CHAPTER-7:

IMPROVEMENT OF TYRE TREAD COMPOUNDS BY TREATMENT OF CARBON BLACK WITH BENZYL TRI-ETHYL AMMONIUM CHLORIDE (BTEAC)

7.1 Introduction

Surface chemistry is a unique feature of carbon black it is associated with presence of various types of functional groups such as carboxylic acids, lactone, ketone, hydroxyl, different sulphur, and nitrogen containing groups etc., The presence of surface functional groups on carbon black benefits in interaction and or reaction of carbon black with the rubber molecules during the compounding [1-2]. Carbon black plays a fundamental role in dispersion of filler, filler-filler interaction, filler-polymer interaction etc. in rubber matrix in line with the surface area, structure, and aggregates size distribution parameters. The intensity of interaction depends on the chemical structure of rubber molecules and extent of surface functional groups presents on carbon black surface.

By modification on chemical nature of rubber molecules and surface chemistry of carbon black, the filler dispersion, filler-polymer interaction, and filler-filler interaction in the rubber matrix have been improved. Wu et al. [3] modified rubber molecules with dimethyl amino multi functionalization to increase the compatibility of rubber molecules with carbon black and observed improvement of carbon black dispersion in the modified rubber matrix, and consequently it caused enhanced tensile strength, elongation at break, and skid resistance properties of rubber compounds. Kirino [4] modified carbon black surface chemistry with a silane compound having an amino group and used the same in a rubber blend system consisting of a second rubber modified with maleic anhydride and showed that the combined modification resulted in improvement of carbon black dispersion in the rubber blend system and consequently caused enhancement of abrasion resistance property and reduction of heat buildup property. Herd et al. [5] functionalized carbon black by using ozone, peroxide, amine treatment and studied the effect of those functionalized carbon black with functionalized rubber system where the rubber molecules are functionalized along the polymer chains and the same led to reduction of hysteresis energy loss, enhancement of abrasion loss of rubber compounds. Thus, it has been established functionalization of carbon black or rubber or both are the potential ways of improving rubber compound properties by enhancing the filler-polymer interactions, reducing the filler-filler interaction, and improving the filler dispersion in rubber matrix.

In this study, an attempt has been made to increase the dispersion of carbon black in rubber matrix, to reduce the hysteresis loss, to improve the mechanical strength and to optimize magic triangle properties of tyre tread compounds by enhancing the affinity of carbon black with the rubber molecules. To carry out the same, surface chemistry of carbon black was modified by treatment with benzyl try ethyl ammonium chloride (BTEAC), which is likely to functionalize carbon black surface by reacting with carbon black surface functional groups.

7.2 Carbon Black Functionalization with Benzyl Tri Ethyl Ammonium Chloride (BTEAC) and its Properties

7.2.1 Treatment of Carbon Black by BTEAC Treatment

In this study ASTM grade carbon black, N330 was functionalized by benzyl try ethyl ammonium chloride having concentration of 0.5 wt%, 1.0 wt% and 1.5 wt% with respect to the carbon black. The functionalized carbon black has been characterized by different carbon black properties and compared with corresponding control non-treated carbon black. BTEAC mixed with carbon black and the mixture was refluxed by heating at 100°C for 60 minutes in presence of excess distilled water and followed by cooling to room temperature. The mixture was washed repeatedly by distilled water in a Gooch crucible for removal of un-reacted BTEAC and then it was dried in oven at 125°C for 3 to 4 hours until complete removal of moisture. The modified carbon black was collected inside desiccator for the further study. A blank run was also carried out by taking the same carbon black sample and refluxed it as above to have identical condition without adding BTEAC. The treatment of carbon black with BTEAC is assumed to cause functionalization by reacting with benzyl, ethyl groups and the amine derivate of BTEAC with the functional groups of carbon black surface. A schematic representation of carbon black functionalization is shown in

Fig-7.1, where the different oxygen containing groups of carbon black attached with functional groups of BTEAC.

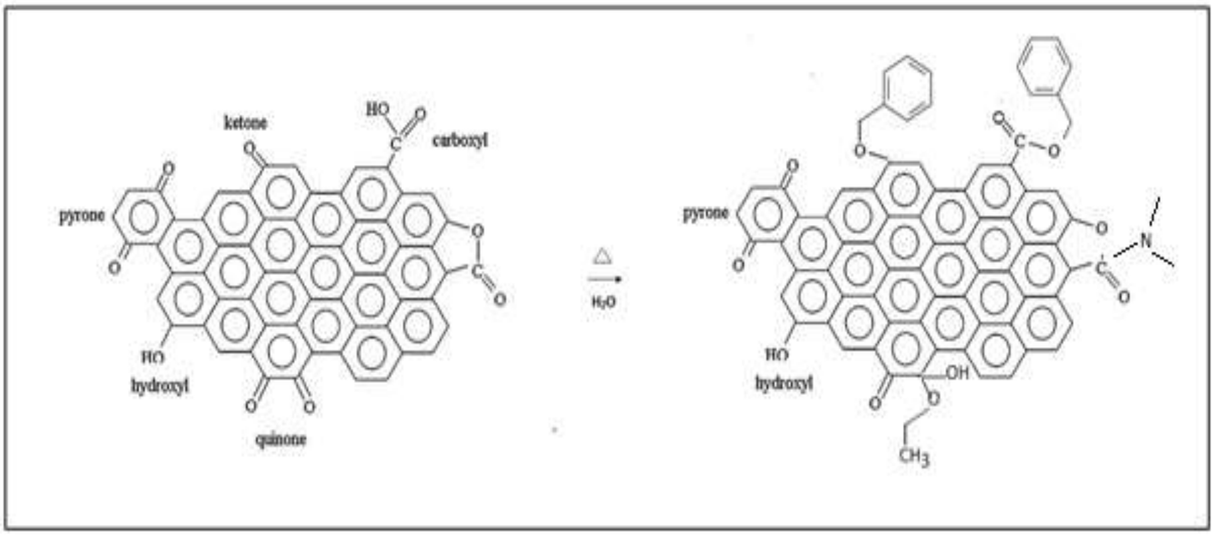

Fig-7.1: Schematic representative of reaction mechanism between benzyl tri ethyl ammonium chloride and carbon black

7.2.2 Carbon Black Properties on BTEAC Treatment

On functionalization of carbon black with BTEAC, the ethyl, benzyl and amine derivative groups are likely to get attached on carbon black surface. It has been described that surface area of carbon black was represented by IAN as well as by NSA measurement. The surface area of control carbon black and BTEAC treated carbon black are shown in Table-7.1, where it has been seen BTEAC treated carbon black provides lower IAN as compared to non-treated control carbon black, whereas NSA of BTEAC treated carbon black is marginally affected and provides similar range of NSA value in comparison to control carbon black.

Functionalization of carbon black leads to formation of bulky organics groups on carbon black surface, which causes restriction for the penetration of iodine molecules to adsorb on carbon black surface during the IAN measurement, as a result less iodine molecules get adsorbed on carbon black surface, resulting less IAN value. This becomes more intense for increased concentration of BTEAC treated carbon black. However, while measuring nitrogen surface area the adsorption of nitrogen molecules is hardly restricted by surface functional groups due to smaller size of nitrogen molecules, as a result on BTEAC treatment NSA value of experimental carbon black is less affected compared to IAN. The structure property as measured by OAN and COAN has least affected by the chemical treatment and it shows a marginal reduction of the same.

In the measurement of aggregate size distribution, the carbon black is sonicated at very high frequency for 20 minutes to segregate the aggregates from the agglomerates. In the aggregate size distribution measurement, the attached functional groups are not accounted due to very smaller size of functional groups in comparison to the aggregate size. The aggregate size distribution parameters of carbon black are shown in Table-7.1 which indicates aggregate size and aggregate size distribution remain intact for BTEAC treated carbon black.

Aggregate size distribution of carbon black was carried out by using BI-DCP, and it is seen on treatment of carbon black with BTEAC the aggregate size distribution of same does not change and the mean, mode and FWHM values of the treated carbon black remain similar to that of non-treated carbon black with similar pattern of aggregate size distribution as shown in Fig-7.2.

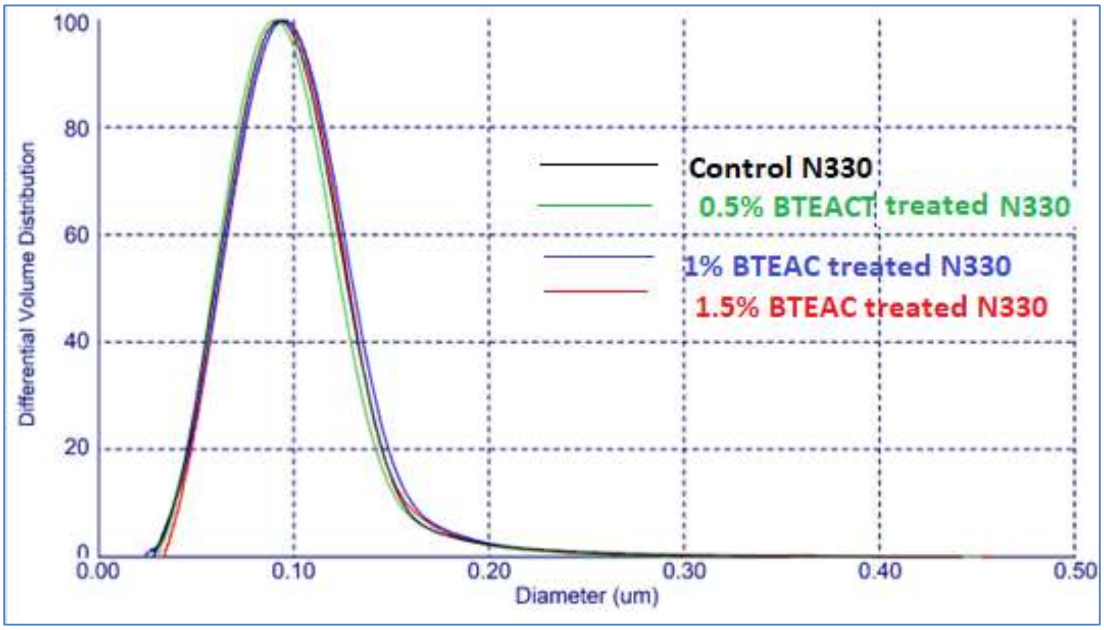

Fig-7.2: *Aggregate size distribution of carbon black on BTEAC treatment and comparison with control carbon black.*

Table7.1: Properties of Carbon black

	UoM	N330 control	0.5% Treated 330	1.0% Treated N330	1.5% Treated N330
IAN	g/Kg	85.0	81.5	78.3	76.4
NSA	m^2/g	80.1	78.8	78.1	77.5
OAN	ml/100g	101.1	98.2	97	95.5
COAN	ml/100g	85.3	84.1	85.8	83.2
pH	-	6.1	7.2	7.8	8.3
Mean	nm	101	100	98	102
Mode	nm	94	94	92	93
FWHM	nm	67	69	68	68

7.2.3 Thermogravimetric (TG) Analysis of Carbon Black to Estimate Functionalization

Thermogravimetric analysis of functionalized carbon black was used to investigate the extent of functionalization of carbon black surface due to treatment with BTEAC. The TG analysis was carried out in inert atmosphere with a temperature sweep from 50°C to 800°C, and at this temperature sweep the functional groups present on carbon black would decompose, and as a result the weight of the carbon black would be lost. This was detected by TG analysis. On decomposition, the functional groups removed from carbon black as volatile organic compounds, and which is termed as volatile matter loss of carbon black [6].

It is seen, control carbon black shows a volatile content loss of 0.89 wt% on thermal treatment from 100°C to 800°C as shown in Fig-7.3. The wight loss after 100°C was considered for measurement of volatile matter loss due to decomposition of its surface functional groups, as below the same temperature, the moisture present in carbon black had evolved. On treatment with BTEAC, the carbon black possesses higher extent of functional group, which increases with increase BTEAC concentration. The TG analysis of the experimental carbon black shows a higher volatile loss compared to the control carbon black and it is seen that a maximum volatile loss of 1.54% occured with the carbon black which was functionalized with maximum concentration of BTEAC. Thus, TG analysis establishes that BTEAC treatment creates increased functional groups on carbon black surface, and which were lost while the same is thermally treated to 800°C in an inert atmosphere.

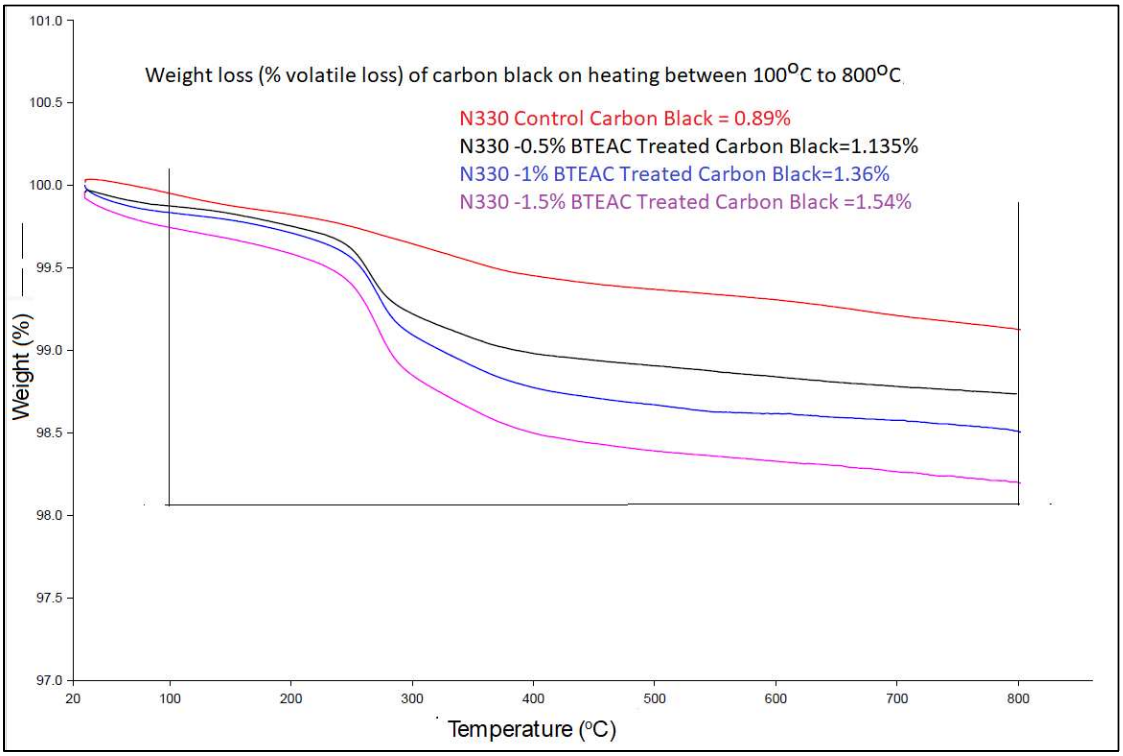

Fig-7.3: *Thermogravimetric analysis of BTEAC treated carbon black vis-à-vis non-treated carbon black.*

7.2.4 High Resolution Transmission Electron Microscopic (HRTEM) Analysis:

Transition electron microscopic analysis of carbon black were carried out to visualize and investigate the changes occurred on carbon black structural morphology and particle size upon treatment of BTEAC. HRTEM analysis was carried out for control N330 carbon black and the experimental carbon black, treated with 1% BTEAC treated carbon black to compare their structural morphology. The high-resolution transition electron microscopic images of carbon black are shown in Fig-7.4, and it signifies that structural morphology of carbon black does not change by treatment with BTEAC. The image 'A' represents the TEM of control carbon black while the image 'B' represents the same of experimental carbon black treated with 1% BTEAC and both the images observed similar fashion of structural configuration. TEM analysis was further explored to calculate the particles diameters of carbon black by particle size measurement software as shown in Fig-7.5.

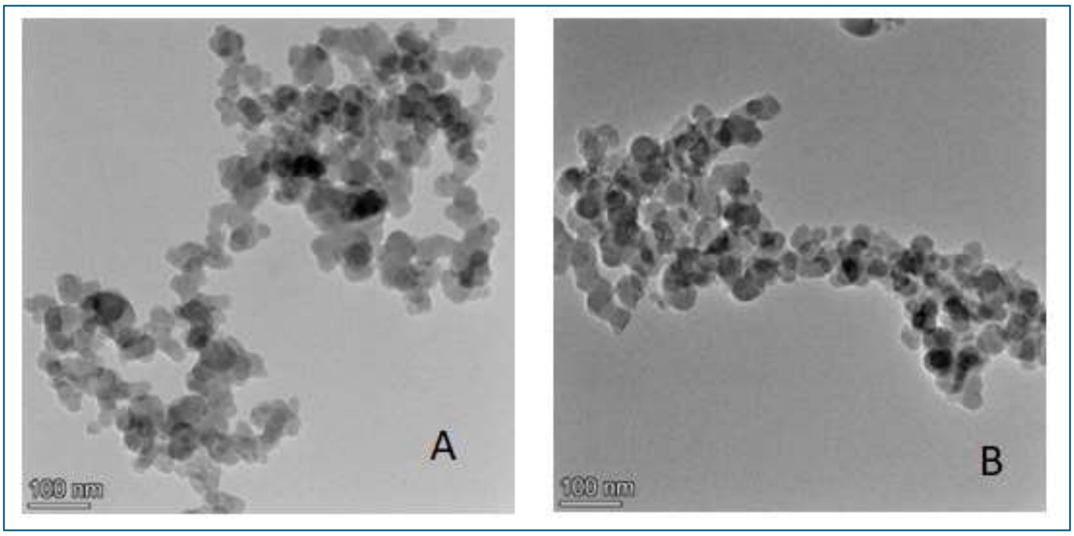

Fig-7.4: *Transmission electron microscopic analysis on aggregate and structural views of BTEAC treatment of carbon black (A) N330 Control carbon black (B) BTEAC treated N330 carbon black.*

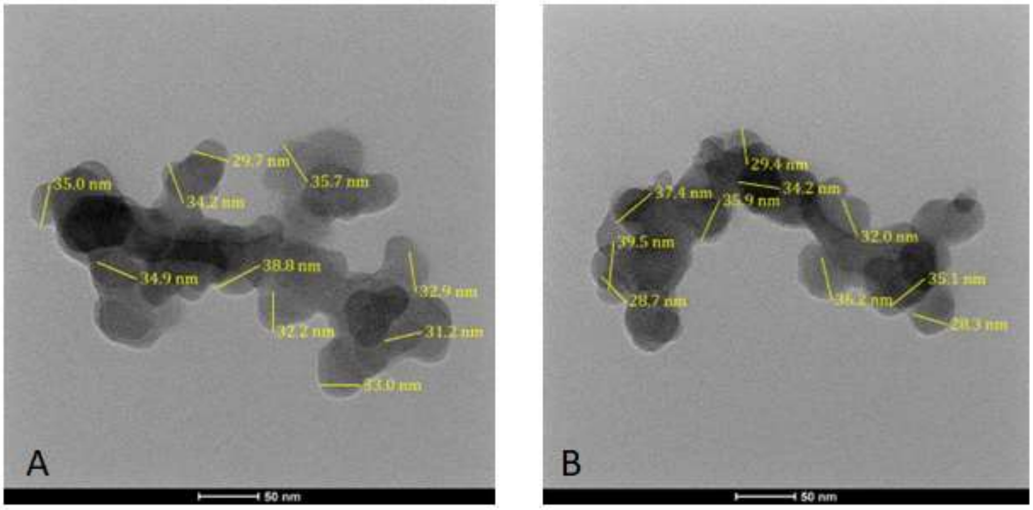

Fig-7.5: Transmission electron microscopy to visualize particle size of carbon black (A) N330 Control carbon black (B) BTEAC treated N330 carbon black.

It is seen that control N330 carbon black has particle size 29.7 nm to 38.8 nm with average particle size of 33.76 nm. Similarly, TEM study of BTEAC treated carbon black shows its particle size also ranges from 28.3 to 39.5 nm with an average particle diameter value of 33.68 nm. This indicates that on treatment of BTEAC, the structural morphology and particle size remains intact.

7.3 Effect of BTEAC Treated Carbon Black in Rubber Compound Properties

Carbon black on treatment with BTEAC changes its surface chemical nature. The modified surface is associated with enhanced functionality with benzyl groups, ethyl groups and amine derivative groups. Due to change in functionality the nature of chemical interaction of modified carbon black with different rubber molecules are supposed to alter in comparison to the non-treated carbon black,

The extent of carbon black surface functionalization depends on dose of BTEAC, and it is observed that with increased in BTEAC dose the extent of functionalization in carbon black increases, which was demonstrated by TG analysis. Hence carbon black with different concentration of BTEAC treatment leads to different extent of functionalization and which would cause a dissimilar characterization of interaction with the rubber molecules based on the chemical structure of the same. In this part of the study ASTM grade N330 has been functionalized with various concentration of BTEAC and effect of the same has been studied in tyre tread compounds.

7.3.1 Rubber Compounding

To investigate the effect of BTEAC treated carbon black, two type of tyre tread compounds have been selected based on solution styrene butadiene rubber and emulsion styrene butadiene rubber with combination of butadiene rubber. The detail rubber formulations are shown in Table-7.2 The control compound for each rubber system is characterized with non-treated N330 grade carbon black while the experimental compounds are characterized by functionalized carbon black as treated with different percentage of BTEAC. The mixing and compounding were carried out in two stage of mixing using laboratory Banbury and followed by two roll mixing mill as described in Chapter-3.

Table-7.2: Rubber compound formulation

	SB0	SB0.5	SB1.0	SB1.5	SS0	SS0.5	SS1.0	SS1.5
SSBR	0	0	0	0	80	80	80	80
SBR1712	110	110	110	110	0	0	0	0
BR	20	20	20	20	20	20	20	20
N330 carbon black	50	0	0	0	50	0	0	0
0.5% BTEAC Treated N330 carbon black	0	50	0	0	0	50	0	0
1.0 % BTEAC Treated N330 carbon black	0	0	50	0	0	0	50	0
1.5% BTEAC Treated N330 carbon black	0	0	0	50	0	0	0	50
Zinc Oxide	5	5	5	5	5	5	5	5
Stearic Acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
TDAE Oil	0	0	0	0	10	10	10	10
6PPD	1	1	1	1	1	1	1	1
M.C. Wax	2	2	2	2	2	2	2	2
CBS	1	1	1	1	1	1	1	1
Sulphur	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2

7.3.2 Curing Characteristics

Curing characteristics of rubber compounds are shown in Table-7.3, and it is found that lower values of Ts2, Tc50, Tc90 are obtained with BTEAC treated carbon black based rubber compound compared to the corresponding control compound**.** BTEAC is basic in nature, and it is seen that BTEAC treated carbon black provides high pH of carbon black, which demonstrates BTEAC treatment of carbon black increases its basic characteristics.

Carbon black with high basicity increases the effectiveness of accelerators which are also basic in nature and consequently increases the curing efficiency of rubber compounds. Earlier Hard et al. [7] demonstrated that on treatment of carbon black with amine compound, the basicity of carbon black surface was increased which resulted in substantial reduction of optimum curing time of the corresponding rubber compound.

Table-7.3: Curing characteristics of rubber compounds

	ML	MH	Delta Torque	Ts2	Tc50	Tc90	Cure rate index (CRI)
SS0	6.50	33.00	26.50	2.28	5.41	6.00	26.88
SS0.5	6.30	32.50	26.20	1.37	3.47	4.44	32.55
SS1.0	6.10	31.00	24.90	1.08	2.70	3.61	39.57
SS1.5	5.80	30.40	24.60	0.97	2.41	3.36	41.92
SB0	5.42	25.89	20.47	4.08	6.31	16.01	8.38
SB0.5	5.50	26.08	20.58	3.46	5.63	14.17	9.34
SB1.0	6.28	26.26	19.98	3.37	5.37	14.00	9.41
SB1.5	5.93	26.05	21.12	3.18	5.43	13.79	9.43

It is seen BTEAC treated carbon black resulted reduction of scorch time, 50% cure time, optimum cure time and consequently increased the cure rate index (CRI) of the experimental rubber compounds compared to the control compound. CRI signifies the rate of curing reaction takes place and higher values of CRI for experimental compounds in comparison to corresponding control compound indicates reduction of curing cycle which is a desirable phenomenon of BTEAC treated carbon black.

7.3.3 Dispersion Analysis by Atomic Force Microscopy

Dispersion of carbon black in rubber matrix are categorised 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 depends on intensity of stress, agglomerate cohesiveness and affinity of carbon black towards rubber molecules. Thus, carbon black having more compatibility to rubber compound will have more tendency to breakdown into aggregate fragments to form smaller size carbon black aggregate fragments in the rubber matrix and will results improved filler dispersion.

The dispersion of carbon black in rubber matrix has been investigated by 3D microscopic image analysis and the quantitative analysis of surface roughness is studied by atomic force microscopy (AFM) [8-9]. In the AFM study, the images were captured using tapping mode and phase imaging study. A small piece of the rubber sample was cut by a sharp razor and the freshly cut surface carefully exposed for microscopic analysis, which characterize the carbon black dispersion and distribution in rubber matrix by the image analysis. Atomic force microscopy analysis for the present study was carried having image dimension of 5-micron X 5-micron, which is shown in Fig-7.6.

In the AFM images, the brighter phase represents the carbon black particles, and the darkest phase represents the rubbery material. The height of the brighter phase was measured by the height measurement software and the same represents the size of carbon black unit present in rubber matrix. The highest in brighter phase height indicates larger carbon black units present in rubber matrix due to the agglomeration [10-11]. AFM studies were carried out for the control compounds and the experiment compound, consisting of 1% BTEAC treated carbon black for both the rubber system, i.e, for emulsion SBR-BR system and SSBR-BR system. This study demonstrates the change in filler dispersion in rubber matrix for BTEAC treated carbon black with non-treated control carbon black in both the rubber compound systems.

In each AFM topography the height of the bright phase is clearly recognizable by the height scale in ‘nm’ along the Z-axis. While comparing AFM topography between control compound with the experiment compound, it is observed that the height and sizes of the brighter phases are maximum for the control compounds in comparison to the experimental compounds in both the rubber system. These results reveal that, larger size of carbon black agglomerates are exists in control compounds and the size of carbon black agglomerates reasonably reduced in the experimental compounds due to improved dispersion of BTEAC treated carbon black.

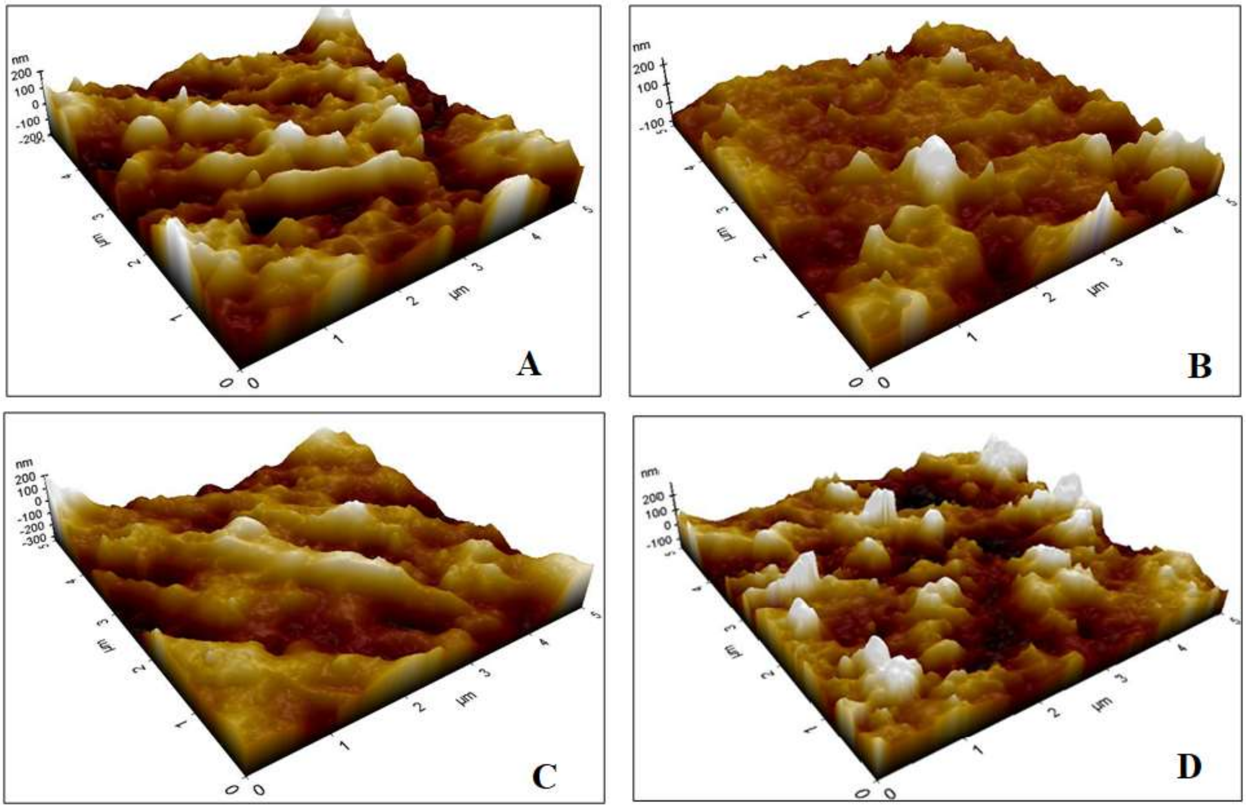

Fig-7.6: *AFM images of compounds (a) AFM image of control compound based on SSBR-BR system (SS0), (b) AFM image of 1.0 % BTEAC modified carbon black based compound based on SSBR-BR (SS 1.0), (c) AFM image of control compound based on emulsion SBR-BR system (b) AFM image of 1.0 % BTEAC modified carbon black based on emulsion SBR-BR system (SB1)*

To get better insight of surface characteristics of AFM topography, the quantitative analysis of surface topography was studied by measurement of amplitude or height parameters. The most common and significant amplitude or height parameters of AFM surface topography as represented here are average roughness (Ra), root mean square roughness (Rq) and ten-point height (Rz). The height parameters such as Ra, Rq and Rz values of AFM topography are the measure of surface roughness and the highest values of those parameters indicate higher surface roughness i.e., poor filler dispersion in the rubber matrix [12-13].

The valley to peak distance or total roughness is a significant quantitative parameter of surface roughness measurement of AFM topography. In the AFM image while the number of peaks and the valleys are significantly high, the value of average roughness and root square roughness may be affected and in such case valley to peak distance or total roughness could be a better interpretation parameter for the clarification of surface roughness of AFM topography. Valley to peak distance or total roughness is the sum of maximum profile peak and the maximum profile valley depth. In the AFM analysis to represent the roughness of surface topography average of valley depths and peak heights is considered and which is termed as ten points height (Rz). Ten-point height (Rz) is, thus, the distance in height between average height of five height peaks and average of five deepest valleys along the measurement length of surface profile. Hence, higher value of Rz indicates highest surface roughness associated with the topography. The quantitative AFM analysis data are shown in Table-7.4 and the lower values of Ra, Rq and Rz for the experimental compounds compared to the corresponding control compound demonstrate that rubber compounds consisting of BTEAC treated carbon black have lower surface roughness associated with the respective AFM topography and it indicates an improvement of filler dispersion in the rubber matrix due to modification of carbon black with BTEAC treatment.

Table-7.4: Quantitative Data of AFM Topography

	Ra (nm)	**Rq (nm)**	**Rz (nm)**
SS0	42.78	53.80	408.04
SS1.0	28.32	37.43	309.40
SB0	53.64	68.01	505.20
SB1.0	30.21	39.05	339.94

7.3.4 Bound Rubber Content

Bound rubber is termed as the part of rubber which is bound by the filler to form an immobilized rubber layer which is formed by adsorption of rubber molecules on filler surface. Bound rubber content depends on several factors, such as, characteristics of carbon black, loading of total filler, the kind of elastomer, the mixing technique e.g., mixing temperature and time [14].

Bound rubber content of the compounds is shown in Fig-7.7, which shows that carbon black functionalised with BTEAC has higher bound rubber content than respective compound having non treated regular carbon black. This is attributed to the addition functional groups on carbon black surface, which interact with rubber molecules more intensely and results strong interactive bonding between them and consequent formation of greater extent of bound rubber.

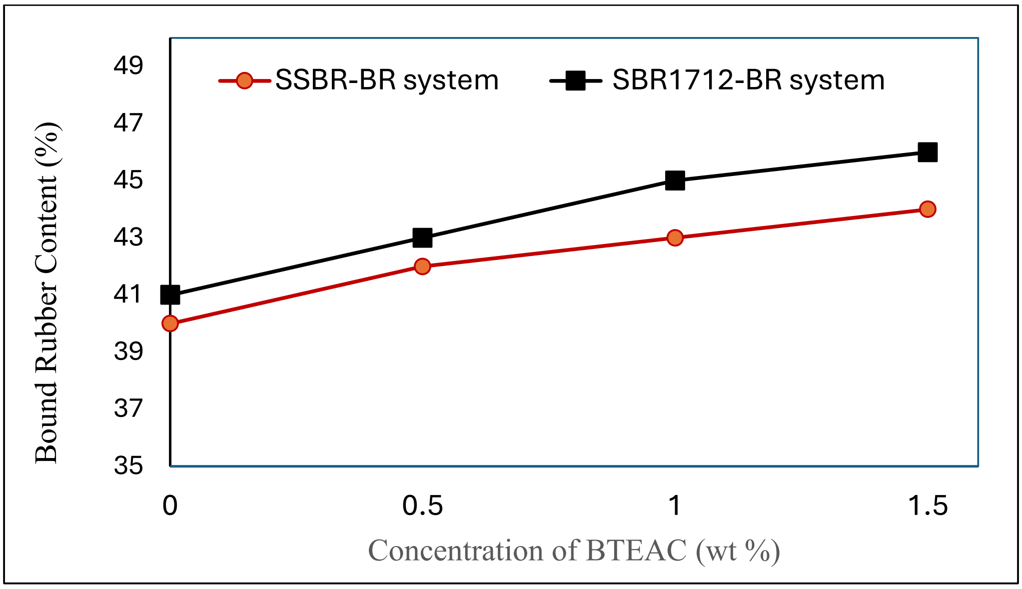

Fig-7.7: Bound Rubber Content of Compounds with concentration of BTEAC in carbon black

7.3.5 Rubber Process Analysis and Payne Effect

Payne effect of compounds was measured by Rubber Process Analyzer (RPA). The rubber compounds were deformation under shear strain amplitudes of 0.1% to 100%. The disruption and displacement of filler network resulted a steady fall of shear modulus, the fall of shear modulus of the compounds with shear strain are shown in Fig-7.8. In this present study, by treatment of carbon black with BTEAC, carbon black becomes increasingly compatible with rubber molecules that leads to reduction of propensity of carbon black inter aggregate network formation. Hence rubber compound consisting of functionalized carbon black shows significantly lower shear modulus at lower shear strain region, and as a consequence, has lower fall of shear modulus on application of strain. As a result, carbon black shows reduced Payne effect when treated with BTEAC in both the rubber systems as shown in Table-7.5.

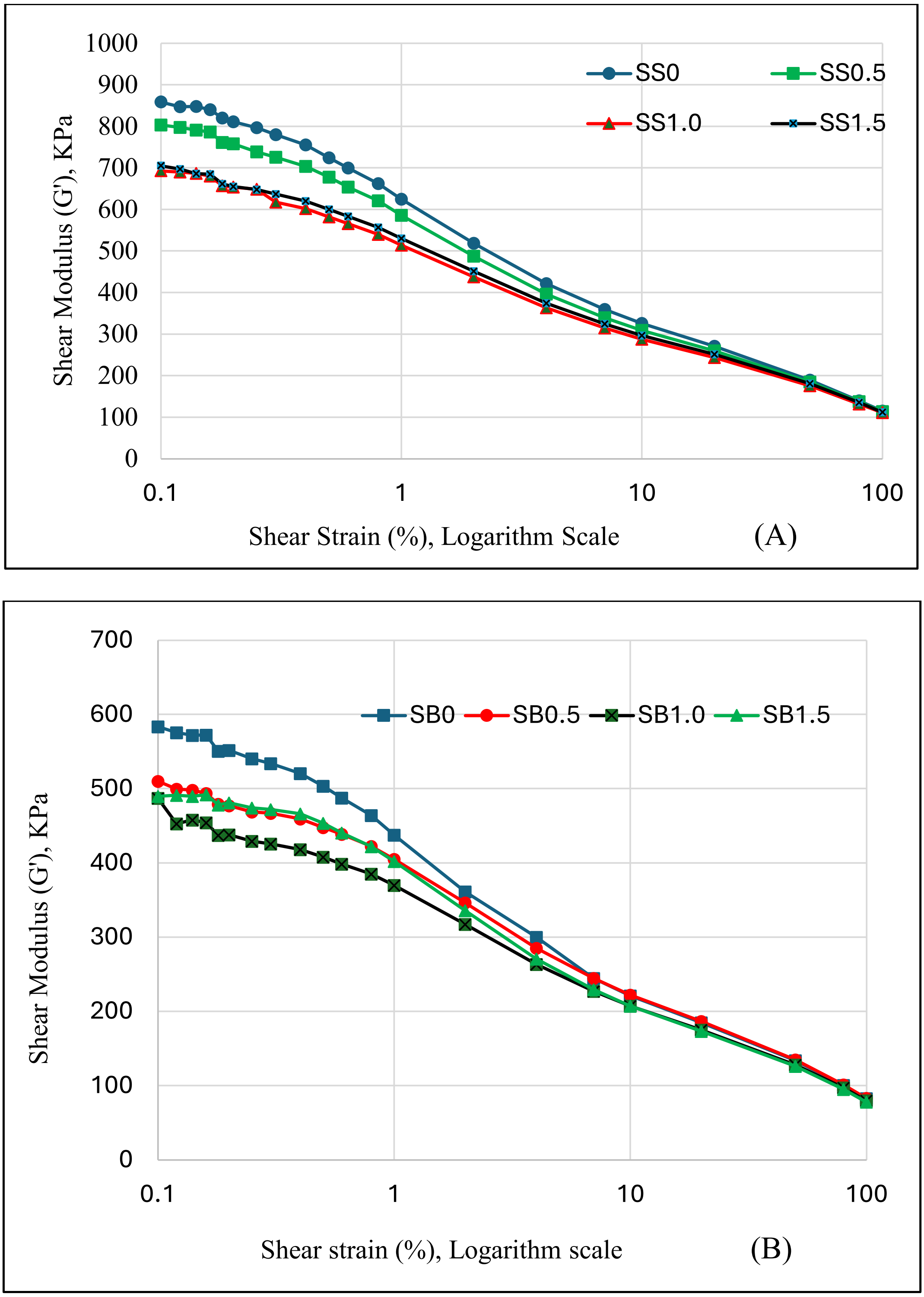

Fig-7.8: Trend of shear modulus of compound with strain amplitude (A) SSBR-BR compounds (B) SBR1712-BR compounds

Table-7.5: Shear modulus and Payne effect of rubber compounds

	Shear Modulus at 0.1% shear strain ($G'_{0.1}$)	Shear Modulus at 100% shear strain (G'_{100})	Payne Effect $=G'_{0.1} - G'_{100}$
Unit	KPa	KPa	KPa
SSBR-BR Rubber System			
SS0	878	115	763
SS0.5	820	113	707
SS1.0	694	108	586
SS1.5	716	112	604
SBR1712-BR Rubber System			
SB0	583	83	500
SB0.5	510	83	427
SB1.0	487	80	407
SB1.5	490	78	412

7.3.6 Dynamic Mechanical Analysis

Dynamic mechanical analysis of rubber compound was performed to investigate the storage modulus and rolling resistance of rubber compounds. It has been demonstrated in the previous section that on application of shear strain a drastic fall of shear modulus takes place in rubber compound due to the breakdown of filler-filler network which has been characterized by the Payne effect of rubber compound, and the same represents the existence of filler-filler interaction in the rubber compound [15-16]. In this investigation, the cured rubber compounds were deformed under a strain sweep of 0.1% to 5% in the tension mode of deformation, and the change in dynamic storage modulus (E') of the rubber compounds were recorded.

Plotting storage modulus (E') of rubber compound with dynamic strain sweep shows a steady fall in E' value with increasing dynamic strain as shown in Fig-7.9. The reduction in compound storage modulus is attributed to the destruction of filler-filler network in rubber compound due to the deformation of rubber compound. It is seen that, the maximum fall in storage modulus was observed for control compound in comparison to the experimental compounds consisting of functionalized carbon black, which suggests a higher breakdown of filler network in control compound in comparison to the experimental compounds in both the rubber system. Hence the concept of Payne effect is also reflected in dynamic mechanical analysis in case of cured rubber compounds and lower fall in storage modulus in experimental compound confirms enhanced filler-polymer interaction resulted with rubber molecules and the functionalized carbon black [17-18].

The loss tangent value as measured by dynamic mechanical analysis is the representation of hysteresis energy loss of the compound due to deformation of the compounds. During the strain sweep of the specimen from 0.1 % to 5% the loss tangent value of rubber compound was also measured and the trend of loss tangent values with strain sweep is shown in Fig-7.10. It is observed that with increase in strain sweep the loss tangent value increases rapidly and after a certain strain amplitude it becomes plateau. Loss tangent is the ratio of loss modulus to storage modulus of rubber compound, and it has been seen above with increase in strain amplitude the storage modulus falls. Hence at the high strain region rubber compound loses its elastic characteristics, as a result the viscous component of the viscoelastic material predominates which causes high loss tangent value at higher strain amplitude region.

Loss tangent value of rubber compounds containing BTEAC treated carbon black show significant reduction in the entire range of the strain, indicating reduction of hysteresis energy loss of rubber compounds upon treatment of carbon black with BTEAC. The dynamic mechanical analysis was carried out at 60°C temperature and 10 Hz frequency which indicates tanδ measured in this condition relates to the rolling resistance property of tyre tread compounds [19]. It is to be noted that on treatment of carbon black with 0.5% of BTEAC the reduction of loss tangent is very limited however a significant reduction of loss tangent value appeared when carbon black was treated with 1.0% and 1.5% BTEAC in both the rubber system though the reduction of tanδ was more significant in SSBR-BR system compared to the emulsion SBR-BR system.

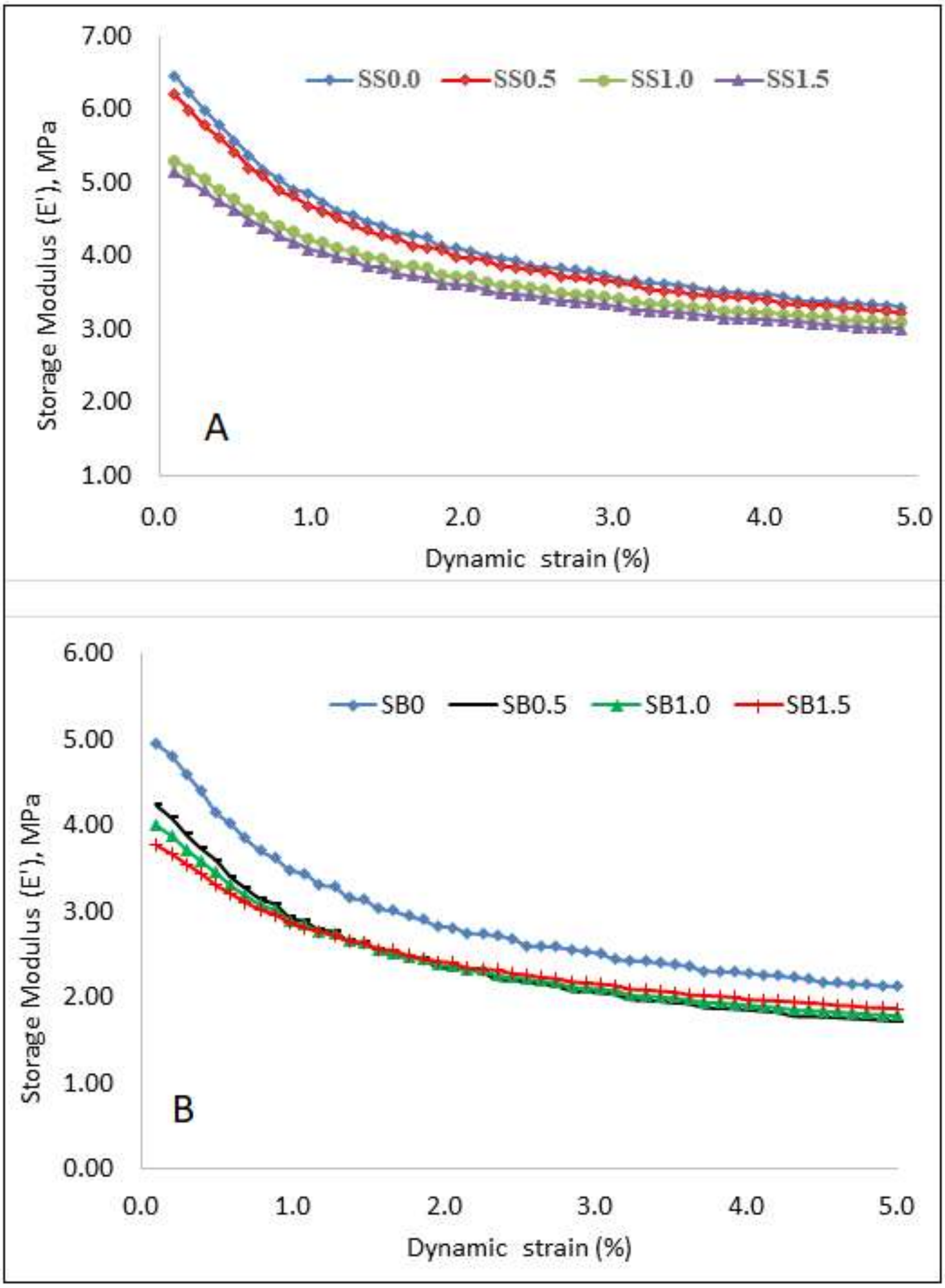

Fig-7.9: Trend of storage modulus with strain sweep at 60°C (A) SSBR-BR compounds, (B) SBR-BR compounds.

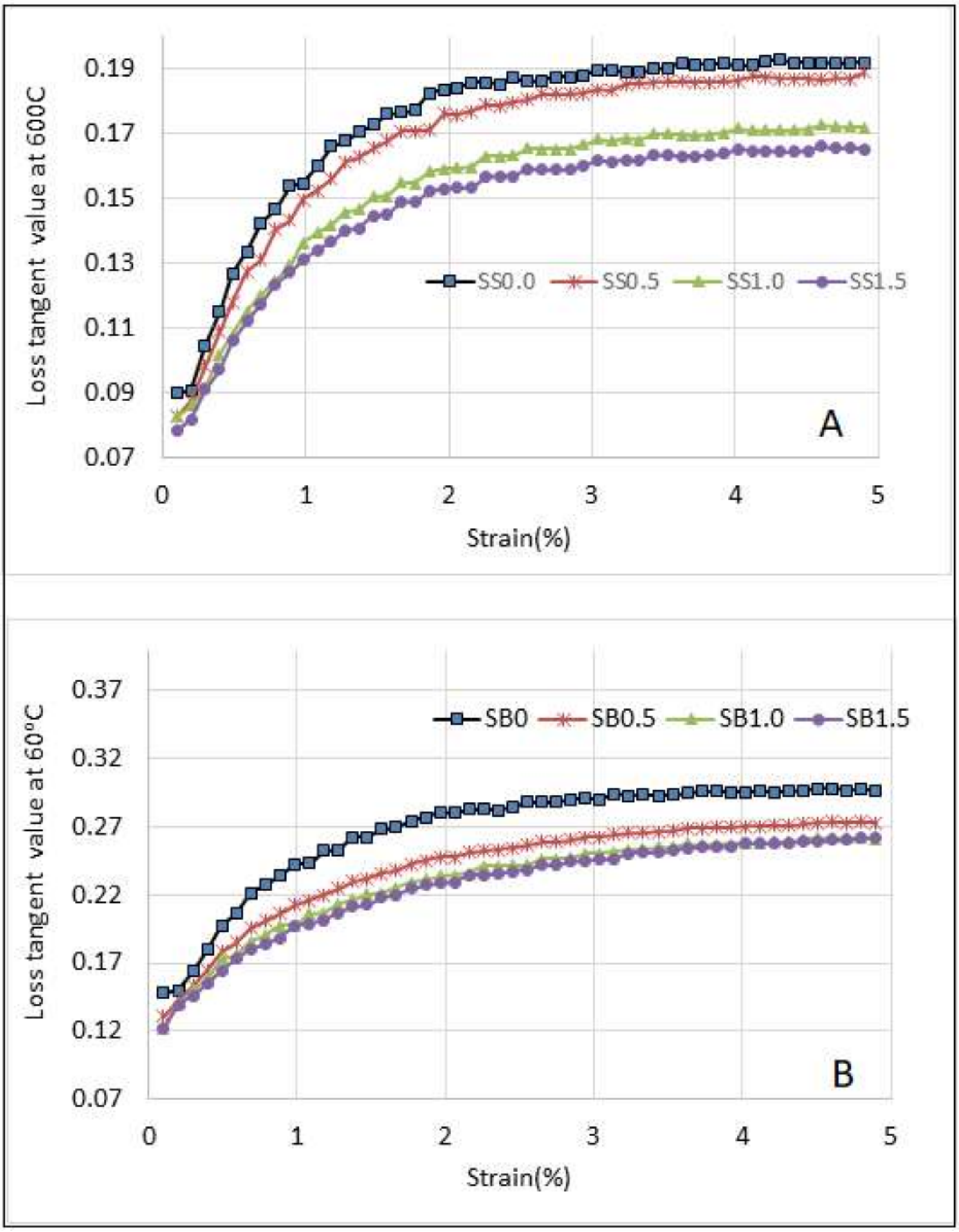

Fig-7.10 Trend of loss tangent value with strain sweep at 60ºC (A) SSBR-BR compounds (B) SBR1712-BR compounds.

7.3.7 Physical Properties of Rubber Compounds

Physical properties of the compounds determine the strength and durability of finished materials. The physical properties of carbon black filled rubber compound is primarily dependent on morphological characteristics of same along with the inherent characteristics of rubber molecules for a fixed loading of compounding ingredients. The physical properties of rubber compounds such as tensile strength, elongation at break, modulus and abrasion resistance. Treated carbon black are comparable with respect to the compound of non-treated carbon black as shown in Fig-7.11, where the changes in physical properties of rubber compounds are shown with use of increased BTEAC treatment carbon black.

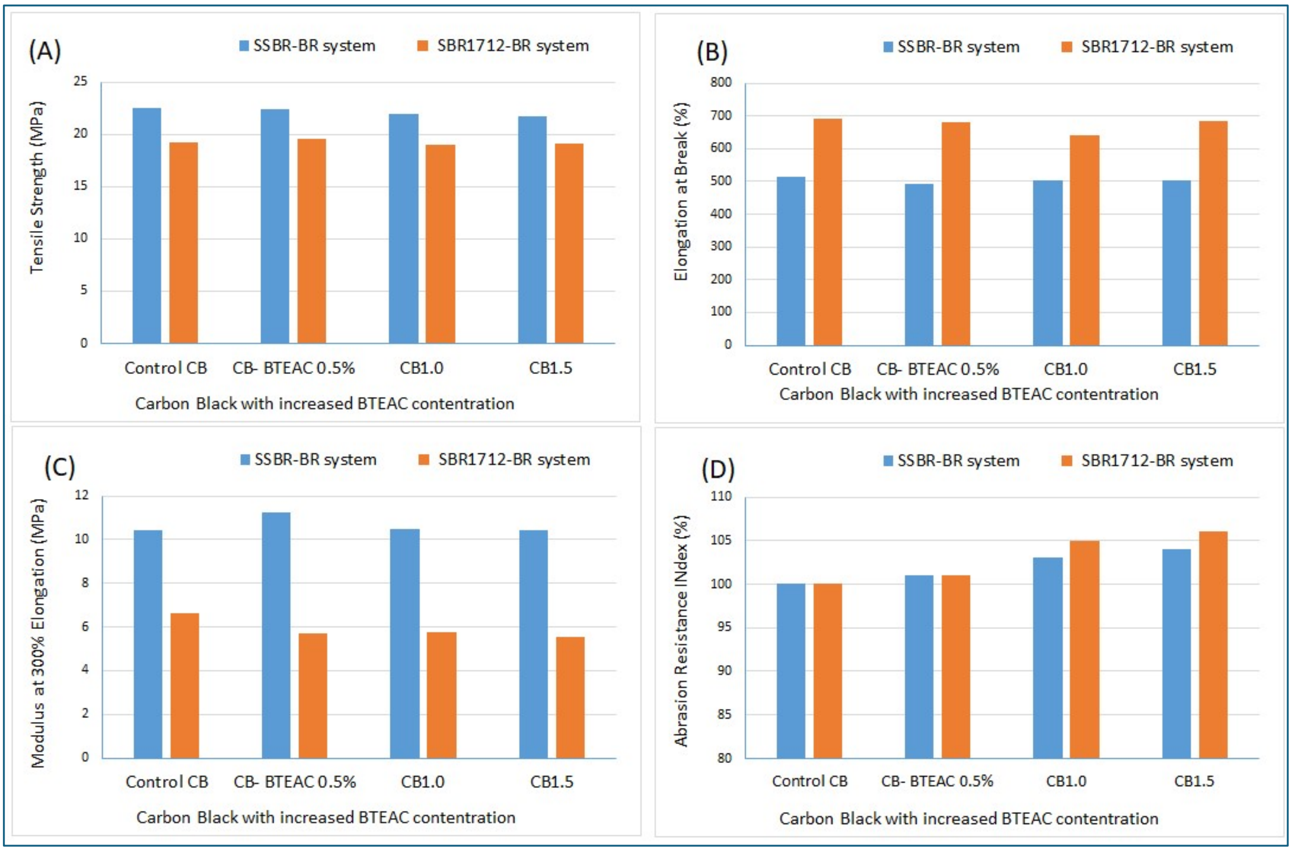

Fig-7.11: Mechanical properties of rubber compounds (A) Tensile strength (B) Elongation at break (C) Modulus at 300% elongation (D) Abrasion resistance Index

The abrasion resistance of rubber compound is one of the important properties, which relates to the durability and life of rubber articles. Abrasion resistance of the compounds is represented by abrasion resistance index and higher value of the same represents improvement of abrasion resistance property. ARI of the rubber compounds implies that an improvement in abrasion resistance property can be possible by using BTEAC treated carbon black and the same is marginally impactful while carbon black was treated with higher dose of BTEAC. The increased abrasion resistance property of the experimental rubber compounds is caused due to the improved filler dispersion in rubber matrix when the carbon black was treated with BTEAC

7.4 Effect of Loading and Optimization Rubber Compound Properties for Tyre Tread Compounds

Carbon black on functionalization with BTEAC the compatibility of the same with rubber molecules is increased, which resulted in superior filler dispersion, lowering of Payne effect, low hysteresis energy loss in rubber compounds etc. as described earlier. Several studies were carried out on the effects of filler loading on rubber compounds properties. Dutta et al [20] described change in elastic modulus (E') of rubber compound with carbon black loading in term of volume percentage (ϕ) and described a linear relationship between elastic modulus and the loading of carbon black (ϕ), where elastic modulus of rubber compound is increasing with increasing volume percentage of carbon black. They further demonstrated the trend of loss tangent ($\tan\delta$) value of rubber compounds with volume percentage (ϕ) of filler and they have established the peak value of $\tan\delta$ decreases with increased volume percentage (ϕ) of carbon black.

Payne effect of rubber compounds varies with extent of filler-filler network formation ability in the rubber matrix and the same varies with loading of filler present in the rubber compounds. Frohlich et al [21] investigated the different rubber vulcanizates properties with different loading of carbon black and established that there is significant reduction of shear modulus appeared while carbon black loading is reduced. The lower shear modulus of the rubber compounds is caused due to presence of reduced filler-filler interaction in the rubber matrix and the same leads to lower Payne effect in rubber compounds. Several literatures demonstrates that with increase of carbon black loading on rubber compounds, there is increase in modulus, abrasion resistance and hardness of rubber compound appeared [22-23]

In this part of the study rubber compounds with different filler loading have been studied where carbon black used were functionalized with BTEAC treatment and the same has been compared with non-treated carbon black.

7.4.1 Rubber Compounding

ASTM grade N220 carbon black was functionalized with 1% benzyl tri ethyl ammonium chloride and the study of different phr of functionalized carbon black was carried in a model emulsion SBR-BR based compounds. Functionalized carbon black taken from 45 phr to 65 phr and the comparative evaluation of compound was carried out with 55 phr of non-functionalized control carbon black.

Table-7.6: Formulation of rubber compound with different filler loading

	SB0-55	**SB1-45**	**SB1-50**	**SB1-55**	**SB1-60**	**SB1-65**
SBR1712	110	110	110	110	110	110
BR	20	20	20	20	20	20
N220 Carbon Black	55	0	0	0	0	0
Functionalized N220	0	45	50	55	60	65
ZnO	3	3	3	3	3	3
ST ACID	2	2	2	2	2	2
TMQ	1	1	1	1	1	1
CBS	1.2	1.2	1.2	1.2	1.2	1.2
Retardard (PVI)	0	0.15	0.15	0.15	0.15	0.15
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5

The mixing of compounds and testing procedure are described in Chapter-2 and the condition of testing are as per for the respective types of rubber compounds.

7.4.2 Rubber Process Analysis

The carbon black inter-aggregate distance is greatly dependent on the population of carbon black particles in a definite rubber matrix, and which is proportional to the loading of carbon black incorporated in the rubber matrix. Hence rubber compound having higher dosing of carbon black with definite surface area and structure would lead to greater extent of carbon black network formation, i.e., filler-filler interaction.

In this experiment, different rubber compounds are associated with either different loading of carbon black or different surface modified carbon black such as control compound is associated with 55 phr non-treated carbon black, while the experiment compounds are characterized with BTEAC treated carbon black but with different filler loading of 45 phr to 65 phr. Thus, while comparing Payne effect of experimental compounds with the same of control compound a synergy effect of carbon black functionalization and the filler loading need to be accounted.

The shear modulus of rubber compounds with strain sweep is shown in Fig-7.12. It is seen a steady fall of shear modulus with increase of strain sweep. The shear modulus of compound (SB1-65) shows very high at lower strain region (0.1% shear strain). Rubber compound (SB1-65) consists of highest filler loading of 65 phr, hence in this compound the interaggregate of filler becomes least which causes increased filler-filler interaction and results high shear modulus of rubber compound. On increase of shear strain the filler-filler networks break down, as a result the shear modulus of rubber compounds reduces.

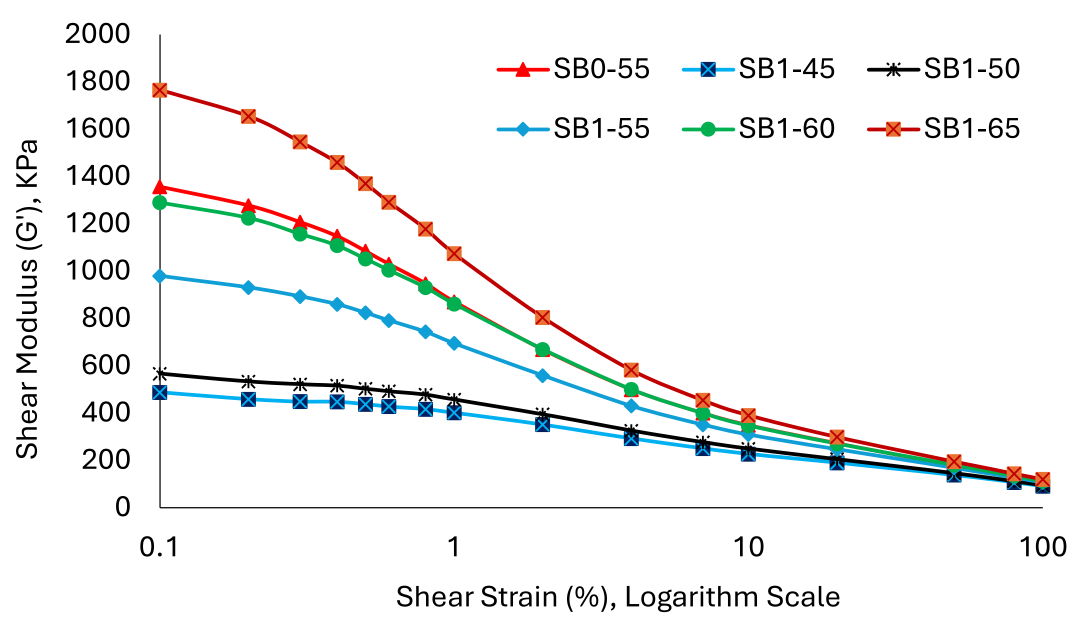

Fig-7.12: Trend of shear modulus of rubber compound with shear strain amplitude

On application of very high shear strain (100% shear strain), it is assumed to be complete destruction of filler-filler network and in this case the variation of shear modulus among rubber compounds is primarily contributed by the hydro-dynamic effect due to incorporation of dissimilar filler loading. In this case rubber compound comprising high dose of filler provides high shear modulus as shown in Table-7.7.

Table-7.7: Shear modulus of rubber compound at different strain amplitude and Payne effect of same

	Unit	SB0-55	SB1-45	SB1-50	SB1-55	SB1-60	SB1-65
Shear modulus ($G'_{0.1}$) @ 0.1% Strain amplitude	KPa	1357	488	567	980	1291	1766
Shear modulus (G'_{100}) @ 100% Strain amplitude	KPa	109	92	95	107	113	120
Payne Effect ($G'_{0.1}$ -G'_{100})	KPa	1248	396	472	873	1178	1646

Payne effect of experimental rubber compound is plotted graphically with the filler loading as shown in Fig-7.13. It is seen Payne effect of the compound increases rapidly with the increase of filler loading because of higher filler-filler network formation takes place with increasing filler loading. Payne effect of control compound consisting of 55 phr non-treated carbon black is also placed in the same diagram and the same is plotted as a single dot at 55 phr of filler loading. It is observed Payne effect of control compound placed above the Payne effect of experimental compound, having 55 phr filler loading, in the same diagram, here with the identical filler loading of 55 phr, experimental compound provides less Payne effect compared to control compound because of its increased filler-polymer interaction due to addition of BTEAC treated carbon black. While comparing Payne effect of experimental compound associated with 60 phr filler loading it shows that the same provides marginally lower Payne effect compared to the control compound in spite of having 5 phr higher filler loading. It has been described that with increased filler loading the Payne effect is supposed to be increased due to enhanced filler-filler interaction, however, in this case due to addition of BTEAC treated carbon black, the filler-polymer interaction is increased in such a level that it counters the increased filler-filler interaction as caused by addition of 5 phr extra filler loading.

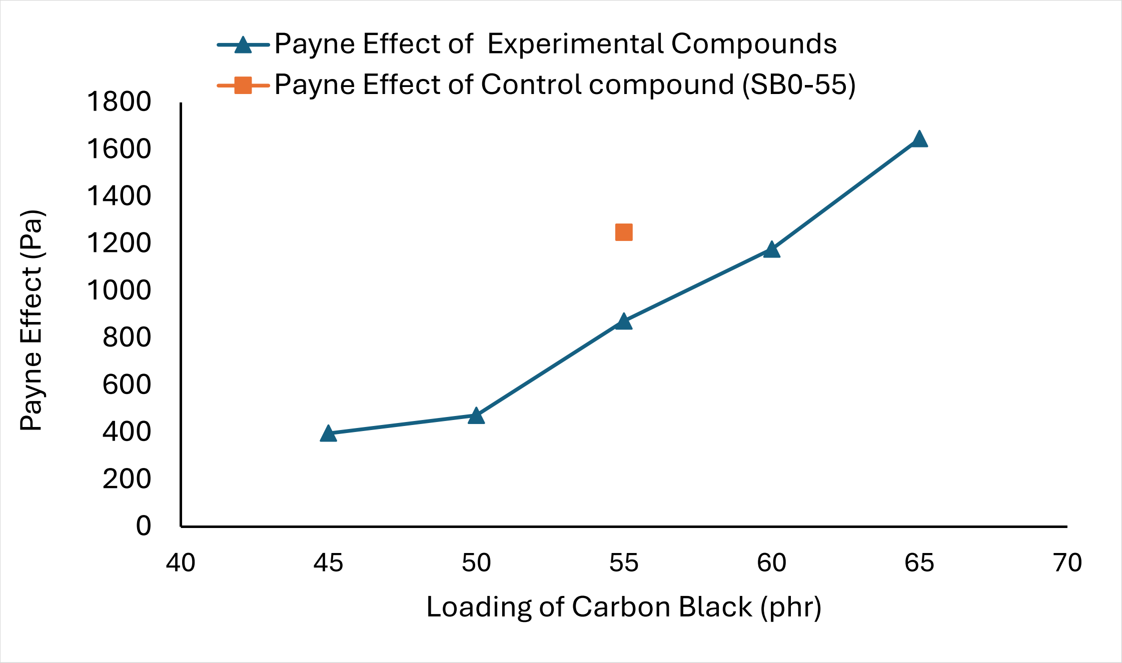

Fig-7.13: Trend of Payne effect with loading of carbon black and compare with Payne effect of control compounds.

7.4.2.1 Mechanical Properties

It has been described that BTEAC treatment of carbon black has little impact on mechanical properties of rubber compounds. The mechanical properties of rubber compounds are practically change due to increase of carbon black loading from 45 phr to 65 phr. On increase of carbon black loading the hardness, modulus and abrasion resistance of rubber compound are increased. Thus, the experimental compound with 65 phr carbon black loading provide highest compound hardness, modulus and abrasion resistance among all the compound however the same provide slight lower tensile strength.

Rubber compounds SB55 and SB1-55, both comprise of similar carbon black loading of 55 phr. It is seen experimental compound, SB1-55 provides slightly high abrasion resistance index compared to control compound SB55. As SB1-55 compound is based on BTEAC treated carbon black, hence the same provides superior filler-polymer interaction and filler dispersion in rubber matrix, which causes advantage to abrasion resistance property.

Table-7.8: Mechanical properties of rubber compounds

	Unit	SB55	SB1-45	SB1-50	SB1-55	SB1-60	SB1-65
Tensile Strength	MPa	21.2	20.56	20	20.29	20.71	18.81
Modulus at 300% Elongation	MPa	12.11	9.41	10.33	12.34	13.1	13.78
Elongation at break	%	463	507	468	445	434	399
Abrasion Resistance Index	%	100	84	89	105	112	118

7.4.2.2 Effect of Filler Loading on Rolling Resistance and Wet Tract Propery of Tyre Tread Compound

Dynamic mechanical analysis measures the loss tangent value of rubber compound at different measurement condition and the loss measured at 60°C and 0°C represents the rolling resistance, and wet skid resistance of tyre tread compound respectively [24]. Loss tangent value of rubber compounds largely depends on rubber compounding, and it has significant corelation with filler loading. McDonald and Hess [25] established a co-relation of loss tangent value of rubber compound with effective carbon black loading into the same and the co-relation of the same is shown in the equation (7.1).

$$1 + Log\ tan\delta = C_1\phi + C_2 Log\ (S\phi) + C_3 \qquad (7.1)$$

Where ϕ represents effective carbon black volume fraction, S is the surface area of carbon black and C1, C2, C3 are the constants which depend on the strain amplitude of dynamic mechanical analysis. Thus, loss tangent (tanδ) value of rubber compound increases with increase in carbon black loading for a specific surface area of carbon black. The tanδ values measured at different temperature are shown Fig-7.14, which indicates tanδ values for the experimental compound increases with increase of carbon black loading from 45 phr to 65 phr.

The tanδ values measured at 60°C show that experimental compounds (SB1-60 and SB1-65) provide lower tanδ compared to control compound (SB0-55) in spite of having high carbon black loading. In the experimental compound BTEAC treated carbon black was used which caused lowering of tanδ value compared to non-treated carbon black. The influenced of BTEAC treatment effect on tanδ value in such a effective manner that tanδ value of functionalized compounds (SB1-60 and SB1-65) remains lower than the control compound (SB0-55) instead of having higher filler loading and the same would provide lower rolling resistance in tyre tread compounds.

Another fundamental characteristic of tyre tread compound is wet traction which is indicated by tanδ value measured at 10 Hz and 0ºC temperature and high tanδ value indicates superior wet traction property. BTEAC treatment results in lowering of tanδ value compared to the control compound with a similar filler loading of carbon black, however increase in caron black loading, experimental compounds result in increase of tanδ and the trend of the same is shown in Fig-7.13. It indicates that with similar loading (55 phr) of carbon black, BTEAC treated carbon black provides around 5% lower wet traction property compared to the control carbon black. However further increase of functionalized carbon black, the wet traction property of rubber compound becomes superior to the control carbon black, and it is seen rubber compound with 65 phr filler loading provides beyond 10% improvement of wet traction property.

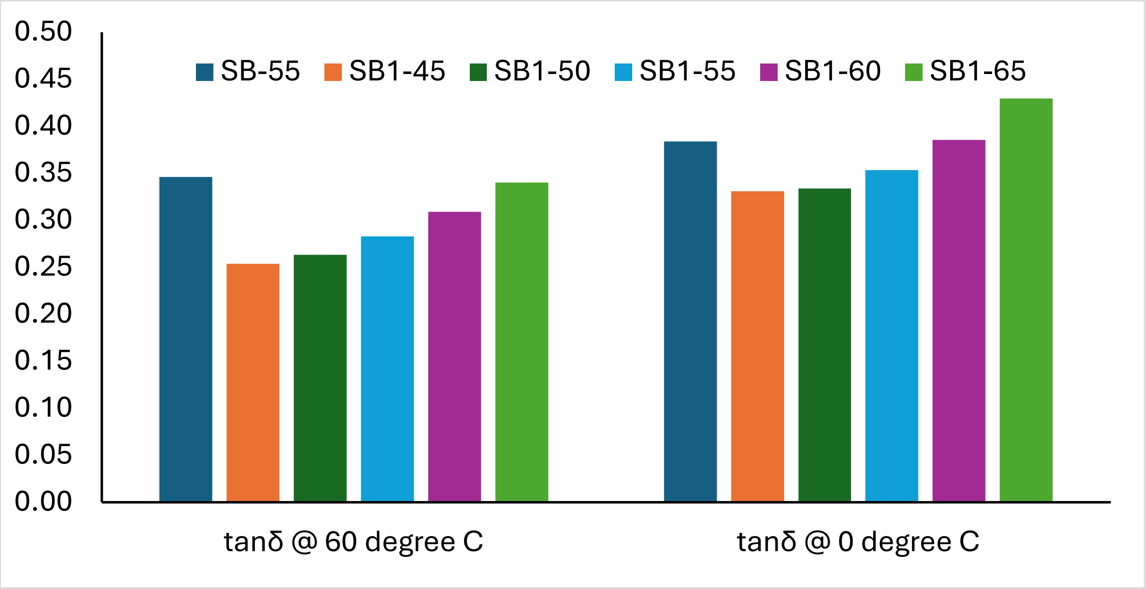

Fig-7.14: Trend of tanδ values of rubber compounds measured at 60ºC and 0ºC.

The storage modulus of rubber compound represents inherent strength of the material which increases with increase in carbon black, and it is seen rubber compound associated with increased filler loading provides enhanced storage modulus value. The detailed parameters of dynamic mechanical analysis include storage modulus, loss modulus and tanδ of rubber compound, measured at 60°C are shown in Table-7.9.

Table-7.9: Dynamic Mechanical Analysis of Compounds at 60°C

Compound ID	Storage Modulus (MPa)	Loss Modulus (MPa)	Tanδ
SB55	5.04	1.74	0.35
SB1-45	3.73	0.95	0.25
SB1-50	3.84	1.01	0.26
SB1-55	4.67	1.32	0.28
SB1-60	5.64	1.74	0.31
SB1-65	6.97	2.37	0.34

7.4.2.3 Magic Triangle Properties

A perfect magic tringle of tyre tread compound refers to low rolling resistance, high wet traction and improved abrasion resistance properties, however achievement of all the properties at a same time remains a challenged in tyre technology.

In this investigation, control compound is based on 55 phr of N220 carbon black, while the experimental compounds are consisting of functionalized N220 carbon black from 45 phr to 65 phr filler loading. It has been seen that an increase of carbon black loading wet traction and abrasion resistance properties of rubber compound improves, while rolling resistance property deteriorates. However, due to effect of BTEAC treatment the experiment compounds (SB1-60 and SB1-65) still provides improved rolling resistance, i.e., lower rolling resistance in comparison to the control compound.

Magic triangle properties of each experimental compound was compared with the same of control compound individually and for the different experimental compounds a dissimilar characteristics of magic tringle properties were observed as shown in Fig-7.15. In the magic triangle plots the abrasion resistance is represented by abrasion resistance index and higher value of same indicates

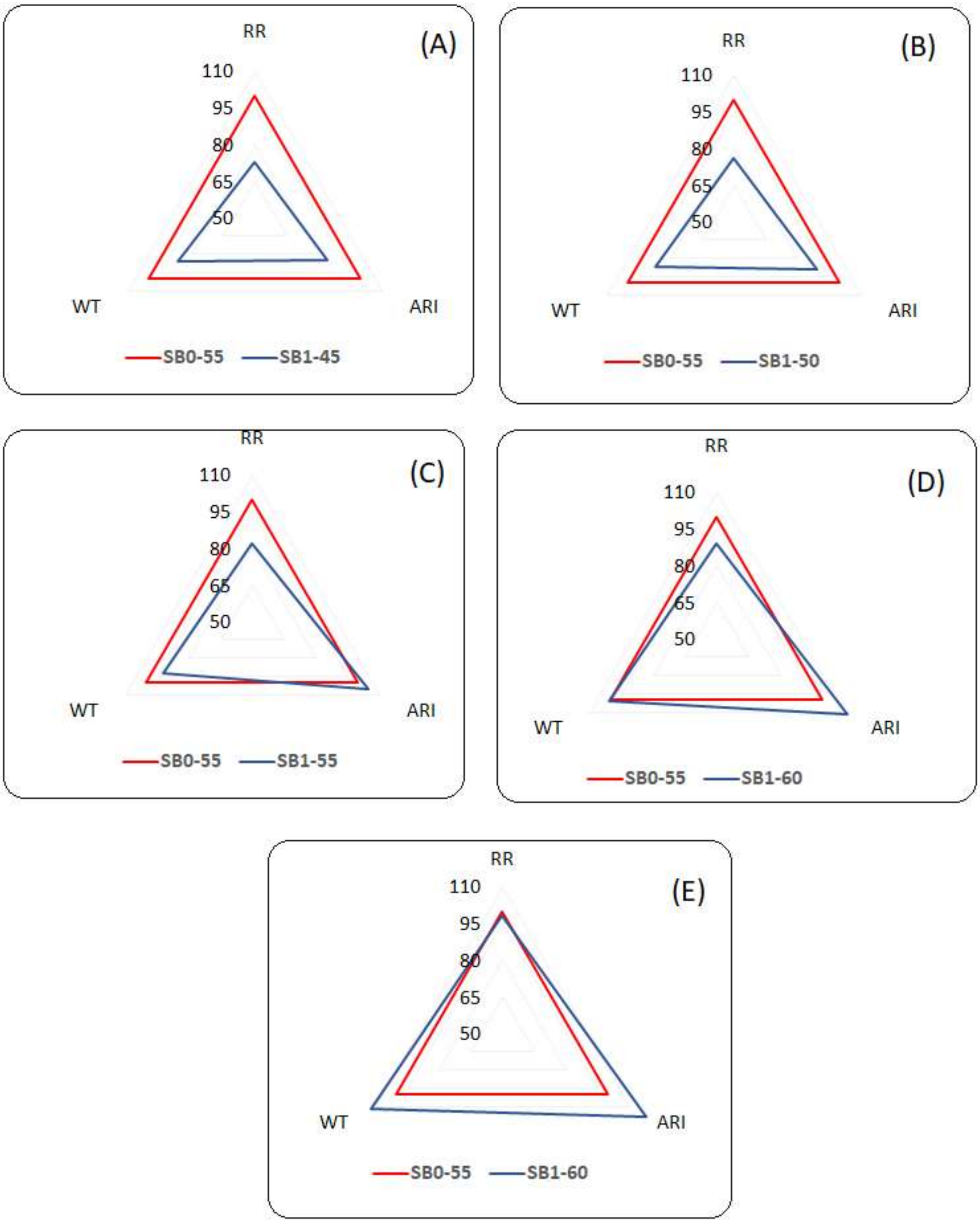

Fig-7.15: *Magic triangle properties of rubber compounds (A) SB0-55 compound vis-à-vis SB1-45 Compound (B) SB0-55 compound vis-à-vis SB1-50 Compound (C) SB0-55 compound vis-à-vis SB1-55 Compound (D) SB0-55 compound vis-à-vis SB1-60 Compound (E) SB0-55 compound vis-à-vis SB1-65 Compound* improved abrasion resistance, while rolling resistance and wet traction properties are represented by tanδ values at 60°C and 0°C respectively. Lower tanδ at 60°C indicates lower rolling resistance, which is desired property, while high value of tanδ value at 0°C indicates high wet traction property, which benefits in braking and safety of vehicles. In each of the magic triangle the rolling resistance, wet traction, and abrasion resistance properties of reference compound (SB0-55) was considered as 100.

Magic triangle (A) & (B) represent BTEAC treated carbon black consisting of 45 and 50 phr filler loading indicates significantly lower rolling resistance property compared to reference carbon black due to lower carbon black loading as well as functionalization of the same with BTEAC. However, the same provides deterioration in wet traction and abrasion resistance property. While in the

magic triangle (C), where control compound as well as experimental compound both have identical filler loading of 55 phr, it is seen BTEAC treated carbon black provides significant reduction of rolling resistance and marginal improvement in abrasion resistance with slight deterioration of wet traction property, hence here, the magic triangle properties signify a preferred choice for low rolling resistance tyre tread compound.

The magic triangle properties of compound SB1-60 (D) and compound SB1-65 (E) show a significant improvement in abrasion resistance property compared to reference compound. The increase in abrasion resistance property is due to use of BTEAC treated carbon black and more significantly due to use of higher filler loading. On comparing rest of the magic triangle properties, these compounds provide different trend of properties to each other. Compound SB1-60, corresponds to magic triangle (D), associated with 5 phr higher filler loading compared to control compound, provides substantial reduction of rolling resistance without affecting the wet traction property, while compound SB1-65, corresponds to magic triangle (E), associated with 10 phr higher filler loading provides similar rolling resistance property with control compound but it provides significant improvement in wet traction property as well as abrasion resistance property. Instead of having higher filler loading neither of compound SB1-60 or compound SB1-65 shows any deterioration in rolling resistance property due to use of BTEAC treated carbon black which resulted strong filler-polymer interaction in these compounds in comparison to the non-treated carbon black. Hence BTEAC treatment of carbon black has potential to provides a different set of magic tringles properties for different tyre tread compounds such as low rolling resistance tyre tread compound, high durable tyre tread compound as well as high safety and low rolling resistance tyre tread compounds based on the suitable area of applications.

7.5 Conclusion

The treatment of carbon black with BTEAC provides increased functionality in carbon black surface. On treatment of carbon black with BTEAC, the pH of carbon black increases. Hence it is plausible by BTEAC treatment, amino derivatives are attached on carbon black surface.

Thermogravimetric analysis indicates a substantial weight loss of the BTEAC treated carbon black which confirms a large quantity functionalized groups are attached to carbon black surface. Simultaneously on BTEAC treatment there is a reduction of iodine adsorption number of carbon black which indicates presence of bulky groups attached on carbon black surface, hence functionalization of carbon black with BTEAC could cause attachment of benzyl and ethyl groups on the carbon black surface. Functionalization of carbon black with BTEAC treatment does not alter the basic morphological characteristics of carbon black such as particle size, aggregate size, aggregate shape, and aggregate size distribution etc.

On treatment of carbon black with BTEAC the surface chemical nature of carbon black was modified, possibly by attachment of ethyl and benzyl groups of BTEAC on carbon black surface through different functional groups present on carbon black at the same time amine part of BTEAC could attached to carbon black. Hence, it makes carbon black more compatible with rubber molecules, as a result, the filler-polymer interaction is increased and consequently the propensity of filler re-agglomeration as well as filler network formation is reduced. It is noted that dispersion and distribution of carbon black aggregates in the rubber matrix were significantly reduced by treatment of carbon black with BTEAC and comparatively lower size of carbon black agglomerates are formed as compared to nontreated control carbon black, AFM study of the rubber compound revealed the same. Due to the enhanced dispersion of BTEAC treated carbon black the abrasion resistance of rubber compound is improved,

Lower filler-filler interaction and the improvement of filler-polymer interaction of treated carbon black with respect to the control compound help in reducing Payne effect of the compounds up to

25%. BTEAC treated carbon black further reduces hysteresis energy significantly in both the rubber system, which was measured at 60°C. Hence treatment of carbon black with BTEAC leads to low rolling resistance for tyre tread compound.

Hence BTEAC treatment of carbon black results in significant change in its surface chemical nature and which causes enhanced rubber properties in emulsion SBR-BR rubber compound as well as in SSBR-BR rubber system. It has been noted that the experimental carbon black has enhanced efficacy towards the SSBR based rubber system in comparison to the emulsion SBR system and the same is probably caused because of polar polymeric ends present in SSBR rubber molecules due to the living polymerization of the same.

BTEAC treatment of carbon black can benefit in increase of filler loading without any detrimental effect. It is observed that due to increase of filler loading by 5 phr, the abrasion resistance, stiffness and wet traction property of rubber compounds increase.

Rubber compound with 65 phr carbon black loading provides significant improvement in wet traction and abrasion resistance properties keeping comparable rolling resistance as compared to control compound consisting of 55 phr of non-treated carbon black. Hence, enhancement of BTEAC treated carbon black loading can be considered as suitable approach for high performance passenger car tread applications where wet traction property is essential, more over the same will benefit in durability and stiffness of tyre tread.

In the case of rubber compound, SB1-60, where 5 phr higher carbon black loading was taken in compassion to the control compound. In this case due to incorporation of functionalized carbon black the abrasion resistance is increased significantly and the efficiency BTEAC is so significant it provides reduced rolling resistance property in comparison to control compound without affecting the wet traction property. In addition to the same it provides enhanced modulus and stiffness of rubber compound compared to the control compound.

Thus, incorporation of 5 to 10% phr higher BTEAC treated carbon black can be considered as preferred selection for specific tyre tread compounds includes electric vehicle tyre tread compound where reduced rolling resistance, enhanced abrasion resistance and high compound stiffness are essential.

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