CHAPTER 3:
MATERIALS AND METHODS

In the present research carbon black was modified by different methods. The modified carbon black was characterized and used as filler in rubber compounds. The influence of the modified carbon black in rubber compound performance was then evaluated particularly for tyre tread applications. The materials used for the present studies and the different experiments, testing and the characterization procedures have been discussed in this chapter.

3.1 Raw Materials Used in the Studies

The raw materials used in these studies, were collected from different sources of India and other nations.

- The key raw materials for the studies are different grade of carbon black which were collected from PCBL Limited, India.
- General purpose rubbers commonly used in tyre tread compounds were also used for the present studies. Natural rubber of grade ISNR 3CV was supplied by Rubber Board, India.
- Emulsion styrene butadiene rubber (grade SBR1712) with consisting of 37.5% oil extended and solution styrene butadiene rubber with 27.5% oil extended were procured from Lanxess AG, Germany.
- Poly butadiene rubber (PBR) with 98% Cis content was collected from Reliance Industries Limited, India.
- Zinc oxide was procured from Mittal Pigment Private Ltd, India. which was used as accelerator activator
- Micro crystalline (M.C.) collected from Repsol Chemicals, India, which is used as process aids which is characterized with a specific gravity of 0.915.
- Stearic acid having iodine number of 9 (max.) and acid number of 185-215 was collected from VVF Ltd, Mumbai, India, which acts as accelerator activator as well as processing aids for the rubber compounding.

- Treated distillate aromatic extract (TDAE) oil was supplied by Hansen and Rosenthal (Hamburg, Germany), used as rubber process oil.
- 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ), N-(1,3-dimethylbutyl)-N-phenyl-p-phenylenediamine (6PPD), N-Cyclohexyl-2-benzothiazole sulfenamide (CBS) were supplied by National Organic Chemical Industry Limited, Mumbai, India, which are used in rubber compound as antioxidant, anti-ozonant and accelerator for rubber vulcanization respectively.
- Sulfur, used as vulcanizing agent for rubber which has a assay of greater than 99% and a acidity of around 0.01 % , the same was procured from Jaishil Chemical Industry, India.
- N-(Cyclohexylthio) phthalimide (CTP) which is used as pre-vulcanization inhibitor (PVI) supplied by Finorchem Limited, Gujarat, India.
- Benzyl tri ethyl ammonium chloride was supplied by Sigma Aldrich, Germany. Carbon black of different grades was collected from PCBL Limited, India.

3.1.1 Carbon Black

The carbon black used in this study was produced in furnace process of manufacturing by incomplete combustion of heavy aromatic petroleum oil, which is termed as carbon black feedstock (CBFS). Carbon black used as reinforcing filler which provides strength into rubber compound, and simultaneously it enhances heat buildup, filler-filler interaction, hysteresis energy loss in rubber compounds [1-3]. Carbon black is characterized by its morphological characteristics such as particle size, surface area, structure, aggregate size and aggregate size distribution pattern, surface chemical property etc, which have been discussed in Chapter-2.

Based on the characteristics of carbon black there are different grades of carbon black available. Different ASTM grade carbon black and newly developed carbon black grades with customized morphological characteristics were produced by PCBL Limited and used in this study. Carbon black is identified by its unique nomenclature, which was done in accordance with ASTM D1765 where different digits of carbon black nomenclature provide their own significance. The first numerical digit of carbon black nomenclature represents particle size and surface area of carbon black and carbon black with different first digit and its corresponding particle size and surface area. In these research work ASTM grade N330 and N220 as well as different new developed grades based on the engineered morphological features were used which were produced by furnace process of manufacturing by PCBL Limited.

3.1.2 Rubbers

Rubber are primarily long chain hydrocarbon molecules which are characterized with high molecular weight and provide superior flexibility, elongation and toughness. Rubbers are produced naturally or synthesized in chemical process by using different monomers. Rubber is the most important and major part of tyre tread compound and in general around 40 to 60% of tyre tread compound is associated with rubber, thus, performance of tyre tread compound is largely influenced by types and characteristics of rubbers used into the same [4]. There are different types of rubbers are used in tyre tread compound based on the area of applications and types of vehicles. In this study different types of rubber were used such as natural rubber, different grades of styrene butadiene rubber (SBR), poly butadiene rubber (PRB) etc.

3.1.2.1 Natural Rubber (NR)

NR is chemically pure poly-cis-1.4 isoprene, which contains more than 99.9 % of cis 1, 4 structural units. The macromolecules of NR are characterized by long carbon-carbon chains, regular, flexible, and practically linear in nature. It has glass transition temperature (Tg) of -70°C, which indicates its superior rubbery characteristics. The structural geometry of NR results its very good elastic properties and assists to undergo spontaneously crystallization while the same is extended under stress, which is called strain induced crystallization and due to the stain induced crystalline, NR provides superior tensile strength in the rubber compound application [5-6].

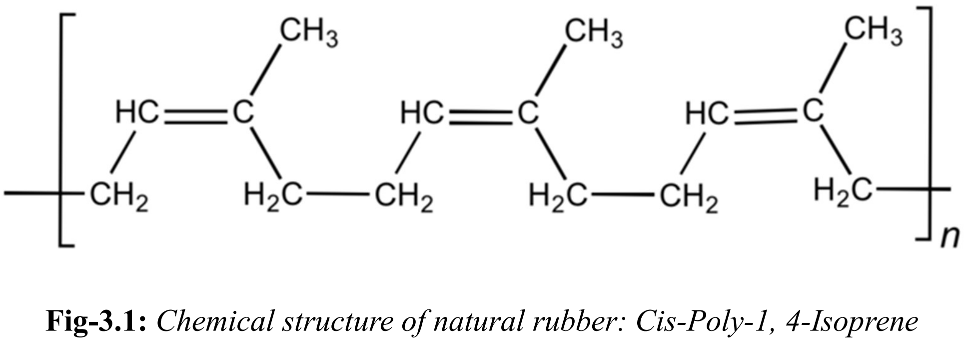

Fig-3.1: *Chemical structure of natural rubber: Cis-Poly-1, 4-Isoprene*

NR is obtained from Hevea Brasiliensis tree and produced by tapping of Havea Brasilia tree by which the latex is collected from the tree. After collection of the latex from tree, it is coagulated, which is basically the destabilization and aggregation of latex particles. The coagulation is carried out either naturally or by various techniques by addition of an acid, salts, or polymeric coagulating agent into the latex under a continuous agitation. The second stage of NR preparation involves drying of the coagulated latex through evaporation, spray drying etc [7-8]. Due to the natural process of manufacturing, NR contains different impurities like dirt, gel, ash content, and based on the same gradation of NR is carried out. There are different grades of Indian standard NR having different composition of impurities which are shown in Table-3.1. ISNR 3CV is one of the most superior Indian standard NR grades, characterized with least dirt content and ISNR 3CV grade NR with Mooney viscosity of 60 MU has been used in present study [9].

Table-3.1: Gradation of natural rubber and properties of the same.

	ISNR 3 CV	**ISNR 3 L**	**ISNR 5**	**ISNR 10**	**ISNR 20**	**ISNR 50**
Dirt percent by mass (Max)	0.03	0.03	0.05	0.1	0.2	0.5
Volatile matter, percent by mass (Max)	0.8	0.8	0.8	0.8	0.8	0.8
Ash, percent by mass (Max)	0.5	0.5	0.6	0.75	1	1.5
Nitrogen, percent by mass, Max	0.6	0.6	0.6	0.6	0.6	0.6
Plasticity retention index, PRI (Min)	60	60	60	50	40	30
Colour code	Black	Black	Green	Brown	Red	Yellow

3.1.2.2 Polybutadiene Rubber (PBR)

Polybutadiene rubber is one of most important general purpose synthetic rubber used in tyre tread compounds. It is formed by the polymerization of 1,3-butadiene monomer by a Ziegler–Natta catalyst in solution based polymerization. Polymerization of butadiene involves formation of ‘cis’ as well as ‘trans ‘forms of isomerism and extent of each configuration depends on the condition of manufacturing and the nature of catalysts [9].

The properties of polybutadiene rubber is greatly dependent on the ‘cis’ content and ‘trans’ content in its micro-structural configuration, for example, polybutadiene rubber with high ‘cis’ content results in high elasticity and is characterized with very low glass transition temperature, which results in excellent rubbery behavior in nature. Poly butadiene rubber is characterized with superior wear resistance, high rebound, and low hysteresis properties, which makes it superior choice for tyre application particularly for tyre tread compound and around 70% of the total polybutadiene rubber produced is consumed in tyre compounds [10].

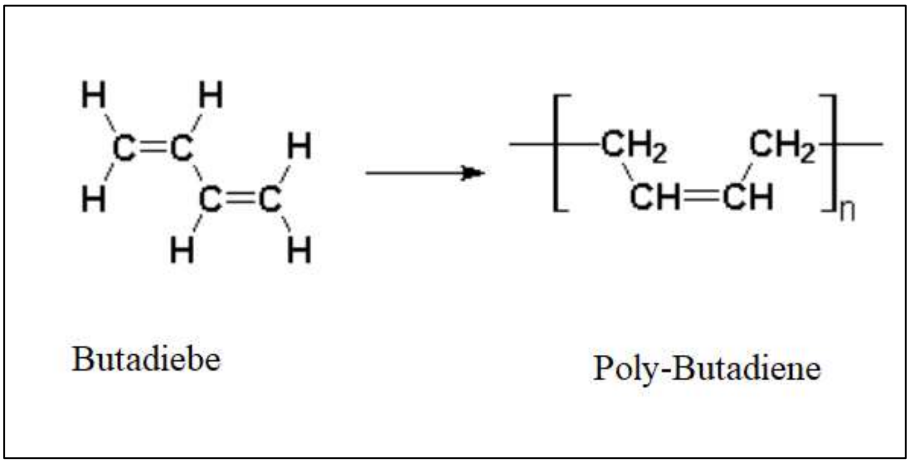

Fig-3.2: *Chemical structural unit of polybutadiene rubber (cis-configuration)*

3.1.2.3 Styrene Butadiene Rubber

Styrene-butadiene rubber (SBR) is made by copolymerization of styrene and butadiene monomers, and it is one of most important rubbers used in tyre application. The properties of SBR are dependent on several factors such as styrene and butadiene content, micro-structure, stereo chemistry of styrene and butadiene units etc. In the microstructural orientation of SBR, the butadiene structural units can arrange in cis-1,4 configurations as well as in trans-1, 4 configuration or in 1, 2 (vinyl) configuration which has been controlled by the manufacturer process and the catalyst used in the manufacturing. It has been noticed higher extent of styrene and 1, 2 butyl structural content contributes to the increase glass transition temperature and terns towards plastic nature of SBR [11-12].

Styrene-butadiene rubbers are clarified based on the types of manufacturing process and the most common process of SBR manufacturing is emulsion polymerization, in which the polymerization is initiated by free radical catalyst. SBR manufactured in this process is characterized by very high molecular weights, broad molecular weight distribution, high level of branching, and usually consists substantial extent of gel content, which practically reduces Mooney viscosity of rubber and benefits in processing during rubber compounding.

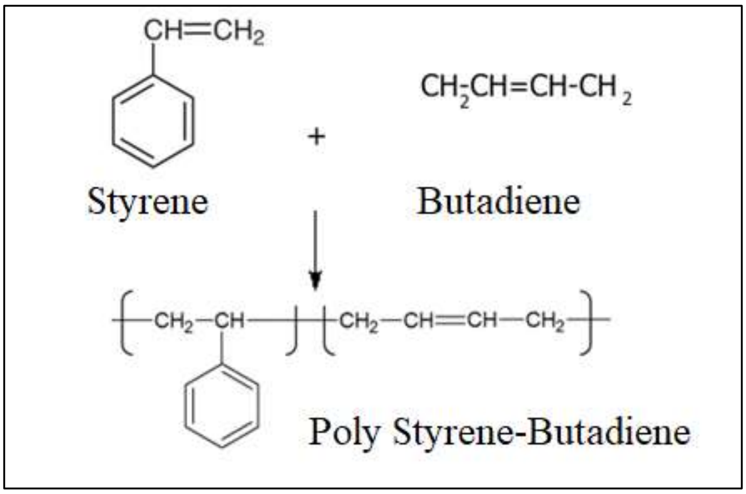

Fig-3.3: *A schematic representation of Styrene butadiene rubber molecular unit formation by reaction of styrene and butadiene monomers*

Styrene-butadiene rubbers are clarified based on the types of manufacturing process and the most common process of SBR manufacturing is emulsion polymerization, in which the polymerization is initiated by free radical catalyst. SBR manufactured in this process is characterized by very high molecular weights, broad molecular weight distribution, high level of branching, and usually consists substantial extent of gel content, which practically reduces Mooney viscosity of rubber and benefits in processing during rubber compounding.

Another common method of SBR manufacturing is an anionic solution polymerization process, which involves more control of polymerization over the emulsion polymerization and leads to a very narrow molecular weight distribution with less chain branching in the backbone structure. In this manufacturing process, polymerization of styrene and butadiene is initaited alkyl lithium initiator (e.g., butyllithium) where usually a hydrocarbon solvent such as hexane or cyclohexane is used. In this process of polymerization, the reaction kinetics is controlled by reaction temperature and polymerization takes places at lower reaction temperature of around 5°C, is called as cold polymerization where a conversion of 60-80% polymerization could take place, whereas polymerization takes place at high reaction temperature of around 50-65°C provides higher conversion of up to 90%, which is called as hot polymerization [12]. In this polymerization technique the monomers undergo complete depletion, which causes living and reactive chain ends in the backbone structure and generates polar chain ends. SSBR with polar chain ends adds benefit to interact or react with different chemicals, fillers and rubber compounding ingredients, which impact on mechanical and dynamic behaviors of rubber compounds.

SSBR is further characterized with its enhanced functionality by reacting with specific functionalizing agents, which are added during the manufacturing of the same through solution polymerization and the same is called functionalized SSBR (FSSBR). It has been established that several types of functionalized SSBR were synthesized by anionic polymerization based on characterization of functionalizing agents and needs of end applications. In the functionalization process a major part of functionalization are carried out with the living and reactive ends of SSBR molecules however, with control polymerization conditions the functionalization also could be possible with in-structure functionalization [13]. Hence the functional groups could be associated at the chains ends of the SSBR molecules as well as within the structure unit of the molecules.

A schematic representative of a few possible FSSBR molecular configurations is shown in Fig-3.4, where different types of functional groups are denoted by A and B. The configuration of the functional groups A and B is primarily controlled by manufacturing condition, types of catalyst, concentration of different chemicals etc [14].

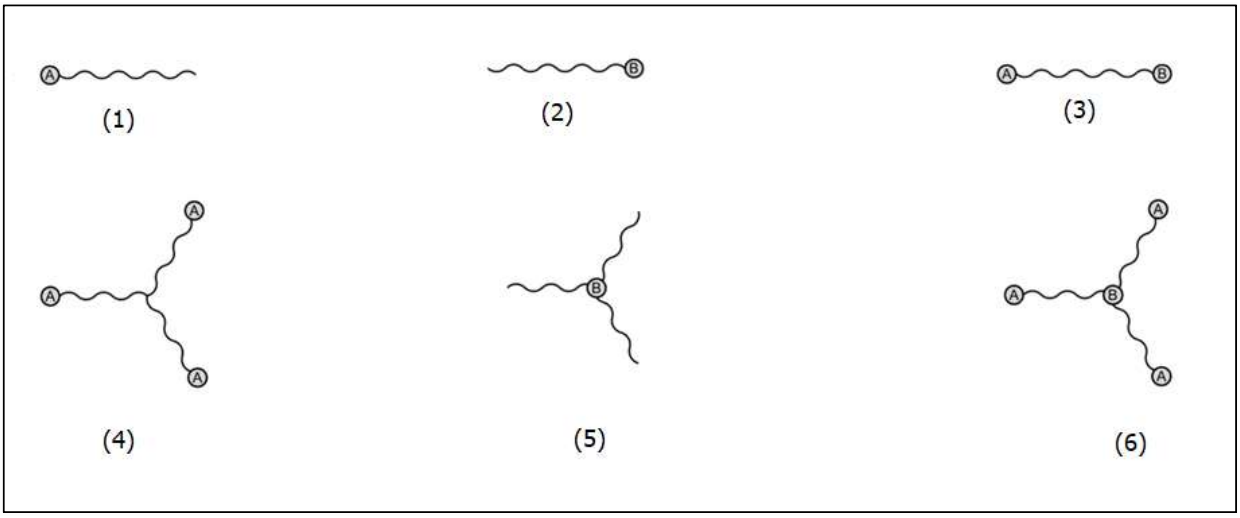

Fig-3.4: *Modes of functionalization at different ends of functionalized SSBR*

3.1.3 Process Oil for Rubber Compounding

Process oils are basically low molecular weight hydrocarbon compounds, which act as plasticizer in rubber compound. The low molecular weight of the process oil embodies themselves between the polymeric chains of rubber molecules and spaces them apart, causing free volume or swelling in the polymeric materials. In this mechanism, process oils make rubbery materials softer and reduce its viscosity thereby increases ease of processibility.

Incorporation of filler in rubber compound leads to increased compound viscosity due to the hydrodynamic effect, which increases with increased filler loading. On incorporation of certain high loading of filler into the rubber compound, the viscosity of the system reaches to such a level that processing of rubber compound becomes difficult, and in this case incorporation of process oil in rubber formulation plays crucial role on reducing the compound viscosity, benefitting in rubber processability [15]. The effect of process oil is largely dependent on its compatibility with the rubber molecules. It has been seen that aromatic types process oils are commonly used in rubber compounds based on NR, SBR, BR, however for rubber molecules characterized with least double bond in backbone structure like EPDM, the paraffinic type of oil are preferred as processing aids.

In this present study treated distillate aromatic extracted (TDAE) oil is used as process oil which has high viscosity-gravity constant and low poly aromatic hydrocarbon content in comparison with commercially available aromatic oil for the rubber compound application [16]. High aromatic oils, which are readily used as rubber process oils, contain high concentrations of polycyclic aromatic hydrocarbons, which are carcinogenic as well as posing a threat to the environment. Since the beginning of 2010, the use of high aromatic process oils has been restricted under the EU regulation 1907/2007 and use of non-carcinogenic oils have been focused. The specification of the TDAE oil as used in present study is shown in following Table-3.2 and supplied by Hansen & Rosenthal (Hamburg, Germany).

Table-3.2: Characteristics of TDAE process oil

Properties	**TDAE (Viva Tec 500)**
Density at 15ºC, Kg/m^3	950
Refractive index at 20ºC	1.53
Kinematic viscosity, mm^2/s at 100ºC	18.8
Flash point COC, ºC	272
Pour point, ºC	27

3.1.4 Anti-Degradation Agents

It has been seen that elastomer-based products suffer irreversible changes to their required design properties during service which causes loss of mechanical properties and alterations in surface aspect of the materials. These changes happen in rubber articles due to the degradation of rubber molecules over time as caused by air oxidation, ozonation, heat, light, high energy radiation and high humidity etc. In order to combat these changes anti-degradants are used in rubber compounds [17-18].

2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) is one of most common antioxidants used in tyre tread application, which is characterized with highly persistent, non-blooming in nature, and it has minimal effects on processing as well as curing characteristics of rubber compounds. It offers in excellent resistance to oxidative degradation of rubber even at lower dosages of around 1 phr. Anti-ozonant used in rubber compound acts as ozone scavenger to protect rubber molecules from the ozone oxidation and resist the deterioration of mechanical strength of rubber articles due to the ozone oxidation. There are different types of anti-ozonant used in rubber compounding such as N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD), N-phenyl-N' isopropyl-pphenylenediamine (IPPD), N,N'-diphenyl- PPD (DPPD) etc. however, in this study the 6PPD has been used as anti-ozonant which is one of most common anti-ozonants used in tyre tread application [19].

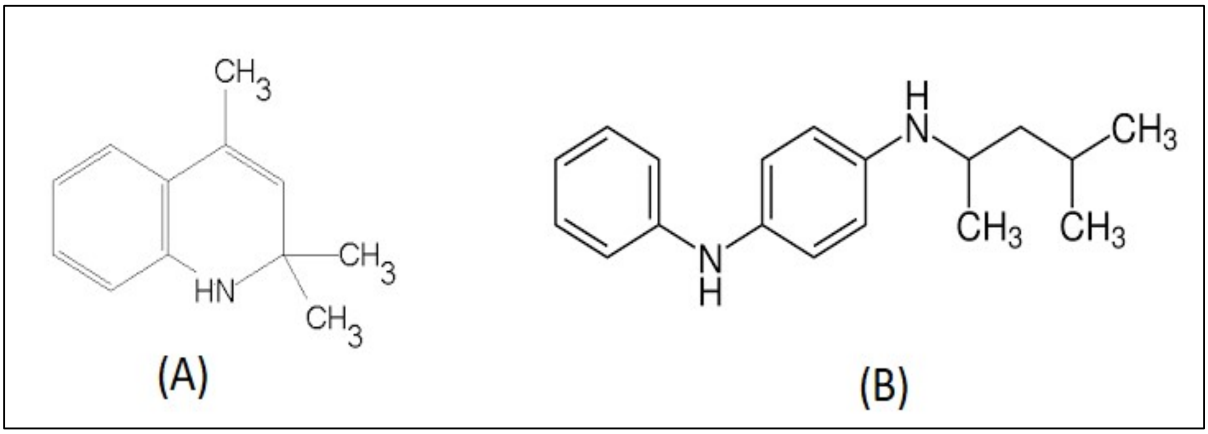

Fig-3.5: *Chemical structure of (A) 2,2,4-trimethyl-1,2-dihydroquinoline (TMQ) and (B) N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)*

3.1.5 Micro-Crystalline Wax (M.C. Wax)

Microcrystalline waxes (M.C. Wax) are basically polymeric hydrocarbons with ‘C’-units between 30 and 80. The M.C. Wax, most commonly used in rubber compound, is characterized with C-unit in between 45 and 55, which are extremely branched in chemical structure. M.C. wax added in rubber compounding as processing aids. In practice general purpose was blooms and creates barriers on rubber surface, which acts as anti-ozonant by restricting ozone to interact with rubber molecules at the same time the blooming of wax creates whitist appearance on rubber article surface. The movement of wax to the surface of a rubber part depends on several variables such as molecular weight, carbon number of the wax molecules, chemical structure of wax, concentration of the wax added in the rubber, loading of filler, chemical structure of rubber molecules etc. Wax with branched chemical structure, blooms slowly to the surface of rubber articles. M.C. Wax is too bulky in molecular configuration to bloom sufficiently to create an ozone barrier on rubber surface, hence microcrystalline wax has least effect on surface appearance of rubber articles, and it is used as processing aids in rubber compounding [20].

3.1.6 Stearic acid

Stearic acid is a very common compounding ingredient for rubber formulations which is chemically octadecanoic acid and consists of 18 carbon units in its backbone structure. Stearic acid attributes key role in rubber compounding performance as accelerator activator in presence of zinc oxide as it forms zinc stearate and increases the efficiency of accelerator in the curing of rubber compound. Stearic acid for rubber applications further provides lubrication and improved viscosity as well as a softer texture for the finished product [21].

3.1.7 Zinc Oxide

Zinc oxide is an inorganic compound which occurs as a white powder in nature and largely used in rubber products as an accelerator activator for vulcanization of rubber. ZnO further acts as filler and benefits in resistance against heat, abrasion and helps guard against ultraviolet degradation [22]. As stated, zinc oxide forms zinc soap in presence of stearic acid and increases its solubility in rubber compound where ZnO forms an accelerator complex and benefits in vulcanization reaction of rubber molecules.

3.1.8 N-cyclohexyl-2-benzothiazolesulfenamide (CBS)

CBS is used as accelerator which enhances the efficacy of vulcanization reaction between rubber and sulfur. CBS is one of most popular accelerators used in rubber industry due to its delayed action as well as faster cure characteristics during the vulcanization reaction [24]. CBS provides a wide range of crosslink densities depending on its loading. CBS is usually incorporated in the rubber compound at the end of mixing cycle along with the curing agent, sulfur keeping rubber compound temperature of around 110 to 110ºC.

3.1.9 Sulphur

Sulphur, used in rubber compounding, acts as curing agent, which cross-links rubber molecules through chemical reaction which is called vulcanization of rubber compound. Crosslinking of rubber molecules converts the long chain molecules into the three-dimensional elastic network, which provides strength, stability, and elasticity into rubber compounds. Element sulfur is the most widely used as general-purpose curing agent in the rubber industry. Elemental sulfur is a solid, crystalline material at ambient temperature, which is termed rhombic sulphur. In the ambient condition rhombic sulphur forms cyclic octatomic chemical structure of formula S8 [23]. The rhombic sulfur has least compatibility with rubber molecules and due to its low molecular weight, it migrates within rubber compound which is known as blooming.

Another form of sulfur used in rubber compound is polymeric insoluble sulfur which is commonly used in natural and synthetic rubbers where restriction of sulfur blooming is essential. Due to very high molecular weight and polymeric configuration of insoluble sulfur the migration of same is limited in rubber compounds.

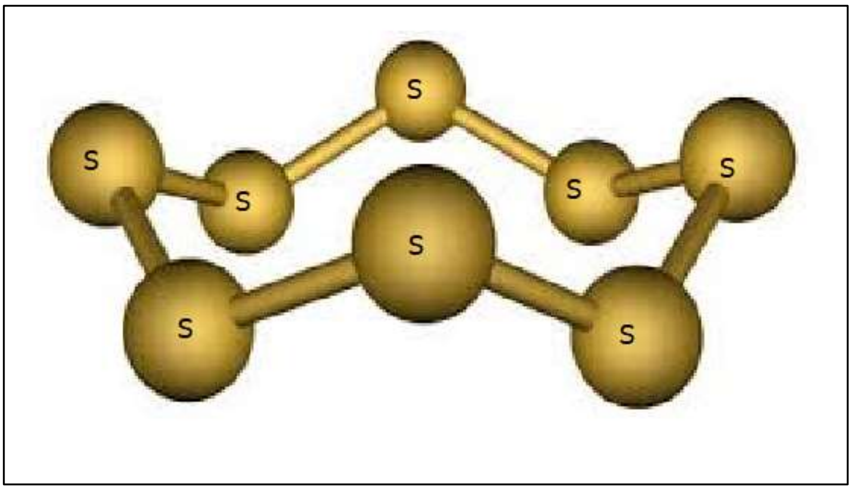

Fig-3.6: *Chemical structure of rhombic Sulphur* (S_8)

3.1.10 Pre-vulcanization agent (PVI):

PVI added in rubber compound to control the scorching of rubber compound during processing, it has been observed that sulfenamide accelerators such as CBS, can be effectively retarded using small proportion of PVI without affecting their rate of cure. The most common PVI used in rubber compound is N-(Cyclohexylthio) phthalimide (CTP) which has been also used for the present studies.

3.2 Testing and Characterization of Carbon Black

In this study carbon black was modified and the effect of the same has been studied in rubber compound for tyre tread compound improvement. Hence different testing and characterization of carbon black as well as rubber compounds were carried out to investigate the carbon black characterization and effect of the same in rubber performance. The details testing and characterization method for carbon black as well as rubber compounds are described below.

3.2.1 Nitrogen Surface Area

Nitrogen surface area measurement is most potential method to determine surface area of carbon black. It is measured by Brunauer, Emmett, and Teller's (BET) principle where total surface area as well as the external surface area of the carbon black are measured by calculating the amount of nitrogen adsorbed on carbon black surface at liquid nitrogen temperature. The total surface area is expressed as nitrogen surface area (NSA) while the external surface is expressed by statistical thickness surface area (STSA). The total nitrogen surface area (NSA) value is calculated from the adsorption of nitrogen by specific weight of carbon black which includes external carbon black surface area as well as surface area associate with micropores of diameters less than 2 nm. Hence a difference between NSA and STSA determines the extent of porosity associated with the carbon black. [25]. The NSA and STSA of carbon black was measured by using nitrogen surface analyser (Model: NOVA 2200E, Anton Paar, Austria) according to ASTM D6556 test method.

3.2.2 Iodine Adsorption Number

Iodine adsorption number is the measure of carbon black surface area as it is based on the amount of iodine molecules adsorb on the surface of carbon black. A higher amount of iodine adsorbs on a specific weight of carbon black signifies a higher portion of available surface area for the carbon black. Iodine adsorption measurement is carried out by chemical method, where the measurement is accomplished by mixing a known weight of dried carbon black with a known volume of iodine solution of known iodine concentration. The mixture was shaken to ensure complete wetting of carbon black particles by iodine solution, and the mixture is then allowed to settle for a given period. Due to the vigorous shaking of carbon black the iodine molecules from the solution are absorbed on carbon black surface and then the mixture is centrifuged to separate carbon black from the solution. The iodine present in centrifuged solution is back titrated by sodium thiosulfate, and it demonstrates the amount of iodine adsorbed on carbon black and represented as gm of iodine adsorbed per kg of carbon black (g/kg unit) [26].

3.2.3 Measurement of Carbon Black Structure

Carbon black structure refers to its primary structure as well as secondary structure, which are associated with aggregates and the agglomerates of carbon black respectively. Carbon black aggregation as well as agglomeration causes void volume inside carbon black structural units and the void volume determines the extent of carbon black aggregation or agglomeration. It has been further demonstrated that carbon black associated with highest void volume, is characterized by high structure property [27-28]. Hence the structure of carbon black was measured by determining the void volume presents per unit weight of carbon black.

The basic equipment used to measure carbon black structure is Absorptiometer (Brabender® Absorptometer "C"). Absorptiometer measures the volume (ml) of oil consumed per specific weight of carbon black (100 gm) which is called oil absorption number (OAN) of carbon black. As carbon black exists in the form of agglomerates, hence OAN represents carbon black structure associated with the agglomeration, i.e., secondary structure property. In the oil absorption number measurement, the most common oil used is di- butyl phthalate (DBP), which terns OAN also as DBP number.

In the measurement of OAN or DBP, a known weighed carbon black sample is taken into the mixing chamber of Absorptometer equipment. Inside the mixing chamber, shaft blades are present, which are attached to a motor drive. It measures the torque while the blades rotate inside the chamber. During testing of OAN, oil is added to carbon black dropwise and the blade rotates to mix the oil with carbon black. The added oil is absorbed in the void of carbon black, as a result viscosity of the mixer increases which causes higher torque generation to rotate the blades. When the carbon black voids are filled completely with the oil, then the extra added oil build up a high viscosity mud or paste of carbon black as a result it causes a sudden peak of torque requirement to rotate the blades, as a result the rotor gets tripped. The volume of oil required to trip the rotation of blades is measured and calculated as oil absorption number of the carbon black.

The primary structure of carbon black is represented by compressed oil absorption number (COAN). In the measurement of COAN value carbon black is compressed or crushed by hydraulic pressing of 24,000 psi which causes complete breakdown of carbon black agglomerates. During crushing, the agglomerates are broken down and the carbon black is characterized with only the presence of primary structural units aggregates. In this condition carbon black is tested for oil absorption number as stated above and the oil absorbed by carbon black under this compressed condition is called compressed OAN or compressed DBP number, which represents the extent of carbon black aggregation.

Fig-3.7: *Absorpotometer Equipment (Brabender® Absorptometer "C")*

3.2.4 pH Testing

The pH of a carbon black was measured by a pH meter, in this method water slurry of carbon black is prepared by suspending a definite amount of carbon black in neutral de-ionized water with constant agitation. pH of the slurry as measured by pH-meter, represents pH of carbon black as per ASTM D1512. pH of carbon black indicates presence of acidic or basic functional groups in carbon black surface and it is believed to affect cure rate tendencies in rubber compound applications [29].

3.2.5 Aggregate Size Distribution:

Aggregate size distribution was measured by Brookhaven Instrument Disc Centrifuge Photosedimentometer (BI-DCP) Particle Size Analyzer, Brookhaven Instruments, USA. The measurement is based on the principle of photo sedimentation where diameter of aggregates measured in term sedimentation time based on Stokes Law, as shown inequation (3.1), where the aggregates are considered as spherical in shapes [30].

$$t = \frac{18\eta_f . \ln\{\frac{R_d}{S}\}}{\omega^2 . \Delta\rho . D_p^2} \tag{3.1}$$

In this method, a small part of carbon black dispersion is injected into the meniscus of a rotating hollow disc filled spin fluid having viscosity, η_f. The disc rotates with a speed of ω, as a result, the particles with diameter, D_p scatter outward due to the centrifugal force. The detector placed with a radian distance of R_d, detects the particles. Here 't' is the time required to traverse the particles from the meniscus having radial distance of S to the detection point which is calculated by the Stokes Law of sedimentation.

Each aggregate of the carbon black dispersion is detected with respective detection time which is inversely proportional to the diameters of aggregates hence carbon black aggregates smaller in diameter are detected first. Hence based on the on the detection time, the aggregate size (Dp) was measured by BI-DCP Disc Centrifuge Particle Size Analyzer

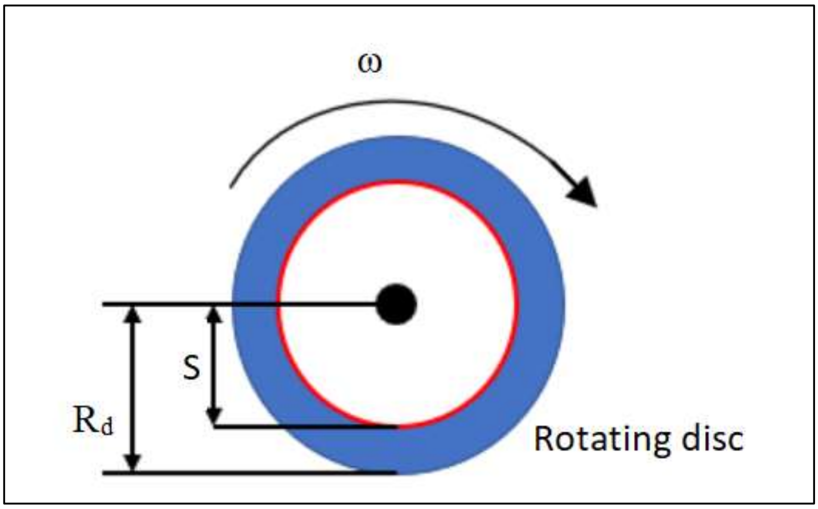

Fig-3.8: *Schematic representation dispersion injection distance (S) and detection distance (R_d)*

In the measurement of aggregate size distribution by BI-DCP sedimentation method, around 10 mg of carbon black powder is mixed with 2 mL of 100% ethanol in a 20 ml vial. The suspension undergoes sonication in a 30 mW sonic bath for 5 minutes to dampen the sample and later 6 mL of a 0.1 vol% TritonX-100 aqueous solution is added to the suspension to scatter the particles. The suspension solution undergoes sonication with a sonic probe for 10 minutes keeping the solution in an ice-bath. In this process the carbon black agglomerates are broken down to discrete units of aggregates which remain stabilized in the solution due to presence of dispersing agent TritonX-100 [31].

To analysis the aggregate size and aggregate size distribution by BI-DCP, initially 15 mL of a 0.1 vol% TritonX-100 aqueous solution, the spin fluid is injected into the non-spinning disc of BI-DCP. 2 ml 100% ethanol was added to spin fluid and followed by 0.2 ml carbon black suspension solution was added while the disc starts revolving with a rotation speed of 10000 rpm. The carbon black aggregates are scattered centrifugally, due to the revolution of disc, and the same were detected by a bean of LED light detector. The time to traverse to the detection point is detected by detector and called the detection time, which in inversely proportional to the square of aggregate size as per Stoke's law. In this method size of each aggregate present in the system was measured and by measuring the same aggregate size distribution of carbon black is portrayed and rest of the aggregate size distribution parameters such as mean, mode, FWHM, d10, d90 etc. were measured.

3.3 Carbon Black Modification

In this work carbon black was modified to enhance the performance of tyre tread compounds and the modification of carbon black were carried out by different methods. Firstly, the carbon black modification was conducted during the manufacturing process where carbon black with different morphological characteristics were made in the furnace process of manufacturing. In addition to this, the commercially available carbon black were further modified by post treatments where carbon black was treated with ozone gas and benzyl triethyl ammonium chloride (BTEAC) surface modifier.

3.3.1 Modification of Carbon Black During Manufacturing

In the furnace process of carbon black manufacturing heavy aromatic oils are used as feedstock which are called carbon black feedstock (CBFS). During the manufacturing CBFS is injected into the reactor through a nozzle along with automized flow of air. Here fine droplets of oil were injected enter the furnace reactor through automizer nozzle where finely droplets oil particles are partially combusted in presence inadequate air. Due to the combustion of CBFS, it generates very high temperatures of 1200°C to 2200°C in the reactor zone of the furnace. The increase in temperature depends on the amount of oil injected, amount of air supplied and extent of oil combusted. In the high temperature of reactor zone, part of the CBFS is combust partially and the rest of the oil is decomposed and form different hydrocarbon, CO_2, CO gases and carbon particles. The reaction of carbon black formation is stopped by addition of co-current flow of water in the reactor, which is called quenching of carbon black.

Injection of CBFS was carried out by multiple nozzles placed circumferentially in the reactor which is called choke section of reactor. In a reactor the multiple chock section is possible for the injection of oil into the reactor. A schematic representation of carbon black reactor is shown in Fig-3.9, where location of choke section, quench position and distance between them has been shown. In the furnace process of manufacturing, different types of carbon black were produced by monitoring the manufacturing and processing conditions, such as position, numbers of nozzles, distance between choke to quench, position of different nozzles in different choke section, volume of CBFS flows, ratio of CBFS to automized air etc. In addition to different processing condition an additive (K+ salt solution) is also added to furnace reactor with proper controlled of flow rate in order to optimize carbon black secondary structure [32].

Carbon black development has been carried out during manufacturing by change in processing conditions, monitoring CBFS to air ratio, monitoring CBFS injection points and monitoring the distance of quench from the choke section. The morphological development of carbon black has been focused primarily on tailor made aggregate size, aggregate size distribution, particle size, surface area and the structure. The aggregate size and aggregate size distribution of carbon black were modified primarily by change in CBFS concentration in different choke sections and by monitoring the distance of quench from the CBFS injection points. The particle size and surface area modification of carbon black was monitored CBFS to air ratio and the temperature of reaction where the structure was controlled by quench location as well as by monitoring the K^+ salt concentration [33].

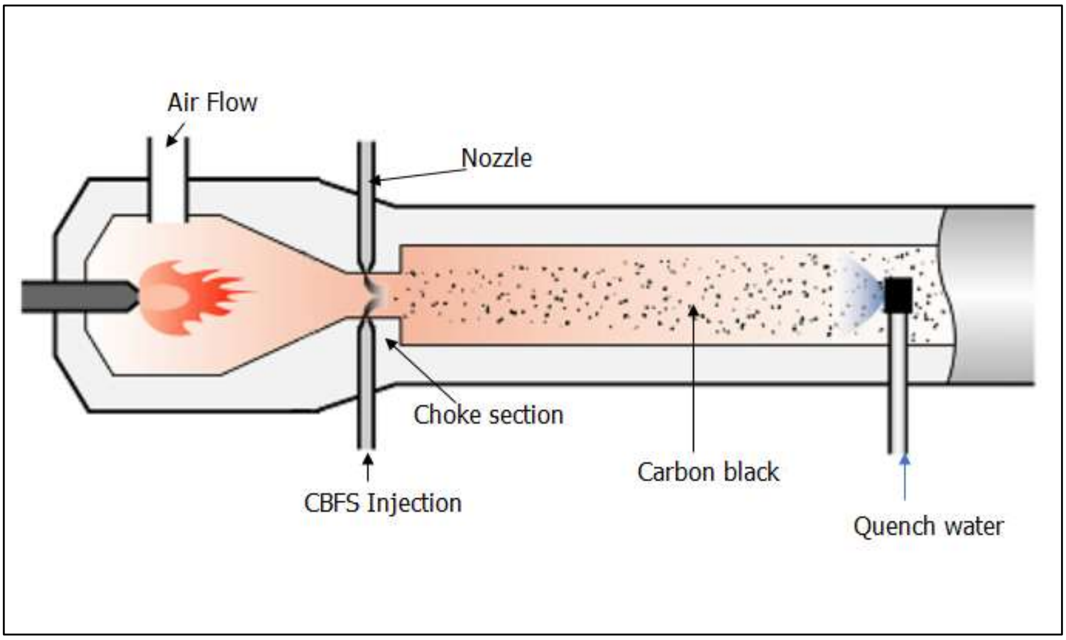

Fig-3.9: *Schematic representation furnace reactor for carbon black manufacturing*

3.3.2 Ozone Treatment of Carbon Black:

Commercial carbon black grade, N330 was post treated with ozone oxidation method where carbon black was treated with a flow of ozone gas over different times of ozone exposure. The time of ozone exposure determines the extent of carbon black oxidation. The oxidation method was developed in PCBL Limited proprietary method where ozone is generated from air oxygen and the same was impinged on carbon black with a ozone flow rate of 3 gm per hours, keeping the reactor at room temperature.

3.3.3 Treatment of Carbon Black with BTEAC

Here carbon black was treated with quaternary ammonium salt, e.g., benzyl tri-ethyl ammonium chloride. The treatment would likely functionalize carbon black by benzyl and ethyl groups as well as by the amins derivative part of the chemical through chemical reaction with different functional groups present on carbon black surface such as ketone, carboxylic acid, lactone etc.

The treatment was carried out by mixing BTEAC with carbon black with different concentrations such as 0.5%, 1.0 % and 1.5% with respect to the carbon black by weight. The mixture was refluxed by heating at 100°C for 60 minutes in presence of excess distilled water and followed by cooling the mixture to room temperature. The mixture was washed repeatedly by distilled water in a Gooch crucible for removal of un-reacted BTEAC and then it was dried in oven at 125°C for 3 to 4 hours until complete removal of moisture. The modified carbon black was collected inside desiccator. A blank run of respective carbon black was also carried out by taking the same carbon black sample and refluxed it as above to have identical condition without adding BTEAC.

3.4 Rubber Compounding and Testing

3.4.1 Mixing of Rubber Compound

Carbon black was mixed with rubbers along with different chemicals based on the specific recipe for individual study. Mixing of rubber compound was carried out by Laboratory Banbury (Model: BB2, M/S: Kobelco, Japan) and followed by Two roll mill mixing machine (SMX. LAB.613.ASTM, Santosh Machinery Pvt. Ltd, India). In the Banbury mixing the rubber is mixed with different chemicals and with carbon black while the dumped compound from Banbury is taken for shaping and sheeting in a two-roll mixing mill. The mixing of the rubber compounds was carried out in two stages of mixing. In the first stage a master batch compound was prepared where rubber was mixed carbon black along with different chemical except the curing agent. The masterbatch compound was prepared in Banbury at a compound dump temperature of 145-150°C, at 60 rpm for 5 minutes where the rubber is mixed with carbon black and chemicals except curatives.

The final stage of the mixing was carried out to mix masterbatch compound with the curing agents such as accelerators, sulfur, PVI etc. In this process the Banbury operated at much lower rotor speed of 45 rpm and at a mixing temperature of 100°C temperature for 3 minutes. The dumped compounds were processed in the two-roll mill to perform the sheeting of rubber compound for both masterbatch compound as well as final batch compound. During mixing the batch weight of rubber compound was monitored in such a way that the fill factor during mixing remained around

0.7, i.e., 70% volume of the Banbury mixing chamber is filled with rubber compound while 30% remains unfilled [34-35].

3.4.2 Rubber Process Analysis

Rubber Process Analyzer (Model-Premier RPA, Alpha Technology, USA)) is a used to characterize the rheological properties of viscoelastic materials, i.e, rubbers. In the RPA, a rotational twist is applied to the specimen, which causes a shear strain within the specimen and on application of strain a part of energy is lost due to its viscous characteristics and rest of the energy is stored due to its elastic part.

The shear modulus of uncured rubber compound is measured with strain sweep. The rubber compound is placed inside a biconical cavity encapsulated between two dies. The rubber compound gets deformed while the bottom die of the cavity starts rotating and causing a shear strain in the rubber compound. The upper die of the cavity remains stationary, and the same relates to high modulus transducer, which measures the torque as applied on upper cavity by the rubber compounds. The torque is applied to lower cavity to provides pre-determined shear strain into the rubber compound, the shear strain causes viscous shear stress as well as elastic shear stress within the sample and only elastic shear stress creates torque generation on the upper cavity, and the same is measured by help of high torque transducer.

In this test method Payne effect of rubber compound was measured, by measuring the shear modulus of rubber compound with different shear strain applied in the rubber compound and same was measured by Rubber Process Analyser. In the study the rubber compound was deformed under a shear strain sweep of 0.1% to 100% at a temperature of 70°C. The shear strength of rubber compound corresponding to respective strain sweep were recorded and Payne effect of rubber compound was calculated by subtracting shear modulus of rubber compound at high shear strain (100%) from the same measured at initial shear strain (0.1%) of the compound [36].

3.4.3 Rheological Characteristics

The Rheological characteristics of rubber compound were carried out by Moving Die Rheometer (MDR2000), Alpha Technology, USA. In the rheological study green rubber compound was cured inside moving cavity with oscillating frequency of 1.66 Hz. The torque generated due to cross-linking of rubber compound is recorded at desired temperature of analysis. Curing characteristics of rubber compounds were carried out at 160oC for 60 minutes.

Rheological study measures different torque parameters such as minimum torque (ML), maximum torque (MH) and their difference (delta torque). The important parameters of curing characteristics measured are scorch time (T_s2), 50% cure time (T_c50), optimum cure time (T_c90) and cure time index as shown in equation (3.2).

$$Cure\ rate\ Index = \frac{100}{T_c90 - T_s2} \qquad (3.2)$$

A typical rheological plot is shown in Fig-3.10 where the torque of rubber compound is shown with time of curing. It is seen that there is an initial fall in compound torque, which is due to the softening of rubber compound when the same is placed in cavity at the curing temperature of 160°C depending on the types of rubber. After a certain time, rise in torque appears which indicates the cross-linking of rubber compound is started and the time required to increase the torque by 2 units is called as scorch time (Ts2). The curing time of rubber compound is expressed as the optimum curing time (Tc90), which is defined as the time required for 90% curing of rubber compound. The measurement of optimum curing time is based on the defined time for a rubber compound which is required to raise 90% of delta torque (MH-ML) from the minimum torque of rubber compound [37]. It indicates that 90% of rubber is cured on curing of rubber for an optimum curing time. Similarly, 50% curing time is defined as the time required to achieve 50% curing of rubber compound, i.e, time required to raise 50% of delta torque (MH-ML) from the minimum torque of rubber compound. In practice curing time of rubber compound is represented by optimum curing time because rubber is cured at an elevated temperature of 140 to 160°C depending on characteristics of rubbers and the compound formulations. Hence while 90% of curing of rubber compound is completed the further heating of rubber compound is stopped because the rest of the curing is possible while the rubber compound gets cooled down to the room temperature from the elevated curing temperature.

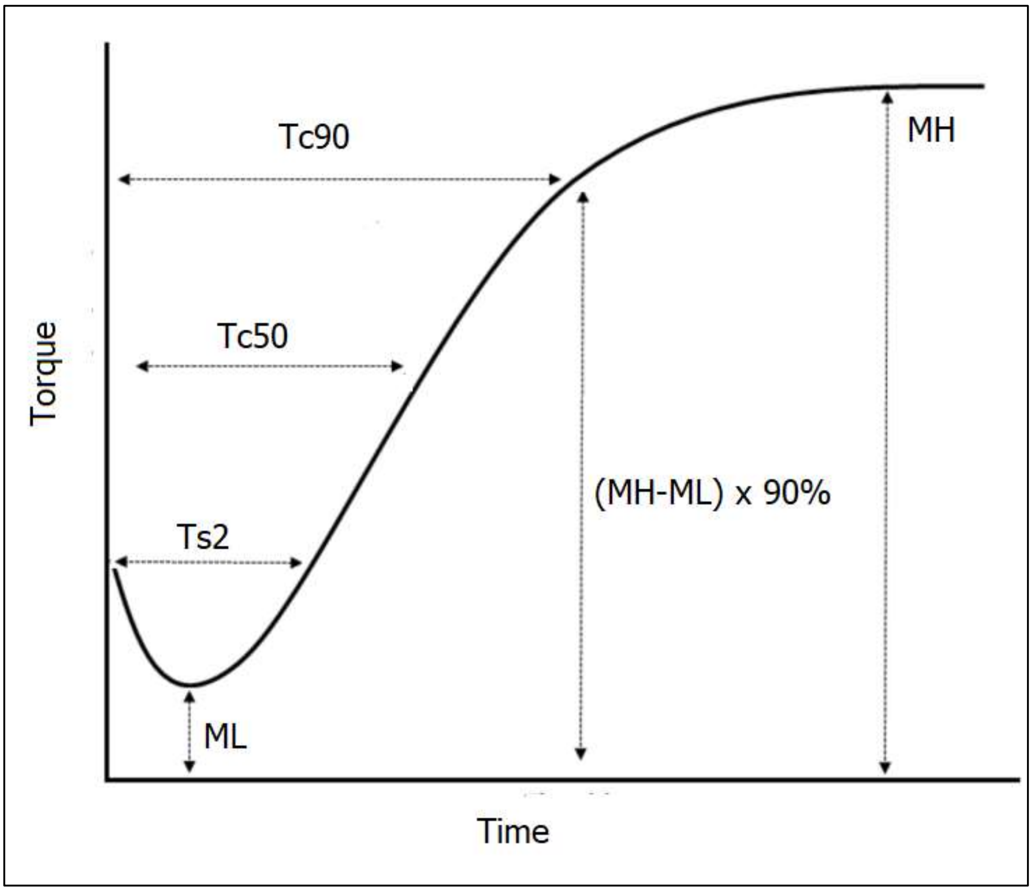

Fig-3.10: *A typical rheological graph of rubber compound*

3.4.4 Mooney Viscosity

Mooney viscosity of rubber compound was measured by Mooney Viscometer of model MV 2000 of Alpha Technology, USA. In the Mooney viscosity measurement, a piece of rubber was placed in a rigid cylindrical cavity where a metal disk is embedded with rubber specimen. The metal disk is slowly rotated clockwise, and the viscosity of rubber compound resists the rotation of the disc. In the Mooney viscosity measurement, the shearing torque, which resists the rotation of a cylindrical metal disk is called Mooney viscosity of rubber compound.

Mooney viscosity of rubber compound basically depends on the size of rotor and according to ASTM D1646, the large rotor has diameter of 38.10±0.03 mm while small rotor has 5.54±0.03 mm. In the present study Mooney viscosity of the rubber compound is measured at elevated temperature of 100°C based on the types of rubber compound and Mooney viscosity of rubber compound is represented by ML(1+4) at 100°C, where M represents Mooney viscosity, L represents large rotor size and 1 represent the pre-heating of rubber compound before Mooney viscosity measurement, 4 represents the duration of Mooney viscosity measurement and the temperature signifies the measurement temperature.

3.4.5 Measurement of Bound Rubber Content

Interaction of carbon black to rubber was studied by estimating the extent of bound rubber. The measurement involved by taking 0.2-0.3 g of uncured rubber compound accurately weighed and cut to small pieces. It was then put to 350-mesh steel wire cage in excess amount of toluene for 120 hrs. After every 24 hours the solvent was changed until it became colourless. It was then kept at room temperature for 24 hours for removal of solvents and finally dried at 100°C temperature in air oven until the complete removal of solvents. It was then cooled in desiccator and final weight of the gel was recorded. The bound rubber is calculated using equation (3.3):

$$\text{Bound rubber content (\%)} = \frac{W_{fg} - WF_f}{WF_P} \qquad (3.3)$$

Where 'W_{fg}' denotes final weight of the gel, 'W' denotes initial sample weight 'F_f' represents the weight fraction of filler, while 'F_p' represents weight fraction of polymer [38].

3.4.6 Compression Molding

A laboratory compression press machine was used for curing and molding of rubber compound for the sample preparation of different test and characterization. In the compression molding the rubber compound are heated to vulcanize there by using different moulds according to standard test method of the testing. The laboratory compression press machine of model-SHP 150, Santosh Machinary- Pvt Limited, India was used. To test tensile properties and dynamic mechanical analysis, rubber samples were prepared by curing of rubber compounds at 100 kg/cm2 pressure having the curing time of $2T_c90+2$ minutes, however for preparation of abrasion resistance sample and heat buildup testing sample, the rubber compounds were cured for $3T_c90$ minutes at 150 kg/cm2 pressure. The curing of samples was done at 145°C for NR based rubber system and at 160°C for SBR based rubber system [39].

3.4.7 Ultimate Tensile Strength Testing

Ultimate tensile strength of rubber compounds was measured by Universal Tensile machine (Model: 3366), Instron, USA as per ASTM D412 using the dumbbell shaped specimen of 6 mm width and 2±0.2 mm in thickness. The specimen undergoes extension with a rate 200 mm/minutes. In this testing tensile stress at different elongation, ultimate tensile strength and elongation at break are reported and the tensile stress at 300% elongation is termed as modulus of the rubber compound at 300% elongation.

3.4.8 Hardness:

Hardness of the rubber compound was measured by Shore-A hardness tester, the equipment is operated automatically, and the needle tip of the hardness measurement press the rubber sample with a fixed load as per ASTM D2230 test method where the sample used is cured rubber compound with dimension of 30 mm diameter and 6 mm thickness.

3.4.9 Abrasion Resistance Measurement

Abrasion resistance of rubber compound was measured by DIN abrasion testing method as following standard test method of ASTM D5963. Rubber samples were abraded while the moving test piece of rubber runs through the surface of an abrasive sheet which was mounted on the revolving drum of DIN abrasion tester. The weight loss of the sample due to the abrasion was measured by analytical balance and was expressed in term of volume loss by means of specific gravity of compound.

Abrasion loss of the rubber compound was represented by abrasion resistance index (ARI). ARI is calculated against the standard sample, which has weight loss of 0.238 g and specific gravity of 1.349 gm/cc. In order to calculate ARI, the abrasion loss of the rubber compound was represented in term of volume loss by using specific gravity of the rubber compound and weight loss of the same due to the abrasion loss. The ratio of the volume loss of a standard rubber sample to that of the test rubber sample is the ARI of the rubber sample.

3.4.10 Dynamic Mechanical Analysis

Dynamic mechanical analysis was carried out to characterize the response in viscoelastic material on application of oscillating force. In the viscoelastic material the oscillating force leads to provide a sinusoidal stress which causes a sinusoidal strain into the same. It has been discussed in Chapter-2, that in sinusoidal stress-strain phenomena there is a time lag between stress sine wave and the strain sine wave, and which is defined as phase angle (δ). DMA measures this sinusoidal stress, strain, and the phase angle at each point of the deformation. These parameters are also used to measure the rest of the dynamic mechanical parameters [40].

Dynamic mechanical analysis is generally carried out in different conditions of testing such as temperature ramp, strain sweep, frequency sweep with time etc. In the present study the dynamic mechanical analysis of rubber compounds was carried out by Dynamic Mechanical Analyzer (DMA300, Metravib, France). Measurement of dynamic properties at different temperatures was carried out by control temperature sweep of the equipment from 0°C to 70°C with a frequency of 10 Hz and at 1% dynamic strain. The testing was also carried out for strain sweep from 1% to 5% strain at constant temperature of 60°C and frequency of 10Hz. In the dynamic mechanical analysis, the loss modulus, storage modulus and loss tangent value of the rubber compounds at different testing conditions are reported where the testing was carried out in a tensile mode of deformation.

3.4.11 Heat Buildup Measurement

Rubber compounds get heated up when the same undergoes repeated deformation, this is called heat buildup property of rubber compounds. Heat buildup was measured by Goodrich Flexometer, (Model: CF 3000, Mon Tech, Germany) as per ASTM D623, where the rubber compound is exposed to cyclic dynamic deformation that causes generation of intrinsic friction inside the rubber compound as a result of which, the test specimens start to heat up due to the viscoelastic nature rubber compound. In this study, heat buildup of rubber compounds was measured by Compression Goodrich Flexometer. In this method a cylindrical shaped cured rubber sample was used. To measure heat buildup, the cylindrical rubber sample of diameter around 17.8 mm and a height of approximately 25 mm was placed between two plates of sample holder under a constant static load of 1 to 2 MPa. At this condition the sample was compressed by sinusoidal dynamic deformation under a frequency of around 30 Hz. Because of the sinusoidal deformation and the intrinsic friction processes, the rubber sample starts to heat up and the increase in temperature was noted by a thermocouple at the bottom or at the top of the cylindrical test sample, the rise in temperature is termed as heat buildup of rubber compound [41].

3.5 Microscopic and Material Characterization of Carbon Black and Rubber Compounds

3.5.1 High Resolution Transmission Electron Microscopy (HRTEM) Analysis

FEG High Resolution Cryo Analytical TEM, JEOL, JAPAN was used to analyze carbon black morphological characteristics as well as dispersion and distribution of the same in the rubber matrix. To analyze the carbon black morphology and its dispersion in rubber matrix by HRTEM suitable sample preparation is essential for each of the experiments which are described below. The HRTEM characterization of the carbon black and rubber samples were carried out at advanced Technology Development Centre (ATDC) in Indian Institute of Technology, Kharagpur, India.

3.5.1.1 Preparation of Carbon Black Sample

Carbon black is associated with agglomerated forms as demonstrated earlier hence the image analysis of carbon black is tedious due to the possibility of particles overlapping with each other. Thus, carbon black was sonicated enough to separate the primary aggregate individually from the agglomerates to obtain clear microscopic image. To achieve the same around 10 mg of carbon black was dispersed in 10 ml of acetone and it was sonicated for 10 minutes and finally a tiny drop of the carbon black dispersion was placed on TEM grid for the HRTEM analysis [42].

3.5.1.2 Preparation of rubber compound sample

The primary step for characterization of carbon black dispersion in rubber matrix by HRTEM is appropriate sample preparation which plays the critical role on image quality and consequently in the interpretation of carbon black dispersion. Cured rubber compound is used for analysis of HRTEM which is cooled in liquid nitrogen by dipping the sample into it and followed by cutting a tiny part of rubber compound with a thickness of around 50 nm by a diamond knife. The cut rubber sample is placed over a TEM grid for the image analysis to visualize carbon black dispersion and distribution in the rubber matrix [43].

3.5.2 Atomic Force Microscopy (AFM)

The micro dispersion characterization of carbon black in rubber compound and surface topography was also imaged by Atomic Force Microscopy (AFM) study. AFM study was carried out by Atomic Force Microscope (Park NX10 system) of Park System, South Korea at Raghupati Singhania Center of Excellence, Mysore, Karnataka, Mysuru, India. Here, rubber sample images analysis was carried out with tapping mode & phase imaging study. A small part of the rubber compound was cut with a sharp razor and the freshly cut surface was exposed to microscopic analysis for analyzing the filler dispersion in rubber compound matrix. Atomic Force Microscopy analysis was carried out in tapping mode of the analysis which results superior resolution without interfering with the surface of the rubber compound samples. The images were captured in phase imaging technique which provides 3D images as well as quantitative data of measurement.

The dispersion characteristics of carbon black filler in rubber matrix such as filler agglomerate size, dispersion, distribution was carried out by visualization of microscopic image analysis such as 3D image analysis and the quantitative analysis of surface roughness [44]. Atomic Force Microscopy analysis for the present study was carried out having different image dimension of 20-micron X 20-micron, 5-micron X 5-micron, 2-micron X 2-micron etc for the different compound. The study involves analysis of AFM topography and analysis of quantitative data for the interpretation of carbon black dispersion and distribution in the rubber matrix.

3.5.3 X-Ray Diffraction (XRD) Analysis

X-Ray Diffraction (XRD) is a non-destructive test method used to analyze the structure of crystalline materials. XRD analysis is used to identify the crystalline phases present in a material. The testing was carried out by using X-Ray Diffractometer, D8 Advanced model of Bruker, UK at Raghupati Singhania Center of Excellence, Mysore, Karnataka, Mysuru, India. A crystal is composed of periodically arranged atoms, molecules or particles in a 3D space, on the other hand, amorphous materials do not possess that periodicity of arrangement where the atoms, molecules, particles are randomly distributed in the 3D space, hence while X-ray reflects from the amorphous phase it scatters in multi-directions with less intensity of multiple X-ray peaks. However, when there is periodic arrangement of atoms the X-rays are scattered only in certain directions and cause high intensity peaks. Thus, in case of amorphous phase X-rays will be scattered in many directions leading to a large bump distributed in a wide range instead of high intensity narrower peaks. The XRD analysis was 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 in accordance with Bruker Bragg's law [45-46].

3.5.4 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of carbon black samples was carried out using Thermogravimetric Analyzer (Model: TGA 8000, PerkinElmer, USA) under a control heating the samples in different gases environment. TG analysis of carbon black was conducted to investigate the presence of volatile matters in carbon black as well as to characterize the crystallinity of carbon black. To analyze the volatile matters, the carbon black was heated in inert atmosphere by using nitrogen gas, however, to characterize crystallinity of carbon black, the sample is heated in oxygen atmosphere where carbon black was undergone an oxidative degradation [58-59]. The samples were heated at a heating rate of 5 to 10°C/min. The control heating of carbon black shows gradual weight loss of the materials due to evolution of low molecular weight volatile matters or oxidation of carbon black depending on the gases environment of testing. The weight loss of carbon black sample on heating was recorded by TG analyzer for the characterization of volatile matters as well as presence of crystallinity [47-48].

3.5.5 CHNS-O Analysis

CHNNS-O analysis was carried out to detect presence of oxygen in carbon black sample. In this method carbon black samples are combustible at high temperatures of 975°C and the presence of elements are detected using the principle of Dumas method by CHNS-O analyzer (Model: Series II, Perkin Elmer, USA).

- ***Reference***

1. *Farida E et al, The effect of carbon black composition in natural rubber compound, Case Studies in Thermal Engineering (2019), 16, 100566.*
2. *Farida E et al, The effect of carbon black composition in natural rubber compound, Case Studies in Thermal Engineering (2019), 16, 100566.*
3. *Spahr ME, Rothon R, Carbon Black as a Polymer Filler, in Polymers and Polymeric Composites (2016), Palsule, S. (eds), A Reference Series. Springer, Berlin, Heidelberg.*
4. *Tim W et al, Shades of grey—tire characteristics and road surface influence tire and road wear particle (TRWP) abundance and physicochemical properties, Frontiers in Environmental Science (2023), 11, 1.*
5. *Nie Y, Gu Z, Wei Y et al, Features of strain-induced crystallization of natural rubber revealed by experiments and simulations, Polym J (2017), 49, 309.*
6. *Bertrand H, Strain-Induced Crystallization of Natural Rubber: a Review of X-ray Diffraction Investigations, Rubber Chemistry and Technology (2011) 84. 425.*
7. *NIIR Board of Consultants and Engineers, The Complete Book on Rubber Processing and Compounding Technology (2006), Publisher: Asia Pacific Business Press Inc.*
8. *Brüning K, Natural Rubber. In: Kobayashi, S., Müllen, K. (eds) Encyclopedia of Polymeric Nanomaterials (2015), Springer, Berlin, Heidelberg.*
9. *White JR and De SK, Rubber Technologist's Handbook, Smithers Rapra Publishing (2001)*
10. *US Patent 5686543A, Process for producing polybutadiene rubber, Inventors: Kyouyu Yasuda Akio Takashima (1996), For JSR Corp*
11. *Sisanth KS et al, 1 - General introduction to rubber compounding, Editor(s): Thomas S, Maria HJ, In Woodhead Publishing Series in Composites Science and Engineering, Progress in Rubber Nanocomposites, Woodhead Publishing (2017), 1.*
12. *US Patent 6372863B1, Synthesis of styrene-butadiene rubber, Inventors: Kerns ML, Xu Z, Christian SM (2000), For Goodyear Tire and Rubber Co.*
13. *Hassanabadi M, Najafi M, Motlagh GH, Synthesis and characterization of end-functionalized solution polymerized styrene-butadiene rubber and study the impact of*

silica dispersion improvement on the wear behavior of the composite, Polymer Testing (2020), 85, 106431

14. *Yamada C, Yasumoto A, Matsushita T et al., Influence of functionalized S–SBR on silica–filled rubber compound propertie,. Functional Composite Mater (2022) 3, 6.*
15. *Chokanandsombat Y, Sirisinha C, Influence of Aromatic Content in Rubber Processing Oils on Viscoelastic Behaviour and Mechanical Properties of Styrene-Butadiene-Rubber for Tyre Tread Applications, Polymers and Polymer Composites (2014), 22, 599.*
16. *Murat O, Karaagac B, Veli D, Substitution of Aromatic Processing Oils in Rubber Compounds, KGK Kautschuk Gummi Kunststoffe (2011), 64, 48.*
17. *Wufan Z et al, Recent progress in the rubber antioxidants: A review, Polymer Degradation and Stability (2022), 207, 110223.*
18. *Cheremisinoff NP, A, Editor(s): Nicholas P. Cheremisinoff, Condensed Encyclopedia of Polymer Engineering Terms, Butterworth-Heinemann, 2001.*
19. *Jia-yao L, Hui-min S, Ting-ting X et al., Rubber anti-aging agent 6PPD and its ozonation product 6-PPDQ: Environmental distribution and biological toxicity, China environment science (2023), 43, 1407.*
20. *Agrawal SL et al, The Effect of Waxes on Rubber Vulcanisates, Progress in Rubber, Plastics and Recycling Technology (2005) 21, 139.*
21. *Ewgenia D, Darina Z, Nina T, Stearic acid in rubber chemistry and technology (2014).*
22. *Heideman G, Datta RN, Noordermeer JWM, Baarle B, Influence of zinc oxide during different stages of sulfur vulcanization, Elucidated by model compound studies, Journal of Applied Polymer Science (2005), 95, 1388.*
23. *Shahrampour H, Motavalizadehkakhky, A. The effects of sulfur curing systems (insoluble-rhombic) on physical and thermal properties of the matrix polymeric of styrene butadiene rubbe, Petrolium Chemictry (2017), 57, 700.*
24. *R.N.Dutta, Rubber Curing Systems, Rapra Review Report, Volume 12, Number 12, 2002.*
25. *ASTM D1512: Standard Test Method for Carbon Black—Iodine Adsorption Number*
26. *STM D6556: Standard Test Method for Carbon Black—Total and External Surface Area by Nitrogen Adsorption*

27. *Sebok EB, Taylor RL, Carbon Blacks, Editor(s): K.H. Jürgen Buschow, Robert W. Cahn, Merton C. Flemings, Bernhard Ilschner, Edward J. Kramer, Subhash Mahajan, Patrick Veyssière, Encyclopedia of Materials: Science and Technology, Elsevier, 2001, 902.*
28. *Spahr ME, Rothon R, Carbon Black as a Polymer Filler. In: Palsule S. (eds) Polymers and Polymeric Composites: A Reference Series. Springer, Berlin, Heidelberg (2016).*
29. *Marius C, Maria LA, Simona A, Chemical and Electrochemical Studies of Carbon Black Surface by Treatment with Ozone and Nitrogen Oxide. Materials Today: Proceedings (2016). 3, 252.*
30. *Walther W, Tscharnuter, Lily Zu, Bruce B. Weiner Characterizing ASTM Carbon Black Reference Materials Using a Disc Centrifuge Photosedimentometer, Journal of Dispersion Science and Technology (2007), 23, 671.*
31. *ISO 15825:Rubber compounding ingredients - Carbon black. Determination of aggregate size distribution by disc centrifuge photosedimentometry.*
32. *Lockwood FC, Van Niekerk JE, Parametric study of a carbon black oil furnace, Combustion and Flame (1995), 103, 76.*
33. *Kuhner G, Voll, Manufacture of carbon black. In: Donnet JB, Carbon Black: Science and Technology, Second Edition (1993), (2nd ed.).*
34. *Fun JF, Mixing Of Rubber, First Published in 1977 by Rapra Technology Limited Shawbury, Shrewsbury, Shropshire, SY4 4NR, UK.*
35. *Anil RS, A Review on Rubber Compound Mixing in Banbury Mixer at Tire Industries, International Journal of Engineering Research and Reviews (2014), 2,106.*
36. *Payne AR, Whittaker RE, Low Strain Dynamic Properties of Filled Rubbers, Rubber Chemistry and Technology (1971) 44, 440.*
37. *Al-nesrawy et al, Effect of Temperature on Rheological Properties of SBR Compounds Reinforced by Some Industrial Scraps as a Filler, International Journal of Chemical Sciences (2016), 14, 1285.*
38. *Sae-oui P, Effects of Blend Ratio and SBR Type on Properties of Carbon Black-Filled and Silica-Filled SBR/BR Tire Tread Compounds, Advances in Materials Science and Engineering (2017), 2017, 1.*

39. *Marina F, Fei WH, Colin H, Cure Simulation of Large Rubber Components: Acomparison of Compression and Extrusion Molding, Rubber Chemistry and Technology (2012), 85, 495.*
40. *ASTM D5026: Standard Test Method for Plastics: Dynamic Mechanical Properties: In Tension.*
41. *Schieppati, J, Schrittesser B, Wondracek A et al, Heat build-up of rubbers during cyclic loading. In Proceedings of the 11th European Conference on Constitutive Models for Rubber (ECCMR 2019), Nantes, France, 25–27 June 2019.*
42. *Randy VW, Aaron T, Kenneth S et al., Carbon Nanostructure Examined by Lattice Fringe Analysis of High-Resolution Transmission Electron Microscopy Images, Applied spectroscopy (2004), 58, 230*
43. *Gontard LC, Knappett BR, Wheatley AEH et al., Impregnation of carbon black for the examination of colloids using TEM, Carbon (2014), 76, 464.*
44. *Shadrinov NV. Atomic Force Microscopic Research of Structural Features of Elastomeric Composite Materials Based on Butadiene Nitrile Rubber. Materials Science Forum (2019), 945, 333.*
45. *Sang-Min L, Sang-Hye L, Jae-Seung R, Analysis of Activation Process of Carbon Black Based on Structural Parameters Obtained by XRD Analysis. Crystals (2021), 11, 153.*
46. *Ungar T et al, Microstructure of carbon blacks determined by X-ray diffraction profile analysis, Carbon (2002), 40, 929.*
47. *Kameya Y, Oxidation-resistant graphitic surface nanostructure of carbon black developed by ethanol thermal decomposition, Diamond & Related Materials (2016), 65, 26.*
48. *Bredin A, Larcher AV, Mullins BJ, Thermogravimetric analysis of carbon black and engine soot—Towards a more robust oil analysis method, Tribology International (2011), 44, 1642.*