

Improvement of Carbon Black Material and Reduction of Tire Rolling Resistance for Benefits of Green Environment

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Abstract

Carbon black is the major filler used in rubber compounds. The extent of carbon black in tire compounds is of the order of 60-70 phr (parts per hundred) this large amount of filler leads to filler-filler interaction and results in extensive hysteresis losses. In spite of numerous efforts put forward to replace carbon black partly by silica the efforts were not very fruitful because all the parameters needed to be satisfied, hence the efforts could not meet the desired criteria. Therefore, of late there is a change in strategy of using carbon black itself as the key filler but in a modified form that will reduce the filler-filler interactions. The impact of filler on rubber compound properties is greatly influenced by its dispersion and distribution nature into the rubber matrix which is greatly dependent on the affinity of filler towards the rubber molecules. Filler with improved affinity towards rubber molecules leads to higher filler -rubber interaction resulting improved filler dispersion and reduce the propensity of filler network formation in the rubber matrix. As low filler-filler interaction and high filler-polymer interaction of modified carbon black results lower extent of filler network, lower extent of hysteresis energy is lost on application of cyclic deformation on the rubber compounds. Thus, tire made up with such types of rubber compounds would have lower hysteresis energy loss during service and would lead to lower tire rolling resistance.

In the present research work an attempt has been made to functionalize carbon black by treating with benzyl tri ethyl ammonium chloride for enhancement of carbon black interaction with rubber molecules. Such treatment causes improved dispersion of carbon black and reduces the inter-aggregates interaction of carbon black in rubber matrix. The compounding of benzyl tri ethyl ammonium chloride treated carbon black was carried out with natural rubber system as well synthetic rubber system such as solution styrene butadiene rubber system. It is observed that due to reduction of re-agglomeration of carbon black aggregates the filler - filler interaction was reduced significantly, leading to lower Payne effect and lower hysteresis loss. As lower hysteresis loss at 60oC temperature of rubber compounds is a measure of tire rolling resistance, thus functionalization of carbon black by benzyl tri ethyl ammonium chloride results lowering of tire rolling resistance and reduces the emission of greenhouse gases by vehicles benefiting the environment.

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I. INTRODUCTION

Air pollution, emission of greenhouse gases from vehicles have been a tremendous concern across the

globe. Different nations have taken different regulations to control the emission of greenhouse gases. Thus, reductions of CO₂ gas, the one of

major component of greenhouse gases, emission become the major mottoes and the primary challenge for automotive transport. It is well understood that wheel of vehicles imparts rolling resistance during operation, and which is one of the reasons for above concern for automotive industries. Rolling resistance, is the energy consumed during rolling of wheel, has significant contribution towards fuel consumption of vehicles as well as on the emission of greenhouse gases.

Thus, reduction of the tyre rolling resistance would play a significant impact on the fuel saving of vehicles and consequently on the reduction of greenhouse gas emission. It has been illustrated that 3 to 6% fuel saving can be possible for passenger car vehicle if a reduction of 30% tyre rolling resistance is achieved and for a heavy-duty truck mostly drive on highway, same proportion of fuel consumption is possible to reduce over a reduction of 20% of rolling resistance [1- 2].

Carbon black is the most significant filler used in tyre compound, which provide strength into rubber compound, i.e. into the tyre. The basic properties of tyre such as wear resistance, rolling resistance, steering response, heat build-up in tyre are greatly influenced by the characteristics of carbon black grades and percentage of carbon black used in tyre compound formulations [1-4]. The basic morphological properties of carbon black are particle size, structure, aggregate size and shape distribution etc, which influence rubber compounding characteristics. Apart from above morphological properties carbon black is characterised with surface chemistry that indicates several organic functional groups such as hydroxyl, ketone, lactone etc as attached on surface of carbon black [5-7].

In this present investigation, an attempt was made to functionalize carbon black by benzyl tri-ethyl ammonium chloride treatment and to study the effect of carbon black functionalization on carbon black dispersion in rubber matrix and the

improvement of filler polymer interaction for the reduction of hysteresis loss of rubber compounds.

II. EXPERIMENTAL

2.1. Materials:

The raw materials used for the present research work were collected from different sources of India and the other nations having standard specifications. Natural Rubber (1X, Indian Standard) was procured from Indian Rubber Board, Kottayam, Solution Styrene butadiene rubber (SSBR) was procured from Lanxess, Germany. Zinc oxide was procured from Mittal Pigment Private Ltd, India. Micro Crystalline (M.C.) Wax having a specific gravity of 0.915 was collected from Repsol Chemicals, India. Stearic acid having iodine number of 9 (max.) and acid number of 185-215 was collected from VVF Ltd, Mumbai, India. TDAE (Vivatec 500) was supplied by Hansen & Rosenthal (Hamburg, Germany). N-1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (6PPD), N-Cyclohexyl-2-benzothiazole sulfenamide (CBS), Tetramethylthiuramdisulphide (TMTD) was supplied by National Organic Chemical Industry Limited, Mumbai, India. Sulfur having assay more than 99% and acidity of 0.01 % was collected from Jaishil Chemical Industry, Mumbai, India. benzyl tri ethyl ammonium chloride was collected from Sigma Aldrich, Germany and carbon black N330 grade having surface area of 82 m²/g and oil absorption number of 100 ml/100 gm was collected from Phillips Carbon Black Limited, India.

2.2. Carbon black sample preparation

Benzyl tri ethyl ammonium chloride is mixed with carbon black having 1% (wt/wt) concentration with respect to carbon black (N330) and refluxed by heating at 100oC for 60 minutes in presence of excess distilled water and followed by cooling the mixture to room temperature. The mixture is washed repeatedly in Gooch crucible by means of distilled water to remove of un-reacted benzyl tri ethyl ammonium chloride (BTEAC) and then it is dried

in oven at 125oC for 3 to 4 hours until complete removal of moisture. The modified carbon black is collected inside desiccator before using. A blank run also carried out by taking only N330 carbon black sample and refluxed it as above to have identical condition of carbon black without adding benzyl tri ethyl ammonium chloride.

2.3. Rubber compounding

The rubber compounding formulations is shown in Table-1. The formulation of different chemicals is based on part of chemical per 100 part of rubber (phr). N0 and SS0 rubber compounds represent control rubber compound of NR and SSBR based rubber while N1 and SS1 represent rubber compounds of NR and SSBR based rubber having carbon black treated with 1% BTEAC.

Mixing of rubber compound was carried out by Laboratory Banbury (Model: BB2, M/S: Kobelco, Japan) and followed by Two roll mill (SMX. LAB.613.ASTM, SantoshMachineryPvt Ltd, India).

Table-1: Formulations of rubber compounds (unit: phr)

	N0	N1	SS0	SS1
NR	100	100	0	0
SSBR	0	0	100	100
N330	50	0	50	0
Treated N330	0	50	0	50
Zinc Oxide	5	5	5	5
Stearic Acid	2.5	2.5	2.5	2.5
TDAE Oil	10	10	15	15
6PPD	1	1	1	1
M.C. Wax	2	2	2	2
CBS	0	0	1	1
TMTD	1.5	1.5	0	0
Sulphur	1.5	1.5	1	1

The mixing of each compound was carried out in two steps, firstly a master batch compound was prepared in Banbury at 60 rpm for 5 minutes with compound dump temperature of 145-150oC. The final mixing was carried out at 45 rpm for 3 minutes at 100-110oC temperature. The dumped compounds were processed on the two-roll mill in order to perform the sheeting of rubber compound for both masterbatch as well as final batch.

2.4 Testing and Characterization

The curing characteristics of the compound are measured by Oscillating Disc Rheometer (ODR2000), Alpha Technology, USA. Curing characteristics for NR based rubber compounds are carried out 145oC for 30 minutes while the same characteristics for SSBR compounds were carried out at 160oC for 60 minutes.

The curing of the samples was done by using a compression moulding machine at 100 kg/cm² pressure having the curing time of 2Tc90+2 (where Tc90 is the optimum cure time as obtained by ODR 2000) minutes. The temperature of curing for analysis of dispersion analysis, dynamic mechanical analysis is 145oC for NR based compound and 160oC for SSBR based compounds.

The dispersion of carbon black in rubber matrix was measured by Disper Grader, Alpha Technology, USA by cutting sharply a piece of cured rubber compound and placed the sharp surface on front of laser light beam source of the equipment. The dispersion and distribution of carbon black aggregates and agglomerates are represented by X value and Y value, which represent the agglomerate size and distribution of carbon black aggregates-agglomerates in the rubber matrix respectively.

Filler-Filler interaction as described by Payne effect was measured by Rubber Process Analyser (Premier RPA), Alpha Technology, USA. The analysis was carried out at 70oC temperature with frequency of 10Hz. The sheer modulus (G') is measured at different deformation level from strain amplitude of

0.07% strain up to 100% strain and the Payne effect is expressed by the difference in G' value at high strain (100%) amplitude from the value at low (0.07%) strain amplitude.

Dynamic characteristics of rubber compounds were analysed by Dynamic Mechanical Analysis (DMA 50), Metravib, France at 60°C temperature, 10 Hz frequency and 0.1 % dynamic strain. The storage modulus, loss modulus and loss tangent ($\tan\delta$) value at 60°C were reported.

III. RESULT AND DISCUSSION

3.1. Curing Characteristics

Benzyl tri ethyl ammonium chloride is basic in nature thus while we treat carbon black with benzyl tri ethyl ammonium chloride increases the efficiency of accelerators which are also basic in nature. Because of this phenomenon carbon black on functionalization with benzyl tri ethyl ammonium chloride reduces the curing time of compound to achieve the optimum curing of compound. The curing characteristics of the compounds are shown in Table-2.

Table-2: Curing Characteristics of rubber compounds

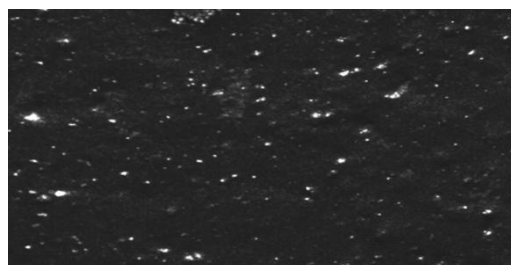
#Parameters, unit of measurement	N0	N1	SS0	SS1
Ts2, minutes	3.95	3.14	1.79	1.31
Tc90, minutes	15.41	8.82	10.12	7.26

#Ts2 is scorch time, Tc90 is the optimum curing time

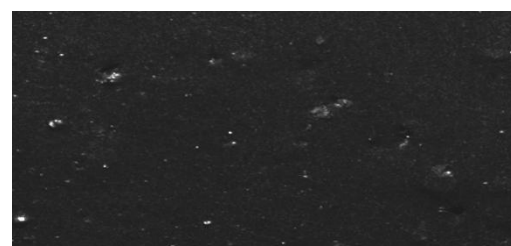
3.2. Dispersion Analysis

Dispersion of carbon black in rubber matrix are classified by ‘rupture’ and ‘erosion’ mechanism, Rupture mechanism involves rapid breakdown of carbon black agglomerate into aggregate due to shear force applied during mixing procedure and erosion mechanism is the detachment of smaller size

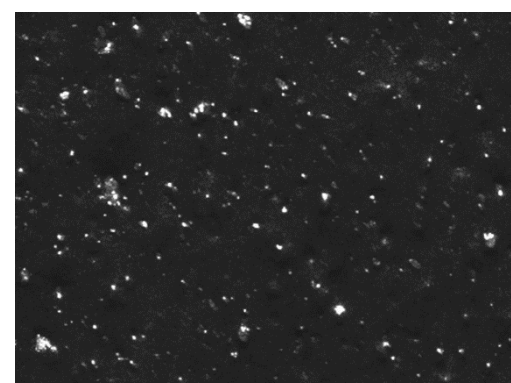
aggregate from the outer layer of agglomerate which is caused by even application of very low shear stress during the mixing. The kinetics of erosion process is depending on intensity of stress, agglomerate cohesive and consequently the affinity of carbon black towards rubber molecules. Thus, carbon black more compatibility to rubber compound will have more tendency to breakdown aggregate fragments to form smaller size carbon black aggregate fragments in the rubber matrix and will results improved dispersion characterize, which is illustrated in Table-3, Fig-1. Fig-1(a) and (c) represent the dispersion of non-treated carbon black in NR compound (N0) and SSBR compound (SS0) respectively while Fig 1(b) and (d) represent the dispersion of treated carbon black in NR rubber compound (N1) and SSBR (SS1) respectively.



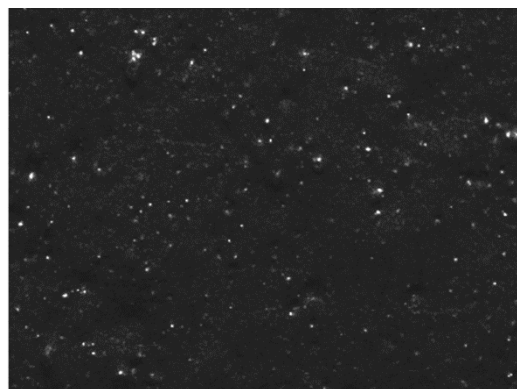
(a)



(b)



(c)



(d)

Fig -1: Dispersion image of carbon black for (a) Control NR compound (N0), (b) Modified NR compound (N1), (c) Control SSBR compound (SS0) of (d) Modified SSBR compound (SS1)

The white spot represents poorly dispersed carbon black agglomerates in rubber matrix, larger number of white spots in Fig-1 (a) signifies poor dispersion and distribution of carbon black than treated carbon black which is represented Fig-1 (b) having comparatively lower white spots [8-9]. Similar trend of lower white spots appeared for treated SSBR compound (SS1) also with respect to corresponding non treated compound (SS0) as shown in Fig 1 (d) and (c) respectively. Table-3 shows that on treatment of carbon black benzyl tri-ethyl ammonium chloride chemical gives to 95.5% carbon black dispersion in NR rubber matrix with respect to 83.5% for non-treated carbon black and the average aggregate size in the rubber matrix of 8.5 nm against 10.9 nm of non-treated carbon black. Similar trend of observation appeared for SSBR compounds as shown in Table-3.

Table -3: Dispersion properties of compounds

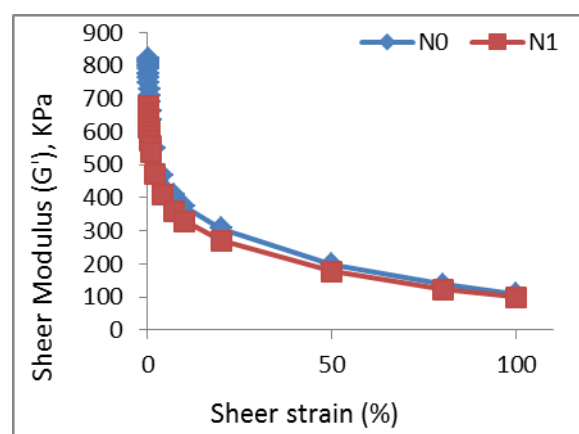
	N0	N1	SS0	SS1
X Value	7.3	8.7	6.9	9.3
Y Value	8.7	9.2	8.8	9.7
White area (%)	7.1	3.7	7.2	3.1

Dispersion (%)	83.5	95.5	86.4	97
Average aggregate size (um)	10.9	8.5	10.9	7.9

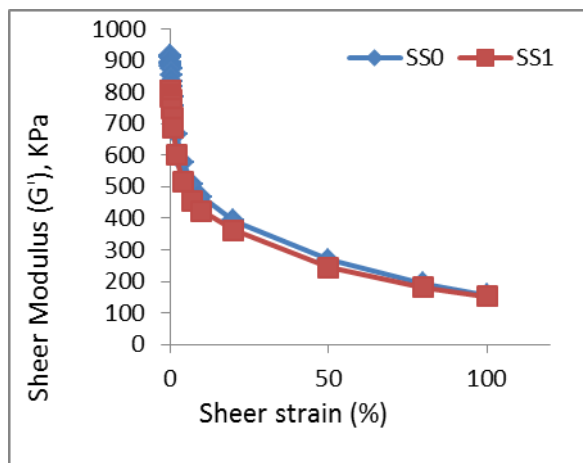
3.3. Rubber Process Analysis and Payne Effect:

Payne effect is the measure of sheer modulus changes by application of strain and which is measured by Rubber Process Analyzer [10-11]. During mixing of carbon black with rubber a sheer stress is developed which results breakdown of carbon black agglomerates into the basic unit of carbon black termed as aggregates. Carbon black aggregates in the rubber matrix always have tendency to re-agglomerate due Van der Wall force of interaction and form branched, higher size agglomerate network in rubber matrix. This tendency of re-agglomeration is increased with loading of carbon black increases the filler –filler interaction. While carbon black has increased interaction with rubber matrix due to functionalization, these will have comparatively lower tendency to re-agglomerate and provide superior dispersion and distribution in rubber matrix and results lower filler networks [10-13].

On application stress, the component of sheer modulus falls due to break down of the carbon black network among agglomerates and aggregates. This



(a)



(b)

Fig-2: Shear Modulus with respect to strain sweep for (a) NR based compounds (b) SSBR based compounds

phenomenon is called as ‘Payne effect’. Thus, it is obvious rubber compounds involving lower extent of filler network would have less propensity of filler network breakdown and consequently result lower ‘Payne Effect’ which is represented by difference of shear modulus of the compound at lower strain application substrate that of higher strain.

In this present investigation carbon black is modified by incorporation of benzyl and ethyl groups on surface of carbon black, it is quite consequent that due to presence of those groups, carbon black becomes more compatible with rubber molecules and there is an increase tendency of carbon black interaction with rubber molecules which leads to reduction of interaction among carbon black aggregate in the rubber compound matrix. The Payne effect of treated carbon black rubber compounds show a significant reduction with respect to their corresponding rubber compound based on control untreated carbon black as shown in Fig-2.

Table-4: Rubber Process Analysis (Stain sweep)

Parameters, unit of measurement	N0	N1	SS0	SS1
Shear Modulus at 0.1%	821	676	914	802

Strain ($G'_{0.1}$), KPa				
Shear Modulus at 100 % Strain (G'_{100}), KPa	109	99	156	153
Payne Effect ($\Delta G = G'_{0.1} - G'_{100}$), KPa	712	577	758	649

3.4. Dynamic Mechanical Analysis

Dynamic mechanical analysis was carried out by Dynamic Mechanical Analyser (DMA50, Metravib, France) at 60oC temperature and 10 Hz frequency to determine loss tangent ($\tan\delta$) of compound. The loss tangent ($\tan\delta$) values at 50 – 80oC are the measure of tyre rolling resistance. It is well understood that rubber compounds with higher hysteresis loss, resulted due to breakdown of filler-filler networks, would have higher $\tan\delta$ value and would exert higher rolling resistance properties while used in tire compounds [1-2, 14-15]. The $\tan\delta$ values at 60oC of the compounds, shown in Table-5, which imply that treated carbon black filled compound has lower $\tan\delta$ value as compared to corresponding non treated carbon black compound for each set of rubber system, which indicates significant reduction of hysteresis loss of rubber compounds as resulted by treatment of carbon black by benzyl try ethyl ammonium chloride. Hence tire with low rolling resistance property can be made while using rubber compounds consisting functionalized carbon black by benzyl try ethyl ammonium chloride.

Table-5: Dynamic Mechanical Analysis at 60oC

	N0	N1	SS0	SS1
Storage Modulus (MPa)	5.47	6.02	4.7	4.38
Loss Modulus (MPa)	1.54	1.55	1.02	0.85
Loss tangent ($\tan\delta$)	0.282	0.257	0.217	0.194

IV. CONCLUSION

The concern towards the greenhouse effect and environment pollution due to increased gas emission by burning of fuel in the field of automotive transport put a significant emphasis to develop fillers, rubbers, chemicals etc in such a way that will help rubber compounders to develop low hysteresis rubber compounds, which would exert low rolling resistance while use in tire application. Here, the functionalised carbon black by treatment of carbon black with benzyl tri ethyl ammonium chloride leads to incorporation of ethyl and benzyl functional groups to the surface of carbon black. The functionalised carbon black makes carbon black increased compatible with rubber molecules to improves the filler-polymer interaction and consequently reduces the possibility of filler re-agglomeration, i.e, reduces the filler-filler interaction which was indicated by reduction of Payne effect of the compounds. Lower Payne effect of functionalized carbon black based compound evidences the improvement of filler-polymer interaction with respect to the corresponding control compounds. This phenomenon helps in reducing hysteresis energy loss, as expressed by loss tangent ($\tan\delta$) value, as well as improvement of filler dispersion and distribution in rubber matrix with reduced extent filler re-agglomeration. Lower loss tangent ($\tan\delta$) value of rubber compounds at 60oC represents the lower rolling resistance of tire. Rubber compound consisting of functionalized carbon black shows approximately 10% reduction of loss tangent ($\tan\delta$) value at 60oC Hence by functionalization of carbon black a design of low hysteresis rubber compound can be made which helps in producing low rolling resistance tire for the benefits of lowering green hose gases emission of transport vehicles.

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