Synopsis of the Thesis Entitled

"Modification of Carbon Black Morphology to Improve Tyre Tread Compound Properties"

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Chapter-1: General Introduction

The climate change due to the emission of greenhouse gas (GHG) is a global issue. The increased rate of GHG emission causes global warming which would have a huge impact on the world's climate and sea levels. It will affect the economic and social development of countries all over the world [1]. The sources of greenhouse gas emissions are mainly caused by human activities because of the burning of fossil fuels for the electricity, heat, and transportation.

The growth of transport industry plays crucial role on the increased emission of GHG across the globe. In the USA, around one-third of GHG emission is caused by transport industry while in India around 14% of GHG is contributed by the same. Thus, reduction of GHG emissions in transport industry is one of the major focuses for the different nations [2-3].

For a vehicle considerable amount of fuel is consumed by tyres, due to rolling resistance. Thus, to cope up with present challenges, low rolling resistance tyres are highly recommended for the transport industry and to make it possible, tyre researchers have been working on various aspects of tyre modification to enhance the tyre performance in line with low rolling resistance. A tyre is composed of several parts such as tread, sidewall, carcass, beads, belts, inner liner etc as shown in Figure 1. Each part of the tyre contributes to the tyre rolling resistance and tread is the major contributor to the same [4].

Figure-1: Different part of a tyre

Tread comes in contact with road thus, along with rolling resistance, other performance properties such as wear resistance, traction, skid resistance and mechanical strength are also important parameters. The performance of tyre tread is monitored by design of tread pattern, formulation of tread compound, speed of vehicles, road condition, vehicle weight etc. A tread is made of rubber compound, which is composed of rubbers, fillers, process oil and many compounding ingredients. Rubber and fillers are the key contributors towards performance of tread compound such as rolling resistance, wear resistance and other performance of tread compounds [5].

Carbon black is the one of most common filler used in tyre compounding and the characteristics of the same impact significantly on rolling resistance, abrasion resistance and mechanical strength of tyre tread compounds. Carbon black with improved affinity towards rubber molecules through chemical interaction or physical interaction or both would lead to increase filler-polymer interaction, reduce filler-filler interaction, and consequently improve the filler dispersion in rubber matrix and boost the tyre tread performances. Carbon black with different surface area, structure property, aggregate size, aggregate size distribution, crystallinity, porosity, and surface functionality have different extent of interaction with different types of rubber molecules. In the 'Chapter-Literature survey' of the synopsis a brief discussion on the same have been deliberated, which not only guides the scope of research but also points to the opportunities of carbon black modification for the improvement of tyre tread compound properties.

Objective of the research work is to improve the tyre tread compound properties by modifying carbon black characteristics. To achieve the same, different approaches were adopted to modify the carbon black characteristics. Attempts were made to induce changes in carbon black surface and structural morphology to make it not only more compatible with rubber but also to reduce the tendency of inter-particle network formation. The same were achieved by different methods involving 1) Optimization of aggregate size distribution of carbon black, 2) Ozone treatment of carbon black to change carbon black morphology and 3) Functionalization of carbon black by chemical treatment. All these modifications were encouraging as they resulted in significant reduction of the rolling resistance of the tyre tread compounds.

The thesis is presented in eight chapters as described below.

Chapter 1 - ***General Introduction:*** Outlines the need and the scope of the investigation.

Chapter 2 - ***Literature survey:*** It includes the present scenario of global concern on rolling resistance of automotive vehicles and consequently outlines the contribution of tyres on the same. It discusses the role of different surface and morphological parameters of carbon black on rolling resistance and other properties of tyre as well as different approaches where carbon black were modified for improvement of tyre tread compound properties.

Chapter 3 - ***Materials and methods:*** Discusses in detail the materials used, experimental methodology adopted, and testing and characterization of rubber compounds carried out to investigate the performance of tyre tread compounds.

Chapter 4 - ***Modification of tyre tread compound by optimized aggregate size and aggregate size distribution of carbon black-*** In this chapter the concept of carbon black structural units such as aggregates are discussed. It demonstrates the effect of carbon black aggregate size, the pattern of aggregate size distribution on the rubber compound performance, which were studied particularly for tyre tread applications.

Chapter 5- C*orrelation of carbon black parameters with rubber compound properties for development of improved tyre tread compounds:* Carbon black is characterized by its aggregate, structure, surface area, particle size etc and each parameter has significant effect on rubber compound properties. In this chapter rubber compound properties are correlated with different carbon black parameters. The correlations were analysed statistically and interpreted by R-square value, and based on the same, the scope of carbon black development for tyre tread compound are drawn.

Chapter 6 –S*imultaneous changes on carbon black surface and structural morphology to improve tyre tread compounds:* Carbon black surface and structural morphology were simultaneously changed by Ozone treatment. In this chapter the morphology changed due to ozone treatment were characterized by TEM, XRD and the effect of ozone treated carbon black were studied in rubber compounds.

Chapter 7- ***Improvement of tyre tread compounds by treatment of carbon black with benzyl tri-ethyl ammonium chloride (BTEAC):*** In this chapter the surface characteristics of carbon black was modified by chemical treatment. The surface characteristics and morphology of carbon. The effect of chemically modified carbon black was studied for the lowering of rolling resistance property of tyre tread compounds.

Chapter 8 - ***Conclusion:*** It demonstrates the outcome of each approach and scope of carbon black modification, which can boost the carbon black performance for tyre tread compound, especially the reduction of rolling resistance. It also covers, how the development of carbon black as stated above, can assist in reduction of global warming, and reduction of greenhouse gases emission.

Chapter-2: Literature Survey

Tyres are very important components of vehicles, which carry the load and provide riding comfort, traction, steering response, braking to the vehicles. The most crucial part of the of tyre is tread, which remains in contact with the road, hence the key performance characteristics of same are rolling resistance, wear resistance, traction, mechanical strength etc. During the movement of vehicles, tyre consumes a portion of the power which is transmitted to the wheels. The power consumed by tyre is termed as rolling resistance and which is caused by mechanical energy losses due to aerodynamic drag associated with rolling, friction between the tyre and road, between the tyre and rim, energy losses due to hysteresis energy loss etc. though, hysteresis energy loss is the major contribution of rolling resistance which is caused due to viscoelastic nature of rubber compound [6]. To enhance the mechanical strength of rubbery material different types of fillers are incorporated into the rubber matrix. On addition of same, the rubber molecules are adsorbed on the its surface and start filler-polymer interaction through the physical interaction or chemical interaction or both. This phenomenon leads to rubber molecular chains converts into immobilized, which hinders the mobility and consequently increases the viscosity and modulus of the compound [7].

Payne attributed that the reinforcement characteristics, achieved in rubber compound due to incorporation of filler, acts as an additive function of few inbuilt strength components, such as polymer network strength, strength due to hydrodynamic effect, strength arises from in-rubber structure and the filler-filler interaction. Payne further demonstrated that on cyclic deformation of rubber compound, the shear modulus of the compound falls due to rupture of the filler-filler interaction. This phenomenon is termed as Payne effect, and which is more intense in the lower strain sweep region of up to 20% strain sweep [8-9].

Tyre tread exhibits continuous rubbing, friction with road during service and leads to loss of rubbery materials from the surface, termed as tread wear. Tread wear leads to loss of tread grooves and resulting loss of tyre steering response, braking forces and tyre life. The wear of rubbery material from tyre tread compound depends on several factors such as tyre compound property, design of tyre tread, speed, weight of vehicles, road condition etc [10].
In order to improve above properties of the tyre tread compound, several attempts were adopted and one of potential attempt is development of raw materials. In this section, different approaches of carbon black development are discussed, and the scope of further development are indicated.

Carbon black is mainly produced in the furnace process by incomplete combustion of heavy petroleum product. During the manufacturing, carbon black particles are fused together and form a clustering chain like units, which are termed as aggregates. The aggregation of carbon black is represented by the carbon black structure and defined as the degree of cluster formation. Higher the number of particles present in aggregates is called high structure carbon black and vice versa. A number of aggregates coming together further form a cluster chain like structure by weak interaction force among them called agglomerates. During mixing with rubber, the agglomerates break down into aggregates, thus, aggregates are the discrete unit of carbon black. Hence performance properties of carbon black in rubber compound significantly dependent on size, shape and number of aggregates present in the system [11-12].

Numerous investigations have been carried out to study the effect of carbon black characteristics on rubber compound properties. Hess et all [13], Parkinson [14] extensively studied the effect of carbon black particle size and surface area on the rubber compound properties. They established that on increase of surface area and reduction of particle size of carbon black leads to increase in Mooney viscosity, tensile strength, wear resistance property, hysteresis energy loss and heat build-up in rubber compound. Li et al. [15] showed that carbon black with different structure properties provides different modulus, hardness, tensile strength, and heat build-up property.

Carbon black aggregate and aggregate size distribution plays significant role on performance of rubber compounds. Stacy et al. [16] and Wang et al [17] showed that carbon black characterized with broad aggregate size distribution provides low hysteresis in rubber compounds in comparison to the narrow aggregate size distribution carbon black. Hironori et al. [18] explained that while carbon black is characterized with broad aggregate size distribution, leads to higher inter-aggregate distance in rubber matrix and consequently results in lower hysteresis loss. Pattern of aggregate size distribution also effects the physical property of rubber compound as demonstrated by Diehl et al [19], where he showed that carbon black with narrow aggregate size distribution results in superior abrasion resistance performance in rubber compounds.

Oxidation of carbon black causes destruction of surface morphology of carbon black in term of change in crystallinity, generation of porosity, change in surface area etc and it could further lead to change of functional groups on carbon black surface [20]. Hence on oxidation of carbon black its performance efficiency towards rubber compound changes drastically based on the method and extent of oxidation.

Carbon black surface is characterized with surface functional groups which is known as surface activity of carbon black. Surface activity can be reasonably defined as the number of active sites in a given weight of carbon black. Surface functional groups are available for bonding to rubber molecules based on the chemical nature of rubber molecules. It is recognized that carbon black with a high amount of surface activity provide higher reinforcement to rubber [21].

Herd et al. [8] functionalized carbon black by using ozone, peroxide, amine treatment and studied the effect of such functionalized carbon black with functionalized rubber system where the rubber molecules are functionalized along the polymer chains. It has been shown the functionalization of carbon black with ozone, peroxide, and amine the hysteresis energy loss, abrasion loss of rubber compounds was reduced substantially in the functionalized rubber system.

Chapter-3: Materials and Methods

3.1 Materials

The raw materials used for the present study were collected from different sources of India and the other nations having standard specifications. The different raw materials used for the research are shown in the Table 1. Carbon black used for the present research were collected from PCBL Limited, India and the same are either N300 series black or N200 series or equivalent to N300 or N200 series black because these series carbon black are commonly used in different tyre tread compounds.

Table-1: Materials and suppliers

Materials	Suppliers
Styrene butadiene rubber (SBR1712)	Lanxess, Germany
Poly butadiene rubber (BR)	Reliance Industries Limited, India
Solution styrene butadiene rubber (SSBR)	Zeon Corporation, Japan
Zinc oxide	Mittal Pigment Private Ltd, India
Micro crystalline (M.C.) wax	Repsol Chemicals, India
Stearic acid	VVF Ltd, Mumbai, India.
N-1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (6PPD)	National Organic Chemical Industry Limited, India
N-Cyclohexyl-2-benzothiazole sulfenamide (CBS)	National Organic Chemical Industry Limited, India
Sulfur	Jaishil Chemical Industry, India
Benzyl tri ethyl ammonium chloride	Sigma Aldrich, Germany
Different grades of Carbon Black	PCBL Limited, India

3.2 Rubber compounding

Mixing of rubber compound was carried out by Laboratory Banbury (Model: BB2, M/S: Kobelco, Japan) and followed by two roll mill mixing machine (SMX. LAB.613.ASTM, Santosh Machinary Pvt Ltd, India). The mixing of the rubber compounds was done 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 where rubber is mixed with carbon black and chemical except curatives. In the final stage of the mixing, the curatives were mixed with the masterbatch compound after a maturation time of minimum 12 hours. In this mixing stage, the Banbury operates at 45 rpm rotor speed at around 100ºC temperature for 3 minutes. The dumped compounds were processed on the two-roll mill to perform the sheeting of rubber compound for both masterbatch compound as well as final batch compound.

3.3 Testing and characterization

Testing and characterization of carbon black and rubber compound were carried out according to standard test method and the details of the same are shown in Table 2.

Table 2: Testing and characterization.

Test parameters	Equipment	Test method/ Remarks
Nitrogen surface area	Brunauer-Emmett-Teller (BET), Anton Par, USA	ASTM D6556
Oil absorption number	Absorptometer, Hi-Tech, Germany	ASTM D2414
Iodine adsorption number	Titration method	ASTM D1510
Aggregate size distribution	BI-DCP Particle Size Analyzer, Brookhaven Instruments, USA	ISO15825
Curing characteristics	ODR 2000, Alpha Technology, USA	Measured at 160^{o}C
Mooney Viscosity	Mooney viscometer (MV2000), Alpha Technology, USA	Represented by ML (1+4) at 100^{o}C
Payne effect	Rubber Process Analyzer (Premier RPA), Alpha Technology, USA.	at 70^{o}C and 10 Hz frequency
Tensile properties	Universal Tensile machine (Model: 3366), Instron, USA	ASTM D412
Abrasion resistance	DIN Abrasion test equipment.	As per ASTM D5963 method
Dynamic mechanical analysis	Dynamic Mechanical Analysis (DMA 50), Metravib, France	Measure loss tangent value
X-Ray Diffraction	XRD equipment, D8 Advance, Manufacturer: Bruker AXS, Germany	Diffraction angle (2θ) value in the range of 3^{o} - 60^{o}

Chapter-4: Modification of tyre tread compound by optimized aggregate size and aggregate size distribution of carbon black.

4.1 Introduction:

In this chapter the pattern of carbon black aggregate size distribution and its effect on tyre tread compound has been discussed. The aggregate size distribution of carbon black is represented by full width half maximum (FWHM) value, which is defined as the width of distribution graph at the 50% height of distribution graph as shown in Figure-2. Higher value of FWHM signifies the broad aggregate size distribution while lower value of the same represents narrow aggregate size distribution [22].

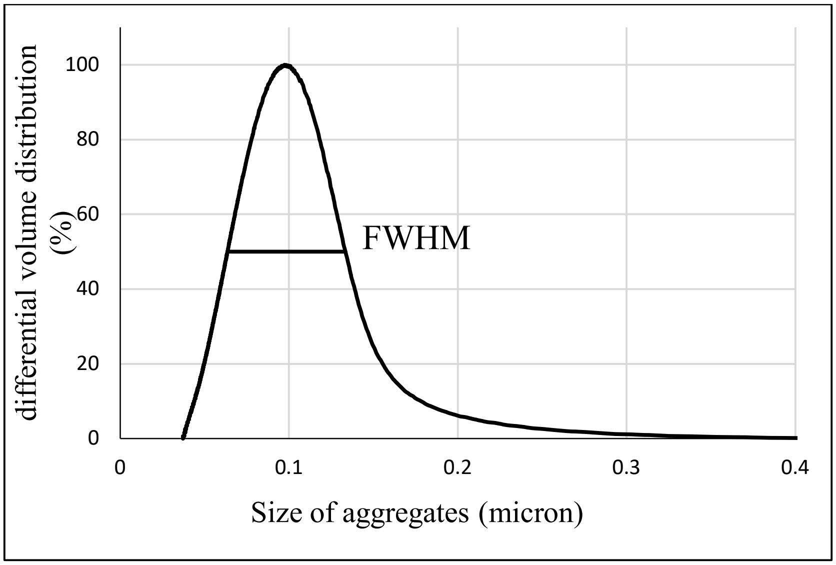


Figure-2: Typical aggregate size distribution of carbon black

The effects of carbon black having different FWHM, and different pattern of aggregate size distribution were studied for tyre tread compound. The experimental carbon black was designed with different FWHM value as shown in Table 3, where Sx-1 is the control carbon black, and Sx-2, Sx-3 are the experimental carbon black.

Table 3: Carbon Black Properties

Parameters	Unit	Sx-1	Sx-2	Sx-3
Iodine Adsorption Number	g/kg	82	82.6	81
OAN	ml/100 g	103.5	101.5	142.4
COAN	ml/100 gm	84	83.2	103
NSA	m^2/g	72	70.5	70.5
FWHM	nm	70	92	104

Carbon black consisting of highest extent of larger size aggregates could lead to different effect on tyre tread compounds compared to the same having relatively lower extent of the larger size aggregates. The extent of bigger size aggregate in carbon black is represented by ‘d90’ of the aggregate size distribution parameters. The d90 value refers that 90% aggregates lie below the ‘d90’ value and rest 10% aggregates have size above the ‘d90’ value. For an example, a carbon black with ‘d90’ value of ‘N’ signifies that 10% of aggregates have diameter greater than ‘N’.

In this chapter the effects of carbon black with different 'd90' value were studied in SBR-BR rubber system having 50 phr of filler loading. The different extent of bigger size aggregates in the different experimental carbon black were achieved by incorporating bigger size carbon black aggregates into the ASTM grade carbon black and the 'd90' value of the corresponding carbon black was measured by the aggregate size distribution analysis.

4.2 Hysteresis energy loss:

The hysteresis energy loss of the compound as represented by the loss tangent value was measured by dynamic mechanical analysis and the same for different rubber compound are shown in Figure 3. It is seen that carbon black, Sx-3, characterized with broad aggregate size distribution (high FWHM value) shows significantly lower loss tangent value compared to the other carbon black. Sx-3 carbon black shows around 20% reduction of loss tangent value compared to the narrowest carbon black Sx-1.

Carbon black aggregates with broad aggregates size distribution has tendency of having higher inter-aggregates distance in the rubber matrix, hence, Sx-3 carbon black with broad aggregate size distribution results in highest separation among the aggregate in the rubber matrix [10]. Due to this reason lower filler-filler interaction is observed in the rubber compound causing lower hysteresis losses in the rubber compound. The loss tangent value of the rubber compound was measured at 60ºC, and it represents the rolling resistance of tyre tread compound. Hence tyre tread compound comprising broader aggregate size distribution results lower rolling resistance property compared to carbon black with narrow aggregate size distribution.

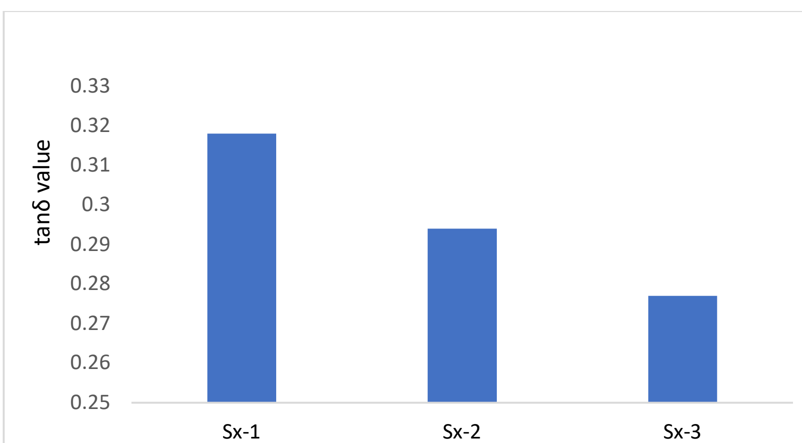
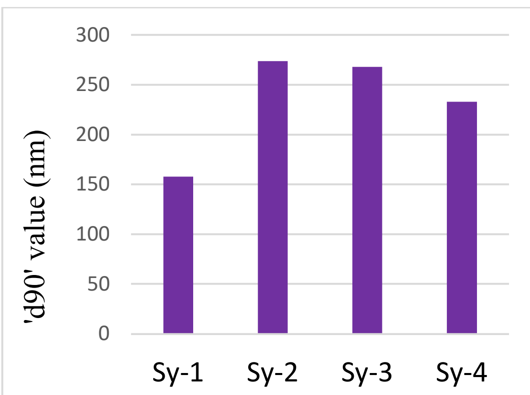


Figure-3: Loss tangent value-, measure of hysteresis loss

In the second set of carbon black the control carbon black (Sy-1) is characterized with ‘d90’ value of 158 nm as shown in Figure-4, which describes that, Sy-1 carbon black is associated with 90% aggregates having diameter up to 158 nm and 10% aggregates have diameter above 158nm. Hence carbon black with high value of ‘d90’ demonstrates that presence high extent of bigger size aggregates in the system. Thus, it is to be said that carbon black Sy-2 and Sy-3 are characterized with higher extent of bigger size aggregates compared to Sy-1 as well as Sy-4 grade carbon black.

The hysteresis loss of rubber compound, as represented by tanδ value and measured at 60°C temperature are shown in Figure 5 and it is observed that carbon black with higher extent of bigger size aggregates provides lower hysteresis loss in comparison with carbon black possessing lower extent of bigger size aggregates.



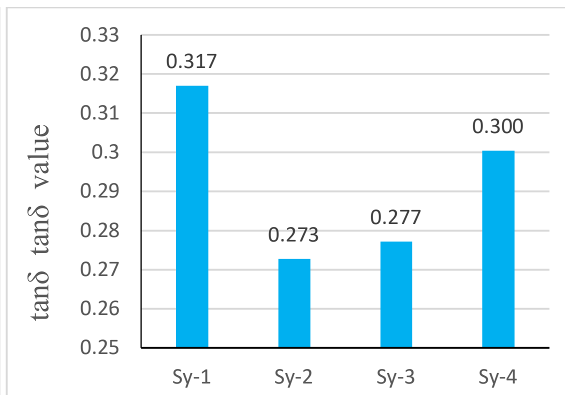


Figure-4: ‘d90’ value of carbon black

Figure-5: Tan delta value (60°C)

4.3 Summary

The carbon black developed for the present study are characterized with broad aggregate size distribution as well as presence of bigger size aggregates. It is seen that carbon black characterized with broad aggregate size distribution with high FWHM value results lower hysteresis energy loss in the rubber compounds. The experiments further concludes that carbon black characterized with higher extent of bigger size aggregates benefits appreciably towards the lowering of hysteresis energy loss of rubber compound. The hysteresis energy loss measured at 60°C temperature, which represents the rolling resistance of tyre tread compounds.

Hence, carbon black characterized with high FWHM value and higher extent of bigger size aggregates are recommended for low rolling resistance tyre tread compound.

Chapter-5: Correlation of carbon black parameters with rubber compound properties for development of improved tyre tread compounds

5.1 Introduction:

Apart from the full width half maximum (FWHM) value the aggregate size distribution of carbon black is characterized with different distribution parameters, such as mean aggregate size ($\bar{X}$), mode of the aggregate size distribution, 'dn' values etc. The mean aggregate size is the arithmetic average size of different aggregates presents in carbon black while mode value is described as the maximum occurrence of aggregate size. The 'dn' is defined as the limit of the aggregate size, which occupy 'n%' of total aggregate volume in the carbon black. [23].

5.2 Carbon Black Properties

The carbon black selected for the present study were characterized with different morphological parameters based on surface area, structure and the aggregate size as shown in Table 4. The structure property of carbon black is measured by oil absorption number (OAN), and it is varied from 110 to 134 ml/100g.

Table-4: Carbon black properties, identified as HP01, HP02, HP03, HP,04, HP05 and HP06

		HP01	**HP02**	**HP03**	**HP04**	**HP05**	**HP06**	**HP07**
OAN	ml/100 g	113.8	114.4	113.9	124	123.5	134	110
NSA	m^2/g	112.3	111.5	114.6	113.3	112.	116.0	112.3
Mean	nm	82	87	103	100	106	105	102
Mode	nm	79	74	98	94	91	104	100
FWHM	nm	62	67	69	66	77	90	67
d10	nm	51	50	64	63	61	59	65

The d10 value of HP02 grade carbon black is 50 nm and the same for HP07 carbon black is 65 nm, the definition of 'dn' value demonstrates that for the HP02 grade carbon black 10% of aggregate having diameter of maximum 50 nm while for HP07 grade carbon black to achieve 10% of aggregate the diameter of aggregate will reach to 65 nm. Hence HP02 carbon black consists of larger extent of smaller size aggregate than HP07 carbon black. Rubber compounding of the carbon black are carried out based on the formulation SBR-BR rubber system with carbon black loading of 60 phr.

5.3 Payne Effect of Rubber Compound and relation with Aggregate size

The Payne effect is the measure of filler-filler interaction in rubber compound, higher the filler-filler interaction results in higher Payne effect [8-9, 24]. In this study Payne effect is correlated with d10 valueazs of corresponding carbon black and is shown in Figure 6. It is visible that Payne effect decreases with increasing of d10 value with a significant 'R-square' value of 0.93 at a confidence level of 95%, which demonstrates that carbon black with higher extent of lower size aggregates leads to higher Payne effect in the rubber compound.

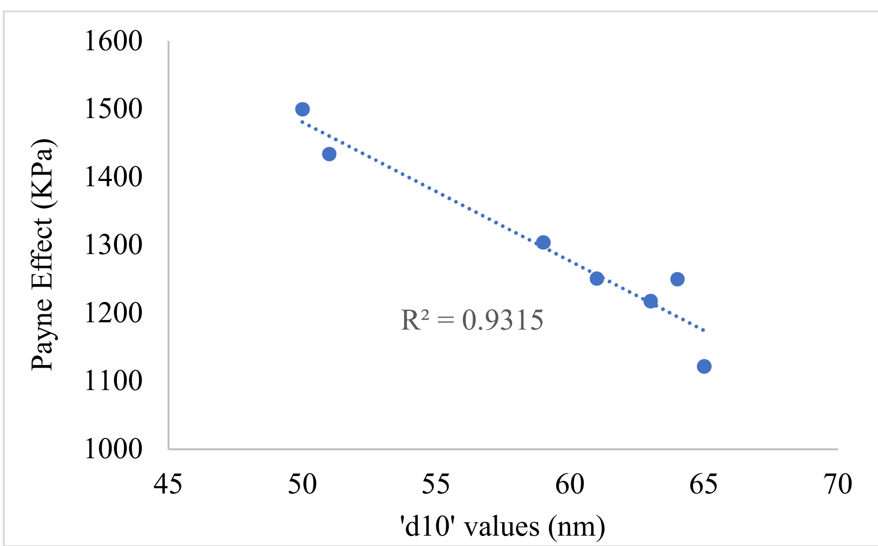


Figure-6: Trend of Payne effect of rubber compound with d10 value of carbon black

5.4 Rolling resistance of rubber compound:

Rolling resistance of tyre tread compound is represented by loss tangent value, measured at 60ºC [25-26]. In this study, the loss tangent value of the same is correlated with FWHM value in combination with the mean aggregate size value of the carbon black. To explore the combined effect of mean value and FWHM value an 'aggregate size distribution co-efficient' parameter (A) has been introduced, which is a function of FWHM and mean value ($\bar{X}$) of carbon black. Aggregate size distribution co-efficient' parameter is defined by an empirical formula as shown in equation (1), where 'n', ' a' and 'b' are the integers.

$$A = \sqrt[n]{a\,\mathrm{FWHM}^2 + b\,(\bar{X})^2} \qquad (1)$$

The value of 'A' changes with the change in 'a', 'b' and 'n' values however for a defined value of the same 'A' value is dependent on FWHM and mean value of individual carbon black.

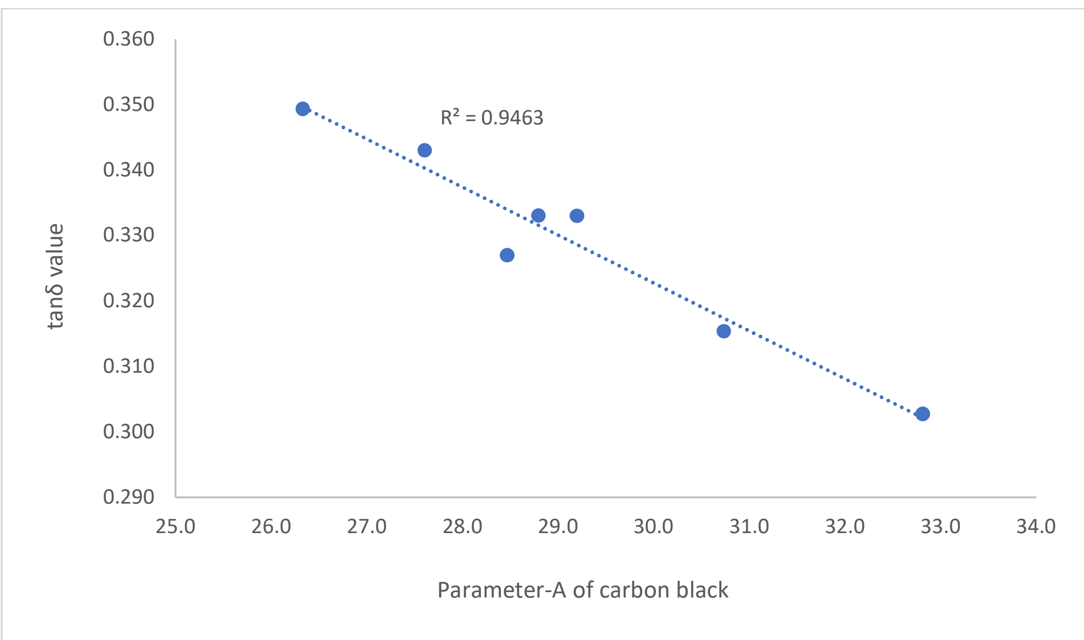


Figure-7: Corelation of loss tangent value with parameter 'A' where n=3, a=4, b=1.

The tanδ value of the rubber compounds as measured by dynamic mechanical analysis is correlated with 'A' value of respective carbon black as shown in Figure 7. It is seen there is a decreasing trend of tanδ values with the 'A' values, which indicates higher 'A' value of carbon black results in low hysteresis property of rubber compound. The correlation factor (R square value) of the graph signifies there is strong relationship of tanδ value of rubber compound with 'A' value of corresponding carbon black, though, the correlation varies with different value of coefficients and indices a, b and n.

5.5 Summary:

The different aggregate size distribution parameters of carbon black such as mean, mode, FWHM, 'dn' etc have significant influence in the rubber compound properties. It is seen carbon black with highest concentration of lower size aggregate, as described by lower d10 value, has increased propensity of filler-filler interaction, and consequently leads to higher Payne effect. It has been established that for carbon black with similar nitrogen surface area the hysteresis property of rubber compound is reduced with increasing 'aggregate size distribution co-efficient' parameter, i.e., with increase of mean aggregate size and FWHM value of carbon black.

Chapter-6: Simultaneous changes on carbon black surface and structural morphology to improve tyre tread compounds.

6.1 Introduction

High-resolution transmission electron microscopy of carbon black morphology described that the basic nanoparticle of carbon black is associated with small graphene flakes layers which are basically arranged towards the surface of particles and gradually diminishing towards the centre [27-28]. Carbon black may undergo several changes on surface morphology on the oxidation of the same and there is a possibility of layer broken down takes place, which could lead to a disordered graphitic structure of carbon black morphology and can cause porosity generation on the surface of carbon black [29].

Moreover, oxidation leads to generation of surface functional groups which covers a part of carbon black surface and restrict the adsorption of nitrogen molecules on carbon black surface during the measurement of carbon black surface area thereby resulting in lower surface area measurement than the expected surface area value.

6.2 Oxidation of carbon black:

Oxidation of carbon black is carried out in Laboratory oxidizer equipment where N330 grade of carbon is oxidized to investigate change in carbon black characteristics. Oxidized carbon black vis -a-vis non oxidized control carbon black is characterized for basic carbon black properties and effect of the same were investigated in tyre tread compound.

6.3 X-Ray Diffraction (XRD) Analysis:

The XRD patterns of oxidized carbon black and non-oxidized carbon black samples are carried out at ambient temperature and from 5 to 90^o (2θ) at a rate of 5^o per minutes and the intensity of diffraction against 2θ is shown in Figure 8. The diffraction pattern of CB shows two broad peaks corresponding to the (002) and (100) planes of the graphite structure respectively, implying that carbon black is an amorphous carbon material with small regions of crystallinity due to graphitic crystallites [30-31]. The intensity of the peak determines the nature of crystallinity, higher intensity of the peak signifies higher extent of crystallinity as the higher

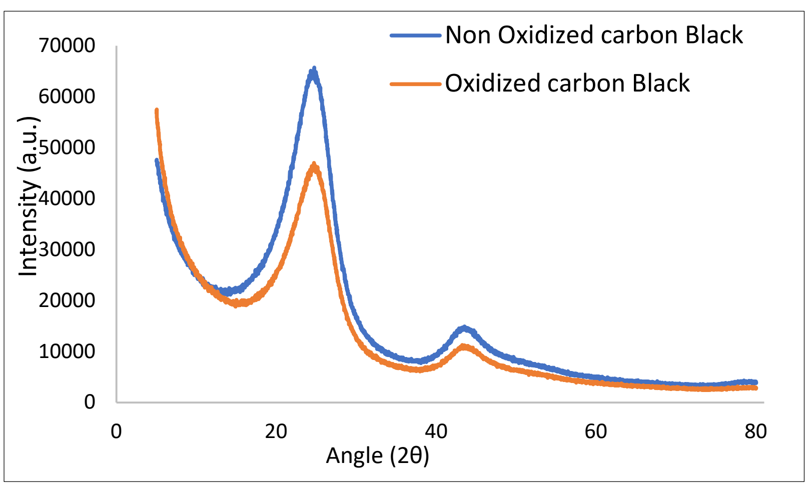


Figure-8: X-Ray diffraction of carbon black

peak is due to the maximum reflections of X-rays from the crystalline planes. The intensity of diffraction corresponding to (002) plane of oxidized carbon black is significantly low as compared to the same for non-oxidized control carbon black. On oxidation of carbon black by ozone treatment, distortion of graphitic plates takes place, which causes reduction of carbon black surface crystallinity and reduction of XRD spectrum peak height.

6.4 Rheological Properties of Rubber Compounds:

The control compound is identified as SS0, and the experimental compound is identified as SS30. On oxidation of carbon black, considerable amount of porosity are generated on carbon black surface as well- as distortion of graphitic layers also takes place, which increase the total surface area of carbon black and leads to higher physical adsorption of rubber molecules on carbon black surface. These phenomena result loss of rubber molecular mobility increase the viscosity of rubber compound. In the rheological study the minimum torque as measured by oscillating disc rheometer and Mooney viscosity expressed as ML(1+4), are the measure of viscosity of rubber compounds. It is seen in Figure 9 and Figure 10, that rubber compound comprising oxidized carbon black result significantly high Mooney viscosity and 'ML' value compared to rubber compound based on control carbon black.

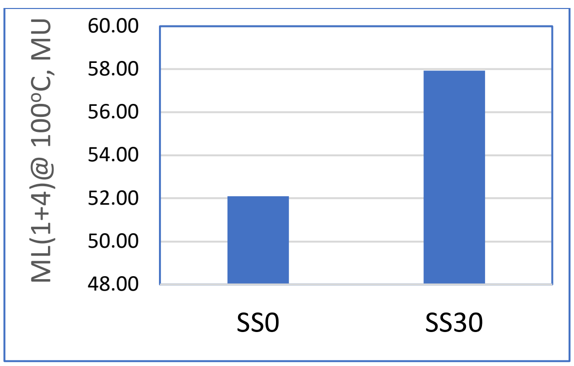


Figure-9: Mooney Viscosity

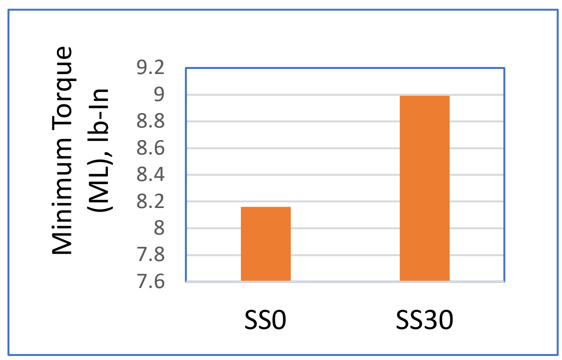


Figure-10: Minimum torque value

6.5 Physical Properties:

Oxidized carbon black with increased effective surface area and generation of pores on carbon black surface, in which rubber molecule chains penetrate, would lead to increased tensile strength of rubber compounds. Due to penetration of rubber molecules into carbon black pores and interaction of rubber molecules with disordered carbon black morphology, the rigidity of rubber molecules is increased. As a result the modulus of rubber compound is also increased as shown in Table-5. The oxidized carbon black result in higher tensile strength and higher modulus as compared to the control carbon black.

Table-5: Physical property of the rubber compound

	Unit	SS0	SS30
Tensile strength	MPa	13.74	15.53
Modulus at 200% elongation	MPa	8.46	9.41
Elongation at break	%	278	299

6.6 Summary:

Oxidation of carbon black increases the carbon black roughness by disordering the crystalline planes and it causes porosity on carbon black. Due to the same, oxidized carbon black increases Mooney viscosity, tensile strength and modulus of rubber compounds and enhances the durability of tyre tread compounds.

Chapter-7: Improvement of tyre tread compounds by treatment of carbon black with benzyl tri-ethyl ammonium chloride (BTEAC)

7.1 Introduction

In this section of the research, an attempt has been made to increase the dispersion of carbon black in rubber system by enhancing the affinity of carbon black towards the rubber molecules. To carry out the same, surface chemistry of carbon black was modified by treatment with benzyl tri-ethyl ammonium chloride (BTEAC), which is likely to functionalize carbon black surface by reacting with carbon black surface functional groups such as ketone, carboxylic acid, lactone etc. Here, influences of BTEAC treated carbon black are studied in SBR-BR based rubber system in comparison with non-treated control carbon black to investigate filler-polymer interaction, dynamic mechanical analysis etc.

7.2 Carbon black sample preparation

Carbon black was mixed with BTEAC having concentration of 0.5%, 1.0 %, 1.5% by weight with respect to carbon black (N330). The mixture was refluxed by heating at 100ºC for 60 minutes in presence of excess distilled water and followed by cooling the mixture to room temperature and finally drying of the sample. Rubber compounding of the carbon black are carried out based on a SSBR-BR rubber system. The rubber compound made with above carbon black are SS0, SS0.5, SS1.0, SS1.5, where the prefix denotes the concentration of BTEAC in the carbon black.

7.3 Rubber-Process Analysis and Measurement of Payne Effect

It is seen that experimental compounds, comprising BTEAC treated carbon black, have lower Payne effect in comparison with corresponding control compound having non-treated carbon black. Hence, it can be interfered that, by treatment with BTEAC the compatibility of carbon black with rubber molecules is increased, which results in increased filler-polymer interaction and reduced filler-filler interaction. The extent of Payne effect reduction for the experimental compounds suggests that the compatibility of carbon black with rubber molecules is more significant when carbon black is treated with 1% of BTEAC.

Table-6: Payne effect of rubber compounds

	Unit	**SS0**	**SS0.5**	**SS1.0**	**SS1.5**
$G'_{0.1}$	Pa	878	820	694	716
G'_{100}	Pa	115	113	108	112
Payne Effect=$G'_{0.1}$ - G'_{100}	Pa	763	707	586	604

7.4 Rheological Characteristics

On treatment of carbon black with BTEAC lower values of Ts2, Tc50, Tc90 are obtained for the experimental rubber compounds, compared to the control compound as shown in Table 7**.** Lower values of Ts2, Tc50, Tc90 increase the cure rate of rubber compounds, which indicates reduction of curing cycle is achieved on treatment of carbon black with BTEAC.

Table-7: Rheological properties of rubber compounds

	SS0	SS0.5	SS1.0	SS1.5
ML	6.5	6.3	6.1	5.8
MH	33.0	32.5	31.0	30.4
Delta Torque (MH-ML)	26.5	26.2	24.9	24.6
Ts2	2.28	1.37	1.08	0.97
Tc50	5.41	3.47	2.70	2.41
Tc90	6.00	4.44	3.61	3.36
Cure rate index [100/(Tc90-Ts2)]	26.88	32.55	39.57	41.92

7.5 Dynamic Mechanical Analysis:

Dynamic mechanical characteristics of rubber compounds, as measured at 60°C, are shown in Table 8. It is seen that loss tangent values of rubber compounds made using BTEAC treated carbon black show significant reduction with respect to the control compound. The maximum reduction of loss tangent value appears with 1.0% and 1.5% BTEAC treatment of carbon black.

Table-8: Dynamic properties of rubber compounds

	Unit	SS0	SS0.5	SS1.0	SS1.5
Storage Modulus	MPa	5.83	5.62	5.07	4.92
Loss Modulus	MPa	1.04	0.96	0.80	0.74
Loss Tangent (tanδ) value	-	0.178	0.171	0.157	0.151

7.6 Summary

On treatment of carbon black with BTEAC, the compatibility of carbon black with rubber molecules is increased. As a result, the filler-polymer interaction is increased, which is demonstrated by the reduction of Payne effect. Hysteresis energy loss of rubber compound is greatly influenced by BTEAC treated carbon black and it is observed a significant reduction of loss tangent value for the rubber compounds consisting of BTEAC treated carbon black as compared to the control compound and which demonstrates that treatment of carbon black with BTEAC benefits towards low rolling resistance tyre tread compounds.

Chapter-8: Conclusion

Carbon black is the most common filler used in tyre tread applications. The modification of carbon black leads to improvement of tyre tread compound properties. It is seen that carbon black morphology with broader aggregate size distribution provides significant impact on reduction of rolling resistance for the tyre tread. A perfect design of carbon black morphology with aggregate size, aggregate size distribution, mean aggregate size and structure property are the key to control the rolling resistance property of carbon black.

FWHM value of carbon black in combination with mean value significantly determines rolling resistance property of tyre tread compound properties. Distortion of surface crystallinity, generation of porosity and surface functionality of carbon black by oxidation of same, has substantial impact on tyre tread compound properties. It has been observed that on modification of carbon black by oxidation the processability, Payne effect, physical property and rolling resistance property of rubber compounds were improved. Carbon black on functionalization with BTEAC, leads to low Payne effect, low rolling resistance for tyre tread compound.

From this research, it is seen that the modification of carbon black can cause a reduction of rolling resistance of tyre tread compound up to 20%. Reduction of rolling resistance for tyre tread compound leads to low fuel consumption of the vehicle. Further, enhancement of abrasion resistance property and mechanical strength of tyre tread compound was also achieved by modifying carbon black. Thus, by modifying carbon black the durability of tyre tread compound can be enhanced and consequently the durability of tyre is increased, which benefits towards the sustainability of tyre technology.

In general, it is demonstrated that on reduction of rolling resistance of tyre by 10%, a reduction of CO_2 emission by 2% is possible for different vehicles. Thus, by modifying the carbon black characteristics there a light of lowering of CO_2 emission by automotive industry appears in the horizon.

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