

Effect of Modified Carbon Black on the Properties of Natural Rubber Vulcanizate

A. K. GHOSH,¹ S. MAITI,¹ B. ADHIKARI,¹ G. S. RAY,² S. K. MUSTAFI²

¹ Materials Science Centre, I.I.T., Kharagpur 721302, India

² Birla Tyres, Balasore 756056, India

Received 5 December 1996; accepted 1 April 1997

ABSTRACT: Rubber-grade carbon black filler HAF(N330) was modified with a plant product (PP; long aliphatic chain substituted phenols), a proprietary item under patent application, in the presence or absence of hexamine (Hexa) or dicumyl peroxide (DCP) to put a flexible moiety in between the carbon black and the elastomer chain in order to improve some of its processing and reinforcement characteristics in natural rubber (NR). The modification process is simple and involves cheap materials. The modified carbon black was characterized and evaluated for its processability as well as reinforcing characteristics in NR vulcanizate. It was observed to show better processing behavior, without any processing aid, such as easy incorporation and uniform dispersion in the rubber phase without abnormal heat generation, and also improved vulcanizate properties, such as tensile strength, flex cracking resistance, and lower abrasion loss, without affecting other properties to a significant extent. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 683–693, 1997

Key words: carbon black modification; flex cracking; bound rubber; abrasion loss; heat buildup

INTRODUCTION

Reinforcement of rubber by carbon black is merely due to the extensive interaction with an elastomer.¹ To achieve the higher interaction of carbon black with an elastomer and to study the exact mechanism of reinforcement, many workers from the past 50 years or so performed carbon black surface modifications by various means.

Gerke et al.² heat-treated carbon black rubber masterbatches followed by vulcanization and showed improved vulcanizate properties, such as lower hysteresis, higher abrasion resistance, and higher electrical resistivity, which is an indication of better carbon black dispersion. Grafting of

oligomers and polymers onto the black surface was initiated by Donnet and co-workers^{3–10} and by Ohkita¹¹ and later on by Tsubokawa and associates.^{12–15} No significant improvement in the reinforcing activity of such grafted carbon black was observed. A number of promoters or coupling agents were developed from time to time and used in various elastomers.¹⁶ In many cases, it was found to improve some properties at the cost of other properties; moreover, their toxic nature kept those agents restricted in use. However, Yamaguchi et al.^{17,18} developed some non-nitroso coupling agents and claimed improved dynamic properties in natural rubber (NR), synthetic polyisoprene, styrene butadiene rubber (SBR), and polybutadiene rubber (BR). Furukawa et al.¹⁹ claimed that modification of carbon black with ethylene glycol, ethanolamine, hexamethylene diamine, 1,2-dimercapto propyl alcohol, or phenyl-

Correspondence to: B. Adhikari.

Journal of Applied Polymer Science, Vol. 66, 683–693 (1997)
© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/040683-11

isocyanate improved SBR vulcanizate properties as a function of the active hydrogen content of carbon black.

But investigations carried out by Vidal et al.²⁰ revealed that the modification of carbon black by methanol and hexadecanol resulted in the reduction of its surface activity. Even modifications with silane compounds (Si 69) also decreased the surface activity and vulcanizate properties in SBR.²¹ So, the surface modification of carbon black indicates a general trend of surface deactivation and subsequent deterioration of vulcanizate properties. Apart from these, in almost all such cases, both the materials and the process of modification are too expensive and time-consuming. Moreover, any improvement in the processing behavior of such modified carbon black is not found in the literature.

We reported earlier some improvements in the processing behavior and reinforcing properties of carbon black modified with a reactive fatty acid and a plant product separately in SBR.^{22,23} With the objectives of low-cost modifications, processing behaviors, and better properties over the existing reported ones, the effect of the plant product (PP)-modified carbon black on processing and reinforcing properties in NR vulcanizate was investigated in this communication.

EXPERIMENTAL

Reactants

Natural rubber (NR; RMA-I, Rubber Board, India), carbon black (N330, Philips Carbon Black Ltd.), *N*-cyclohexylbenzthiazylsulfenamide (CBS; ICI, India), dicumylperoxide (DCP; BDH, England), zinc oxide (BDH, India), plant product (PP; long aliphatic chain substituted phenols, proprietary item), and other chemicals such as acetone AR and toluene AR and commercial grades of stearic acid, sulfur, and spindle oil were used as received.

A simple modification process was developed in the authors' laboratory. One hundred grams carbon black was mixed with 10 g of the PP in acetone in the presence of the requisite amount of hexamine or DCP in a physical blending process. The mixture was air-dried overnight and then heated at a suitable temperature for 1 h.

Characterization of Carbon Black

After treatment, the modified carbon black was extracted with acetone for 60 h and dried to a

constant weight. After extraction, it was subjected to gravimetric analysis to assess the degree of modification and characterized for the I_2 surface area and dibutylphthalate adsorption (DBPA) via ASTM D 1510 and D 2414, respectively. Also, the pH of carbon black samples was measured with an aqueous slurry of the black.

Processing and Vulcanizate Properties

Compounding was performed in an open two-roll mixing mill (laboratory size) at a friction ratio 1.2. In the course of mixing, the temperature of the compound was recorded at a definite time interval. For determination of the bound rubber content, carbon black rubber masterbatches (without curatives) were kept at room temperature for 7 days for conditioning. After this period, the compounds were cut into small pieces and about 0.5 g of the sample was immersed in 250 mL toluene in a stainless-steel wire cage (320 mesh). The solvent was renewed every 24 h, and after 5 days, the samples were taken out of the solvent and vacuum-dried to a constant weight. The bound rubber percentage (BR%) was calculated by the following equation²⁴:

$$\text{BR}\% = [(W_d - F)/R] \times 100$$

where W_d = weight of the dried gel, F = weight of the filler in the gel (same as weight of the filler in the original sample), and R = weight of the polymer in the original sample.

For measurement of the mechanical properties of filled vulcanizate, the compound was cured in a hydraulic press (Carver, Model 2518) under a pressure at 150°C for $t = t_{90}$ as determined by a Monsanto R-100 rheometer. The tensile properties were measured on a tensile testing machine (KMI, Model 1.3D) as per ASTM D 412-51T. The swelling value (Q) was determined with about 0.5 g of the cured rubber specimen (accurately weighed) using toluene as the solvent. After the equilibrium swelling, the sample was taken out and the solvent was blotted from the surface of the sample and weighed immediately. It was then dried under a vacuum at 100°C until constant weight. The swelling value (Q) was estimated from the equation²⁵

$$Q = \frac{\text{swollen weight} - \text{dried weight}}{(\text{original weight} \times 100)/\text{formula weight}}$$

Table I Formulation of Carbon Black (CB) for Modification

CB(N330) Designation	CB (g)	PP (g)	Hexa (g)	DCP (g)
CB I ^a	100	—	—	—
CB II ^b	100	10	—	—
CB III ^b	100	10	1.64	—
CB IV ^b	100	10	—	1.00
CB V ^a	100	10	—	—

^a No heat treatment.

^b Heat-treated at a suitable temperature.

where the formula weight is the total weight of rubber plus compounding ingredients based on 100 parts of rubber.

Abrasion loss was evaluated by a DuPont abrasion tester (Prolific Engineer). Flex cracking resistance was assessed with a De Mattia flex tester (Prolific Engineer) as per ASTM D 813-59. Heat generation was measured by a Goodrich Flexometer with a 143 psi load, 0.175 in. stroke, and cps 30 Hz as per ASTM D 623-78.

Assessment of Dispersion of Carbon black

The dispersion of carbon black was assessed by measurement of the volume resistivity of the cured sample and by scanning electron microscopy (Model Cam Scan Series II) at a 0° tilt angle of the tensile fracture surface after coating the surface with sputtered gold. The volume resistivity of the vulcanized sample (thickness 0.2 cm) was measured using an LCR meter at a frequency of 100 kHz (LCR Bridge Model 921).

RESULTS AND DISCUSSION

Carbon Black Modification

Carbon black contains carbon and other atoms like hydrogen, oxygen, and sulfur.²⁶ These atoms form several organic functional groups on its surface and contribute to the reactivity of carbon black.^{27–29} Moreover, a substantial concentration of free radicals on the surface of the black was also estimated.³⁰ This carbon black was treated with the PP. In actual modification, carbon black was mixed with the PP and hexamine (hexa) or dicumyl peroxide (DCP) using a small amount of acetone followed by heating at a certain temperature for 1 h. Table I presents the composition of

the carbon black used for modification. CB I was used as a control and CB II–CB IV are the modified blacks. In CB V, the PP was kept as a physical mixture with the black and, therefore, no heat treatment was applied to this formulation. The object of this treatment was to attach a flexible chain onto the carbon black surface by the reaction with the PP. In CB II, carbon black is only heat-treated with the PP, whereas in the case of CB III and CB IV, hexa and DCP were used to facilitate the reaction.

Carbon Black Characterization

Table II presents some of the characteristics of the PP-modified carbon black. In one of our earlier publications,²² the attachment of the phenolic moiety of the PP onto carbon black was verified by the reaction of 2,2-diphenyl-1-picryl hydrazyl (DPPH) with the carbon black (modified and control) and by X-ray photoelectron spectroscopy (XPS) analysis of the modified carbon black along with the control. Here, the carbon black was characterized by gravimetric analysis to estimate the amount of the bound PP onto the carbon black, measurement of the I_2 surface area, determination of the structure by dibutylphthalate adsorption (DBPA), and also by measurement of the pH of the aqueous slurry of the black sample to assess the acidic functional group on the surface of the black (Table II). Gravimetric analysis shows a 21.32% attachment of the PP to the carbon black by simple heating (CB II), but the extent of attachment was found to increase up to 37.00% (CB III) and 38.5% (CB IV) by using hexa (CB III) and DCP (CB IV) with the PP during treatment. As the PP contains a long hydrocarbon chain attached to the phenol, both hexamine and DCP are anticipated to react between the PP and the carbon black matrix. Although a detail reaction mechanism of the PP with carbon black is a mat-

Table II Characteristics of Modified Carbon Black (CB)

CB (N330) Designation	Bound PP on CB (%)	I_2 Surface Area (m ² /g)	DBPA Value (mL/100 g)	pH
CB I	—	80.25	102.1	7.2
CB II	21.32	77.10	97.1	6.6
CB III	37.00	76.00	95.1	6.4
CB IV	38.50	75.20	94.4	6.4

Table III Mix Formulations of Rubber Compounds

Ingredients	Formulation No.						
	1	2	3	4	5	6	7
CB I	41	41	41	—	—	—	—
CB II	—	—	—	45	—	—	—
CB III	—	—	—	—	45	—	—
CB IV	—	—	—	—	—	45	—
CB V	—	—	—	—	—	—	45
PP as							
processing aid	—	—	4	—	—	—	—
Spindle oil as							
processing aid	—	4	—	—	—	—	—

Base formulation (phr): NR(RMA-I) : 100; ZnO: 5; stearic acid: 2; CBS: 1; sulfur: 1.75.

ter of future communication, it is believed that the phenolic ring of the PP becomes linked with the phenolic moiety of carbon black by hexamine at the modification temperature through the formation of a phenol formaldehyde-type resin. DCP after decomposition produces cumyloxy radicals which may abstract the hydrogen atom from the carbon black surface and from the hydrocarbon chain of the PP to facilitate the reaction of the long-chain PP with carbon black by C—C linkage.³¹ The increment of the bound PP in the case of CB III and CB IV shows a positive contribution of hexamine and DCP in the modification.

In Table II, it is observed that both the I_2 surface area and the DBPA values are decreased to a small extent by modification. This reduction of surface area and the DBPA value is believed to be due to the presence of the PP as an intimate entity with carbon black. The decrease in pH is also due to the attachment of the phenolic function of the PP on carbon black.

Compounding of Modified Carbon Black in Natural Rubber

To study the effect of modification, the carbon black was compounded with NR to check its efficiency in processing as well as in reinforcement of the vulcanizate. The compounding formulation is presented in Table III. In all the formulations, the carbon black loading was kept fixed to 41 phr for the sake of comparison of the vulcanizate properties (Formulations 4–7 contain 41 phr carbon black and 4 phr pp with or without heat treatment

as detailed in Table I.) As one of the aspects of this investigation was to observe the processing behavior of modified black, no additional processing oil was used in formulations 4–6. The sulfur-to-accelerator level was kept a little higher to obtain the higher amount of the flexible polysulfide linkage.

Processing Behavior of Modified Carbon Black in NR Vulcanizate

During incorporation and dispersion of carbon black, the energy which produces the shearing action is converted into heat and the temperature of the mix is increased. The increment of the temperature and the extensive milling of the compound may cause reduction of the compound viscosity below the optimum level and also produces an adverse effect in the dispersive mixing.^{32,33} To overcome such problems and to achieve a desired level of dispersion during compounding in the internal mixer, different parameters such as ram pressure and rotational frequency are adjusted properly.³⁴ To judge the potentiality of the PP in overcoming such dispersion problems in the processing of the NR compound (as one of the objectives), we monitored the temperature increase of some formulations during milling at a certain time interval. Figure 1 shows increase of the compound temperature as a function of milling time. To observe the extent of chain scission of the polymer during carbon black dispersion, the viscosity-average molecular weight was determined for the uncured compounds. The variance (σ^2) among four to five specimens for the tensile strength and modulus was also calculated to assess the uniformity of carbon black dispersion throughout the entire elastomeric matrix. The results are presented in Table IV. The dispersion was qualitatively judged also by scanning electron microscopy of the tensile fractured surface and by measuring the resistivity of the cured samples. The results are shown in Figure 2 and Table IV, respectively.

The results of the temperature increase with the progress of milling (Fig. 1) showed the highest temperature increase in case of formulation 1 without process oil, lower in formulation 2 containing process oil, and the lowest in formulations 4–6 where PP-modified black was incorporated. Formulations containing the PP-modified carbon black (formulations 5 and 6) showed the lowest chain scission, and formulation 1 (the unmodified control black without oil), the highest chain scission, as evident by the viscosity-average molecu-

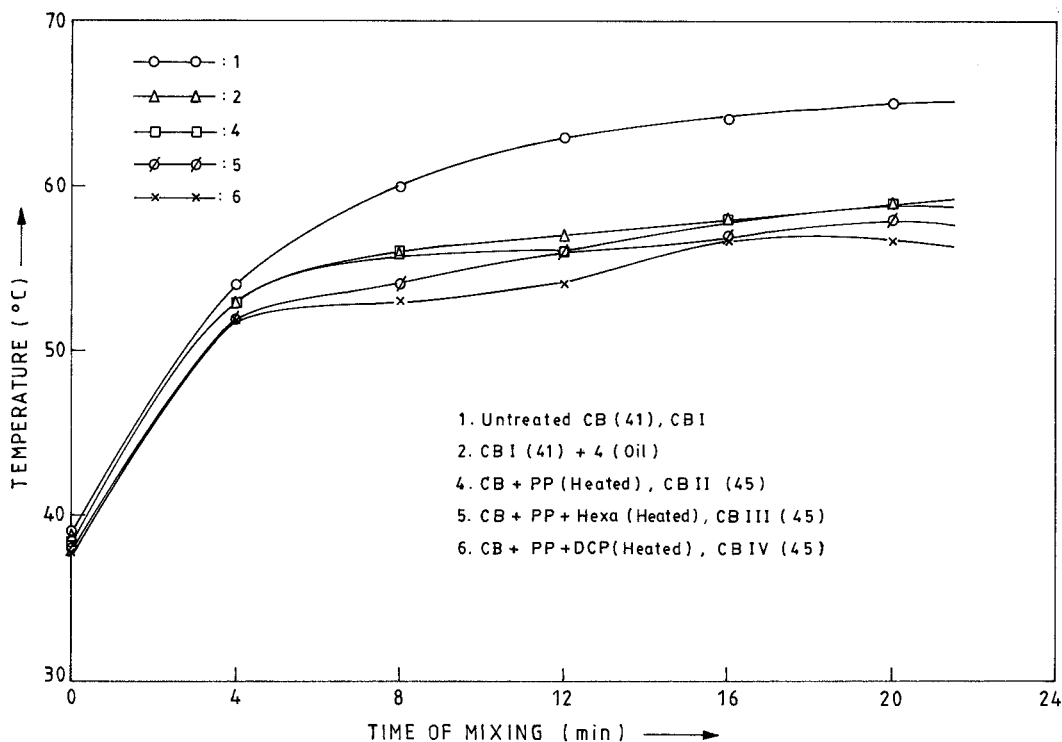


Figure 1 Plot of temperature vs. time during compounding.

lar weight (Table IV). Formulation 2 with process oil showed intermediate chain scission. The uniformity of the vulcanizate properties, such as modulus, tensile strength assessed by estimating the variance (σ^2) among four to five specimens for 200% and 300% moduli, and tensile strength is a function of the uniform dispersion of the reinforcing filler into the rubber matrix. Comparatively lower values of variances (σ^2) of modified black-filled formulations 4–6 over those of controls (formulations 1 and 2) indicate the effectiveness of modified carbon black in its uniform dispersion in the rubber matrix. One of the reasons

for the effectiveness of PP-modified carbon black for better dispersion in rubber is perhaps the lubricating action offered by the long alkyl chain of PP which is attached to carbon black after modification.

Scanning electron micrographs (SEM; Fig. 2) of the tensile fractured specimens showed that modified carbon black-filled samples (formulations 4–6) exhibited better carbon black dispersion in the elastomer matrix than did the control (formulations 1 and 2). These results correlate very well with the variance (σ^2) in the mechanical properties (Table IV). That the modified carbon

Table IV Effect of Mixing on Polymer Molecular Weight and Carbon Black Dispersion

	Formulation No.						
	1	2	3	4	5	6	7
$\bar{M}_v \times 10^{-5}$	1.17	1.36	—	—	1.65	1.62	—
Variance (σ^2) (MPa)							
For 200% modulus	0.125	0.071	0.082	0.061	0.052	0.049	0.106
For 300% modulus	0.141	0.082	0.134	0.072	0.070	0.069	0.160
Tensile strength	0.413	0.322	0.384	0.291	0.210	0.232	0.310
Resistivity (ρ) $\times 10^{-7}$ Ω -cm	5.9	15.4	3.4	—	85.7	117.3	—

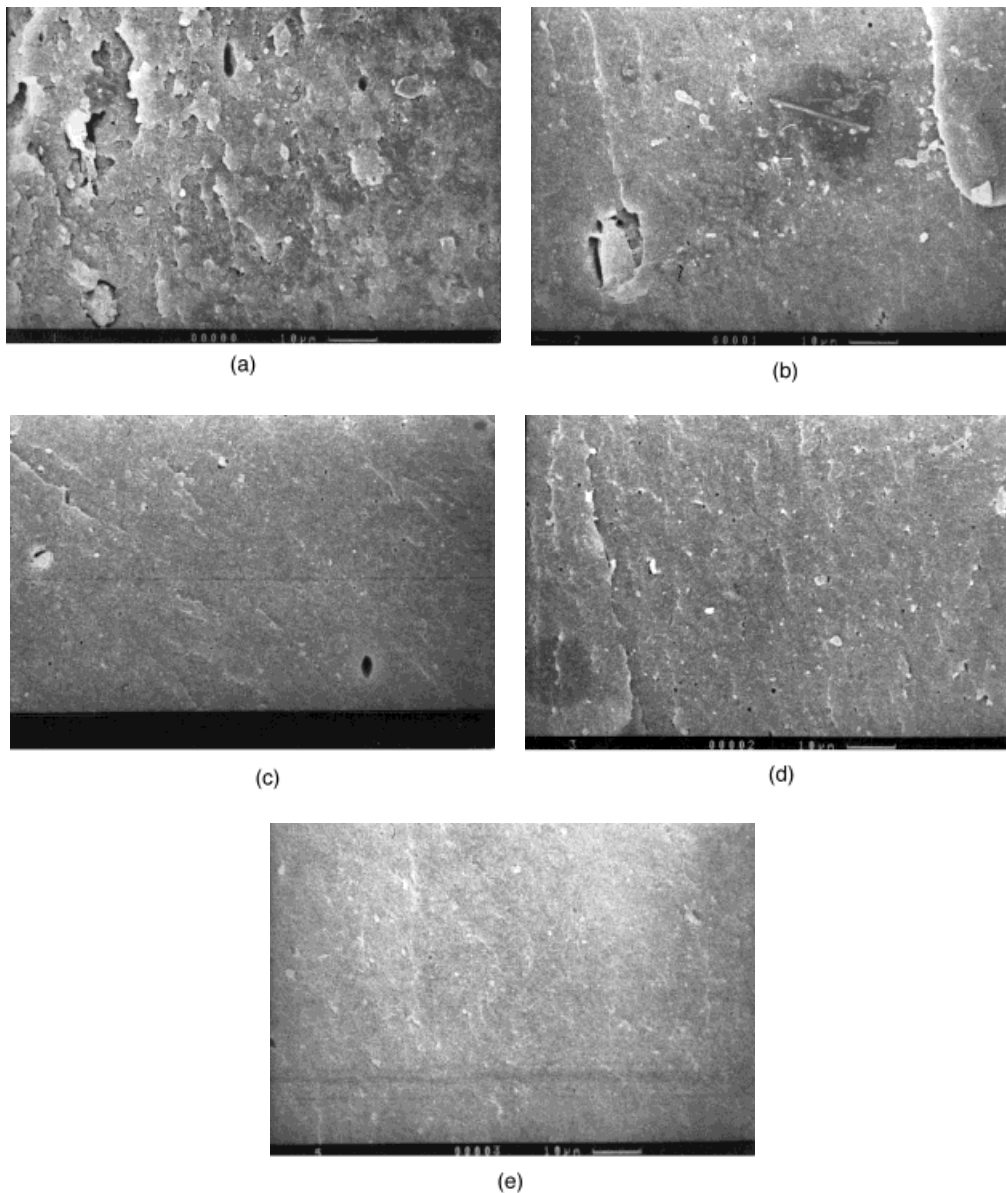


Figure 2 SEM photomicrograph of vulcanizate: (a) formulation 1 (CB I without process oil); (b) formulation 2 (CB I with 4 phr process oil); (c) formulation 4 (CB-II, modified black); (d) formulation 5 (CB-III, modified black); (e) formulation 6 (CB-IV, modified black).

black improves its dispersion in rubber has also been observed by us by the increase in electrical resistivity (formulations 5 and 6). It is known that the resistivity is a function of the dispersion of carbon black in rubber vulcanizate.³⁵ Formulations 5 and 6 show higher resistivity than that of control formulations 1 and 2 (Table IV). These data also correlate well with the SEM and the variances in mechanical properties of cured vulcanizates. Thus, the modification of carbon black with the PP results in improvement of its disper-

sion in the elastomeric phase vis-à-vis the product quality and performance.³⁵

Cure Characteristics

The presence of the PP as a processing aid (formulation 3) or as physically mixed with the black (formulation 7) or the PP-modified carbon black (formulations 4–6) marginally increases the value of the optimum cure time (t_{90}) and scorch time (t_{s2}) (Table V). This is due to the weak acidic

Table V Effect of Modified Carbon Black on Curing Behavior in NR Vulcanizate

Monsanto Rheometer R-100 Data at 150°C	Formulation No.						
	1	2	3	4	5	6	7
Optimum cure time (min)	8.5	8.5	10.0	10.0	10.0	10.5	9.5
Scorch time, t_{s2} (min)	3.0	3.0	3.5	3.5	3.5	3.5	3.5
Extent of cure (dNm)	66.5	56.0	57.0	54.0	55.5	55.5	56.5
Cure rate index (min^{-1})	18.2	18.2	15.4	15.4	15.4	14.3	16.7

nature of the PP which retards the curing reactions, but the modification does not affect the extent of cure in comparison to the standard formulation (formulation 2).

Bound Rubber

Bound rubber is a good measure of the reinforcement of the filler and a function of the filler surface area and its activity.³⁶ It appears to be a general belief from the investigations that the bound rubber formation is attributed to the physical and chemical interaction of the filler with carbon black. Chemical interaction takes place between the polymer radicals generated in chain scission by milling and the carbon black active sites³⁷ and may also be the reaction of the polymer with the active sites of carbon black which are generated in course of milling.³⁸ Wolff and co-workers³⁹ also reported that physical adsorption of the polymer on carbon black plays a prominent role in bound rubber formation. The effect on the bound rubber formation of carbon black modified with the PP was studied and the results are presented in Table VI. On a comparative basis, it is observed that there is around a 4% decrease of bound rubber in the modified black-filled formulations over one control formulation (formulation 1). Such a decrease in the bound rubber content is attributed to the small coverage of the carbon black surface by the modifying agent. This effect was reflected by the decrease of I_2 surface area and the DBPA structure of the carbon black after modification with the long-chain PP (Table II). The slight decrease in bound rubber and, hence, the decrease in carbon black rubber interaction are required for the better flexing property of the rubber composite, particularly in tire application under cyclic stressing. But the modified black formulations 4–6 do not show any significant difference of bound rubber content with formulation 2. Moreover,

both formulations 3 (PP as the processing aid) and 7 do not show any improvement of the bound rubber content.

Vulcanizate Properties

Tensile Properties

Tensile properties include 200 and 300% moduli, tensile strength, and % elongation at break (EB). The results of all the formulations containing modified and unmodified carbon black are presented in Table VI and also in Figure 3. It is observed from the results that modification of carbon black with PP decreases both 200 and 300% moduli to a very small extent. The modulus is a measure of the stiffness of the vulcanizate contributed by carbon black and is a function of the loading, surface area, and structure of carbon black. At higher strain, the value also depends on the filler–polymer interaction.³⁹ In this study with the same loading level of carbon black in all the formulations, the small decrease of the modulus in the modified black formulations is attributed to the decrease of rigid filler–polymer interaction. The highest value of the modulus in formulation 1 without process oil supports the higher rigid filler–polymer interaction but the value decreases when process oil is used in the mix (formulation 2). The lower value of both 200 and 300% moduli in formulation 3 (PP as the processing aid) and formulation 7 (PP as the physical mixture with carbon black) also indicates the decrease of filler–polymer interaction. These observations are in tune with the fact that the low extension modulus is a function of rubber crosslink density which may be correlated here with the filler–polymer interaction density. Further, those results are corroborated by the observations in the swelling value (Q) and bound rubber content (Table VI). It is well known that carbon black has a marginal

Table VI Effect of Modified Carbon Black on Vulcanizate Properties and Bound Rubber Content

	Formulation No.						
	1	2	3	4	5	6	7
Vulcanizate properties							
200% modulus (MPa)	3.9	3.2	2.9	3.0	2.9	2.8	2.7
300% modulus (MPa)	9.4	8.5	8.3	7.9	8.0	8.1	7.8
Tensile strength (MPa)	18.0	18.6	19.8	21.1	23.1	23.0	20.0
Elongation at break (%)	460	502	545	575	590	570	560
Hardness (Shore A)	66	62	62	60	61	62	61
Abrasion loss (%) in 1000 cycles	1.39	1.46	1.62	1.21	1.09	1.04	1.74
Flex cracking resistance in K Cycles							
Initiation	30	41	45	61	65	71	42
Growth	50	76	70	110	122	133	72
Heat buildup (°C)	19	17	23	—	19	19	22
Goodrich compression set (%)	11.0	10.5	13.9	—	11.6	11.5	13.2
Swelling value (Q)	3.1	3.5	3.9	4.1	3.7	3.6	3.9
Bound rubber content (%)	28.6	26.4	24.4	24.7	23.9	24.5	23.1

effect on the tensile strength of NR vulcanizate because of the latter's unique strain-induced crystallization. In the present investigation using modified carbon black, it was observed that tensile strength values are increased over the control at the same effective loading of carbon black (Table VI). But formulations 3 and 7 do not bring any improvement of this property. So, it is worth mentioning that the modification of carbon black is associated with the improvements of the ultimate properties in NR vulcanizate.

In the case of modified black formulations, the percent elongation at break (% EB) is maximum,

indicating the higher flex fatigue life.⁴⁰ Formulations 2, 3, and 7 show also the higher % EB and it is believed to be due to the process oil and PP present as a physical mixture with carbon black. The observation of tensile strength and elongation at break is explained by both the decrease of the rigid filler-polymer interaction and the strain-induced crystallization. With increase of the filler-polymer interaction (modulus), elongation at break decreases. Since the interaction is reduced by modification of carbon black, % EB increased, inducing more crystallization and, hence, tensile strength.

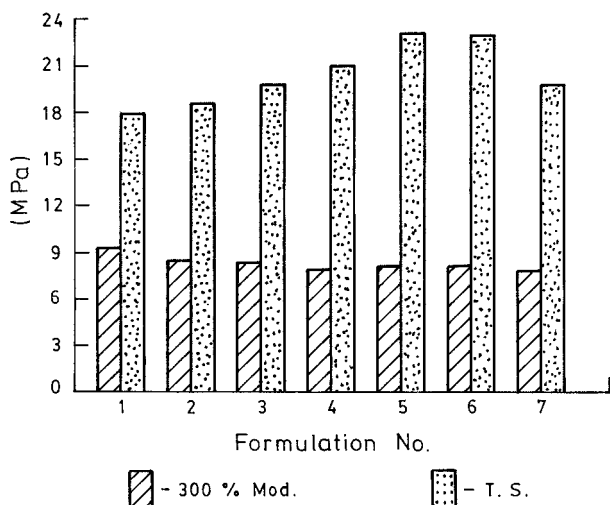


Figure 3 Effect of modified carbon black on 300% modulus and tensile strength of NR vulcanizate.

Heat Buildup

Goodrich heat buildup gives a measure of the dynamic properties of rubber vulcanizates. It is observed from the heat buildup results in Table VI that the modification of carbon black leads to a much smaller increase of heat buildup than that of the control formulations. Fabre and Bertrand⁴¹ pointed out a relation of heat buildup with the bound rubber content. By attaching some chemical promoters to carbon black, they showed that as bound rubber increases heat buildup decreases in the butyl rubber vulcanizate. The results imply the dependence of the carbon black rubber interfacial interaction density on the heat buildup properties. These aspects were also supported by the work of Kurimoto and Yamaguchi.⁴² Modification of carbon black by the dinitrodiamine compounds resulted in a decrease of the heat buildup property

in the NR vulcanizate. The present study of carbon black modification with the PP results in a small decrease of bound rubber content (Table VI), i.e., the decrease of carbon black rubber interfacial interaction density. This leads to the small increase of the heat buildup property of the NR vulcanizate in modified black formulations (formulations 4–6) over the control formulation 2.

There are some earlier reports relating the state of cure to the heat evolution^{43,44} during stretching. It was found that under constant load, however, heat evolution decreases with increase in the state of cure (crosslink density). Some recent studies point out the relationship of heat generation with the crosslinking systems and the crosslink density.^{45,46} Higher crosslink density decreases the heat generation. Since the swelling value (Q) is a measure of crosslink density, comparatively higher swelling values in formulations 4–6 indicate the lower crosslink density and higher heat buildup (Table VI). Formulation 3 (PP as the processing aid) and formulation 7 show the highest value of Q and, consequently, the lowest crosslink density and therefore the highest values of Goodrich heat buildup. The values of the Goodrich flexometer permanent set (Table VI) also support the findings. Since in this case modification of carbon black by the PP decreased the crosslink density, the small increase in heat buildup is justifiable.

Flex Cracking and Abrasion Resistance

Resistance to crack initiation and growth on flexing is one of the essential dynamic properties needed by the rubber articles in dynamic application. So, this property must be achieved at a desired level to obtain a longer service life. Both the crack initiation and the growth during cyclic stresses are functions of the nature of the elastomer, but they also depend on carbon black.⁴⁷ Both the resistance to crack initiation and growth results are included in Table VI and in Figure 4. It is observed that modified carbon black-filled formulations show quite higher resistance to both crack initiation and growth compared to all other formulations (1–3 and 7). Campbell pointed out the dependence of the de Mattia fatigue flex life on the crosslinking system.⁴⁸ At a certain ratio of sulfur-to-accelerator concentration, the flex life becomes optimum. The higher fatigue flex life of the modified black-filled compounds is probably due to the insertion of a long hydrocarbon chain with the carbon black in the course of modifica-

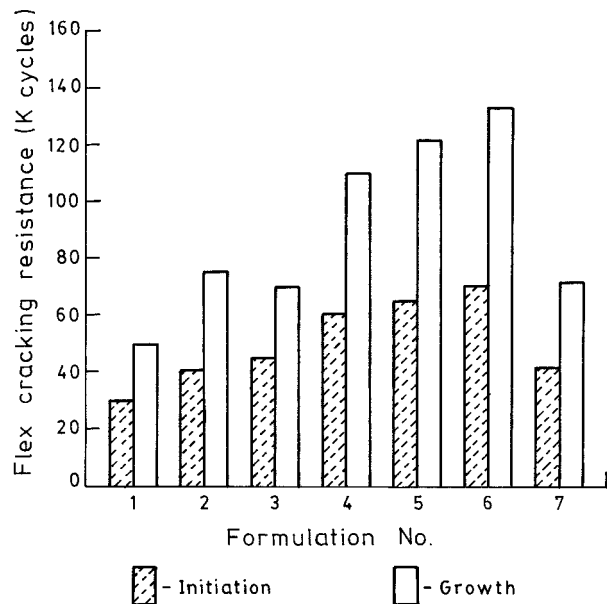


Figure 4 Effect of modified carbon black on flex cracking resistance (both initiation and growth) of NR vulcanizate.

tion. The flexible bridge operating between carbon black and rubber may be partially responsible for the relief of the localized stresses at a dynamic condition.^{49,50} The unmodified carbon black without process oil (formulation 1) showed the least value of both crack growth and initiation resistance. This result is a reflection of the rigid interaction of carbon black with rubber, which is insufficient to relieve the stresses during cyclic operation. The moderately higher value in formulations 2, 3, and 7 are merely due to the process oil (formulation 2) and the PP as the processing aid (formulation 3) and the PP physically mixed with the black (formulation 7).

Abrasion resistance, i.e., the percentage of volume loss after 1000 cycles of revolution, was recorded in a DuPont abrader and the results are presented in Table VI and in Figure 5. It is observed that modification of carbon black with the PP leads to a higher resistance to abrasion (compare formulations 4–6 with the rest). Carbon black has been reported to play an important role in abrasion resistance. In a recent review, Medalia⁵¹ clearly described the effects of carbon black on the abrasion and the tread wear. In an intense search, he pointed out that there are different mechanisms of action of carbon black on road wear. There was an early report that the treatment of carbon black played a prominent role toward the abrasion resistance.⁵² Many researchers

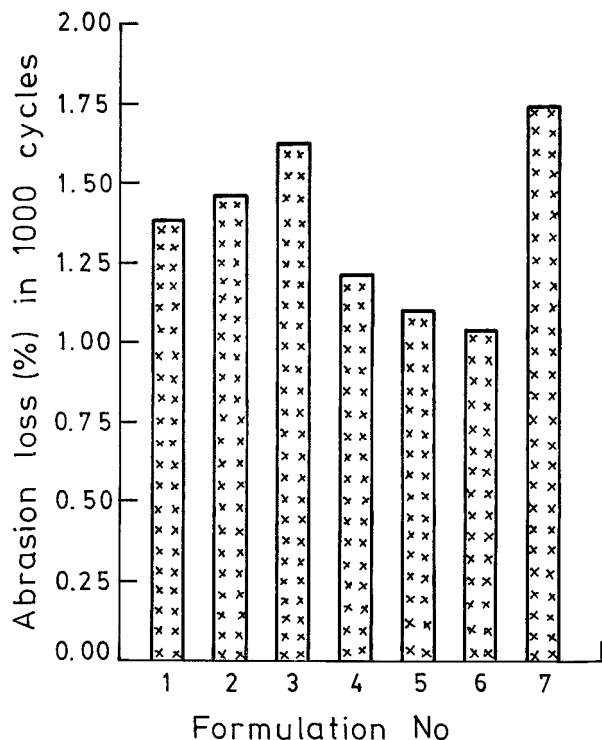


Figure 5 Effect of modified carbon black on abrasion resistance of NR vulcanizate.

improved the abrasion resistance of different vulcanizates after modification with various agents. The improvement of abrasion resistance in the present investigation is due to the modification of the carbon black surface with PP. In the authors' opinion, the improvement of abrasion resistance in NR may be a function of better carbon black dispersion and the chemically bound flexible chain with the carbon black which retards the polymer to be abraded out from the surface. The highest value of abrasion loss in formulations 3 and 7 is probably due to the presence of oil which causes polymer dilution and thus affects the resistance during abrasion.⁵³

CONCLUSION

It appears from the experimental observations on both carbon black modification with the PP and its performance in rubber that the PP moiety is acting as a flexible bridge between the carbon and the rubber matrix. This flexibility offered by the PP decreased slightly the filler-polymer interaction, which decreased the stiffness of the filler-

rubber composite, resulting in improved flex cracking resistance.

The authors thankfully acknowledge the generous help of Mr. S. Mitra and Mr. D. Dutta for the SEM and Dr. D. Bhattacharya and Mr. B. Panda for the resistivity measurements.

REFERENCES

1. E. M. Dannenberg, *Rubb. Chem. Technol.*, **59**, 512 (1986).
2. R. H. Gerke, G. H. Ganzhorn, L. H. Howland, and H. M. Smallwood, U.S. Pat 2,118,601 (1938).
3. J. B. Donnet, G. Henrich, and G. Riess, *Rev. Gen. Caout.*, **39**, 583 (1962).
4. J. B. Donnet, L. Geldreich, G. Henrich, and G. Riess, *Rev. Gen. Caout Plast.*, **41**, 519 (1964).
5. J. B. Donnet and G. Henrich, *J. Polym. Sci.*, **46**, 277 (1960).
6. J. B. Donnet, G. Peter, and G. Riess, *J. Polym. Sci.*, **22**, 645 (1969).
7. J. B. Donnet, A. Vidal, G. Riess, and L. Geldreich, *Rev. Gen. Caout. Plast.*, **47**, 1289 (1970).
8. J. B. Donnet, G. Riess, and G. Majowski, *Eur. Polym. J.*, **7**, 1065 (1971).
9. E. Papirer, J. B. Donnet, G. Riess, and N. Van Tao, *Angew. Makromol. Chem.*, **19**, 65 (1971).
10. A. Vidal, PhD Thesis, Faculte de Sciences, Universite de Strasbourg, 1970.
11. K. Ohkita, N. Kitahara, and H. Yamazaki, *J. Soc. Rubb. Ind. (Jpn)*, **38**, 13 (1965).
12. N. Tsubokawa, T. Jian, A. Yamada, and Y. Sone, *Polym. Bull.*, **16**, 249 (1986).
13. N. Tsubokawa, A. Kuroda, and Y. Sone, *J. Polym. Sci. Polym. Chem.*, **27**, 1701 (1989).
14. N. Tsubokawa, K. Fujiki, and Y. Sone, *J. Polym. Sci. Polym. Chem.*, **24**, 191 (1986).
15. N. Tsubokawa, K. Kobayashi, and Y. Sone, *Polym. Bull.*, **17**, 87 (1987).
16. J. O. Harris and R. W. Wise, in *Reinforcement of Elastomers*, G. Kraus, Ed., Interscience, New York, 1965, Chap. 9.
17. T. Yamaguchi, I. Kurimoto, K. Ohashi, and T. Okita, *Kautsch. Gummi Kunstst.*, **42**, 403 (1989).
18. T. Yamaguchi, I. Kurimoto, H. Nagasaki, and T. Okita, *Rubb. World.*, **199**(5), 30 (1989).
19. J. Furukawa, S. Yamashimo, J. Shimori, and T. Kotani, *Jpn. Pat.* 7,120,886 (1971).
20. A. Vidal, Shi Zhi Hao, and J. B. Donnet, *Kautsch. Gummi Kunstst.*, **44**, 419 (1991).
21. W. D. Wang, A. Vidal, G. Nanse, and J. B. Donnet, *Kautsch. Gummi Kunstst.*, **47**, 493 (1994).
22. A. K. Ghosh, B. Adhikari, and S. Maiti, *J. Polym. Mater.*, **12**, 285 (1995).
23. B. Adhikari, *J. Polym. Mater.*, **9**, 175 (1992).

24. J. J. Brennan, T. E. Jermyn, and B. B. Boonstra, *J. Appl. Polym. Sci.*, **8**, 2687 (1964).
25. C. R. Parks and R. J. Brown, *Rubb. Chem. Technol.*, **49**, 233 (1976).
26. M. L. Studebaker, *Rubb. Chem. Technol.*, **30**, 1400 (1957); R. C. Bansal, J. B. Donnet, and F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, 1988.
27. H. P. Boehm, *Adv. Catal.*, **16**, 198 (1966).
28. J. B. Donnet, *Carbon*, **6**, 161 (1968).
29. D. Rivin, *Rubb. Chem. Technol.*, **44**, 307 (1971).
30. G. Kraus and R. L. Collins, *Rubb. World*, **139**(2), 219 (1958).
31. E. M. Dannenberg, M. E. Jordan, and H. M. Cole, *J. Polym. Sci.*, **31**, 127 (1958).
32. H. M. Edmondson, in *Institute of Rubber Industrial Conference*, April 1969.
33. J. R. Bourne, *New Sci.*, **33**, 334 (1967).
34. H. Palmgren, *Rubb. Chem. Technol.* **48**, 462 (1975).
35. W. M. Hess, *Rubb. Chem. Technol.*, **64**, 386 (1991).
36. B. Meissner, *Rubb. Chem. Technol.*, **68**, 297 (1995).
37. W. F. Watson, *Ind. Eng. Chem.*, **47**, 1281 (1955).
38. A. M. Gessler, *Proc. Int. Rubb. Conf.*, 249 (1967).
39. S. Wolff, M. J. Wang, and E. H. Tan, *Kautsch. Gummi Kunstst.* **47**, 873 (1994).
40. F. S. Conant, in *Rubber Technology*, M. Morton, Ed., Van Nostrand Reinhold, New York, 1986, p. 146.
41. R. Fabre and G. Bertrand, *Rev. Gen. Caout. Plast.*, **42**, 405 (1965).
42. I. Kurimoto and T. Yamaguchi, *Jpn. Kokai Tokyo Koho JP 01,275,666* (1989).
43. A. E. Juve and B. S. Garvey, Jr., *Ind. Eng. Chem.*, **36**, 212 (1944).
44. J. F. Svetlik, W. S. Howard, W. T. Cooper, and H. E. Railsback, CD 2610, Report to Reconstruction Finance Corp., Dec. 6, 1951.
45. T. Kempermann, *Rubb. Chem. Technol.*, **55**, 391 (1982).
46. E. Meinecke, *Rubb. Chem. Technol.*, **64**, 269 (1991).
47. E. S. Dizon, A. E. Hicks, and V. E. Chirico, in *ACS, Rubber Division Manufacturing Conference*, Denver, 1973, Paper No. 23.
48. D. S. Campbell, *J. Appl. Polym. Sci.*, **14**, 1409 (1970).
49. W. Cooper, *J. Polym. Sci.*, **28**, 195 (1958).
50. B. A. Dogadkin, Z. N. Tarasova, and I. I. Goldberg, in *Proceedings of the 4th Rubber Technology Conference*, London, 1962, p. 65.
51. A. I. Medalia, *Kautsch. Gummi Kunstst.*, **47**, 364 (1994).
52. C. W. Sweitzer, K. A. Burgess, and F. Lyon, *Rubb. World*, **143**(5), 73 (1961).
53. J. T. Byers, in *Rubber Technology*, M. Morton, Ed., Van Nostrand Reinhold, New York, 1986, p. 83.