CHAPTER-6:
SIMULATANEOUS CHANGES ON CARBON BLACK SURFACE AND STRUCTURAL MORPHOLOGY TO IMPROVE TYRE TREAD COMPOUNDS

6.1 Background

Carbon black is made of spherical primary particles which are associated with tiny nano-structural units having graphitic layers of crystallites phase and amorphous phase in nature. A schematic representation of carbon black morphology is shown in Fig-6.1, and it is seen that carbon black particles consist of a carbon black 'core' which is surrounded by graphitic layers of crystallites, while the core is basically characterized in amorphous in nature [1].

Houska et al [2] emphasized the structure of carbon black in terms of graphite structure, and they suggested that carbon black micro-structure consists of a numerous number of small graphite layers with diameters in the order of 20A^{o}. They further demonstrated that few numbers of these graphitic layers of structural units are associated together and form a 'group of graphitic layers which are randomly oriented and connected through Van der Waals force of interaction. Jawhari, et al. [3] analyzed carbon black morphology through Raman spectroscopy and described that the carbon black consists of limited crystallinity in its structure and the crystalline region of carbon black are mainly distributed towards the skin region of carbon black. Gruber et al, characterized carbon black through high-resolution transmission electron microscopy and described that the basic nanoparticle of carbon black is associated with small graphene flake layers which are basically arranged towards the surface of particles and gradually diminishing towards the center of the particles [4].

In line with surface morphological phenomena, carbon black is characterized by different surface chemical functional groups which are formed during the manufacture of carbon black in the furnace process of manufacturing. A schematic representation of surface functional groups is shown in Chapter-2 which concludes that major oxygen containing functional groups are

associated on carbon black surface [5-6]. A carbon black associated with large extent of amorphous characteristics possesses maximum extent of functional groups, since surface functionalization of carbon black largely takes place in the amorphous regions of carbon black compared to the crystallite parts [5].

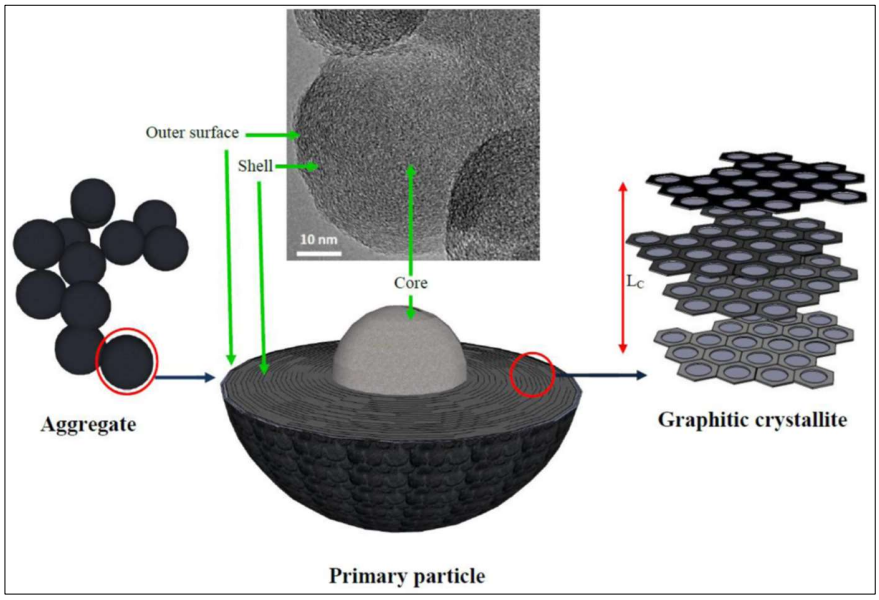


Fig-6.1: Schematic representative of carbon black surface morphology and functionality

Several investigations have been carried out towards the pattern of surface morphology, the surface functional groups of carbon black and their influences on the rubber application properties. It has been demonstrated in previous studies, that carbon black morphology as well as the surface functional groups can be altered by heat treatment, chemical treatment, oxidation, plasma treatment etc [6-7].

Since carbon black surface is characterized by a part of amorphous nature and partly graphitic layers, it causes existence of partial crystalline structural unit on its surface. Oxidation of carbon black may cause several changes on surface morphology, and on achievement of specific oxidation limit, the possibility of change in extent of crystallization could takes place. Oxidation of carbon black could cause a change in surface textures of carbon black, which could change the surface area of carbon black that leads to change in its surface porosity, surface crystallinity, surface

roughness etc [8-9]. The extent of carbon black characteristics modification truly depends on the route of oxidation as well as on the extent of the oxidation. Additionally, oxidation causes a change in surface functionality of carbon black.

In the current investigation, carbon black has been oxidized by treatment of the same with ozone under a controlled condition and the changes on carbon black morphological structure as well surface chemistry is discussed. The effect of such modified carbon black on rubber compound properties are also elaborated.

6.2 Ozone Treatment of Carbon Black and Characterization of Change in Surface Phenomena

6.2.1 Ozone Treatment Method of Carbon Black

Oxidation of carbon black has been carried out in Laboratory oxidizer equipment as described in Chapter-3. In this investigation, N330 grade of carbon was oxidized by treatment of carbon black with ozone and on oxidation the morphological characteristics of carbon black were susceptible to change. To investigate the change in carbon black morphology, the carbon black was oxidized for 30 minutes, and the oxidized carbon black vis -a-vis non oxidized control carbon black were characterized for different carbon black features, include HRTEM, XRD, surface functionality, thermogravimetric analysis, FESEM analysis and basic carbon black colloidal parameters etc.

6.2.2 Characterization of Carbon Black on Ozone Treatment

6.2.2.1 High Resolution Transmission Electron Microscopy Analysis

High Resolution transition electron microscopy (HRTEM) analysis of carbon black was carried out to visualize and investigate the changes that occurred on carbon black surface morphology due to ozone treatment. The high-resolution transition electron microscopic images of carbon black are shown in Fig-6.2, here the high magnification of carbon black surface illustrates the nature of

microstructural crystallography associated on the surface. It is observed that a major part of graphitized layers, as shown by thin layers, are arranged, and packed together in a crystallographic fashion. The arrangement of thin graphitic layers signifies the nature of crystallinity associated on carbon black surface.

HRTEM study was analyzed for comparing the nature of crystallography change and fashion of graphitic layers arrangement between control carbon black as well as ozone treated carbon black. HRTEM study reveals that a portion graphitized micro layers are poorly arranged for oxidized carbon black as compared to the control carbon black. Hence, it signifies that the oxidation of carbon black through bombard of ozone gas the crystallinity of carbon black surface was diminished, and the amorphous characteristics are generated on carbon black surface [10]. The distortion of graphitic layers of crystallites is clearly recognized by rough surface of experimental carbon black in comparison with the control carbon black by the help of very high magnification of microscopic image as shown in Fig-6.2 .

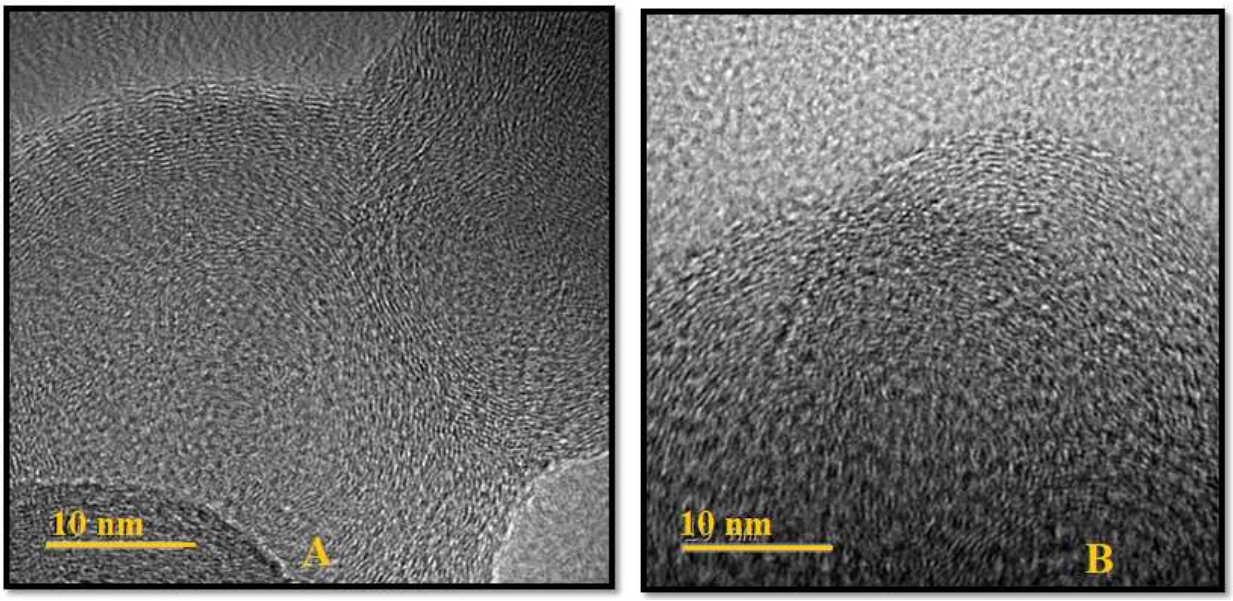


Fig-6.2: *High-resolution transition electron microscopy (HRTEM) of carbon black (a) non-oxidized carbon black (b) oxidized carbon black with ozone treatment.*

Further oxidation of carbon black leads to generation of functional groups on carbon black surface, which are basically oxygen containing organic functional groups. On oxidation carbon black morphology tends towards amorphous nature due to destruction of graphitic microstructural

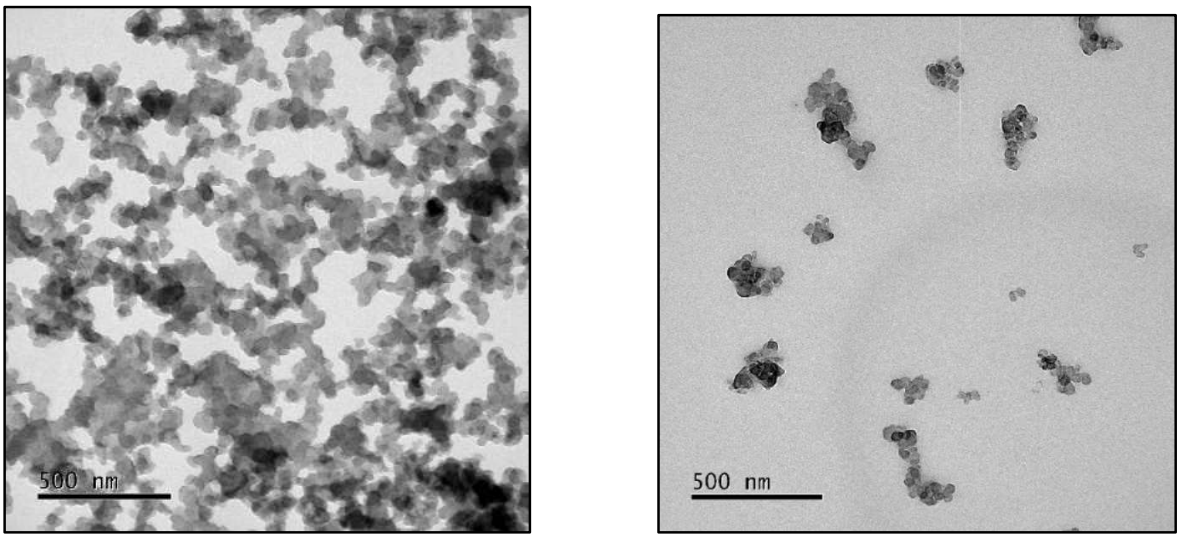
arrangement. The increased amorphous characteristics of oxidized carbon black also leads to generation of functional groups as carbon black amorphous parts are prone to generate surface functional groups.

The added functional groups of oxidized carbon black increase the hydrophilicity of carbon black attributed to generation of oxygen containing functional groups. ASTM furnace black does not possess enough hydrophilicity to be dispersible in water while increased surface functionality of ozone treated carbon black possesses enough hydrophilicity which can make it sufficiently dispersible in water.

The increased hydrophilicity of carbon black due to ozone treatment is characterized by HR-TEM analysis by dispersing the same in distilled water. In this study, carbon black was dispersed in distilled water in an ultrasonic bath at high vibrating frequency, which assists in segregation of aggregates from each other and make a water dispersion of carbon black. As ASTM grade carbon black, eg N330, does possess enough polarity, the aggregates of the same tend to interact with each other and lead to re-aggregation in the dispersion medium. While on oxidation the polarity of carbon black is enhanced, and which could provide enough hydrophilicity on the same to make a comparatively stable dispersion of oxidized carbon black compared with non-oxidized carbon black [18]

HRTEM of these carbon black dispersions was carried out after a defined time of disperse preparation. In this study, after 30 minutes of disperse preparation, a tiny drop of disperse was put on the grit of HRTEM analysis, and then the grit was allowed in hot environment to evaporate the water for around one hour. The carbon black particles deposited on grit surface were analyzed for HRTEM.

The HRTEM of carbon black is shown in Fig- 6.3, it is observed that control carbon black shows a network structure of agglomerates, where the aggregates are connected to each other as shown in Fig-6.3 (a), while in case of oxidized carbon black, the aggregates are well separated from each other and remains as discreate aggregates in the system as shown in Fig 6.3 (b). The high network formation of non-oxidized carbon black is caused due to the re-agglomeration tendency by Van der Waals force of interaction while on oxidation of carbon black, it becomes sufficiently hydrophilic in nature which is able to form stable dispersion of carbon black with adequate separation among the aggregates in the aqueous medium.



(a) (b)

Fig-6.3: *HRTEM images of carbon black aggregates/agglomerates suspended in water-dispersion* (a) non-oxidized carbon black, where aggregates form agglomeration (b) Oxidized carbon black *by Ozone treatment for 30 minutes where aggregates remain discrete particles and scattered in the system.*

6.2.2.2 X-Ray Diffraction (XRD) Analysis and Characterization

X-Ray Diffraction analysis was carried out to investigate the structural characteristics of crystalline materials to identify the crystalline phases present in the material. A crystal is composed of periodically arranged tiny structural units, atoms, planes etc, while amorphous materials do not possess that periodicity, where the structural units are randomly distributed in its structure. Hence, for crystalline structure, while there is periodic arrangement of atoms/structural units, the X-rays scatter only in certain directions during the XRD analysis and the same causes a high intensity peak of the X-rays, however, in case of the amorphous phase X-rays would be scattered randomly in many directions due to disordered arrangement of structural units. As a result, X-ray diffraction from amorphous material surface would provide a lower peak intensity compared to crystallite structure. XRD analysis of carbon black was studied by different investigators to characterize the structural construction of the same and indicates that carbon black is composed of small crystallite region which were made up of parallel graphitic layers [12].

The XRD patterns of carbon oxidized carbon black and non-oxidized carbon black samples are carried out at ambient temperature, with a scanning range of 5 to 90° at a scanning rate of 5° per minute. The diffraction intensity at different diffraction angles (θ) are measured and plotted the same with 2θ value. The diffraction pattern of CB shows two broad peaks corresponding to the (002) and (100) planes of the graphite structure, respectively, and the intensity of the peak determines the extent of crystallinity [13].

The XRD of carbon black is shown in Fig-6.4, where it is seen the high intensity diffraction peak corresponds to (002) plane appears near to 2θ value of around 26° while the peak corresponds to (001) plane appears near to 43°. It is seen that the intensity of diffraction corresponding to (002) plane of non-oxidized control carbon black is substantially high as compared the same of oxidized control carbon black. A reduced XRD intensity peak of ozone treated carbon black signifies presence of reduced crystallinity and increased amorphous characteristics compared to control carbon black. In TEM analysis of carbon back post ozone treatment, a distortion of graphitic plates takes place, which causes distortion of surface crystallinity and same has been confirmed by the reduced XRD peak corresponds to (002) plane as well as (100) plane.

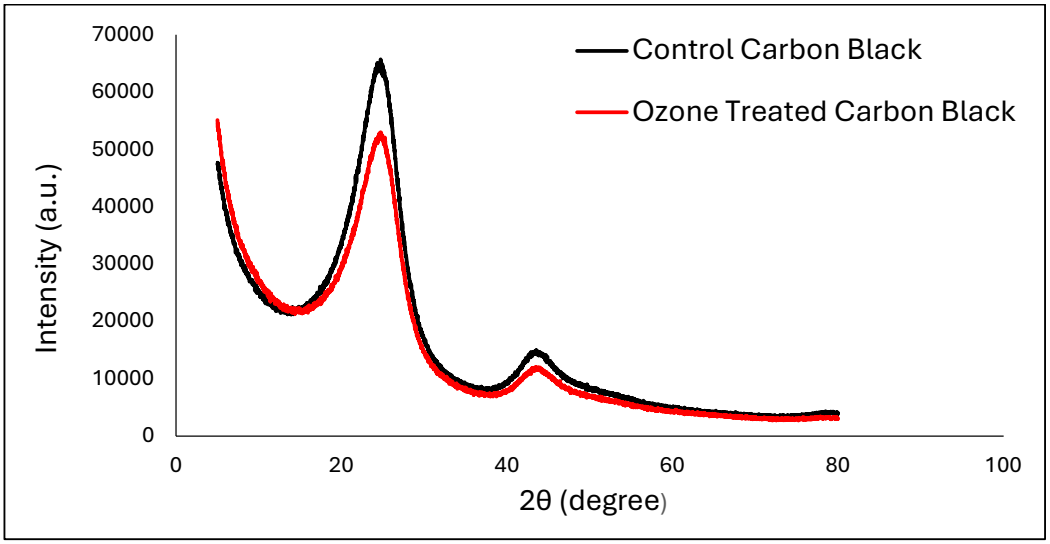


Fig-6.4: *XRD Pattern of control carbon black and ozone treated carbon black.*

6.2.2.3 Thermogravimetric (TG) Analysis and Study of Crystallinity

The study of crystallinity is further characterized by thermogravimetric analysis where the concept of oxidative degradation is applied to investigate the change in crystallinity on carbon black due to oxidation by ozone treatment. The inherent characterization of carbonaceous material reveals that the graphitic and crystallite arrangement is highly resistant to oxidation and the oxidation resistance increases with increased graphitized structure of same [14]. It is seen that on ozone treatment carbon black surface; the morphological structure is changed and arrays of graphitization get distorted to increase the amorphous nature of carbon black.

The change in crystallinity of carbon black was detected by study of oxidation stability and the same was carried by TG analysis under heating of carbon black at oxygen gas environment with a control heating of 10°C per minute. The TG analysis of carbon black is shown in Fig-6.5, where it is seen that over the control heating of carbon black there is a slow weight loss of the materials due to removal of volatiles present in carbon black and after a certain time of heating a steady fall in carbon black weight is observed which is caused due to burning of carbon black in presence of oxygen, i.e. it indicates oxidative degradation of carbon black has started.

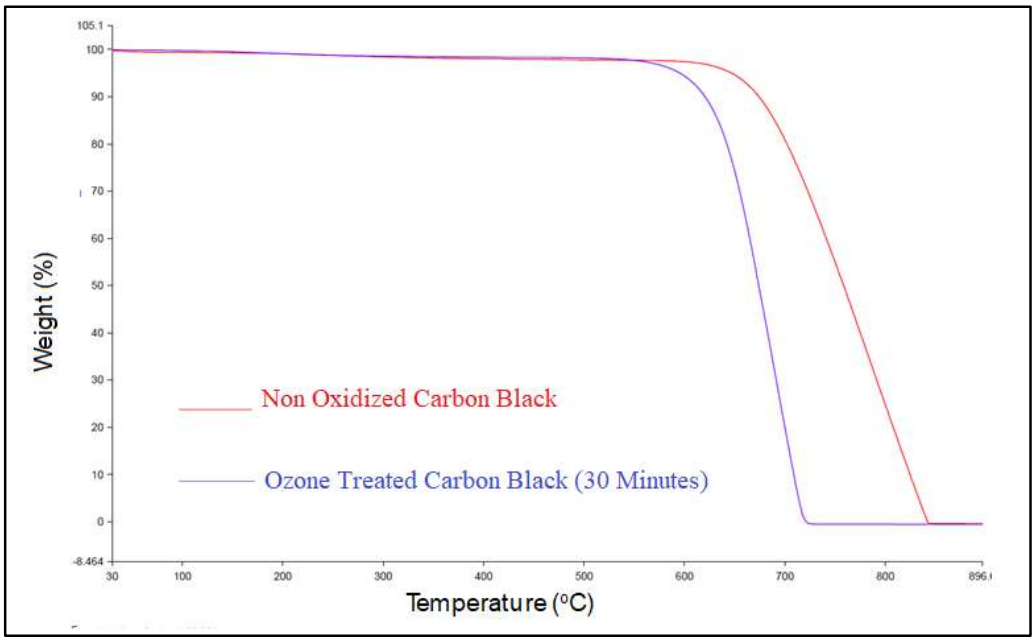


Fig-6.5: *Thermogravimetric analysis of carbon black in presence of oxygen atmosphere*

It is seen the onset of oxidation started for non-oxidized at around 575°C and completed at above 800°C, while ozone treated carbon black shows the oxidation started at around 575°C temperature, however the same completed at 720°C, i.e, oxidative degradation of ozone treated carbon black occurs rapidly. Hence it indicates the oxidation stability of carbon black is reduced on treatment of carbon black with ozone and the same results due to its increased amorphous nature, caused by distortion of graphitic structural arrangement on ozone treatment.

6.2.2.4 Changes in Carbon Black Properties on Ozone Treatment

Nitrogen surface area measurement of carbon black is based on B.E.T equation where the external surface area of carbon black is measured by statistical thickness surface area (STSA) and total surface area of same is measured by total nitrogen surface area (NSA value). NSA value of carbon black indicates the surface area associated with external surface area as well as the pores present on surface. Due to the smaller size, nitrogen molecules enter into the pores of carbon black and adsorbed inside the pores which resulting in additional surface area, while external surface area does not count the pores present on carbon black surface. Hence the ratio of NSA to STSA is proportional to the porosity on carbon black and is considered as a measure of carbon black surface porosity [15-16].

The properties of control carbon black as well as oxidized carbon black are shown in Table-6.1, it indicates that STSA value of oxidized carbon black is similar to control carbon black, however the NSA value of the oxidized carbon black is substantially higher. The high NSA value of oxidized carbon black indicates the presence of numerous numbers of pores generated on carbon black surface and causes a considerable change in carbon black morphology. The increased porosity of oxidized carbon black is represented by its increased NSA to STSA ratio value compared to the same of non-oxidized carbon black [17].

Iodine adsorption number is also a measure of carbon black surface area, and it is represented by the amount of iodine adsorb on a defined amount of carbon black. The higher the iodine adsorption number indicates a high surface area of carbon black. On oxidation numerous numbers of functional groups are generated on carbon black surface which restricts the adsorption of bulky iodine molecules on its surface during the iodine adsorption number measurement, as a result on

oxidation carbon black results with low iodine adsorption number compared to non-oxidized carbon black.

The structure of the carbon black is measured by oil absorption number which indicates the milliliter of oil absorbed per 100 gm of carbon black. Carbon black on oxidation does not change its basic structural configuration and the oil absorption number of carbon black is almost similar. CHNS-O analysis was carried out to measure presence of oxygen in carbon black, and it is seen increased oxygen content observed with oxidized carbon black which is caused by generation of oxygen containing functional groups on carbon black surface due to the ozone treatment.

Table-6.1: Carbon black properties

	Unit of Measurement	**Non-oxidize carbon black**	**Oxidized carbon black (30 minutes)**
Iodine Adsorption Number (IAN)	(mg/Kg)	82	77
Nitrogen Surface Area (NSA),	(m^2/g)	73	78
Statistical thickness Surface Area (STSA),	(m^2/g)	69	70
Ratio between NSA and STSA	-	1.06	1.11
Oil Absorption Number (OAN)	ml/100g	101	102
Compressed OAN	ml/100g	84	84
Oxygen Content	Wt%	0.2	0.51

6.2.2.5 Measurement of Volatile Matters Present in Carbon Black and pH of Carbon Black

Carbon black on heating at high temperature in absence of oxygen results in a major part of carbon black surface functional groups getting removed from the surface in term of volatile matters. On heating carbon black in absence of oxygen the functional groups are thermally decomposed, as a result carbon black partially losses its weight and the weight loss of carbon black indicates the extent of functional groups lost due to the thermal decomposition [18].

The heating of the carbon black was carried out in absence of oxygen to restrict the ignition of carbon black and to make sure the loss of weight was caused due to the loss of functional groups on thermal degradation. The testing of volatile matters measurement was carried out according to

DIN53552 test method, where carbon black was heat treated till 900°C in presence of inert gas. The volatile matters of carbon black due to the heat treatment are shown in Fig-6.6 and it indicates ozone treated carbon black resulted in greater loss of volatile matters. Hence on oxidation of carbon black by ozone, several functional groups were generated on carbon black, and which were removed as volatile matters on thermally decomposition in absence of oxygen and as a result volatile matters for ozone treated carbon black becomes higher compared to control carbon black.

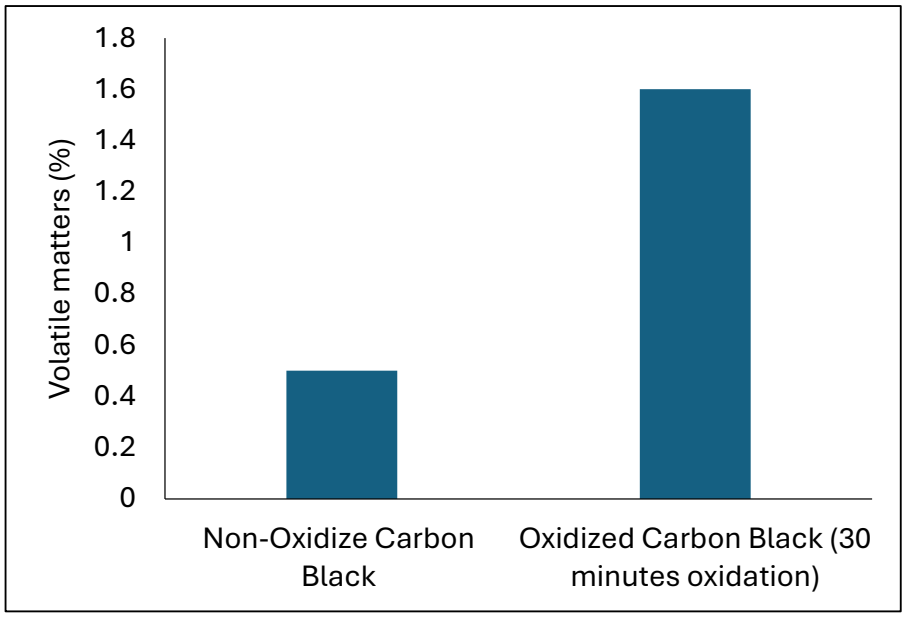


Fig-6.6: *Increased in volatile content due to functionalization of carbon black.*

On oxidation, several functional groups generated on carbon black surface as confirmed by TGA analysis and the functional groups are primarily characterized with oxygen containing groups, as a results, carbon black tends toward acidic nature and consequently pH of carbon black is reduced which is shown in Fig-6.7. It is seen that carbon black on ozone treatment gets acidic and pH of the same is reduced to 5.5 form its initial pH of 7.5. The reduction pH signifies the presence of acidic surface functional groups on carbon black surface. The oxidized carbon black is then thermally treated in an inert atmosphere and on thermal treatment of oxidized carbon black in inert atmosphere the surface functional groups of carbon black are lost in term of volatile matters, and then pH of the carbon black is again measured. It is seen that, on heat treatment of oxidized carbon black the pH of the same is increased to 8, which is even higher than the control carbon black. It

indicates on thermal treatment the acidic functional groups generated on carbon black surface are lost as a result carbon black loses its acidic characteristics and which causes its increased pH.

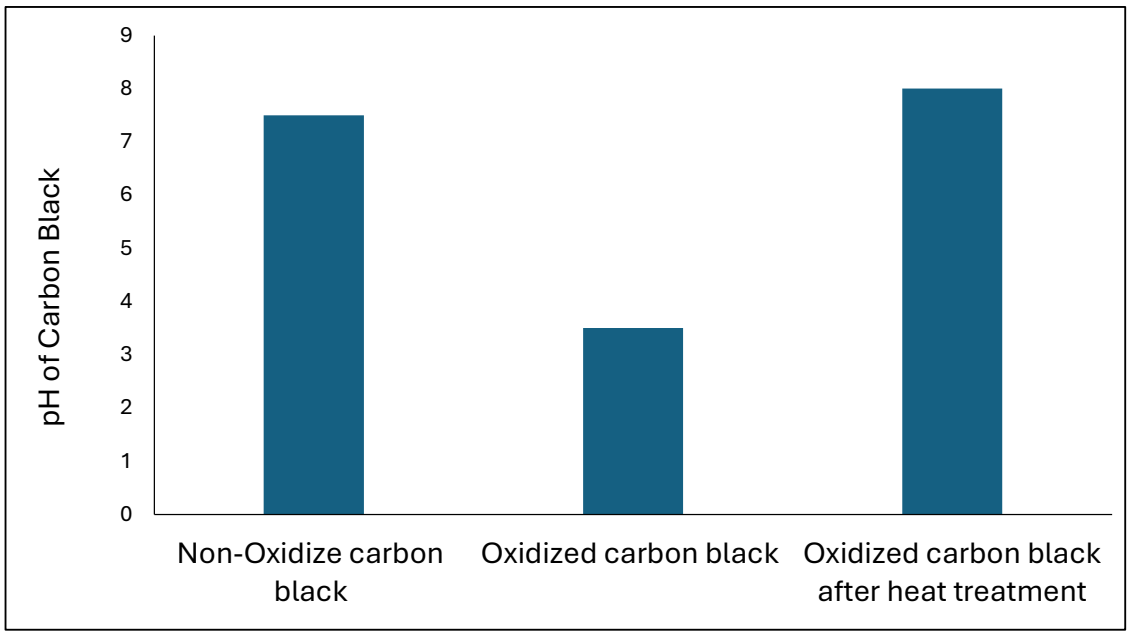


Fig-6.7: *pH of carbon black- changes due to presence of functionalized*

6.3 Investigation of the Effect of Ozone Treated Carbon Black in Rubber Compound Properties for Tyre Tread Compounds.

The modification of carbon black by post treatment with ozone gas causes a disorientation of the arrays of graphitic layers on the carbon black surface, which results in reduction of crystallinity consequently, it increases the amorphous behavior of the same. The amorphous part of the carbon black provides irregularities on its surface and may cause enhanced physical attachment with rubber molecules. Moreover, oxidation leads to an increase in porosities on carbon black surface where rubber molecular chain ends attempt to penetrate. Carbon black surface morphology assists in formation of functional groups on its surface as Scanning Tunneling Microscopy (STM) study of carbon black indicates, the functional groups bonded to carbon black majorly at its amorphous phase areas [1]. It has been demonstrated that on oxidation of carbon black leads to increased

surface functionality due to formation of higher active sites for the functionalization and leads to formation of large numbers of new functional groups as well as modify the existing functional groups of carbon black.

Thus, post treatment of carbon black by ozone changed its functionality, crystallite textures, surface porosity etc., which affects the rubber reinforcement of carbon black. In this part of the investigation, carbon black has been post-treated with ozone and the effect of ozone treated carbon black has been carried out in a model tyre tread compound and compared the same with non-treated control carbon black.

Here an attempt has also been made to investigate the effect of oxidized carbon black with different levels of ozone oxidation and to do the same, carbon black was oxidized for 15 minutes, 30 minutes and 60 minutes and compared with control carbon black.

6.3.1 Carbon Black Properties

N330 grade carbon black was ozone treated for different time interval such as 15 minutes, 30 minutes and 60 minutes, and the treated carbon black designated as CBO-15, CBO-30 and CBO-60 respectively. It is expected that they would have different level of changes in the surface morphology. The properties of these experimental carbon black vis-à-vis control carbon black, identified as CBO-0, are shown in Table-6.2.

It is seen with increase in ozone treatment time the carbon black results in increased porosities as represented by increased NSA/STSA ratio. The carbon black sample CBO-60 has the largest NSA value of 79 m^2/g and comparable STSA value, hence the same results in higher value of NSA/STSA ratio among all the carbon black, indicating its larger porosity on the surface due to higher extent of oxidation. The volatile matter, oxygen contents of carbon black increase with increase oxidation time, which indicates the increase functionalization of carbon black with increase oxidation time, however, the difference of the same between CBO-30 and CBO-60 is marginal which indicates scope of further functionalization is limited after oxidation for 30 minutes, similarly pH of experimental carbon reduces with increase in oxidation time and the difference of the same between CBO-30 and CBO-60 remains marginal.

Table-6.2: Colloidal parameters of carbon black with different ozone treatment time

	Unit	CBO-0	CBO-15	CBO-30	CBO-60
IAN	mg/Kg	82	81	77	76
Nitrogen Surface Area (NSA)	m^2/g	73	75	78	79
STSA	m^2/g	69	69	70	70
NSA/STSA	-	1.06	1.09	1.11	1.13
Oil Absorption Number (OAN)	ml/100g	101	102	102	102
Compressed OAN	ml/100g	88	87.1	86.8	87
Oxygen Content	%	0.2	0.23	0.51	0.55
Volatile content	%	0.5	1	1.6	1.7
pH	pH unit	7.5	7	5.5	5

The carbon black grades are further characterized by change in crystallinity with increase ozone treatment time by XRD study. The XRD spectra of the carbon black are shown in Fig-6.8, and it is seen with increase of oxidation time the crystallinity of carbon black is reduced, which is demonstrated by reduced peak height of diffraction intensity (2θ) at 26° and 43°corresponds to (002) plane as well as (100) plane. The lowest peak height of XRD plot is associated with carbon black, which was ozone treated for maximum time of 60 minutes which is indicative of its low crystallinity and increased amorphous characteristics compared to rest of the carbon black samples.

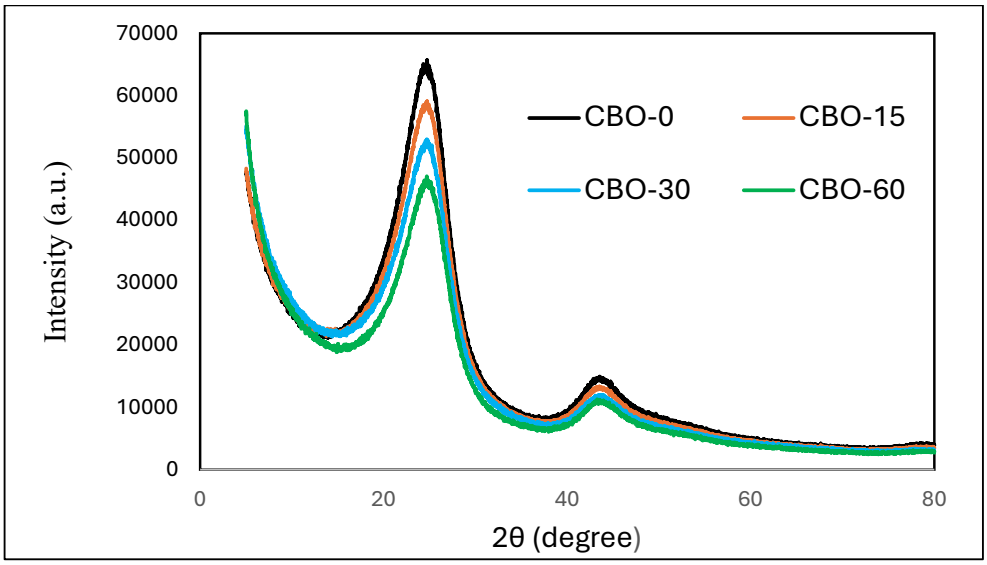


Fig-6.8: *XRD pattern of carbon black characterized with different oxidation time*

The oxidation stability of the carbon black samples was measured by TG analysis and the results are shown in Fig-6.9. It shows that carbon black CBO-60 has least thermal stability in oxygen atmosphere followed by CBO-30 and CBO-15 and the maximum stability is observed with control carbon black, CBO-0. The least oxidative degradation stability of ozone treated carbon black indicates presence of increased extent of amorphous region as compared to the non-treated control carbon black (CBO-0) and the increase amorphous characteristics is more prominent when ozone treatment time is increased.

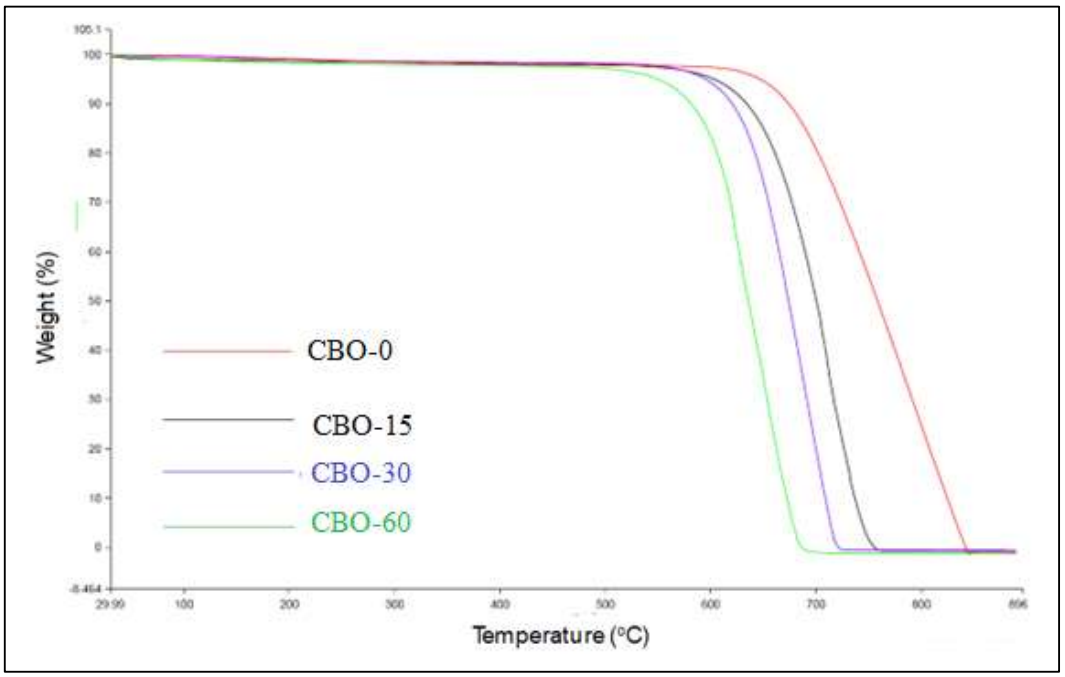


Fig-6.9: *Thermogravimetric analysis, in presence of oxygen atmosphere, of carbon black characterized with different ozone treatment time.*

6.3.2 Rubber Compound Properties of Ozone Treated carbon Black

Oxidation of carbon black results in morphological changes and generation of large number of functional groups on carbon black surface. To investigate the effect of these changes on rubber compound properties different types of rubber systems were selected for this study such as solution SBR-BR system (SSBR:BR =80:20) and emulsion SBR-BR system (SBR1712:BR =110:20). Carbon black loading was taken 50 phr for each of the compounds, keeping all other compounding ingredients identical. The detailed formulation and identification of compounds are shown in

Table-6.3. The mixing and compounding of rubber compounds were carried out in two stage mixing process by use of laboratory Banbury followed by two roll mixing mill as described in Chapter 3.

Table-6.3 A: Rubber compounding Formulation (unit: phr)

A. Compounding formulation of different rubber system compounds		
Ingredients	SBR1712-BR Based Compound	SSBR-BR Based Compound
BR	20	20
SBR1712	110	0
SSBR	0	80
Carbon Black	50	50
Zinc Oxide	5	5
Stearic Acid	2.5	2.5
TDAE Oil	5	20
M.C.Wax	2	2
CBS	1	1
Sulphur	1.2	1
B. Compound identification of rubber compounds consisting different oxidized carbon black		
Type of carbon black (N330) consisting in compounds	Identification of SBR1712-BR Based Compound	Identification of SSBR-BR Based Compound
Compound consisting of non-oxidized N330 Carbon black	SBO0	SSBO0
Compound consisting of 15 minutes Oxidized N330 Carbon black	SBO15	SSBO15
Compound consisting of 30 minutes Oxidized N330 Carbon black	SBO30	SSBO30
Compound consisting of 60 minutes Oxidized N330 Carbon black	SBO60	SSBO60

6.3.2.1 Rheological Properties of Rubber Compounds:

In the reinforcement of carbon black filled rubber compound, the rubber molecules are physically adsorbed on carbon black surface, leading to entanglements of rubber molecules on the carbon black surface, which is increased with increase in carbon black surface area. Similarly, the entanglement of rubber molecules increases with surface irregularity of carbon black. It is seen on oxidation the effective surface area is increased due to generation of pores on carbon black surface

and at the same time the surface morphology of the carbon black gets an irregular arrangement of graphitic layers, as a result larger extent of rubber molecular entanglement could be possible with carbon black. Rubber molecules with high entanglement or adsorption on filler surface, provides high Mooney viscosity, high torque during the rheological study [19]. In the rheological study the minimum torque was measured by oscillating disc rheometer and Mooney viscosity was measured by Mooney viscometer, which is expressed by the ML(1+4) value. The Mooney viscosity and ML value of rubber compound are shown in Fig-6.10 which indicates carbon black with increase in oxidation time leads to high Mooney viscosity in rubber compound. Hence, the increase of surface porosity and distortion graphitization morphology of carbon black leads in increased Mooney viscosity of rubber compounds.

Along with surface morphological changes, oxidation leads to generation of different functional groups on carbon black surface, which are acidic in nature and causes on reduction of carbon black pH. The accelerators used in rubber are basic in nature, hence due to increased acidity of carbon black the efficiency of accelerator is reduced towards vulcanization reaction. As the acidity of carbon black increases it tends to react with the basic natured accelerator. Hence with the increase in extent of carbon black oxidation the curing time of rubber compound is increased. The curing characteristics of the compounds are shown in Table-6.4, which shows high scorch safety and increased scorch time observed with experimental rubber compounds in both the rubber system.

Table-6.4: Curing characteristics of the compounds

	Mooney Viscosity	**ML**	**MH**	**Ts1**	**Ts2**	**Tc50**	**Tc90**
Unit	MU	lb-in	lb-in	Minutes	Minutes	Minutes	Minutes
SBO0	48	6.87	40.14	3.15	3.5	4.73	7.23
SBO15	48.2	7.06	39.41	3.7	4.02	5.37	8.31
SBO30	48.9	7.53	38.3	3.89	4.2	5.69	9.06
SBO60	49.1	7.56	38.21	4.11	4.43	6.22	10.37
SSB0	54.3	8.16	36.84	3.08	3.47	4.83	8.47
SSB15	56.5	8.77	35.6	2.94	3.31	5.03	10.51
SSB30	57.3	8.86	33.98	2.82	3.23	5.41	12.01
SSB60	58.4	9.22	33.44	3.14	3.8	7.71	12.37

6.3.2.2 Transmission Electron Microscopy (TEM) Analysis of Rubber Compounds

Transmission Electron Microscopy (TEM) analysis of rubber compounds was carried out to visualize the carbon black dispersion and its distribution in rubber matrix. Carbon black mixing in rubber matrix, involves the application of shear-forces, which benefits in dispersion and distribution of carbon black homogeneously in the matrix. It is to note, that even when carbon black is dispersed uniformly in the rubber, the carbon black aggregates tend to flocculate in the post-mixing stages like storage, extrusion, or vulcanization, which results re-agglomeration of carbon black aggregate. Re-agglomeration creates localized accumulation of carbon black, which causes a dense area of carbon black in rubber matrix. Simultaneously, for a fixed carbon black loading, the same phenomenon also creates some carbon black free space (void), i.e., less carbon concentrate region with increased inter-aggregate separation of carbon black in the rubber matrix. [20].

TEM image analysis for rubber compound is based on the phenomena that carbon black filled unstrained rubber compounds interpreted as two-phase system involving a dark phase, which refers to the presence of carbon black and a light phase, representing the rubbery material. The dark phase created by carbon black because to its high specific gravity compared to rubbery phase, though the darkness of the phases varies, due to the presence of carbon black concentration in the corresponding location in the matrix. While the carbon black particles overlap each other, the dark phase becomes more intense, which is caused due to high flocculation or inadequate dispersion and aggregated structure of carbon black.

As stated, for a particular dosage of carbon black, due to overlap of carbon black as well as due to flocculation of carbon black, some region of rubber matrix become free of carbon black, which leads to generation of light space or void space in the microgram images. Thus, TEM microgram images consisting more light space area signifies major area of rubber matrix free from presence of carbon black due to inadequate dispersion or flocculation of carbon black.

TEM analysis of rubber compounds comprising oxidized carbon black as well as non-oxidized carbon black was shown in Fig-6.9, where the experimental compound is associated with oxidized carbon black, that has been ozone treated for 30 minutes. The TEM analysis demonstrated a comparative study of change in filler dispersion and distribution between 30mmitnute ozone

treated carbon black and non-treated control carbon black in both the selected rubber systems, i.e, in SSBR-BR and emulsion SBR1712-BR. This investigation would conclude the effect of ozone treated carbon black in filler dispersion and distribution in the rubber matrix in compassion with control carbon black.

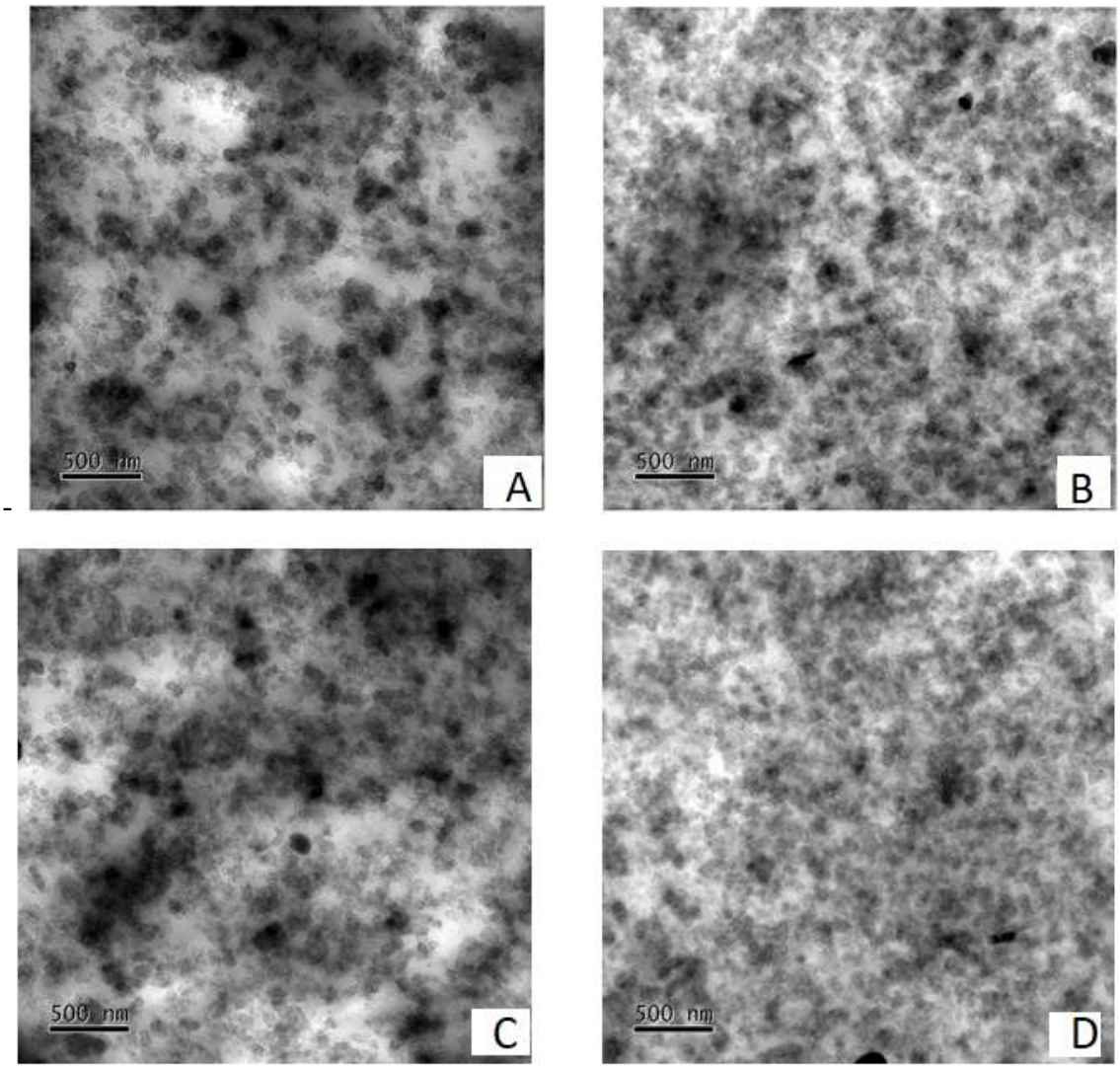


Fig-6.10: *TEM of rubber compounds (A) Controlled SBR-BR compound, (B) Experimented SBR-BR compound (SBO-30) where 30 min ozone treated carbon black used, (C) Control SSBR-BR compound, (D) Experimented SSBR-BR compound (SSBO-30) where 30 min ozone treated carbon black used.*

The TEM images show the control compound is associated with maximum volume of light spaces and bigger size of dark spots are scattered in the micrographic image in comparison to the experimental compound. The dark portion of the images demonstrates the presence of carbon black and the larger in size of the dark phase represents the localized and agglomerated carbon black which is caused due to inadequate filler dispersion in rubber matrix. It is also seen that the localized and agglomerated carbon black causes void volumes in rubber matrix just in vicinity to the dark phase which indicates poor filler dispersion for the control compound for both the rubber system selected. The TEM images of experimental compound signify a suitable filler dispersion in rubber matrix as the dark phases due to carbon black are scattered throughout the matrix and there are presence of less void volumes in the rubber system due to local filler loading and which is due to comparatively poor dispersion and distribution of filler.

Thus, on ozone treatment of carbon black, numerous pores are formed and crystal structure changes towards amorphous nature and several functional groups attached on carbon black surface, which causes then carbon black to interact with rubber molecules comparatively more strongly and increases the dispersion and distribution of carbon black in rubber matrix as visualized through microscopic study in both rubber systems.

6.3.2.3 Rubber Process Analysis

Payne effect of rubber compound is the measure of filler-filler interaction and filler-polymer interaction in rubber matrix. Carbon black characterized with enhanced interaction with rubber molecules provides lower Payne effect in the rubber compound [21-22]. The Payne effect of rubber compound was measured by Rubber process analyzer and the same for the corresponding rubber compound is shown in Fig-6.11. Here the trend of Payne effect of rubber compound with ozone treatment time of corresponding carbon black is shown and compared with corresponding control compound.

It is seen that the Payne effect of rubber compound decreases while the same consists of ozone treated carbon black and rubber compound with increase of ozone treatment time of carbon black corresponding rubber compounds shows more reduction of Payne effect. Thus, it indicates while carbon black is modified with ozone treatment, it enhances its compatibility with rubber molecules and leads to reduced filler-filler interaction and increase filler-polymer interaction.

While comparing efficiency of ozone treated carbon black on Payne effect in different rubber system, it suggests that ozone treated carbon black provides more affinity toward SSBR based rubber system, e.g., SSBR-BR system as compared to emulsion SBR1712-BR system. It has been observed that with increased oxidation time of carbon black the Payne effect of SSBR-BR rubber system falls steadily as compared to the same of emulsion SBR-BR rubber system. SSBR rubber is characterized by anionic polymerization and consists of living and reactive sites in its backbone structure, hence while the same is mixed with ozone treated carbon black possessing of increased functionality causes increased chemical interaction with the carbon black consequently, the Payne effect of rubber compound is reduced more effectively.

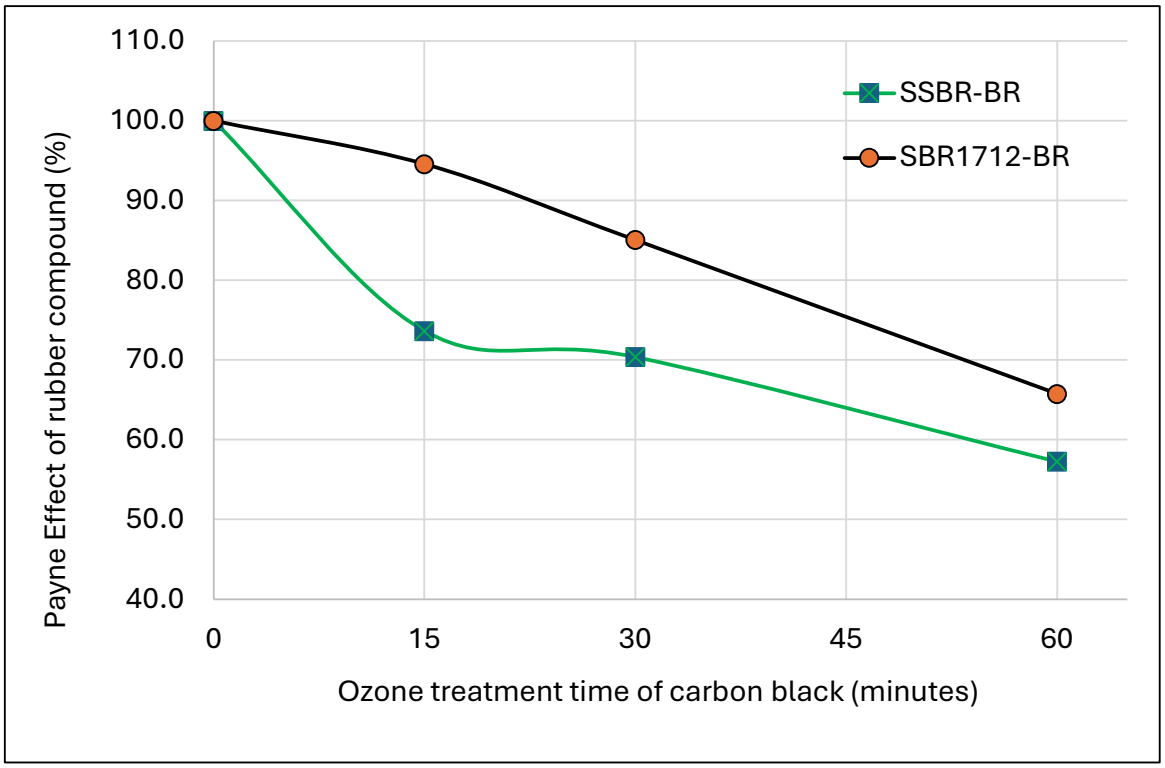


Fig-6.11: *Trend of Payen effect of rubber compound with ozone treatment time of corresponding carbon black.*

Table-6.5: Rubber process analysis and Payne effect of rubber compounds

SSBR-BR System	Unit	SSBO0	SSBO15	SSBO30	SSBO60
Shear modulus at high strain (G'_{100})	KPa	2109	1613	1547	1284
Shear modulus at low strain ($G'_{0.1}$)	KPa	157	176	174	167
Payne Effect (G'_{100}-$G'_{0.1}$)	KPa	1952	1438	1374	1118
SBR1712-BR System		SBO0	SBO15	SBO30	SBO60
Shear modulus at high strain (G'_{100})	KPa	583	510	487	490
Shear modulus at low strain ($G'_{0.1}$)	KPa	83	83	80	78
Payne Effect (G'_{100}-$G'_{0.1}$)	KPa	501	427	407	412

6.3.2.4 Physical Properties:

Ozone treated carbon black possesses considerable amount of surface porosities and is characterized with increased amorphous features in its surface morphology due to distortion of graphitic layers on oxidation. In rubber compounded with carbon black, the rubber molecules form multiple rubber shells surrounding the carbon black particles. Heinrich et al. [23] demonstrated that the rubber shells are of estimated thickness of is 0.7 nm approximately. The formation of rubbery shell causes increased interaction between rubber and carbon black and leads to restriction of motions of rubber molecules and hence increases the Mooney viscosity and modulus of rubber compound.

The modulus of rubber compound is shown in Fig-6.12, it shows a significant improvement of compound modulus observed while ozone treated carbon black is used and with increase in extent of ozone treatment period the change in modulus becomes more prominent. The ozone treated carbon black provides high compound modulus due to the surface porosity and increased amorphous nature of surface morphology which restricts the movement of rubber molecules due to physical interaction of carbon black with the rubber shells.

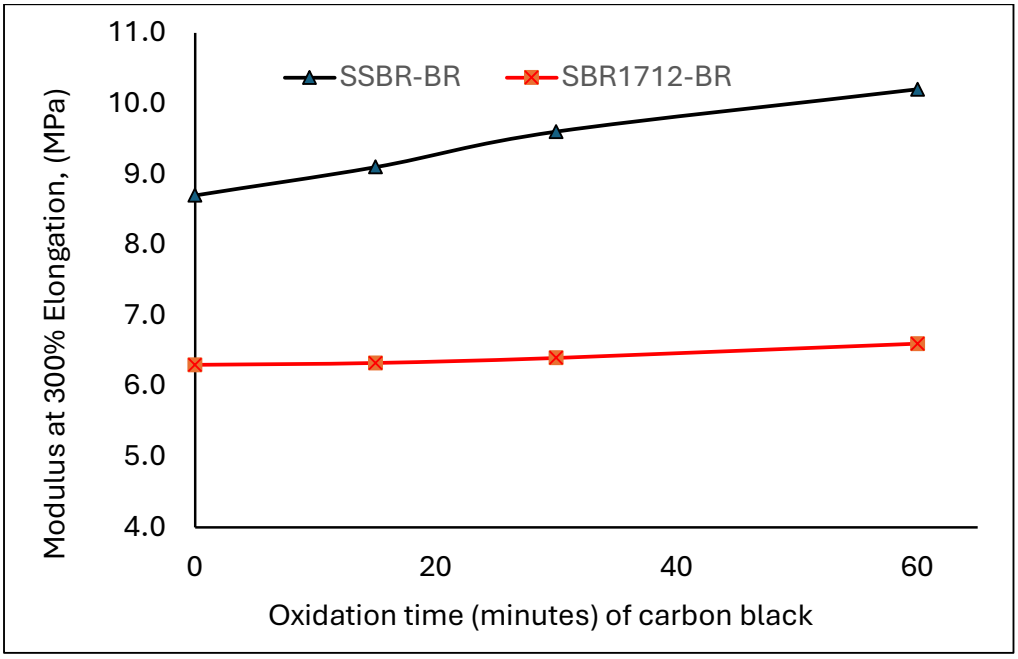


Fig-6.12: *Trend of modulus of rubber compound with ozone treatment time of corresponding carbon black.*

It is seen the extent of modulus enhancement is more prominent for the case of SSBR system as compared to SBR1712 based rubber system. The high modulus observed with SSBR based compound with ozone treated carbon black, is attributed to the restriction of movement of rubber molecules due to presence of high vinyl groups in its backbone structure. SSBR rubber, characterized with high vinyl content and its micro-structure configuration, provides high modulus as compared to oil extended emulsion SBR1712.

Carbon black with high surface area results in high tensile strength and abrasion resistance properties in rubber compound application. The oxidized carbon black gets enhanced surface area, as well as surface functional groups. The surface functional groups provide enhanced compatibility with rubber molecules causing added advantage of filler dispersion in rubber matrix as seen in transmission electron microscopy. The effective high surface area and enhanced filler dispersion of ozone treated carbon black provides enhanced tensile strength as well as superior abrasion resistance in rubber compound as shown in Fig-6.13 and Fig-6.1 respectively. The effectiveness of ozone treated carbon black is increased with increased ozone treatment time of the carbon black and it is more effectiveness with SSBR rubber system due to its high polarity.

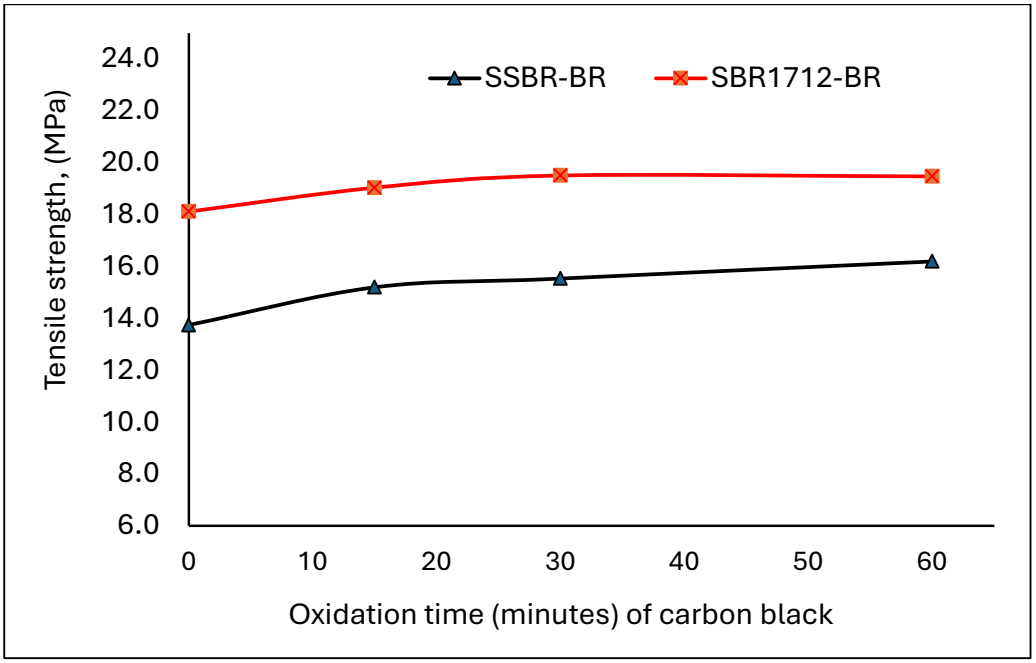


Fig-6.13: *Trend of tensile strength of rubber compound with ozone treatment time of corresponding carbon black.*

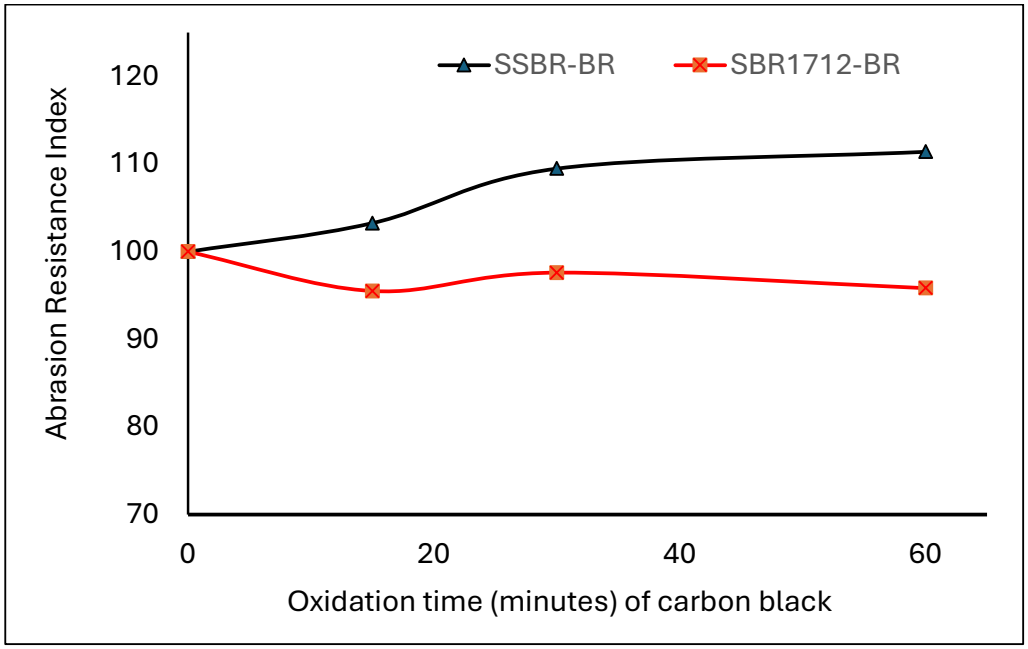


Fig-6.14: *Abrasion resistance index of rubber compounds*

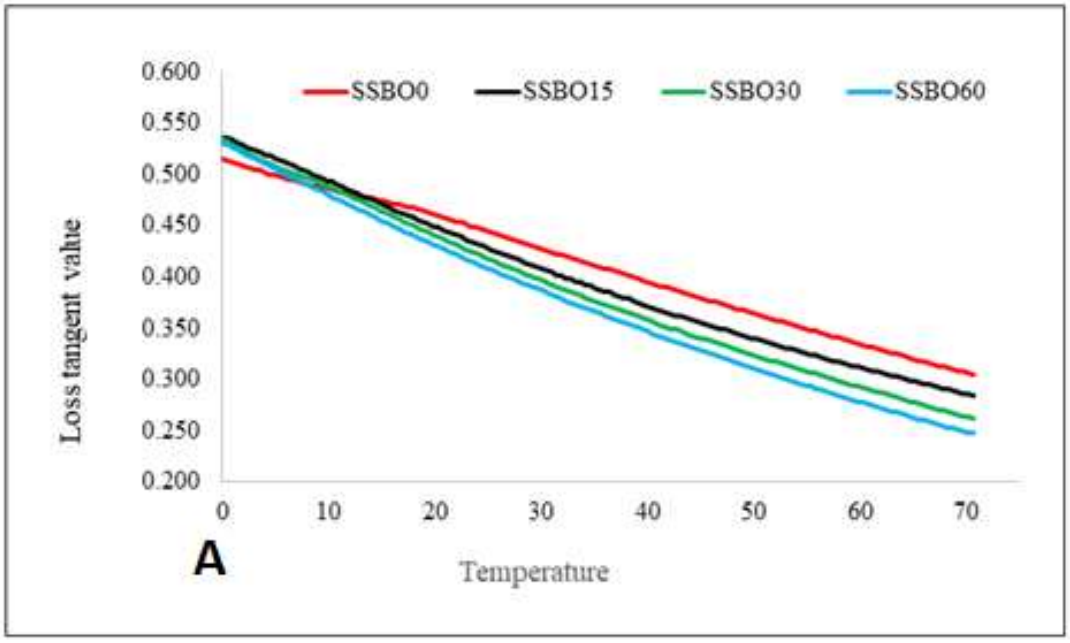
6.3.2.5 Dynamic Mechanical Analysis:

Dynamic mechanical analysis was carried out to characterize stiffness, hysteresis loss of rubber compound in different temperatures. Dynamic mechanical analysis was conducted from 0°C to 70°C temperature and hysteresis loss as expressed by loss tangent value (tanδ) of 60°C temperature and 0°C temperature was monitored, because tanδ at 60°C represents the rolling resistance of tyre tread compound and the same at 0°C represents wet grip performance for tyre tread compound [24-25].

The trend of tanδ value of rubber compounds with temperature are shown in Fig-6.15 for SSBR-BR rubber system and SBR1712-BR rubber system. The plots are used to calculate tanδ value of each compound at different measurement temperatures of 60°C as well as at 0°C which is shown in Table-6.6. It has been seen that while carbon black was treated with ozone the tanδ value of rubber compound at 60°C has decreased significantly, which indicates reduction of rolling resistance for the tyre tread compounds.

The extent of the tanδ value reduction varies with the time of ozone treatment of carbon black. It is observed that with the increase of ozone treatment time the reduction of tanδ becomes prominent. SSBR rubber with its inherent polarity has enhanced ability to interact chemically with the ozone treated carbon black compared to emulsion SBR1712 grade, as a result SSBR-BR based rubber compounds provides enhanced efficiency toward the dynamic characteristics and significantly reduces the tanδ. It is seen by use of ozone treated carbon black around 18% reduction in tanδ value has been achieved.

The wet grip performance of rubber compounds shows that ozone treated carbon black provides mixed performance on the same. The highest tanδ at 0°C indicates high wet grip property and it is seen that ozone treated carbon black provides enhanced tanδ value at 0°C temperature for SSBR-BR rubber system, hence in this rubber system ozone treated carbon black provides enhanced benefits in wet grip property, however, in case of emulsion SBR1712-BR rubber system, ozone treated carbon black provides marginal low tanδ value at lower temperature range of 0°C which indicates slight low wet grip property is resulted by use of ozone treated carbon black for SBR1712-BR based tyre tread compound however the same provides significantly lower rolling resistance.



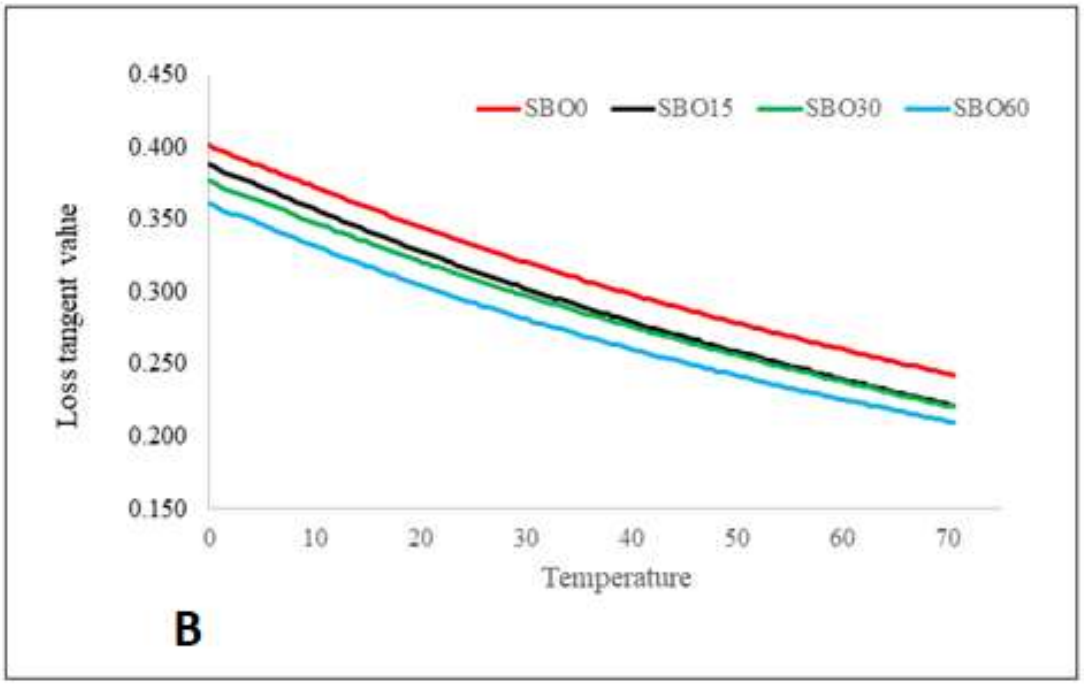
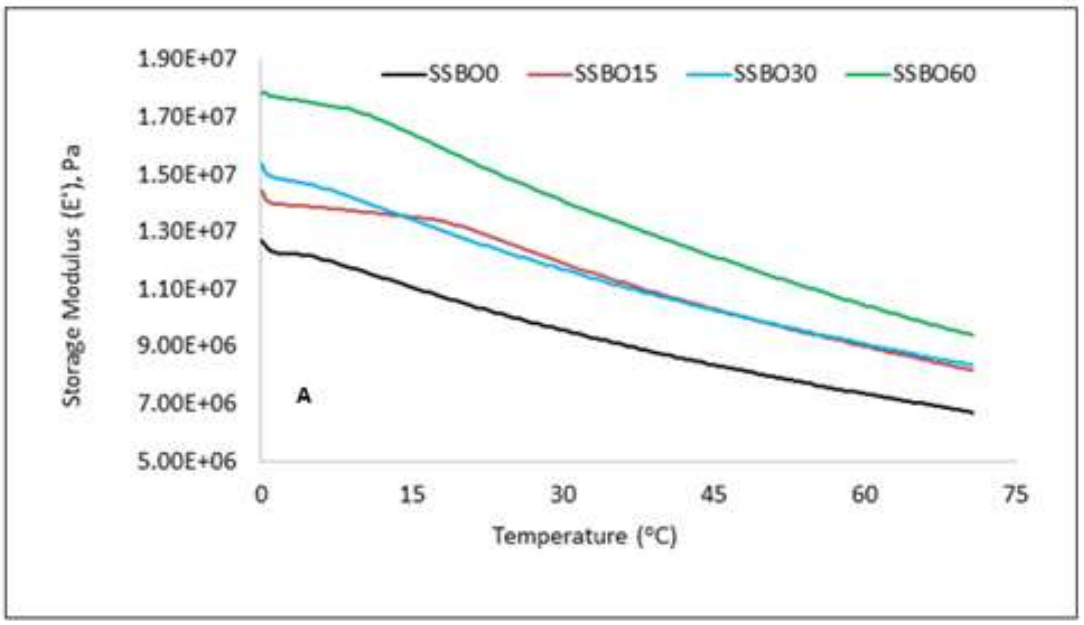


Fig-6.15: *Trend of loss tangent value of rubber compound with temperature scan (A) of SBR1712-BR rubber compounds (B) SSBR-BR rubber compounds*

Table-6.6: Dynamic Mechanical Properties of Rubber Compounds.

Dynamic Mechanical Analysis (at 60°C)				
SSBR-BR System	SSBO0	SSBO15	SSBO30	SSBO60
Storage Modulus (E'), MPa	7.36	9.01	9.1	10.5
Loss Modulus (E''), MPa	2.47	2.81	2.67	2.92
Tanδ	0.335	0.312	0.293	0.278
SBR1712-BR System	SBO0	SBO15	SBO30	SBO60
Storage Modulus (E'), MPa	5.84	6.58	6.69	6.63
Loss Modulus (E''), MPa	1.52	1.58	1.60	1.50
Tanδ	0.261	0.240	0.238	0.226
Dynamic Mechanical Analysis (at 0°C)				
SSBR-BR System	SSBO0	SSBO15	SSBO30	SSBO60
Storage Modulus (E'), MPa	12.7	14.4	15.3	17.8
Loss Modulus (E''), MPa	6.53	7.71	8.19	9.42
Tanδ	0.515	0.535	0.536	0.529
SBR1712-BR System	SBO0	SBO15	SBO30	SBO60
Storage Modulus (E'), MPa	7.28	8.18	8.24	8.29
Loss Modulus (E''), MPa	2.93	3.17	3.10	2.99
Tanδ	0.402	0.388	0.376	0.361

The stiffness of rubber compounds is expressed by its storage modulus (E') value and the trends of storage modulus of rubber compounds with temperature are shown in Fig-6.16 in both the rubber systems. The trends of storage modulus indicate that carbon black on ozone treatment provides enhanced compound stiffness compared to non-treated carbon black in the entire range of measurement temperature and the same at 60°C are shown in Table-6.5. It indicates a significant improvement of compound stiffness by around 20% has been achieved by use of oxidized carbon black. SSBR rubber system with polar back-bone structure and unique micro-structure characteristics provides enhanced efficiency towards ozone treated carbon black as compared to emulsion SBR system. It provides a higher extent of improvement in compound stiffness, which benefits the stability of tyre tread compound, inbuild strength of the material [26-27].



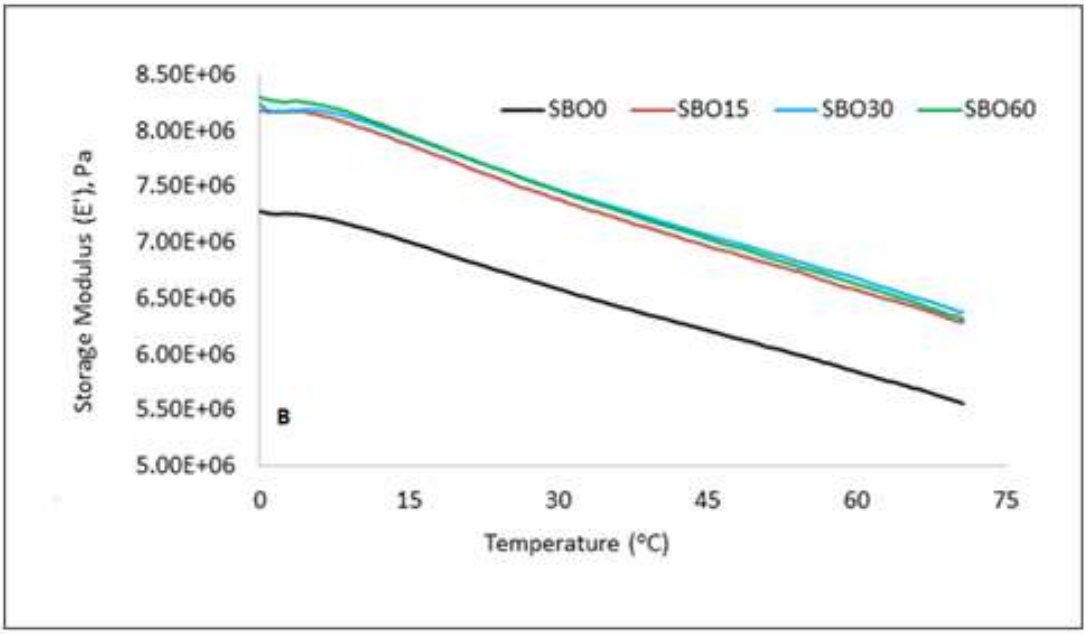


Fig-6.16: *Trend of storage modulus of rubber compounds with temperature scan (A) of SBR1712-BR rubber compounds (B) SSBR-BR rubber compounds*

6.3.2.6 Magic Triangle Properties for Tyre Tread Compounds

Optimization of magic triangle properties always remains in prime focus while development of tyre tread compound. Magic triangle properties of tyre tread compound refers to abrasion resistance, rolling resistance and wet traction properties which are represented here by abrasion resistance index, tanδ value @ 60ºC and tanδ value at 0ºC respectively. An increase in abrasion resistance index represents superior abrasion resistance, lower tanδ value @ 60ºC indicates low rolling resistance and high, tanδ value @ 0oC represents enhanced wet grip properties [28].

The magic triangle properties of rubber compounds are studied for both rubber systems, eg. SBR1712-BR system as well as in SSBR-BR system. The effect of ozone treated carbon black has been investigated on magic triangle properties of tyre tread compounds and compared with non-treated control carbon black. The magic triangle properties of rubber compounds in SBR1712-BR system as well as in SSBR-BR system are shown in Fig-6.17 and Fig-6.18 respectively. It indicates that ozone treated carbon black provide enhanced abrasion resistance and reduced rolling resistance properties in tyre tread compound based on SBR1712-BR rubber system at the cost of wet traction properties as wet traction property indicator (tanδ value @ 0ºC) of experimental rubber compounds reduces in the same direction of rolling resistance property (tanδ @ 60ºC).

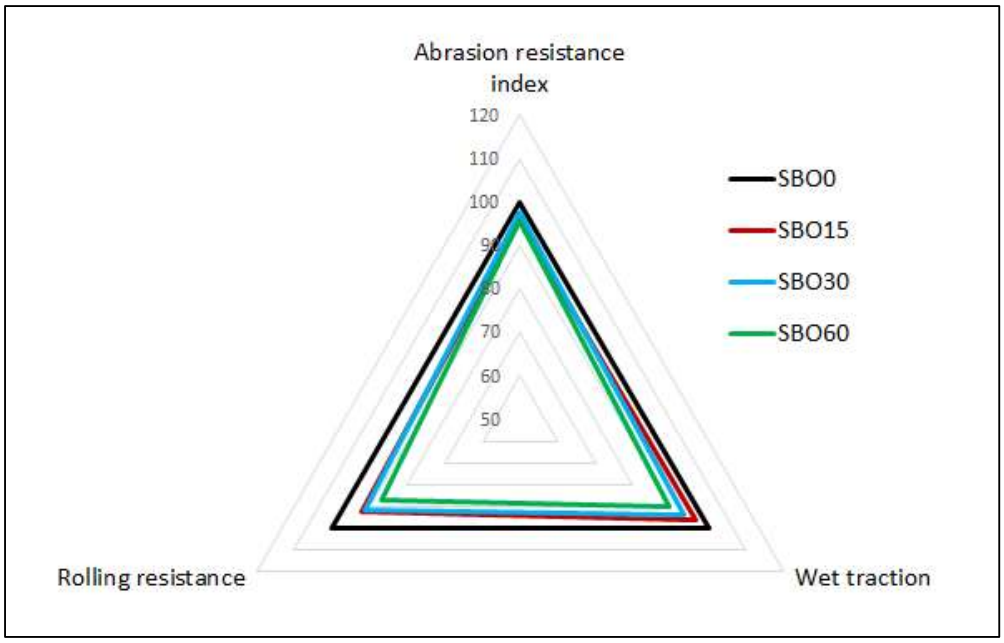


Fig-6.17: *Magic triangle properties of different SBR1712-BR rubber compounds*

While describing the magic tringle properties of ozone treated carbon black in SSBR-BR system, it appears to be the perfect magic triangles for tyre tread compounds. Here it is seen a significant reduction of rolling resistance was achieved by keeping other magic tringle properties either intact or improved. In the concept of magic tringle properties, it has been demonstrated that to improve any of these properties usually leads to deterioration of either any one property or in the worst case remaining two properties. However, in this case none of the properties deteriorate with improvement of overall magic triangle properties. The best magic triangle is observed with oxidized carbon black of 60 minutes of ozone treatment, in this case, a reduction of around 17% rolling resistance, 11% abrasion resistance and around 4% wet traction improvement are observed.

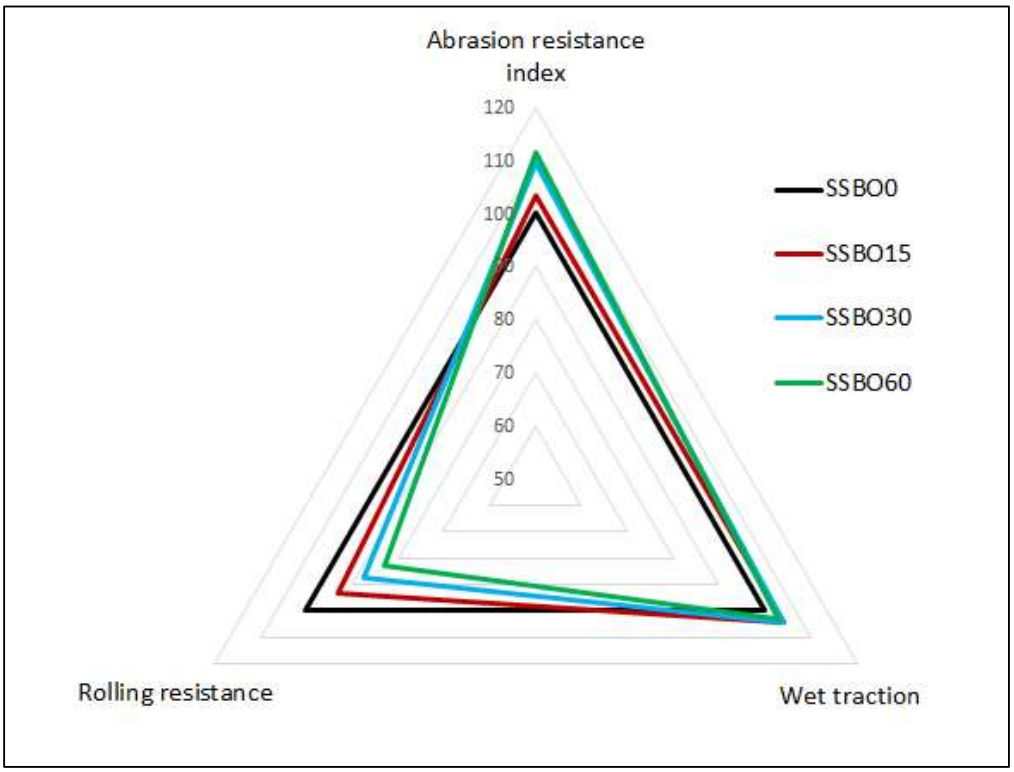


Fig-6.18: *Magic triangle properties of different SSBR-BR rubber compounds*

6.4 Conclusions

Carbon black is characterized by its unique morphological composition, which consists of different layers of graphitic units. The extent as well as the pattern of graphitic layers associated in carbon

black determines its crystalline and amorphous behavior. It has been seen a proper method of ozone treatment on carbon black as stated above, could cause a disintegration of the crystallinity.

It has been demonstrated; on ozone treatment the microstructure arrangement of carbon black morphology is changed significantly. The reduction of crystallinity and increase of amorphous characteristics of carbon black due to ozone treatment is confirmed by XRD analysis where a reduced X-ray diffraction peak intensity appears for ozone treated carbon black compared to control carbon black. Ozone treatment of carbon black further demonstrates its low oxidation stability and the same is caused due to its increase amorphous characteristics which is prone to oxidation in comparison to crystalline part of carbon black. The TEM analysis also clearly depicts the distortion of surface morphology. The distortion of graphitic arrays caused a lowering of carbon black surface crystallinity. Oxidation causes generation of porosities on carbon black surface which increases its nitrogen surface area, measured by BET surface area measurement, however, it does not affect significantly on structure property of carbon black.

Further oxidation of carbon black by ozone treatment generates a considerable amount of surface functional groups on carbon black surface which results in increase of amorphous characteristics of carbon black. The increase functional groups are primarily oxygen containing groups which makes carbon black acidic in nature, as a result ozone treated carbon black is characterized with low pH value. However, the functional groups are liable to thermal decomposition in inert atmosphere, causing high volatile matter, which is an interesting characteristic of ozone treated carbon black. Thus, oxidation of carbon black with ozone treatments causes generation of surface porosity, distortion of surface crystallinity and increase of amorphous nature, generation of large number of surface functional groups on carbon black.

The ozone treated carbon black was studied in different types of model tyre tread compounds. It is noted that a tyre for electric vehicles is characterized with unique features for its performance during service. Electric vehicles generate sufficiently high and instant mechanical torque, hence the tyres for EVs should have enhanced stiffness and high wear resistance properties to withstand the torque. Moreover, the tyres should have been characterized with low rolling resistance property, which can extend battery life as well as minimize the frequency of battery charging.

Ozone treated carbon black low rolling resistance property in tyre tread compound based on SBR1712-BR as well as SSBR-BR rubber system. It is observed that due to presence of living polar groups in SSBR molecules, SSBR-BR system provides superior performance in rolling

resistance reduction compared to SBR1712-BR rubber system. In the above, it has been seen that ozone treated carbon black is characterized with increased surface porosity, high amorphous behavior, and high surface functional groups which benefits in rubber reinforcement with enhanced filler dispersion, that results in enhanced mechanical strength, high storage modulus and superior wear resistance properties in new generation tyre tread compound system based on SSBR-BR.

Thus, a combination of SSBR rubber system with ozone treated, modified carbon black could be considered as preferred materials for the new generation tyre technology for EV applications, where rolling resistance, mechanical strength, abrasion resistance and tyre stiffness are addressed properly without sacrificing the safety, i.e., wet traction property. Ozone treated carbon black further benefits in tyre tread compound based on emulsion SBR rubber system, where the same provides significant reduction of rolling resistance property.

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