CHAPTER-4:

MODIFICATION OF TYRE TREAD COMPOUND BY OPTIMIZED AGGREGATE SIZE AND AGGREGATE SIZE DISTRIBUTION OF CARBON BLACK

Carbon blacks with different aggregate size distribution results in different performance of rubber compounds. Aggregate size distribution parameters of carbon black refer to pattern of aggregate size distribution, mean aggregate size, mode of aggregate size, differential volume distribution (dV/dD), cumulative distribution, d_{10}, d_{90} etc. which are measured by disc centrifuge method as stated in Chapter-2 [1].

In this part of the study carbon black have been developed by the furnace process of manufacturing by changing process parameters to obtain carbon black with different aggregate size distribution and the effect of the same have been investigated in tyre tread compound in comparison with commercially available ASTM grade carbon black. The experiments have been designed in two parts. In the first part of the studies, the effect of different FWHM of carbon black were investigated while in the second part of these study the different value of dV/dD of carbon black has been discussed and effect of the same in tyre tread compound has been explored.

4.1 Study the Effect of Carbon Black Aggregate Size Distribution with Different FWHM Value on Tyre Tread Compounds

FWHM is a key carbon black aggregate size distribution parameter, which indicates the pattern of aggregate size distribution. Carbon black with higher value of FWHM is characterized with broad aggregate size distribution while the least value of the same signifies narrow aggregate size distribution of carbon black [2-4]. To investigate the role of carbon black aggregate size distribution in rubber compounds, different sets of carbon black were selected having dissimilar aggregate size distribution pattern. It has been established that carbon black used in tyre tread compound is primarily determined by its surface area and structure properties, however, a best choice of carbon black for the same application should be proper combination of surface area, structure as well as its aggregate size distribution. In this study, the effects of different FWHM values have been investigated, and at the same time a suitable combination of same with surface area and structure have been discussed which would provide optimum performance in tyre tread compounds

4.1.1 Carbon Black with Different Morphological Features

To investigate effect of FWHM value of carbon black on rubber compound, two sets of carbon black grades were identified. In the first set, ASTM grade carbon black N330 was selected as control carbon black having nitrogen surface area of around 80 m^2/g and the experimental carbon blacks were developed based on similar level of nitrogen surface area but dissimilar in aggregate size distribution. In the second set of carbon black, N134 grade was considered as control carbon black and similarly the experimental grade carbon black was developed based on comparable NSA value but dissimilar FWHM value with N134.

The experimental carbon blacks were developed with tailor made aggregate size distribution and produced in the furnace process. Homogeneous processing conditions of carbon black manufacturing led to narrow aggregate size distribution, however a variation on processing conditions causes manufacturing of carbon with dissimilar aggregate size distribution. The experimental carbon black with broad aggregate size distribution was developed by monitoring the distance of choke section from the quench location in the furnace reactor, where a modified furnace reactor was used to develop carbon black with dissimilar aggregate size distribution by using PCBL proprietary processing conditions of carbon black modification. A schematic design of furnace reactor is shown in Chapter-3.

4.1.1.1 Carbon Black Parameters and Aggregate Size Distribution

In the first set of carbon black, N330 grade taken as control carbon black and identified as Sx-1 and the experimental carbon blacks are identified as Sx-2 and Sx-3 while in the second set of carbon blacks the control carbon black is N134 grade and identified as Sx-4 and while experimental carbon black is identified as Sx-5. The carbon black parameters are shown in Table-4.1 and it is seen that carbon black Sx-1, Sx-2 and Sx-3 are associated with similar nitrogen surface area. Sx-1, Sx-2 carbon black are characterized with similar structure property as represented by OAN and COAN parameters, while Sx-3 carbon black is characterized with very high structure compared to carbon black Sx-1, Sx-2. In case of the second set of carbon black, Sx-1 and Sx-2 are characterized with comparable surface area and structure properties with similar NSA, OAN and COAN Values.

The aggregate size distribution pattern of each set of carbon black is shown in Fig-4.1 and the plots of aggregate size distribution demonstrate the nature of aggregate size distribution. It indicates that Sx-3 carbon black is characterized with broad aggregate size distribution followed by Sx-2 carbon, black while Sx-1 is characterized with narrowest aggregate size distribution among the first set of carbon black. In the case of second set carbon black, Sx-5 is characterized with broader aggregate size distribution compared to Sx-4 carbon black.

Table-4.1: Carbon black Characterization

Parameters	Unit	Sx-1	Sx-2	Sx-3	Sx-4	Sx-5
Iodine Adsorption Number	g/kg	82.0	82.6	81.1	141	142
OAN	ml/100 g	103.5	101.5	142.4	127	126
COAN	ml/100 gm	84.0	83.2	103.1	101	102
NSA	m^2/g	72.3	70.5	70.5	134.6	135.2
FWHM	nm	70	92	104	54	69

The broadness of aggregate size distribution is further characterized quantitatively by FWHM value as shown in Table-4.1. It is seen that FWHM value of Sx-3 carbon black is significantly higher compared to Sx-1 and Sx-2 carbon black, which indicates its substantial broad aggregate size distribution, while Sx-1 is characterized with the least value of FWHM, demonstrating its narrowest aggregate size distribution. Similarly, for the set-2 carbon black, FWHM of Sx-5 carbon black is substantially high with respect to that of Sx-4 carbon black due to its broad aggregate size distribution pattern.

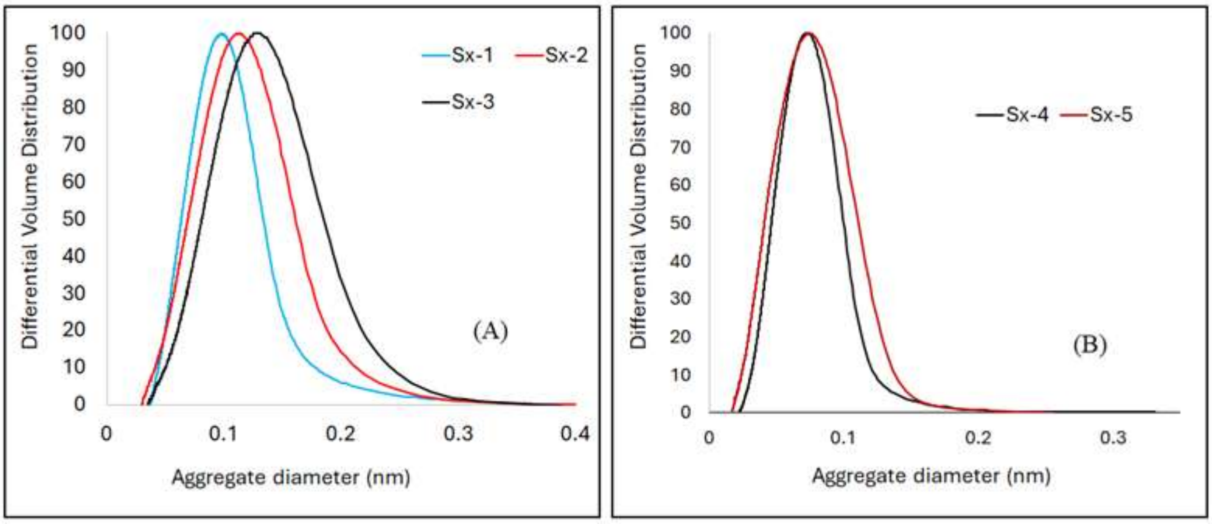


Fig-4.1: *Comparison of aggregate size distribution of carbon black (A) Aggregate size distribution of Sx-1, Sx-2, Sx-3 (B) Aggregate size distribution of Sx-4 and SX-5.*

4.1.1.2 High Resolution Transmission Electron Microscopy (HRTEM)

HRTEM analysis of carbon black was carried out to visualize and investigate structural morphology and particle size of the carbon black. The particle size of carbon black was measured by using a particle size measurement software during the TEM analysis [5-6]. It is established that nitrogen surface area resembles particle size of carbon black. Here, experimental carbon black and the corresponding control carbon black are characterized with similar surface area hence, these carbon black provides similar particle size, as demonstrated by HRTEM analysis.

TEM micrograms of different carbon black are shown in Fig-4.2, which shows that carbon black Sx-1, Sx-2 and Sx-3 are characterized with similar particle size within the range of 25 nm to 45 nm diameters and having average particle size of 31.76 nm, 36.61 nm and 36.41 nm respectively. Carbon black, Sx-4 and Sx-5 are characterized with finer particle size with a range of 12 nm to 25 nm with tentative average particle size of 17.76 nm and 18. 67 nm respectively. These grades are characterized by high surface area due to the smallest particle size of the same as compared to first set of carbon black such as Sx-1, Sx-2 and Sx-3.

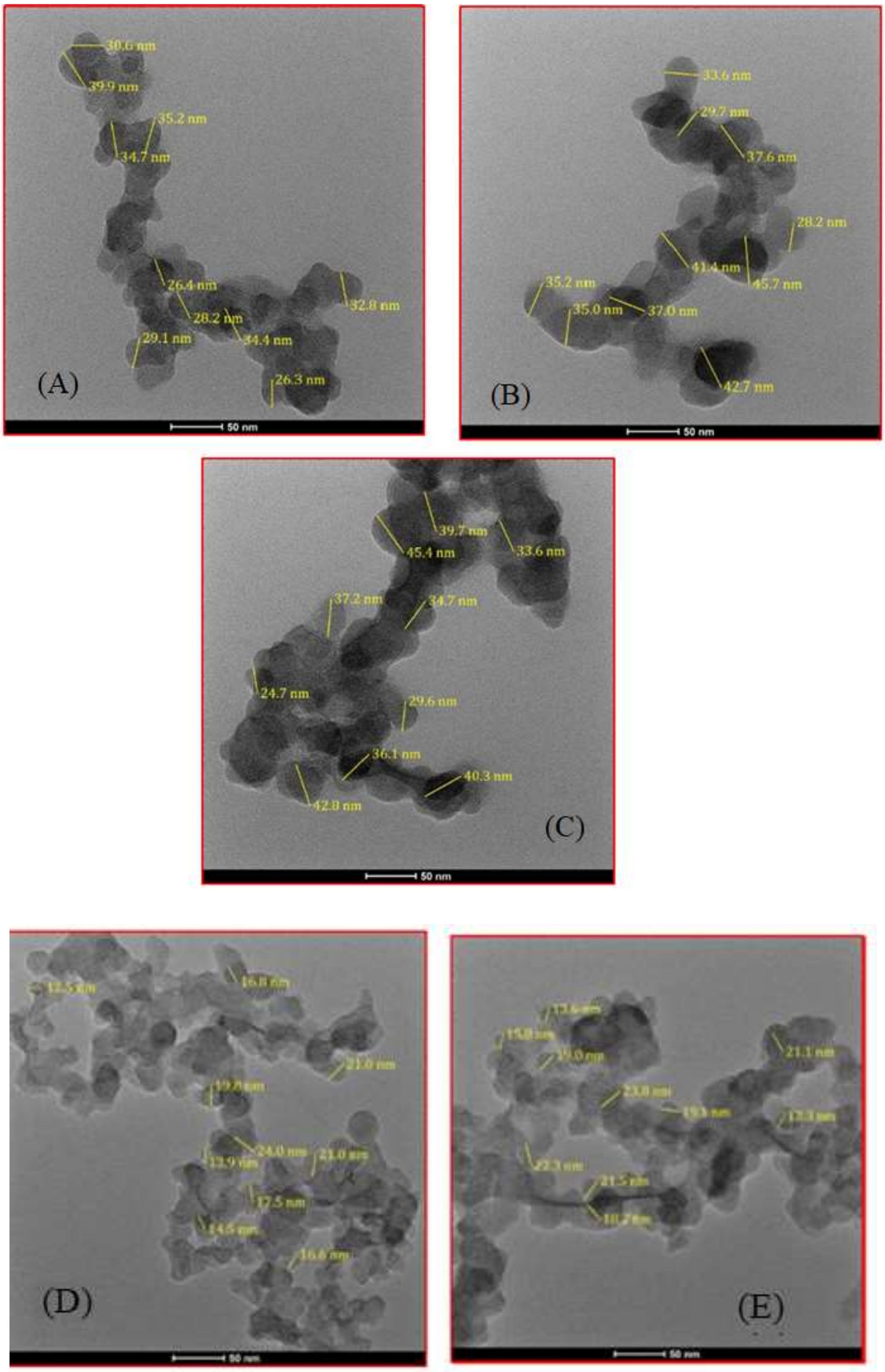


Fig-4.2: *Transmission electron microscopy: (A) Sx-1 carbon black (B) Sx-2 carbon black, (C) Sx-3 carbon black (D) Sx-4 carbon black (E) Sx-5 carbon black.*

4.1.2 Performance of Rubber Compound with Tailored Carbon Black Fillers

Carbon black with high surface area is commonly used in truck-bus tyre tread application in which natural rubber is predominantly used, while comparatively lower surface area carbon black grades are suitably used in passenger car tyre tread compound, where synthetic rubbers are predominantly used [7-8]. In this study Sx-1, Sx-2, Sx-3 carbon black were characterized with moderate surface area; hence these grades were studied in SBR1712-BR based tyre tread compound, while Sx-4 and Sx-5 grade carbon black, characterized with high surface area, were studied in natural rubber-based truck tyre tread compound and the formulations of same are shown in Table-4.2.

Table-4.2 Rubber Formulation (unit: Phr)

Ingredients	Sx-1RC	Sx-2RC	Sx-3RC	Sx-4RC	Sx-5RC
NR	0	0	0	100	100
SBR1712	96	96	96	0	0
BR	30	30	30	0	0
Peptizer	0	0	0	0.2	0.2
Carbon Black (Sx-1)	50	0	0	0	0
Carbon Black (Sx-2)	0	50	0	0	0
Carbon Black (Sx-3)	0	0	50	0	0
Carbon Black (Sx-4)	0	0	0	50	0
Carbon Black (Sx-5)	0	0	0	0	50
TDAE oil	0	0	0	5	5
ZnO	5	5	5	5	5
Stearic Acid	3	3	3	3	3
TMQ	1	1	1	1	1
CBS	1.2	1.2	1.2	0.85	0.85
Sulphur	1.5	1.5	1.5	2	2
PVI	0	0	0	0.2	0.2

4.1.2.1 Rubber Mixing and Compounding

The mixing of rubber compound was carried out in laboratory Banbury followed by two roll mixing mill. The first set of carbon black have been studied in SBR1712-BR system. Two stage mixing procedure was adopted where masterbatch compound was prepared in the first stage of mixing and in the final stage of the mixing the masterbatch compound was mixed with curing agent. In case of NR based compound the mixing was carried out in three stage mixing procedure. In the first stage of mixing masterbatch compounds were prepared and these masterbatch compounds were re-passed in the second stage of mixing without incorporation of any chemicals while in the final stage of mixing the masterbatch compound was mixed with curing agent. The rubber compound made of Sx-1, Sx-2, Sx-3, Sx-4 and Sx-5 grades carbon black were identified as Sx-1RC, Sx-2RC, Sx-3RC, Sx-4RC and Sx-5RC respectively.

4.1.2.2 Curing and Processing characteristics:

The curing characteristics of the rubber compounds are shown in Table-4.3 and it is seen that the optimum curing time, scorch time of the corresponding compounds are comparable to each other for the respective set of carbon black. Hence it implies that broad or narrow aggregate size distribution of carbon black has the least impact on the curing property of rubber compounds. However, it is seen that carbon black characterized with broad aggregate size distribution provides lower minimum torque (ML) value as well as lower Mooney viscosity in rubber compound, as compared to carbon black characterized with narrow aggregate size distribution in both the rubber systems. Hence carbon black with broad aggregate size distribution contributes to ease of processability of rubber compound irrespective of rubber system.

Table-4.3: Curing and processing characteristics of rubber compounds**.**

Parameters	Unit	Sx-1RC	Sx-2RC	Sx-3RC	Sx-4RC	Sx-5RC
ML	lb-in	12.17	12.2	11.82	9.5	8.3
MH	lb-in	54.37	53.47	52.4	42.6	41.9
Ts1	Minutes	7.5	7.07	7.01	4.7	4.8
Ts2	Minutes	8.16	7.8	7.7	5.4	5.4
Tc90	Minutes	12.17	12.2	12.3	10.6	10.4
Mooney viscosity	MU	69.7	66.2	67.5	72.2	67.1

4.1.2.3 Effect of Aggregate Size Distribution on Payne Effect

Carbon black create filler-filler interaction in rubber matrix due to Van der Waals force of interaction, and which results in inter-aggregate networks in the matrix [9]. Carbon black characterized with dissimilar aggregate size plays crucial role toward the Van der Waals force of interaction and finally monitors in the filler-filler interaction in rubber matrix. The interaction among aggregates largely depends on inter-aggregate distance and lower the inter-aggregate distance leads to high Van der Waals force of interaction.

The inter-aggregate distance of carbon black in rubber matrix was derived by Wang et al [10]. They demonstrated the concept, how a carbon black with broader aggregate size creates increased inter-aggregate distance in rubber matrix compared to narrow aggregate size distribution carbon black. They have derived that at a constant filler loading the distance between similar particles changes if the diameters of those particles change i.e, the distance between narrow distribution particles is changed if the particle size distribution terns to broad distribution in nature. They had mathematically showed the same by the following spherical model; and established that for two identical particles of diameter (d), on reduction of a particle diameter by 1/X, the diameter of next particle should be increased by d' and where d' is measured according to equation (4.1).

$$d' = \left[\left(2 - \frac{1}{X^3}\right)^{1/3} - 1\right]d, \tag{4.1}$$

In a typical example, assumed the particle diameter (d) is reduced by half (i.e, 0.5d for X=2) hence the diameter of second particle is increased by 0.2331d by using the above equation. The concept is depicted in Fig-4.3, where the black color spheres (A and B) represent the original ones with equivalent diameter (d) and make a separation between them is δ_o. The diameter of sphere A is halved and leads to new sphere of A' while the diameter of sphere B is increased and leads to a new sphere B' and the resultant separation between the new speres is denoted by δ_o'.

It is portrayed that due to reduction of sphere (A) diameter the smaller sphere (A') makes an increased separation of ½(0.5d) from its original location while the bigger sphere (B') move closer by ½(0.2331d) which make resultant increased in separation of spheres of ½(0.5d - 0.2331d), i.e., 0.1335d. This model demonstrates that particles with dissimilar diameters, more preferably, particles with broad distribution in size create higher inter-particle distance compared to same with similar size or narrow size distribution respectively.

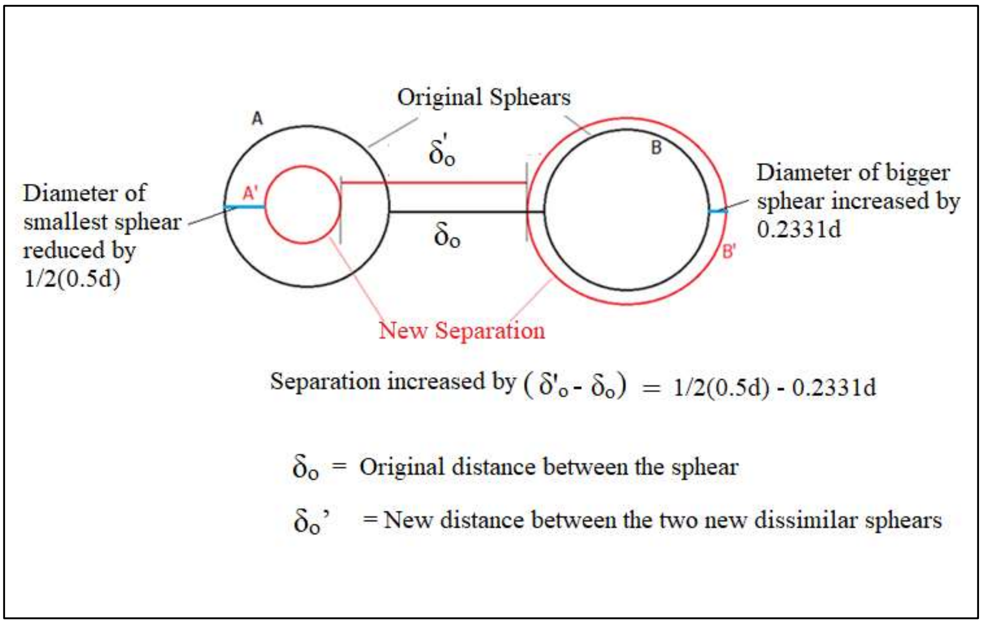


Fig-4.3: *Schematic representative of inter-particle distance with two similar particle size vis-à-vis dissimilar particle size*

The above concept can be applied for carbon black aggregates size distribution and can demonstrate the separation of aggregates in rubber matrix. Thus, carbon black with broader aggregate size distribution results higher interaggregate distance in rubber matrix compared to narrow aggregate size distribution carbon black and results in less propensity of filler-filler interaction.

The existence of filler-filler interaction in rubber compound was studied by rubber process analyzer where shear modulus of rubber compounds is plotted with different strain amplitude on a cyclic deformation of the same. The trend of shear modulus with strain sweeps of rubber compound is shown in Fig-4.4 (A). It appears that rubber compound based on carbon black, Sx-3 provides low shear modulus at lower strain region compared to carbon black Sx-1 and Sx-2.

Sx-3 carbon black is characterized with broad aggregate size distribution compared to Sx-1 as well as Sx-2 carbon black and due to its broad aggregate size distribution, it results in higher interaggregate distance in rubber matrix and as a result, it provides lower filler-filler interaction.

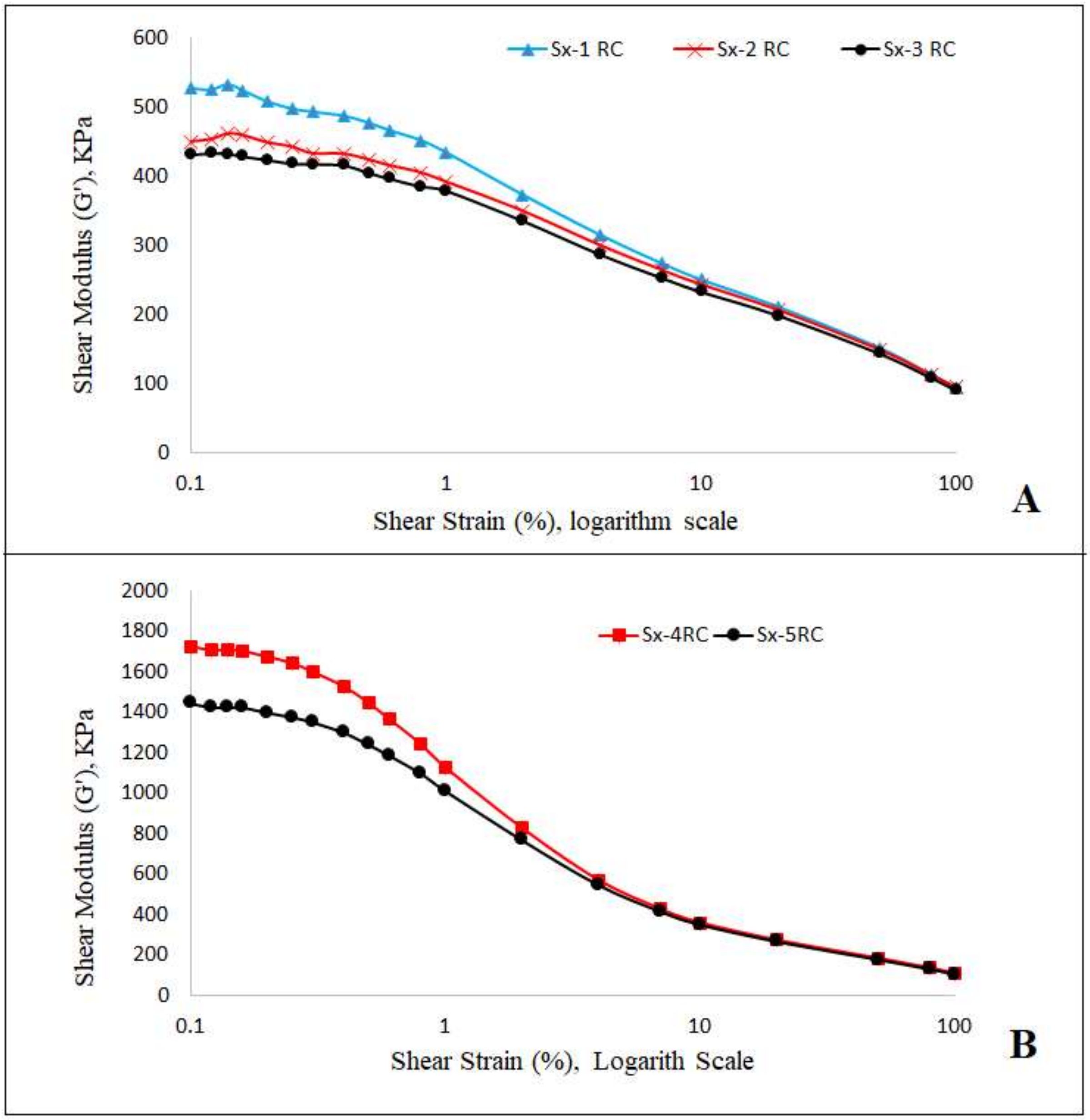


Fig-4.4: *Shear modulus of compound with strain sweep, (A) Compound Sx-1RC, Sx-2RC, Sx-3RC and (B) Compound Sx-4RC, Sx-5RC.*

Similar findings also appear for Sx-5 carbon black in NR compound system, where it provides least shear modulus in the rubber compound at the lower strain region of the deformation as compared to Sx-4 carbon black and which is caused due to the broad aggregate size distribution of Sx-5 carbon black compared to Sx-4 carbon black. The trend of shear modulus of rubber compound Sx-4RC and Sx-5RC is shown Fig-4.4 (B).

The Payne effect of rubber compound further demonstrates the existence of filler-filler network in rubber compound which is shown in Table-4.4. It is obvious that Sx-3 carbon black provides less Payne effect in rubber compound due to association of least filler-filler interaction in comparison to Sx-1 and Sx-2 carbon black. A similar fashion of Payne effect also appeared for Sx-4RC and Sx-5RC rubber compound where Sx-5 carbon black provides less Payne effect as compared to Sx-4 carbon black due to its broad aggregate size distribution. Hence carbon black characterized with broader aggregate size distribution provides high inter-aggregate separation in rubber compound and consequently causes less propensity of filler-filler interaction, as a result it provides lower Payne effect in rubber compounds.

It has been reported in literatures that carbon black with high structure property results in high filler-filler interaction and provides high Payne effect in rubber compound [13-14]. However, contrary to reported data, in our study, it is seen that in spite of having high structure, Sx-3 carbon black provides least filler-filler interaction in rubber compound due to its broad aggregate size distribution and consequently, the same provides least Payne effect in rubber compound. Hence it demonstrates that aggregate size distribution pattern of carbon black is one of potential carbon black parameters which determines its ability to form filler-filler interaction and predominantly monitors the Payne effect in rubber compounds.

Table-4.4: Rubber process analysis of rubber compounds

Parameters	Unit	Sx-1RC	Sx-2RC	Sx-3RC	Sx-4RC	Sx-5RC
Shear Modulus ($G_{0.1}$’) at 0.1% shear strain	KPa	525	458	417	1723	1434
Shear Modulus (G_{100}’) at 100 % shear strain	KPa	94	95	91	110	106
Payne Effect ($G_{0.1}$’-G_{100}’)	KPa	430	363	326	1613	1328

4.1.2.4 Hysteresis Energy Loss and Rolling Resistance:

Hysteresis energy loss of rubber compound was measured by dynamic mechanical analysis in which hysteresis energy loss of rubber compound was represented by loss tangent (tanδ) value.

The measurement was conducted at a temperature of 60°C temperature and 10 Hz frequency under tension mode of deformation and Fig-4.5 shows the tanδ of various rubber compounds.

On comparing the tanδ value of SBR1712-BR rubber compounds where the first set of carbon black (Sx-1, Sx-2 and Sx-3) have been used, it is observed that rubber compound associated with Sx-3 provides lowest tanδ value in comparison to Sx-1 and Sx-2 carbon black. Sx-3 carbon black is characterized with broad aggregate size distribution and the same provides around 20% lower tanδ value than the narrowest aggregate size distribution carbon black Sx-1 while it provides around 10% lower tanδ value in comparison to its nearest broader aggregate size distribution carbon black Sx-2 [4-5]. Similarly, for the second set of carbon black (Sx-4 and Sx-5), Sx-5 carbon black provides for lesser tanδ value compared to Sx-4 carbon black where NR based rubber compound has been used.

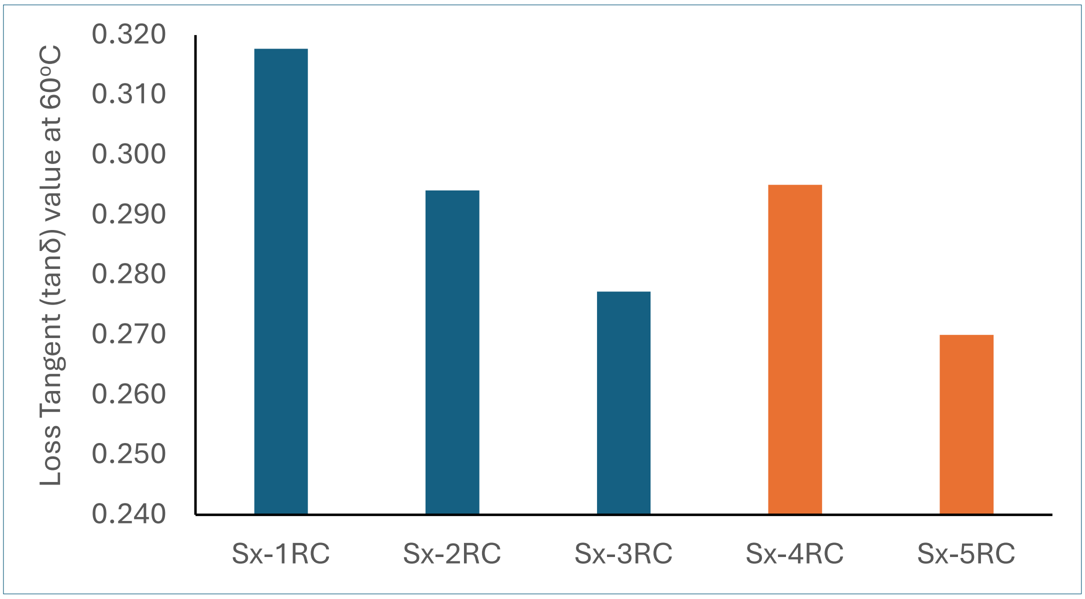


Fig-4.5: *Hysteresis loss (loss tangent value) of rubber compounds, measured at 60°C*

Hence carbon black, characterized with broad aggregate size distribution having high FWHM value, provides low hysteresis property in rubber compound as compared to the same associated with narrow aggregate size distribution with least value of FWHM. Consequently, it provides low rolling resistance property for tyre tread compounds [15].

4.1.2.5 Abrasion Resistance Property

The abrasion resistance property of carbon black filled rubber compound is primarily dependent on the particle size, surface area and structure of carbon black for a specific filler loading in the rubber compound. Carbon black associated with smaller particle size comprises a high surface area, which gives rise to maximum exposure with the rubber molecules. As a result, a higher covering area of rubber matrix is possible with carbon black particles. While carbon black provides a larger extent of exposure in rubber matrix with increased surface area, and it resists rubbing off the rubbery material while the compound is under rubbing with solid surface [16-17].

In addition to surface area, the structure of carbon black also plays a significant role on abrasion resistance property. Carbon black structure is the measure of void volume, and it has been demonstrated that carbon black with high structure is characterized with high inbuild voids. High voids lead to higher occluded rubber, and the same acts as filler in the matrix, as a result abrasion resistance of resistance of rubber compound is enhanced [18-19]. The improved abrasion resistance of high structure carbon black was further explained by the phenomena that rubber compound consisting of high structure carbon black leads to formation of enhanced filler network configurations in the rubber matrix which slows down the rate of abrasion loss. The network structure of filler acts as an inbuild skeleton of rubber articles hence while rubber surfaces are in touch with movable solid surface the skeleton filler structure resists the abrasion of rubber compounds. [20].

It has been described above that carbon black with narrow aggregates size distribution forms higher filler network in the rubber matrix compared to broad aggregate size distribution. Thus, these filler network structure acts as skeleton structures of rubber articles and restrict the abrasion of rubber compounds while the same are rubbing with solid substrate [21]. Hence, carbon black with narrow aggregate size distribution benefits in abrasion resistance of rubber compound which is shown in Fig-4.6. It is seen that Sx-1 carbon black characterized with narrow aggregate size distribution shows marginal improvement in abrasion resistance compared to Sx-2 carbon black. However, it is seen Sx-3 carbon black provides high abrasion resistance property instead of its broad aggregate size distribution as compared to Sx-1 and Sx-2 and the same has been achieved because of its high structure property.

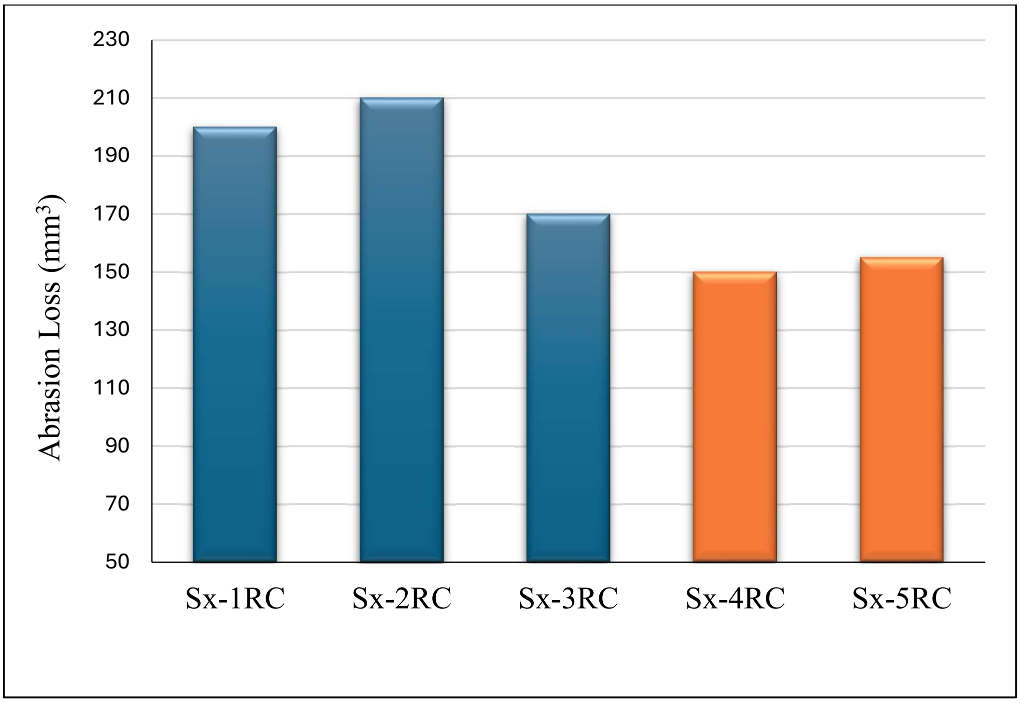


Fig-4.6: *Abrasion loss (volume loss in mm^3) of rubber compound*

Abrasion resistance property of Sx-4 and Sx-5 carbon black in NR system shows that a marginal improvement in abrasion resistance appeared with Sx-4 carbon black over the Sx-5 carbon black due to its narrow aggregate size distribution over Sx-5 carbon black. Hence, aggregate size distribution pattern of carbon black influences the abrasion resistance property of rubber compound, however, for a dissimilar structure property of carbon black with high structure value predominates the abrasion resistance property over the aggregate size distribution

4.1.2.6 Tensile Properties:

Tensile properties of the rubber compounds are described by tensile strength, modulus, and elongation at break etc. As described, the carbon blacks selected for the current investigation are depicted by different morphological characteristics specially in aggregate size distribution. In the case of first set carbon black, eg, Sx-1, Sx-2 and Sx-3 similar level of nitrogen surface area and statistical surface area are observed while the structure property of Sx-3 carbon black is significantly high compared to Sx-1 and Sx-2 grade carbon black. Sx-1 grade carbon black shows a similar level of tensile strength property with Sx-2 and Sx-3 carbon black due to the similar NSA and STSA values. Sx-3 carbon black shows a significant effect on modulus due to its high structure compared to Sx-1 and Sx-2 causing high modulus and lower elongation at break. While for the second set of carbon black, Sx-4 and Sx-5 are characterized with similar surface area and structure properties resulting similar tensile properties.

Table-4.5: Tensile properties of rubber compounds

Parameters	Unit	Sx-1	Sx-2	Sx-3	Sx-4	Sx-5
Tensile Strength	MPa	19.09	18.56	19.02	28.37	27.47
Modulus at 300% Elongation	MPa	5.32	5.6	6.28	14.97	14.8
Elongation at break	%	630	636	641	512	508

4.2 Incorporation of Bigger Size Aggregates into Carbon Black Morphology and Investigate the Rubber Performance for Tyre Tread Compounds.

Aggregate size distribution plot of carbon black is represented by differential volume distribution (dV/dD) against corresponding aggregate size. Differential volume distribution (dV/dD) of the aggregate size distribution graph along Y-axis is the indicative of the extent of corresponding size aggregate present in the system and hence, high dV/dD value for a particular aggregate size indicates the highest extent of same size aggregates present in the system. This phenomenon is described by a typical example, where two model aggregate size distribution (ASD) graphs of carbon black (namely, Carbon Black A and Carbon Black B) are compared as shown in Fig-4.7. It is observed that the dV/dD value of carbon black-A at the aggregate size of 0.1-micron is around 80, while the same for ASD-B is around 50. It indicates that Carbon black-A has a larger extent of aggregates of 0.1-micron aggregate diameter compared to Carbon black-B [1].

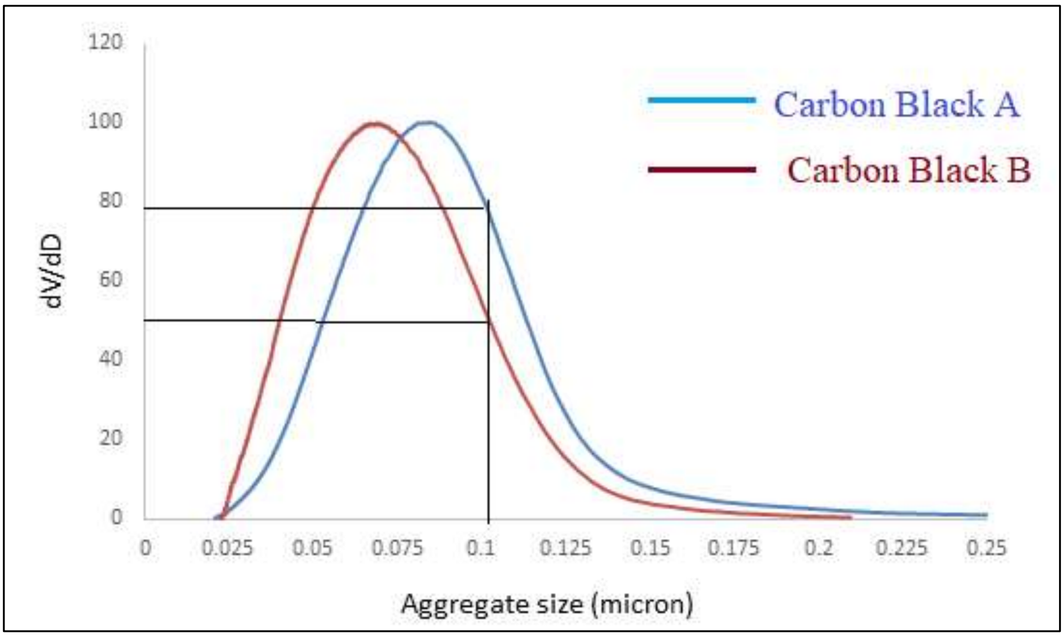


Fig-4.7: Typical example of aggregate size distribution of carbon black with different dV/dD values across the aggregate size.

In the previous section, it has been demonstrated that carbon black with broad aggregate size distribution reduces the hysteresis loss of the rubber compound and consequently it reduces the rolling resistance for tyre tread compound, where broadness of aggregate size distribution has been indicated by FWHM value of corresponding carbon black. FWHM indicates the broadness of aggregate size distribution at 50% height of the plot along the dV/dD axis. Beyond a certain aggregate size, the aggregate size distribution pattern could not be explained by FWHM and in such case dV/dD value needs to be considered for explaining the nature of aggregate size distribution. This phenomenon is well explained by a typical example as shown in Fig-4.8, where two model aggregate size distribution plots are compared. In these plots, it shows that FWHM values of carbon black-1 and carbon black-2 are similar, however, beyond the aggregate size of 150 nm, the aggregate size distribution pattern shows that carbon black-2 is characterized with broad aggregate size distribution in spite of having similar FWHM value. In this region, carbon black-2 is characterized with high dV/dD value compared to Carbon black-1 and making it overall broad aggregate size distribution. Hence, the larger dV/dD value of Carbon black-2 beyond 150 nm aggregate size region signifies that in the bigger aggregate size region (i.e., beyond 150 nm), carbon black-2 is accompanied with larger extent of bigger size aggregates, and it has overall broad aggregate size distribution with long tail aggregate size distribution.

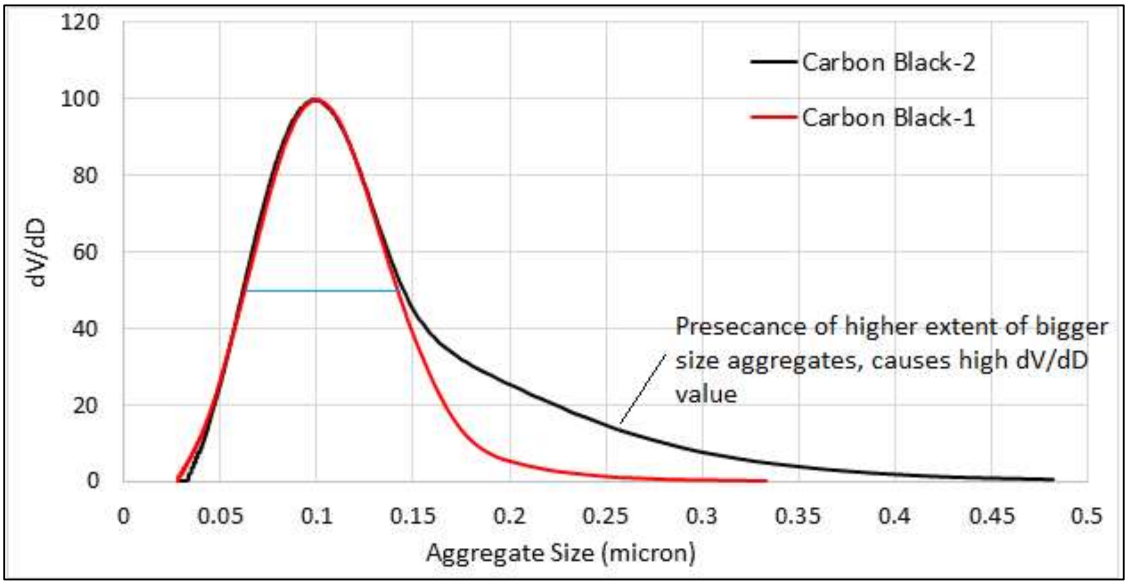


Fig-4.8: *Aggregate size distribution of different carbon black having different extent of large size aggregate with dissimilar characterization of dV/dD at the large aggregate size region.*

In addition to broadness of aggregate size distribution, the size of aggregates plays the crucial role in the rubber reinforcement. In this study the effects of carbon black, characterized with large extent of bigger size aggregates which creates long tail aggregate size distribution, are discussed in the rubber compound properties.

4.2.1 Design of Carbon black Morphology:

In this investigation, ASTM grade N330 has been taken as control carbon black which is characterized with iodine adsorption number of 82 g/kg and oil absorption number of 103.5 ml/100g and is designated as Sy-1. The carbon blacks for this investigation were designed with tailor-made aggregate size distribution maintaining similar surface area with control sample. The experimental carbon blacks are identified as Sy-2, Sy-3 and Sy-4, in which the ASD is designed in such a manner that it is characterized with long tail aggregate size distribution with presence of larger extent of bigger size aggregates compared to the control sample. The tailor-made aggregate size distribution was carried out by incorporating larger size aggregates of carbon black into the system of experimental carbon black. The details carbon black characteristics are shown in Table-4.6 and corresponding aggregate size distribution is shown in Fig-4.9. Here the term $(dV/dD)_{150}$ signifies the dV/dD value of carbon black at 150 nm aggregate size.

Table-4.6: Carbon black parameters of Sy-1, Sy-2, Sy-3 and Sy-4

	Unit	**Sy-1**	**Sy-2**	**Sy-3**	**Sy-4**
Iodine No	g/kg	82	80.8	80.3	81.1
OAN	ml/100g	103.5	100	105	102
COAN	ml/100g	83	84.2	88.3	83.5
NSA	m^2/g	76.3	76.1	75.6	76
Mean	nm	110	143	147	127
Mode	nm	97	74	86	88
FWHM	nm	70	62	77	71
$(dV/dD)_{150}$	-	24.3	35	42.5	28

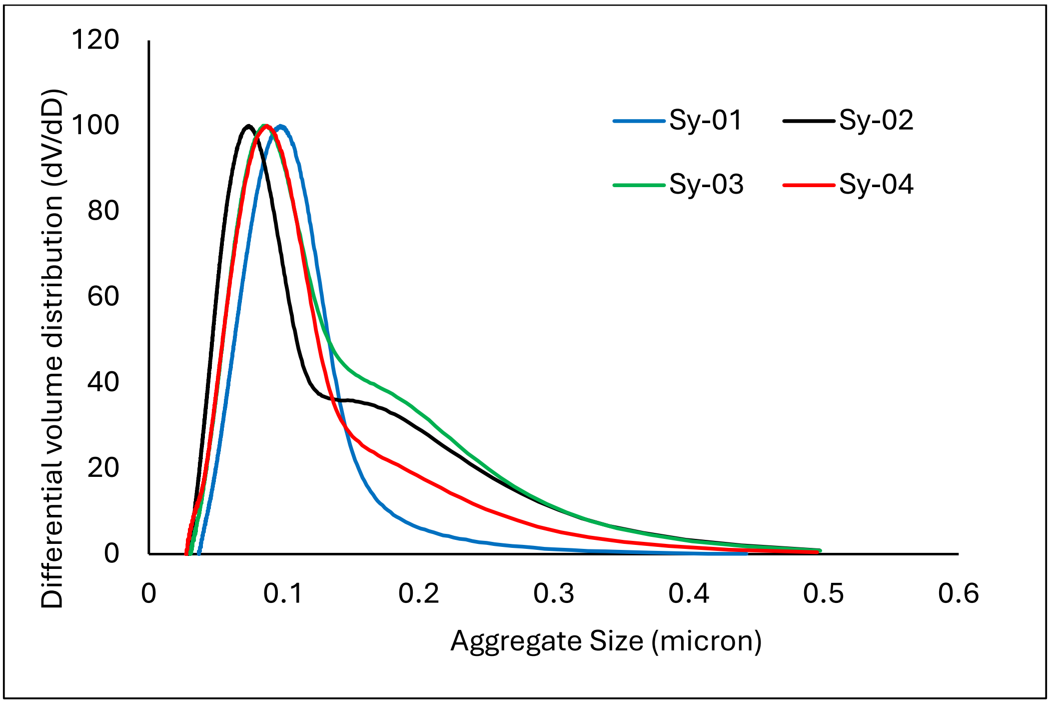


Fig-4.9: *Aggregate size distribution of carbon black with dissimilar dV/dD value at higher aggregate size region.*

It is seen that carbon black Sy-2 is characterized with lower FWHM value and can be said as narrow aggregate size distribution with respect to rest of the carbon black when the broadness of aggregate size distribution is represented by FWHM value. However, while comparing the distribution pattern on the large aggregate size region, it is seen that Sy-2 carbon black is characterized with very long tail aggregate size distribution due to the presence bigger size aggregates to a larger extent compared to Sy-1 and Sy-4. Similar fashion of long tail aggregate size distribution is associated with Sy-3 carbon black.

In a typical value for a larger aggregate size of 150 nm, it is observed that different carbon black has different (dV/dD) value at 150 nm aggregate size due to presence of dissimilar extent of 150 nm aggregates in the respective carbon black. It is seen for Sy-2 grade carbon black the (dV/dD) value at 150 nm aggregate is 35, and the same for Sy-3 and Sy-4 grade carbon black is 42.5 and 28 respectively while it is for control carbon black (Sy-1) is only 24.3. Hence it is demonstrated that higher extent of 150 nm size aggregates is present in Sy-3 grade carbon black followed by Sy-2 grade carbon black, while control carbon black is associated with least extent of bigger size aggregate of 150 nm. Similar trends also appear while moving towards bigger size aggregate region of beyond 150 nm aggregate. Hence overall, Sy-3 carbon black is characterized with higher extent of bigger size aggregates followed by Sy-2 and Sy-4 grade carbon black.

The reciprocal of $(dV/dD)_{150}$ value of the carbon black is graphically represented in Fig-4.10 where the reciprocal value of control sample is high due to its lower extent of bigger size aggregate at 150 nm range.

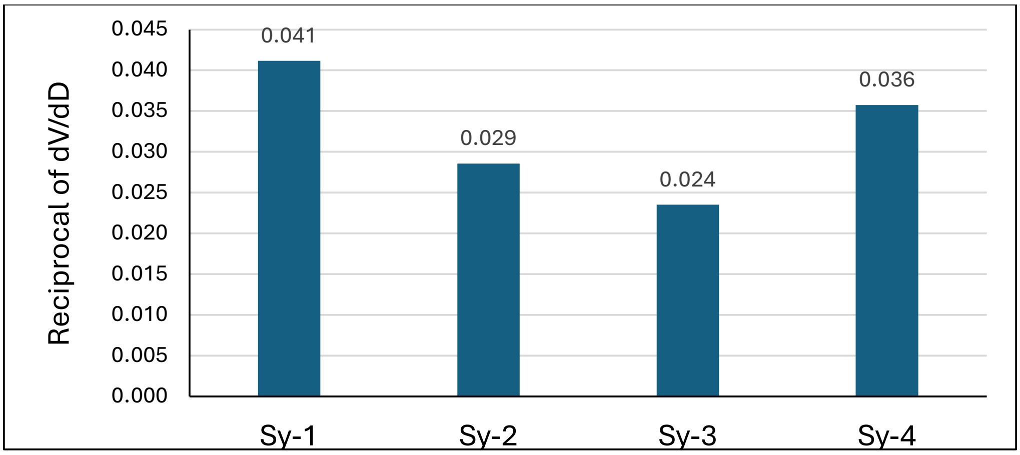


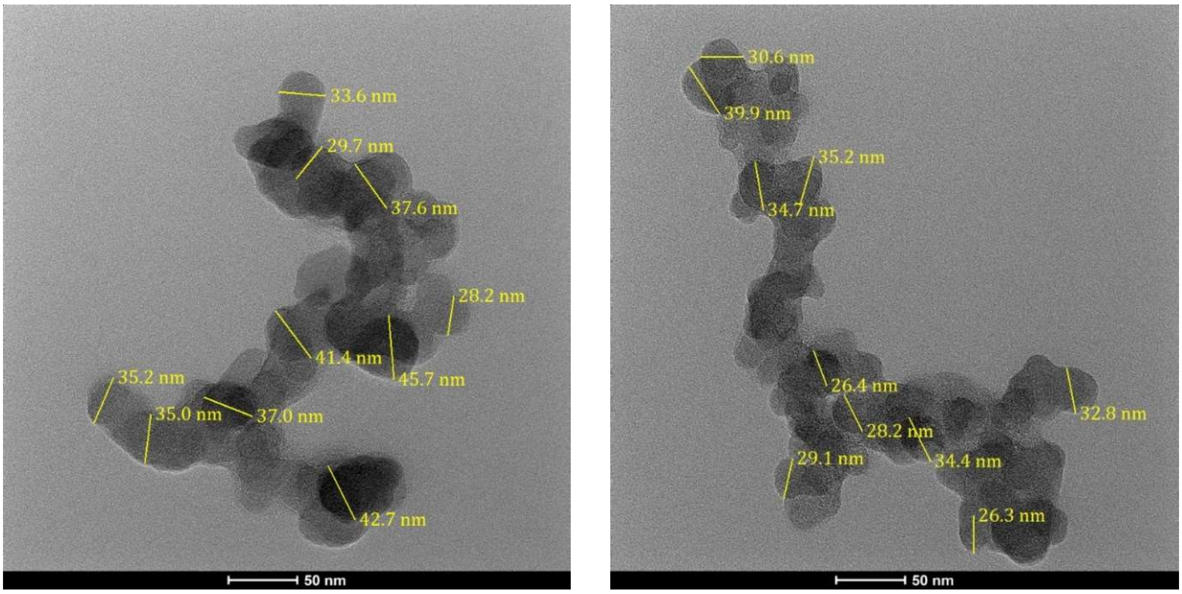
Fig-4.10: *Reciprocal of (dV/dD) value at 150 nm aggregate diameter*

4.2.2 High Resolution Transmission Electron Microscopy

The HRTEM images of Sy-1, Sy-2, Sy-3 and Sy-4 grade carbon blacks are analyzed to characterize the size and shape of different aggregates. Aggregates are built up by fusing several carbon black particles hence, the size of aggregates depends on the size of carbon black particles as well as the number of particles fused together to form the aggregate [22-23]. In practice aggregates associated with larger number of carbon black particles lead to have larger aggregate size. On the other hand, aggregate constructed with bigger size carbon black particles also results in larger aggregate size.

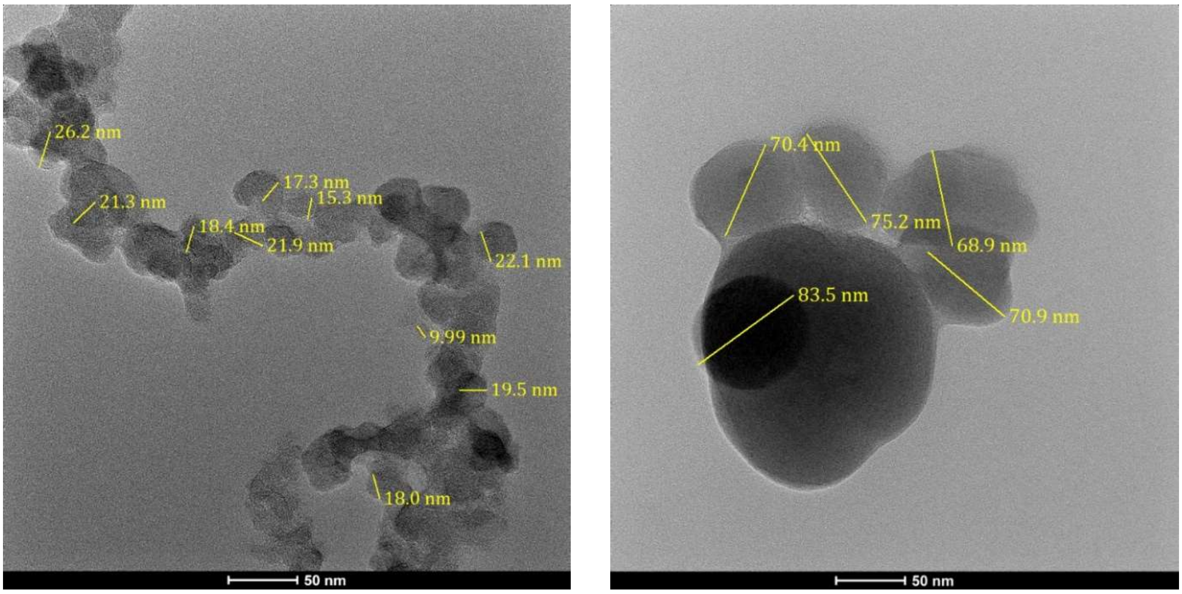
The transmission electron microscopic images of Sy-1 carbon black is shown in Fig-4.11 (a) and (b), it reveals that Sy-1 carbon black consists of particles size ranges from 26 nm to 45 nm and these particles form aggregate having mean aggregate size of 110 nm. Whereas HRTEM analysis shows that different nature of aggregates presents in Sy-2 carbon black as shown in Fig- 4.12 (a) and (b) respectively. The HRTEM of carbon black Sy-2 aggregates demonstrates that it is associated with two different characteristics of aggregates. A part of aggregates is characterized with carbon black particle size of around 17 nm to 26 nm diameter while the other part of aggregates is characterized with larger particles size of around 75 nm to 160 nm and these two dissimilar natures of aggregates provides overall mean value 143 nm. Aggregates construction of Sy-3 carbon black is in similar fashion to that of Sy-2 as shown in Fig-4.13 (a) and (b) where the part of aggregate is constructed with particle size of 20 to 38 nm while the second part of aggregate is constructed with particle size of 70 to 100 nm. TEM images of Sy-4 are shown in Fig-4.14 (a) and (b) and which show aggregates of the same are also characterized with two dissimilar patterns of aggregates having different particles size.

It is seen in the HRTEM analysis that carbon black aggregates constructed with comparatively bigger size particles show spheroidal shape while the same constructed with smaller particles results branched network structural units. It is also seen that aggregate network while made of bigger size particles it makes thick network structural lines, whereas the same made of smaller size particles forms aggregate networks of thinner lines. Hence for a fixed weight of carbon black, aggregates made of smaller size particles form, cumulatively larger length of networks lines compared to the same made of bigger size particles



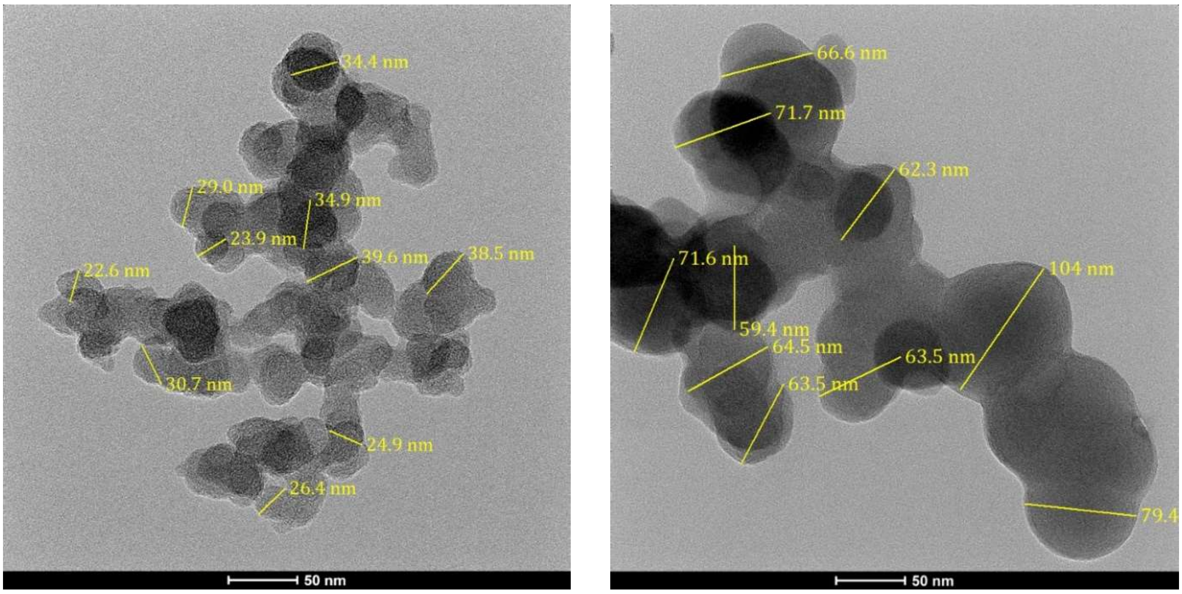
4.11 (a) 4.11 (b)

Fig-4.11: *Transmission Electron Microscopy of Sy-1 Carbon black - (a) aggregate constructed with lower particle size (b) aggregate constructed with similar particle size.*



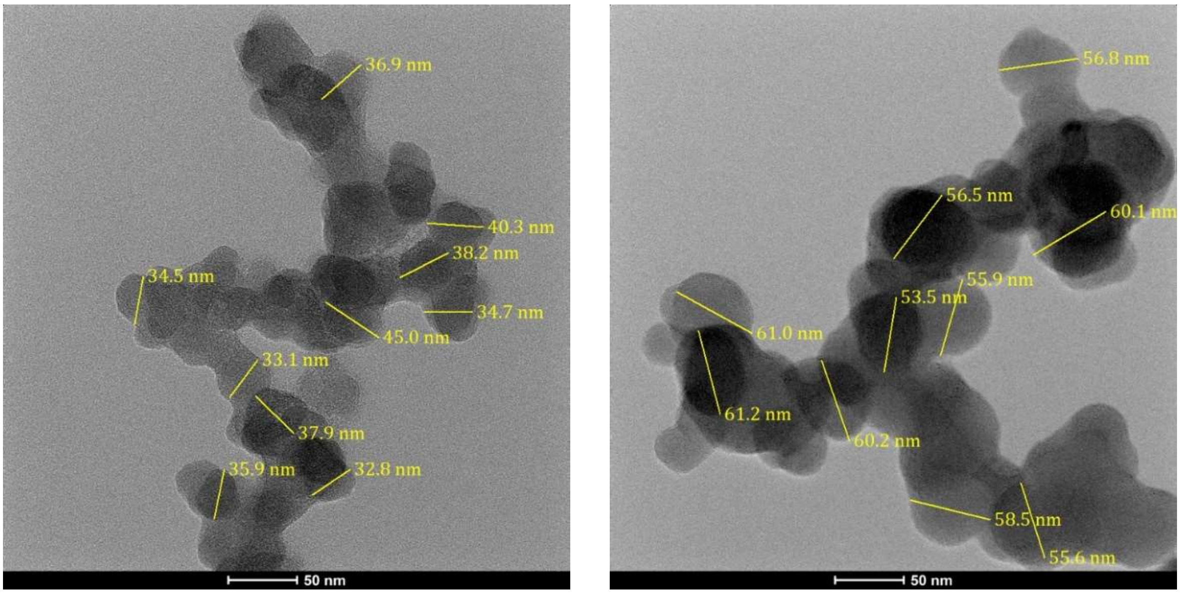
4.12 (a) 4.12 (b)

Fig-4.12: *Transmission Electron Microscopy of Sy-2 Carbon black - (a) aggregate constructed with lower particle size (b) aggregate constructed with bigger particle size.*



4.13 (a) **4.13 (b)**

Fig-4.13: *Transmission Electron Microscopy of Sy-3 Carbon black - (a) aggregate constructed with lower particle size (b) aggregate constructed with bigger particle size.*



4.14 (a) 4.14 (b)

Fig-4.14: *Transmission Electron Microscopy of Sy-4 Carbon black - (a) aggregate constructed with lower particle size (b) aggregate constructed with bigger particle size.*

4.2.3 Rubber Compound Property

Carbon black aggregate size and its distribution play significant roles in rubber compound performance and in this study the effects of differential volume distribution (dV/dD) for the specific aggregate size of carbon black are analyzed. The formulation of the analysis is tabulated in Table-4.7, here four rubber compounds were prepared identified as SyR-1, SyR-2, SyR-3 and SyR-4 by which are based on carbon black Sy-1, Sy-2, Sy-3 and Sy-4 respectively.

4.2.3.1 Mixing and testing:

The mixing of rubber compound was carried out in laboratory Banbury followed by two roll mixing mill as per procedure described in Chapter 3. The mixing of SBR1712-BR compound was carried out in two stage mixing procedure while mixing of NR based compound was carried out in three stage mixing procedure. The rubber compound made of Sx-1, Sx-2, Sx-3, Sx-4 and Sx-5 carbon black are identified by Sx-1RC, Sx-2RC, Sx-3RC, Sx-4RC and Sx-5RC respectively.

Table-4.7: Formulation of rubber compounds (unit: phr)

Ingredients	SyR-1	SyR-2	SyR-3	SyR-4
SBR1712	96	96	96	96
BR	30	30	30	30
Sy-1	50	-	-	-
Sy-2	-	50	-	-
Sy-3	-	-	50	-
Sy-4	-	-	-	50
ZnO	5	5	5	5
St. Acid	3	3	3	3
TMQ	1	1	1	1
CBS	1.2	1.2	1.2	1.2
S	1.5	1.5	1.5	1.5

4.2.3.2 Curing and Processing characteristics:

Aggregate size distribution of carbon black does not show significant difference on curing time, scorch property of rubber compound as shown in Table-4.8, though, it is seen that experimental carbon blacks result lower ML value and lower Mooney viscosity in rubber compound as compared to the control carbon black, Sy-1. One of potential reasons for lower ML and lower Mooney viscosity for experimental compounds is attributed to presence of bigger size aggregate in the respective carbon black used in the rubber compound. It is also seen rubber compound SyR-3 provides least ML value and Mooney viscosity among all the rubber compound due to high $(DV/dD)_{150}$ value of corresponding carbon black, i.e, same is associated with higher extent of bigger size aggregate of diameter 150 nm. Thus, ASD of carbon black demonstrates the ease of processability in rubber compound and the same is achieved by high dV/dD value at the larger aggregate size region.

Table-4.8: Rheological characteristics of carbon black

Parameters	Unit	SyR-1	SyR-2	SyR-3	SyR-4
ML	lb-in	12.6	11.1	10.5	11.7
MH	lb-in	52.65	50.2	50.2	52.1
Ts1	Minutes	7.10	7.22	7.5	7.42
Ts2	Minutes	7.95	8.11	7.99	7.82
Tc90	Minutes	11.65	11.95	11.81	11.93
ML (1+4) at 100ºC	MU	68.2	65.5	64.1	66.0

4.2.3.3 Filler-Filler Network Formation

The formation of filler network in rubber compounds leads to potential source of shear modulus in rubber compound and which are prone to destruction while rubber compound is deformed. The extent of filler network formation is characterized by the features of carbon black aggregates and is measured by Payne effect of corresponding rubber compound [24]. The Payne effect of rubber compound is shown in Fig-4.15, it is observed that rubber compound SyR-3 is characterized with least Payne effect followed by the rubber compound SyR-2. The least Payne of these rubber compounds could be caused due to presence of larger extent of bigger size aggregates in the respective carbon black. Control carbon black associated least extent of bigger size aggregates, indicates high Payne effect in the rubber compound.

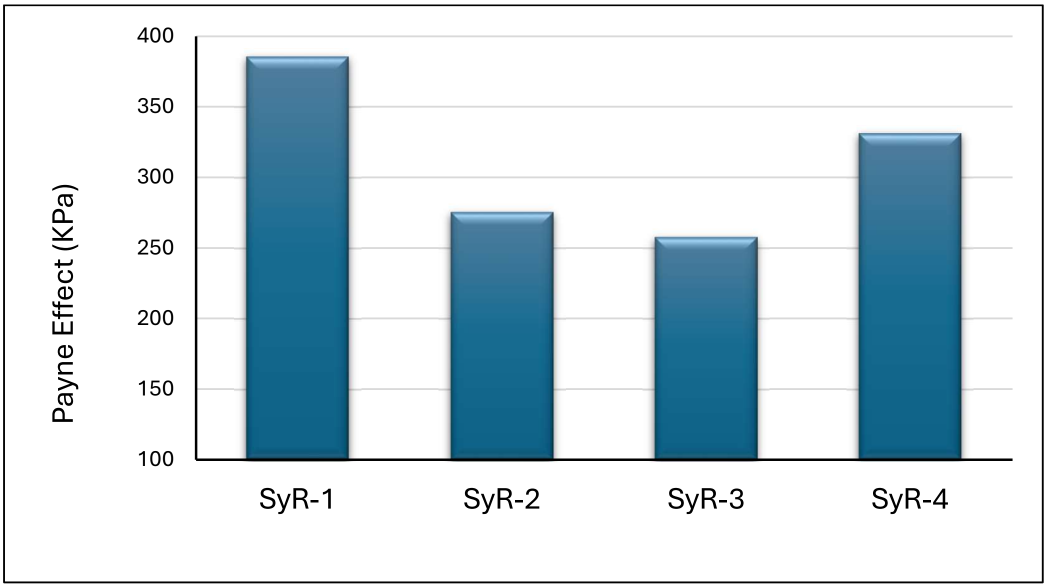


Fig-4.15: *Payne effect of rubber compound*

In this investigation the Payne effect of rubber compound was correlated with the extent of larger size aggregates present in corresponding carbon black. The extent of larger size aggregates present in carbon black was represented by dV/dD value of aggregate size distribution at the larger aggregate size region and which is represented here by $(dV/dD)_{150}$ value, where $(dV/dD)_{150}$ value represents the differential volume distribution (dV/dD) value for 150 nm aggregate size. Hence the carbon black associated with large $(dV/dD)_{150}$ value, indicates, it possesses higher extent bigger size aggregate of 150 nm in the system.

To compare Payne effect of rubber compound with bigger size aggregates present in corresponding carbon black, i.e., $(dV/dD)_{150}$ value, the plot of reciprocal of $(dV/dD)_{150}$ of respective carbon black (as shown in Fig-4.9) is compared with plots of Payne effect. It shows a similar fashion of Payne effect trend with the trend of the reciprocal of $(dV/dD)_{150}$. Hence it demonstrates that Payne effect of rubber compound reduces with reduced reciprocal of $(dV/dD)_{150}$ i.e. with increase of

$(dV/dD)_{150}$. Hence carbon black characterized with high $(dV/dD)_{150}$ value, i.e. characterized with higher extent of bigger size aggregates provides low Payne effect in rubber compounds.

The experimental carbon black with larger size aggregates are made of bigger size carbon black particles, which made aggregates spheroidal in shape and the same leads to least filler-filler interaction in the rubber matrix. It is also stated that experimental carbon black is characterized by a part of aggregates which associates with large size carbon black particles. Due to the large particle sizes, aggregates form thick network structure, hence for a fixed carbon black loading, the thick carbon black network structure cause less filler network distance in the rubber matrix, which results in less filler-filler interaction and consequently less Payne effect in the rubber compound.

4.2.3.4 Dynamical Properties of Rubber Compound.

Dynamical properties of rubber compounds are represented by hysteresis energy and heat buildup of rubber compound under oscillating and cyclic deformation. Hysteresis energy loss of rubber compound is expressed by loss tangent value (tanδ) which was measured by dynamic mechanical analysis at 60°C temperature and the heat buildup properties as measured by rise in sample temperature during the heat buildup measurement by Goodrich Flexometer [25-26]. The tanδ value and heat buildup of rubber compounds are shown Fig-4.16 and Fig-4.17 respectively.

It is seen that tanδ value of experimental compounds (SyR-2 and SyR-3) is substantially low compared to the control compound (SyR-1). The experimental compounds (SyR-2 and SyR-3) consist of carbon black Sy-2 and Sy-3 respectively, which are associated with large value of $(dV/dD)_{150}$ in comparison to control carbon black Sy-1. It indicates carbon black with large value of $(dV/dD)_{150}$ provides low tanδ value in rubber compound.

The tanδ value between SyR-2 and SyR-3 rubber compounds shows that instead of having high $(dV/dD)_{150}$ value of Sy-3 carbon black, it still provides marginal high tanδ value compared to Sy-2 carbon black in the corresponding rubber compound. It is seen that Sy-3 carbon black has comparable surface area with Sy-2 carbon black however the same is associated with marginal high structure properties. It has been studied in different literatures that carbon black with high structure properties adversely effects on hysteresis property in the rubber compound, i.e, carbon black with high structure leads to increase in hysteresis (tanδ) in rubber compound. That is why Sy-3 carbon black due to its high structure, results in high hysteresis compared to Sy-2 carbon black and Sy-3 carbon black exceed the effect of marginal high $(dV/dD)_{150}$ value compared to Sy-2 carbon black. However, due to significantly high $(dV/dD)_{150}$ value, Sy-3 carbon black still provides low tanδ value compared to Sy-4 and control carbon black, Sy-3 in the rubber compound.

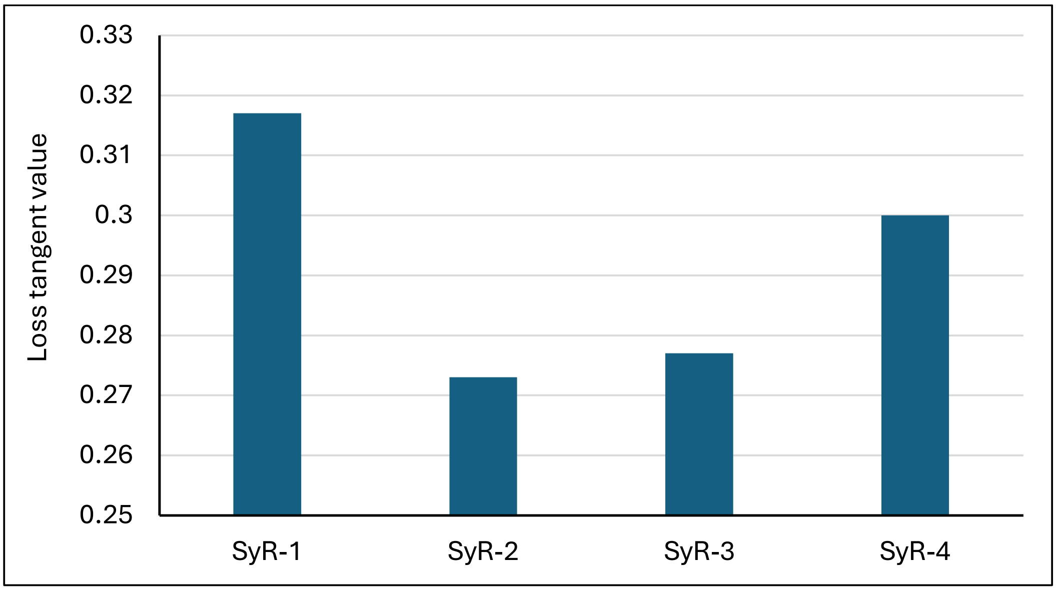


Fig-4.16: *Loss tangent value of rubber compound at 60°C.*

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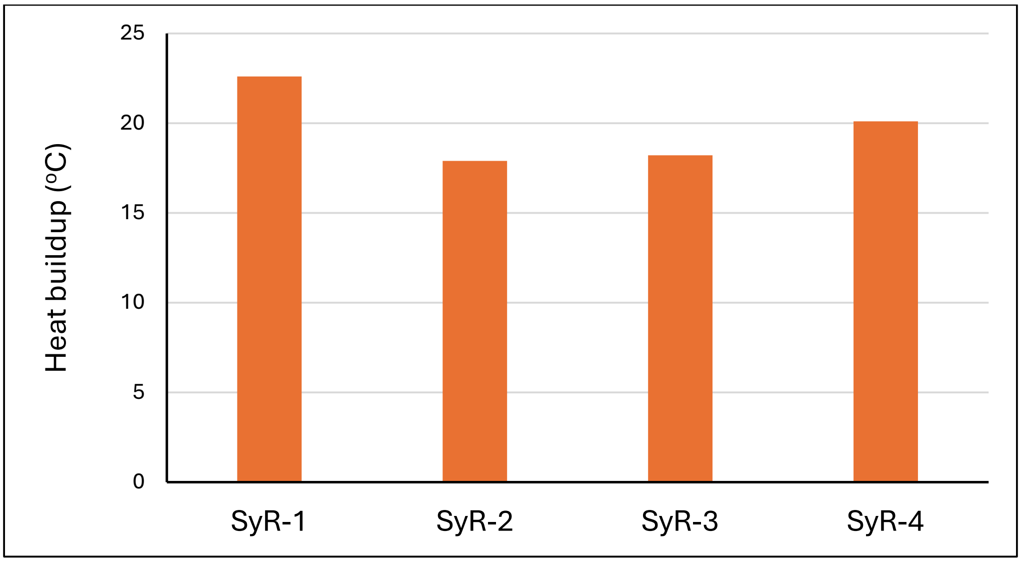

Fig-4.17: *Heat buildup properties of rubber compounds*

Filler-filler interaction, hysteresis loss of rubber compounds relates to the heat buildup property of the rubber compound. Heat buildup property of rubber compounds demonstrates that experimental rubber compounds are characterized with lower heat buildup in rubber compound and the trend of heat buildup indicates carbon black characterized with high $(dV/dD)_{150}$ value causes less heat buildup property. Sy-3 carbon black is associated with marginal high structure as compared to Sy-2 carbon black, which counters adversely against the effect of high $(dv/dD)_{150}$ of Sy-2 carbon black, hence both the carbon black provide similar heat buildup in rubber compound

4.2.3.5 Mechanical Properties of Rubber Compounds:

Mechanical strength of carbon black filled rubber compound primarily depends on surface area and structure of carbon black for a fixed filler loading. However, a tailor-made aggregate size distribution of carbon black can cause substantial impact on mechanical strength of rubber compound. It has been demonstrated that carbon black aggregates with spheroidal or ellipsoidal shaped are lower branched behavior, and these parts of carbon black aggregates lead to inadequate entanglement with rubber molecules [27]. Thus, carbon black with spheroidal or ellipsoidal shaped aggregates results in lower modulus and increased elongation at break of rubber compound. The tensile properties of rubber compounds are shown in Table-4.9, which indicates modulus of rubber compounds substantially increases with lower value of $(dV/dD)_{150}$.

Table-4.9: Mechanical Properties of Rubber Compounds

Parameters	unit	SyR-1	SyR-2	SyR-3	SyR-4
Tensile Strength	MPa	18.2	18.4	17.6	17.0
Modulus at 300% elongation	MPa	5.6	4.5	5.0	5.2
Elongation at break	%	636	700	625	634
Abrasion Resistance Index	%	100	95	99.5	97

The control carbon black is characterized lower $(dV/dD)_{150}$ and is associated with branched aggregate structure as shown by HRTEM study, hence for control carbon black, the rubber molecules has enhanced propensity of form entanglements and consequently results in high compound modulus and low elongation at break. with the rubber molecule due its branched aggregate structure, characterized by HRTEM analysis. HRTEM (Fig-4.11b) depicts that Sy-2 carbon black is characterized by a part of aggregates which is associated with bigger particle sizes, and which are spheroidal in structure. Moreover, the bigger particle size of carbon black makes it less branched. Hence less entanglements of the rubber compound take place with the carbon black resulting in lower modulus of rubber compound among all the carbon black. Therefore, aggregate shape along with aggregate size are considered as the key parameters which could determine the modulus in rubber compounds. Abrasion resistance property of experimental rubber compounds shows marginal deterioration in comparison to the control compound due to the presence of large extent of bigger size aggregates in corresponding experimental carbon black as well the same are characterized with broader aggregate size distribution compared to the control carbon black.

4.3 Conclusions:

Carbon black with broad aggregate size distribution results in increased interaggregate distance and resulting lower filler-filler interaction in rubber compound which causes lower Payne effect. Broad aggregate size distribution of carbon black provides low hysteresis loss in rubber compound and can provides low rolling resistance in tyre tread compounds. It describes that carbon black with narrow aggregate size distribution provides enhanced abrasion resistance property when surface area and structure of the same remain intact however, to achieve the highest abrasion resistance property of tyre tread compound carbon black with narrow aggregate size distribution, high structure and high surface are recommended.

It is also seen that carbon black characterized with larger extent of bigger size aggregates provides long tail aggregate size distribution pattern and, in such case, the FWHM value of the distribution could not be conclusive on the broadness of aggregate size distribution. Hence for these types of aggregate size distribution, (dV/dD) values at the larger aggregate size region are considered as potential aggregate size distribution parameter to demonstrate the pattern of aggregates size distribution. A carbon black associated with bigger particle size forms aggregates of thick network structure and thus, with a fixed carbon black loading, it provides lower length of aggregate network, distributed throughout the rubber matrix.

Carbon black having larger extent of aggregate beyond 150 nm aggregate size as denoted by high $(dV/dD)_{150}$ value, shows significant reduction of filler-filler interaction as compared with control carbon black, N330 and provides low Payne effect in rubber compound. It is also observed that the trend of hysteresis energy loss (loss tangent value at 60°C) of rubber compound is inversely related to the $(dV/dD)_{150}$ value of respective carbon black. It is noticed that by increasing concentration of bigger size aggregates in carbon black the hysteresis loss of rubber compound is reduced by 15%. As a result, it provides low rolling resistance in tyre tread compound.

It is further seen that carbon black, characterized with long tail aggregate size distribution due to presence of larger extent of bigger size aggregates, results in reduced heat buildup property in rubber compound which benefits in performance for tyre tread compound. The low heat buildup property of rubber compound benefits in tyre durability by reducing the chemical degradation of rubber molecules due to the heat generation during service, further it benefits in reducing the energy loss because of lowering the heat buildup.

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