CHAPTER 2:
LITERATURE SURVEY

2.1 Introduction

Climate change due to the emission of greenhouse gas (GHG) is a global issue which would have a huge impact on the world's landscape and sea levels and affects the economic and social development of countries all over the world. The trend of GHG emission growth over the years is rising rapidly as shown in Fig-2.1. The growth of the transport industry plays crucial role on the increased emission of GHG across the Globe. Hence, reduction of GHG emissions in transport industry due to consumption of fossil fuel is one of major motoes for the different nations [1].

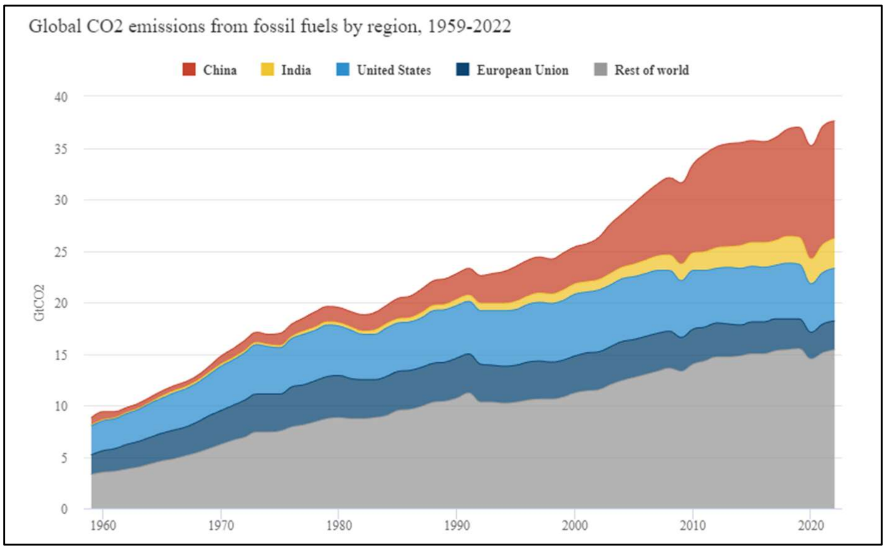


Fig-2.1: *Trend of global greenhouse gas generation till 2020 in terms of carbon dioxide from fossil fuels.*

The basic role of fossil fuel, consumed in the transport industry, is to supply the energy to the vehicle for running. A great extent of the energy used, is consumed by the tyre due to the rolling resistance. Rolling resistance is the energy consumed by tyre to keep movement of the vehicles, which arises from mechanical energy losses due to hysteresis energy of tyre, aerodynamic drag, frictional force between tyre with road and with rim etc [2]. Hence, during the running of vehicles, tyres consume a portion of the power transmitted to the wheels and leaves less energy available for vehicles to move. Rolling resistance causes extra fuel consumption, therefore, a tyre with low rolling resistance property benefits in fuel consumption of the vehicles and would lead to low GHG emission. It has been demonstrated that reduction of rolling resistance of tyres by 30%, can cause around 3 to 6% of fuel saving for the passenger car and the light commercial vehicles while for a heavy-duty truck, bus a reduction of 20% in rolling resistance can lead to saving of around 6% fuel consumption. [3-4].

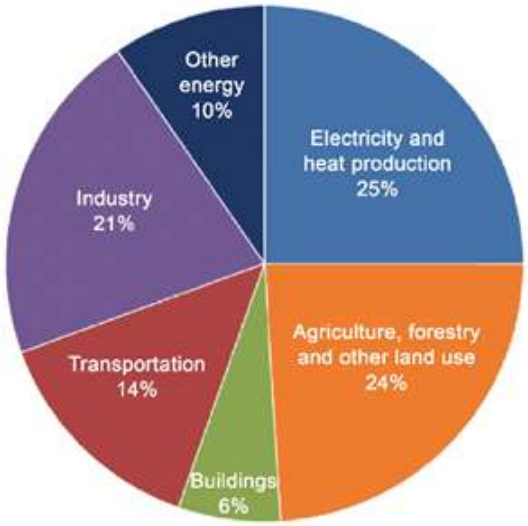


Fig-2.2: *Global Greenhouse Gas Emissions by Economic Sector*

The major effect of rolling resistance is the heat generation due to hysteresis loss of tyre during the rotation, which is caused by the viscoelastic nature of rubber compound used in different components of the tyres [5]. A tyre is composed of several components such as tread, sidewall, carcass, beads, belts, inner liner etc as shown in Fig-2.3 and each part contributes to the rolling resistance of tyre [6-7]. The extent of rolling resistance as contributed by different components of tyre is shown in Fig-2.4, which demonstrates that the major part to rolling resistance is contributed by the tread [8].

Tread is the largest part of tyre, and which comes in contact with road, provides steering response, stability, grip, traction and brake etc. to the vehicles. It is made of thick rubber compound, and is composed of rubbers, fillers and different rubber compounding ingredients such as curing agent, antioxidant, processing aids, accelerator activator etc. The performance of tyre tread is primarily monitored by the characteristics of the raw materials and dose of the same. In a tread major raw materials used are rubber and filler and it is observed around 50 to 60% of tread compound is rubber and around 30 to 40% is filler.

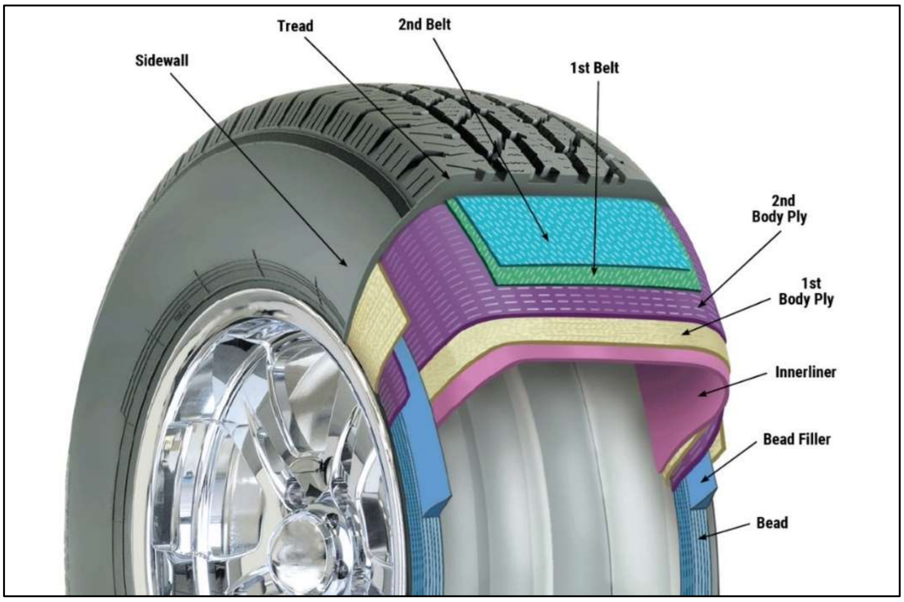


Fig-2.3: *Different components of tyre*

Filler offers the reinforcing in rubber compounds and provide mechanical strength, wear resistance etc into it, however at the same time, it affects adversely on different performance properties of rubber compound, such as increases rolling resistance, reduces resilience, increases heat buildup of rubber compounds depending on the characteristics of fillers, rubbers, rest of compounding ingredients and the compounding recipes. It has been further demonstrated that by adjusting the compounding formulation, and by incorporating modified ingredients or innovative new generation ingredients the performance of rubber compound, e.g., tyre tread compound can be improved to counter the above said adverse effects to the fillers [9].

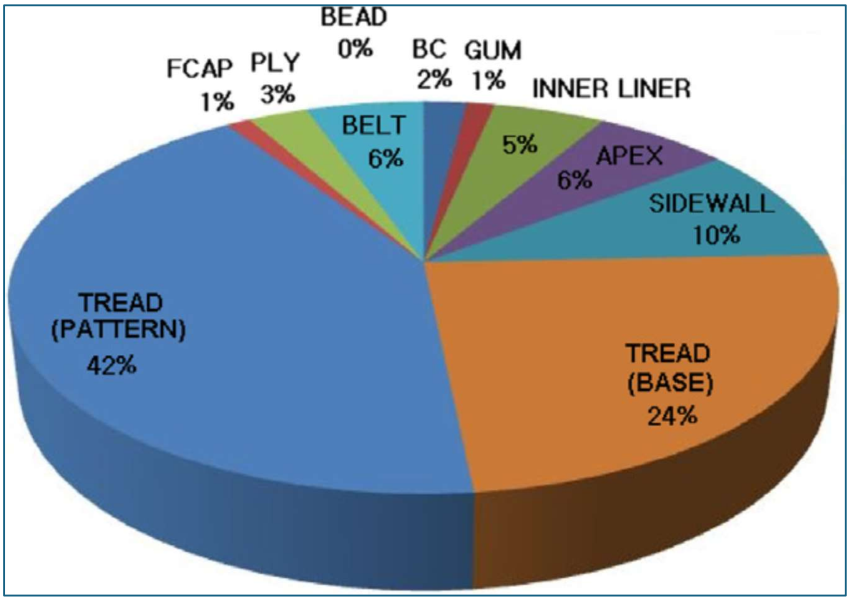


Fig-2.4: *Rolling resistance contributed by different components of tyre*

2.2 Tyre Tread Compounding and Properties

Tyre tread compound comprises different grades of natural rubber or different types of synthetic rubber or blend of these rubbers as the base material, which is reinforced by different types of fillers, such as carbon black, silica etc. It further comprises various rubber compounding ingredients, for examples; processing aids, antioxidants, curing agents, accelerator activators and others specific ingredients to boost processing characteristics and performance of tread compound [9-10]. In general, the performances of tyre tread are expressed by reinforcement characteristics, Payne effect, rolling resistance, abrasion resistance, heat buildup, grip resistance etc. which can be optimized based on the applications and end user's needs by the modification of tread compound recipes. In the subsequent sections the performances of these properties are elaborated.

2.2.1 Reinforcement of rubber compound

Rubber materials are soft in nature and characterized by lower mechanical strength. To make rubber material strengthen fillers are incorporated into the same which enhances the mechanical strength, modulus of rubber materials. Hence reinforcement of rubber compound refers to increase in mechanical strength and modulus of rubber material on incorporation of fillers. The reinforcement of rubber compounds represented by the mechanical strength, achieved in filled rubber compound is represented by the different components of strengths namely polymer network, hydrodynamic effect, in-rubber structure, and the filler-filler interaction. If the strength of material is expressed by shear modulus (G*), then the same can be expressed numerically in terms of the different strength component of rubber compound according to the following equation (2.1).

$$\boldsymbol{G^{*}} = \mathbf{G}_{\boldsymbol{p}} + \mathbf{G}_{\boldsymbol{h}} + \mathbf{G}_{\boldsymbol{r}} + \mathbf{G}_{\boldsymbol{f}} \qquad \textbf{(2.1)}$$

Where G_p represents component of sheer modulus due to polymer network of rubber compound, which arises cross linking formation of rubber molecules due to the vulcanization. 'G_h is due to the hydrodynamic effect, Gr is due to rubber structure and Gf arises due to filler –filler interaction [11-12].

Vulcanization of rubber compounds is the process of chemical reaction where rubber molecules take part in cross linking reaction among them with the help of vulcanizing agents and create network shaped molecular structure [13]. As a result, an inbuild mechanical strength in the compound is generated, which is termed as 'polymer network (G_p). The mechanical strength arises from polymer network is characteristics of polymer's chemical structure, vulcanizing agent, vulcanization conditions etc. In practice rubber molecules with higher concentration of reaction sites lead to higher concentration of networks formation upon vulcanization and which causes generation of higher mechanical strength in the rubber compound [14].

Hydrodynamic effect refers to the increased viscosity of fluid in dispersion of rigid particles in a fluid. An elastomeric system comprising dispersed rigid solid particles such as fillers caused an increase in viscosity, and which is termed as the hydrodynamic effect of elastomeric compound. Guth [15] established a relationship between filled rubber compound viscosity and unfilled rubber viscosity in term of volume fraction of filler as shown in equation (2.2), where η and η_o are the viscosities the filled and unfilled rubber system and φ represents volume fraction of the filler.

$$\eta = \eta_o\,(1 + 2.5\varphi + 14.1\varphi^2) \qquad (2.2)$$

These investigators further stated that for an elastomeric system the shear modulus is increased on addition of filler and the increased shear modulus has a similar relationship with viscosity, hence the shear modulus of elastomeric composites can be defined by below equation (2.3),

$$\mathrm{G} = \mathrm{G}_o\,(1 + 2.5\varphi\ +\ 14.1\varphi^2) \tag{2.3}$$

where G and G_o are the shear modulus of the filled and unfilled system respectively and φ is the volume fraction of the filler. In practice, the fillers incorporated in elastomeric system are non-spherical in nature, and to minimize the effect of irregularity of filler shape, Guth introduced a shape factor, 'f', which is the ratio of the longest dimension to the shortest dimension of the particles and proposed a modified equation (2.4) of shear modulus (G_h), as contributed by hydrodynamic effect in the rubber compound.

$$\mathrm{G}_h = \mathrm{G}_o\,(1 + 2.5\mathrm{f}\varphi\ +\ 14.1\,\mathrm{f}^2\varphi^2) \tag{2.4}$$

The third component of the shear modulus is 'in-rubber structure (G_r), which arises from the filler-polymer interaction through the chemical interaction as well as the physical interaction of filler with the rubber molecules. The chemical groups presence on filler surface can interact with rubber molecules and react with the same to provide enhanced filler-polymer interaction which causes improvement in mechanical strength of the filled rubber compound. The presence of voids on fillers or even rough filler surface, as well as different morphological features of fillers affects the physical adsorption of rubber molecules and results in the component of shear modulus termed as 'in-rubber structure (Gr).

During mixing of filler with rubber a shear stress is developed, which results in the breakdown of carbon black agglomerates into the aggregates. Carbon black aggregates in the rubber matrix have tendency to re-agglomerate due to Van der Waal force of interaction and form branched, network structures and leads to generation of strength in rubber compound which is the component of shear modulus caused as filler-filler interaction [16]. Payne [12] demonstrates that the modulus (G_f)

resulting due to filler-filler interaction is the major component of the shear modulus in filled rubber compound.

2.2.2 Payne Effect of rubber compound

Payne [17] extensively studied the shear modulus (G_f) contributed by the filler-filler networks and established that the filler-filler networks are prone to destruction on application of strain. He further demonstrated that during the deformation of rubber compounds, a drastic fall of compound modulus appears, which is caused due to the breakdown of filler-filler network. The fall in shear modulus on deformation of rubber compound is termed as 'Payne Effect and which is the measure of shear modulus fall during a specific deformation of rubber compounds [18]. A schematic representation of different part of shear modulus are shown in Fig-2.5 where the change in shear modulus has been portrayed as the strain amplitude of rubber compound is increased.

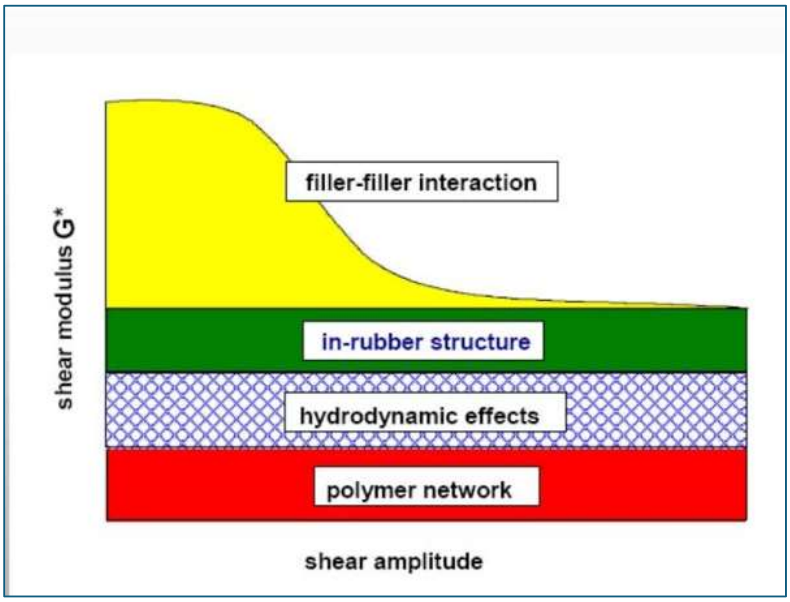


Fig-2.5: *Payne effect and contribution of Shear Modulus for carbon black*

It is seen that, on incrase of strain amplitude the compounents of shear modulus resulted by polymer netwrk (G_p), hydrodynamic effects (G_h) and in-rubber structure (Gr) remain unchanged. However the shear modulus component caused by filler-filler interaction (G_f) shows a different behavior while the shear strain is increased in rubber compound. It is seen that at the lower shear strain amplitude region, the rubber compound is characterized with a very high value of G_f. which is caused by filler-filler network present in the rubber compound. The high value of G_f ultimately results in overall high value of compound total shear modulus (G*). As the strain amplitude increases the filler-filler networks present in rubber compound tend to break, as a result the shear modulus component (G_f) caused by filler-filler networks readily falls. It is also seen that on application of very high strain amplitude the G_f tends to diminish which signifies a complete breakdown of filler-filler network. The change in shear modulus due to breakdown of filler-filler network on application of strain amplitudes is the measure of Payne effect, which is basically the difference between total shear modulus at lower strain amplitude region and the same at higher strain amplitude region.

2.2.3 Hysteresis and Rolling Resistance of Rubber Compounds.

Rolling resistance of tyre is primarily caused by three major factors such as hysteresis energy loss, aerodynamic drag and the frictional force of tyre with rim as well with road. It has been investigated that a major part of rolling resistance of around 90%, is contributed by the hysteresis energy loss, which is generated by cyclic deformation of tyre, due to the viscoelastic nature of tread compound [19]. During rolling, the tyre gets deformed in shape at the contact patch due to load of vehicle. The same contact patch gets back undeformed on the movement of vehicle, and at the same time the next part of the tyre comes in contact with road and gets deformed. Thus, tyres undergo continuous and cyclic deformation during the service, which causes hysteresis energy loss [20].

Hysteresis loss of viscoelastic material is explained by time dependent shear stress value, γ (t). In the cyclic deformation of viscoelastic material, the time dependent shear stress is defined as

$$\gamma (t) = \gamma_o \sin (\omega t) \tag{2.5}$$

here 'ω' is the angular frequency of deformation, γ_o and t are maximum strain and time respectively. For visco elastic material there is a time lag between stress and strain with a phase angle of δ, then the sheer stress response σ (t) is expressed as

$$\sigma(t) = \sigma_o \sin(\omega t + \delta) \qquad (2.6a)$$

$$\text{i.e.,} \quad \sigma(t) = (\sigma_o \cos\delta)\sin\omega t + (\sigma_o \sin\delta)\cos\omega t \qquad (2.6b)$$

Thus, shear stress of viscoelastic material has two components, one is in phase component of $\sigma_o \cos\delta$ associated with its elastic part and the second part is 90° out phase component of $\sigma_o \sin\delta$, which is associated with its elastic components, the same phenomena has been expressed in Fig-2.6 [20-21].

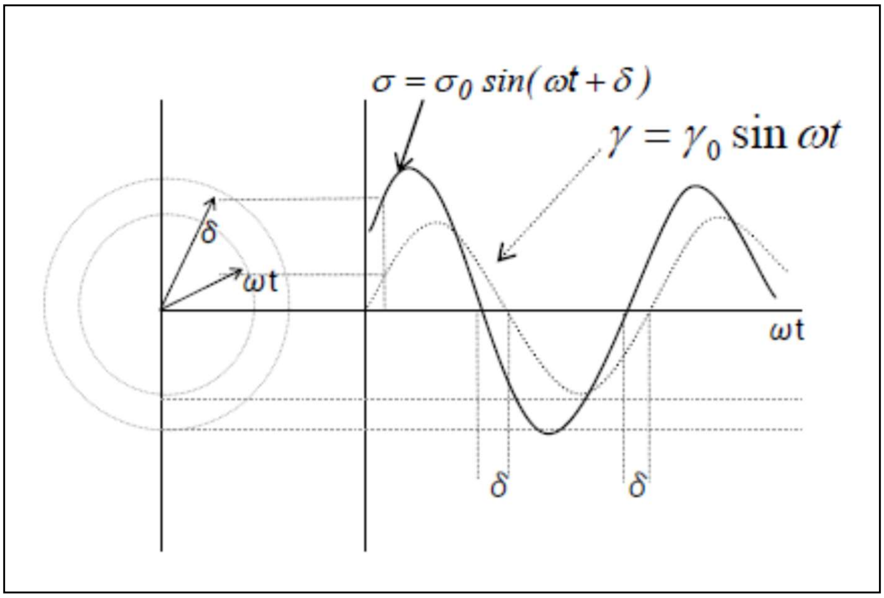


Fig-2.6: *Illustration of applied sinusoidal strain and measured shear stress for a typical viscoelastic material.*

The above equation further expressed as

$$\sigma(t) = \gamma_o [G'\sin\omega t + G''\cos\omega t] \qquad (2.7)$$

where $G' = (\sigma_o/\gamma_o)\cos\delta$ and $G'' = (\sigma_o/\gamma_o)\sin\delta$

G’ is termed as storage modulus of viscoelastic material and G” is termed as loss modulus. The ratio of loss modulus to storage modulus is termed as loss tangent (tanδ) value, which is defined below. Loss tangent value of viscoelastic material represents its hysteresis energy loss, i.e., the energy loss during cyclic deformation of the same.

$$\frac{G''}{G'} = \tan\delta \qquad (2.8)$$

Loss tangent (tanδ) value for rubber compound, as articulated by tanδ value, is measured using dynamic mechanical analysis. A good number of research have been carried to investigate the rolling resistance of the tyre tread compounds by its hysteresis loss (tanδ) property. It has been established tanδ value of rubber compounds measured at 60 to 70°C temperature is an indicative of rolling resistance of tyre [22-23]. Lou [22] demonstrates that rolling resistance of tyre relates with loss tangent (tan δ) value of rubber compounds used in tyre and stated rubber compounds with lower tan δ value results lower rolling resistance in tyre. Hess and Klamp [23] established the correlation of tyre rolling resistance with tanδ value of rubber compound. measured at 60°C, where, they have observed a linear relationship rolling resistance with tanδ value with a positive slop of the graph which indicates with increase of tanδ value of rubber compound the rolling resistance of tyre is increased.

2.2.4 Wer Traction Property of Tyre Tread

Traction refers to the maximum frictional force generated in tyre tread and road surface before any slippage of tyre takes place during the run of vehicle. It is the braking force generated while a driving torque is applied to the tyre, which is basically developed at the contact area of tyre tread and the road surface. In general, vehicles should have sufficiently high traction force which could lead to achieving the minimum acceleration of vehicle without any slippage.

Tractional force of tyre depends largely on characteristics of rubber compound of tread, especially on dynamic characteristics of the same. Moore et al [24] described tractional force in term frictional co-efficient (μ), and which arise from the adhesion force between tyre tread and road surface. They demonstrated tractional force in term of frictional co-efficient (μ) through the empirical equation (2.9) as given below.

$$\mu = [k_1 (P/E)^n + k_2 (E'/P^m)] \tan\delta \tag{2.9}$$

where 'k_1' & 'k_2' are constant and 'm' is an exponent which is equal to approximately 0.2, 'n' is an exponent and is greater than 1 or equal to 1, 'P' is total pressure. Thus, tractional force of tyre has a direct relationship with hysteresis loss of rubber compound (tanδ) and higher value of the same favors the traction property of tyre tread compound [25].

During skidding of vehicles on the wet surface, the frequency and temperature of tyre remain very high of around 105 Hz and 40°C respectively, hence, to express the tractional force of tyre by the tanδ value, it is necessary to measure tanδ value under the testing conditions of very high frequency of 10^5 Hz at a temperature of 40°C [26-27]. The measurement of tanδ value at such a very high frequency is a tedious job and has limited scope of measurement at the laboratory scale. Hence to explore the same Grosh [26] derived a temperature-frequency relationship of dynamic mechanical characteristics for rubber compounds and established a correlation of tanδ measured at different temperature and frequency. It has been proved that tanδ value measured at 10^5 Hz and 40°C is equivalent to the same measured at 0°C and 10Hz frequency. Thus, to predict the traction property of tyre, the tanδ value of tyre tread compound measured at 0°C and 10Hz can be considered. Hence by measuring tanδ value of tyre tread compound at 0oC temperature and 10Hz frequency by dynamic mechanical analysis the wet traction resistance of tyre can be investigated [23].

In practice the wet skid resistance of tyre is measured by different methods and one of potential method of wet skid resistance of tyre is British Portable Skid Tester (BPST). In this method British Pendulum Device is used to measure the wet skid resistance of tyre. The device basically measures the frictional force between a skidding tyre and the road surface and finally represents wet skid data for the tyre which is expressed in terms of BPST (wet skid number). A high BPST (wet skid number) of a tyre represents its high wet skid resistance characteristics [28]. Takino et al [29] established the correlation between BPST (wet skid number) of tyre and tanδ value of corresponding tyre tread compound, which was measured at 0°C and 10Hz frequency by dynamic mechanical analysis. They demonstrated that with the increase of tanδ value of tyre tread compound, measured at 0ºC and 10Hz, the BPST (wet skid number) of corresponding tyre is increased. Their experimental observation was graphically represented, and it was observed a linear relationship between BPST (wet skid number) of tyre and the tanδ value of corresponding tyre tread compound measured at 0ºC and 10Hz frequency as shown in Fig-2.7. Hence it validates that tanδ value of tyre tread compound measured at 0ºC and 10Hz frequency is a potential representative parameter for wet traction property of tyre tread compound.

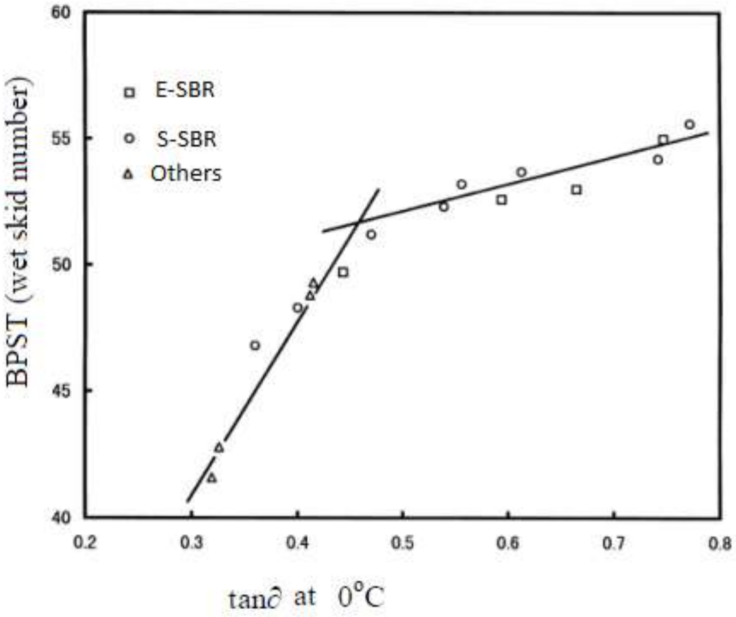


Fig- 2.7: *Correlation of BPST (wet skid number) of tyre and the tanδ value of corresponding tyre tread compound measured at 0ºC and 10Hz frequency.*

2.2.5 Wear Resistance of Tyre Tread

Wear of tyre seems to the tread wear during service, which is causes due to five important factors, according to Maitre [30], such as routes and styles of driving, condition of road surface, season of driving, the vehicle, and the tyre itself. While considering tyre itself as factor of tread wear the geometry, stiffness, mechanical characteristics, and tread compound properties are the key parameters to control wear resistance property. Tread exhibits continuous rubbing, friction with road during the service and leads to loss of rubbery materials which leads to loss of tread grooves, resulting in loss of tyre steering response, braking forces, traction and finally the life of tyres.

During service, the tread wear is carried out different mechanisms namely abrasive wear mechanisms and hysteresis wear mechanism. Abrasive wear loss is caused due to the friction between road surface and tread compound, while the hysteresis loss is caused due to the viscoelastic nature of the rubber compound [31-32].

While the rubbery material of tread comes in contact with road surfaces, the rubber molecules from the tread surface tend to form temporary bonding with the road and results in an adhesion force between the tread compound and the solid surface of the road. The bonding strength between the surfaces depends on weight of vehicles, area of contact path, characteristics of rubber compound and texture geometry of the road. On movement of the vehicles the parts of rubbery material from the tread surface gets abraded due to the bonding strength between rubber molecules and the road surface and loss of rubber compound is called the abrasive wear of tyre tread. The phenomenon of abrasive wear is schematically represented in Fig-2.8.

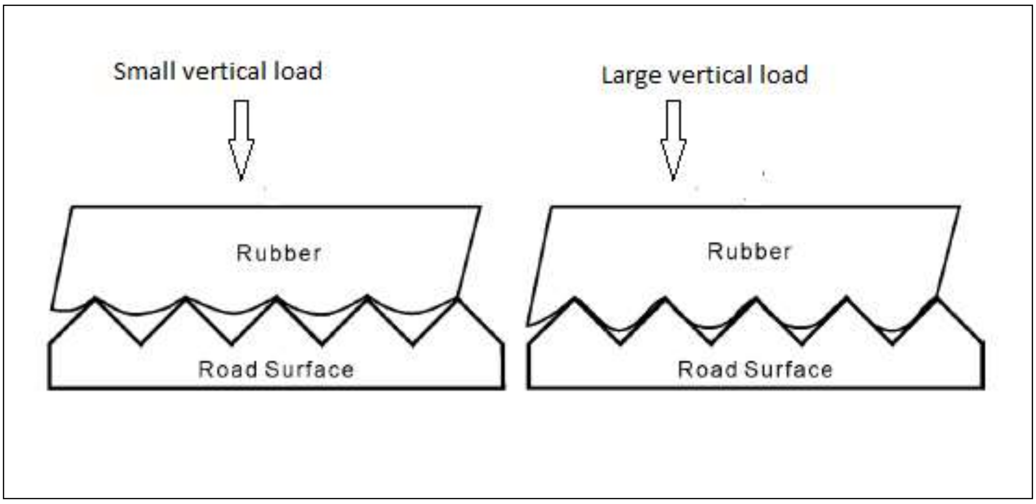


Fig-2.8: *Schematic representation of road texture and abrasive tread wear*

Hysteresis wear is due to the viscoelastic nature of rubber during the bulk deformation of compound while the tyre meets with road surface. It has been described that during the cyclic deformation of tyre, a loss of hysteresis energy takes place as rubber slips over the surface. As rubber deforms, it enfolds on the texture peak and when tyre tends to rise toward higher slope of the texture peak it undergoes high deformation which leads to major possibility of hysteresis wear of rubbery material.

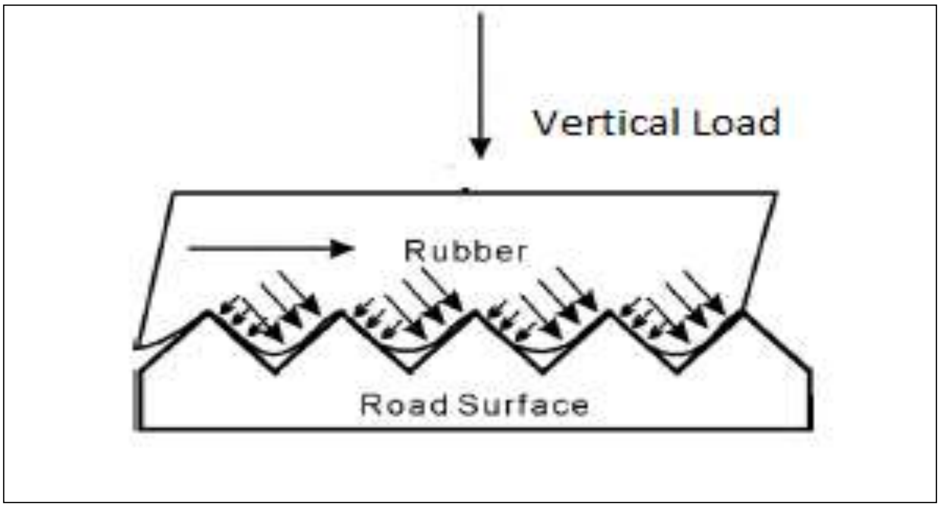


Fig-2.9: Schematic representation of hysteresis wear loss

The wear resistance of tyre tread is greatly influenced by the nature of rubber compound used in tyre tread. The types of rubber, filler types and loading of filler play significant role in the wear resistance of tyre tread compound. It has been seen in different studies that rubber compound based on carbon black provides superior wear resistance performance over the use of silica as reinforcing filler in the tread application. The intrinsic characteristics of carbon black eg, particle size, surface area, structure, aggregate size distribution, surface characteristics effects on abrasion resistance property of tyre tread compound.

2.2.6 Magic Triangle Properties of Tyre Tread

The basic characteristics of tyre tread are associated with three major properties such as rolling resistance, wet traction, and wear resistance. Rolling resistance of tyre signifies fuel efficiency of vehicle and has significant contribution on emission of greenhouse gases hence reduction of rolling resistance of tyre tread compound remains as major focus towards tyre manufacturers. Wet traction of tyre tread relates to the safety of vehicles, riders, and the pedestrians, as the same measures the stability of vehicles on wet road condition and restricts skidding of vehicles. Hence tyre with high wet traction property is highly recommended for the vehicles, especially for the passenger car vehicles. Wear resistance property determines the life of tyre and is the measure of tyre durability.

Hence, for a perfect tyre tread compound, low rolling resistance, high wet traction, and improved wear resistance are highly recommended by the users. The interesting fact is that improvement of all these three properties of tread compound together is difficult, and it has been observed that improvement of one property is at a cost of deterioration of one of other properties. Due to this contradictory characteristic, these properties are known as magic triangle properties of tyre tread compound [33-34]. The concept of magic triangle is schematically represented in the Fig-2.10, where a magic triangle of model fuel efficient tyre tread compound is compared with same of a model control tyre tread compound. The magic triangle property of the control tyre tread compound is shown by the black color plots while green color plot represents magic triangle properties of the fuel-efficient tyre tread compound. In this typical example it is seen that experiment compound has low rolling resistance and high wet traction value compared to control tread compound which provides enhanced fuel efficiency and improved riding safety of vehicle, however, at the same time the experimental tyre tread compounds shows low abrasion resistance property compared to the control tread compound. Hence it indicates the experimental tread compound provides superior rolling resistance and wet traction property but by the cost of abrasion resistance.

In order to balance the magic triangle properties, it is desirable to optimize those properties by improving any of two properties without sacrificing the remaining one or to minimize the deterioration of the same. To optimize the best balance of magic tringle properties of tyre tread, the design of tread pattern and formulation of compound recipe have significant influence. Tyre manufacturers have been working on the development of tyre tread compound and consistently modifying the performance of tyres in line with the present needs and with the trend of tyre technology upgradation. In order to assist in tyre compound development and to move with next generation tyre technology development, different raw materials suppliers are consistently modifying the material characteristics as well as developing the innovative and new generation materials for the tyre applications. The major and prime raw materials for tyre tread compounds are different types of rubbers and fillers such as carbon black, silica etc. In this part of the research plenty of literatures have been surveyed to investigate the carbon black, its effect tyre tread properties, different modification, and development carried out in carbon black to enhance and optimized the performance of tyre tread compounds.

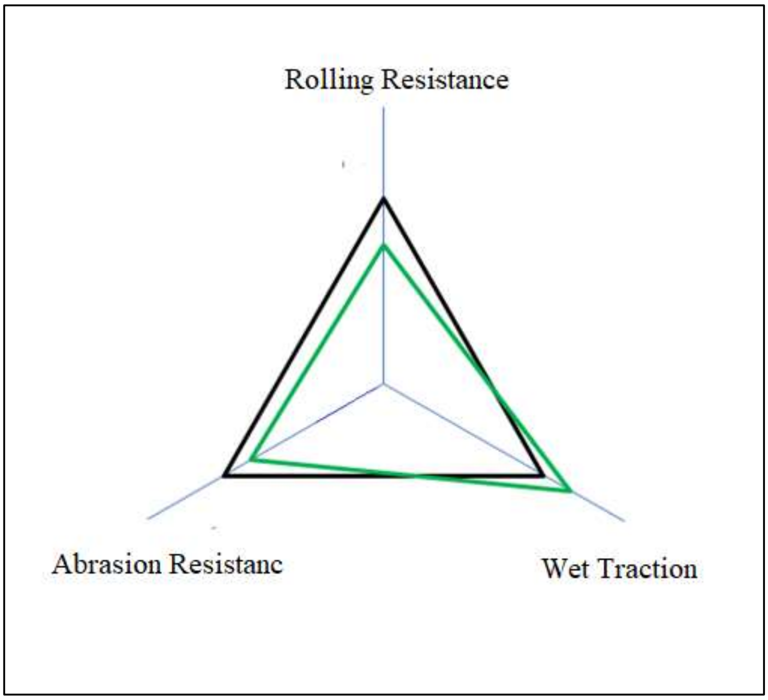


Fig-2.10: *Magic triangle property of tyre tread compound*

2.3 Carbon Black and its Characteristics

2.3.1 History of Carbon Black

Carbon black is an ancient material which was known as early as the third century B.C. where it was used as black pigments, inks etc as produced from the undesired product of soot. However, in the present day, carbon black is widely used in different applications of daily life. Manufacturing of carbon black started in the 19th century, by channel process and the commercial manufacturing was started in early 20th century in the different types of manufacturing process. The furnace process of manufacturing is the most suited carbon black production, due to its bulk manufacturing capability and low cost of production, where carbon black is produced by incomplete combustion of heavy aromatic oil. Other than the furnace process, a few other processes of carbon black manufacture are also well known, such as channel process and the thermal process of carbon black manufacturing [35].

2.3.2 Basic Features of Carbon black

Carbon black is majorly used in rubber compound applications as reinforcing filler, and tyre is the major consumption of carbon black. The other areas of carbon black usage apart from the rubber applications are plastics, fibers, inks, paints, coatings, textiles etc. Carbon black is characterized with several morphological features such as particle size, aggregate, agglomerate, structure, aggregate size distribution, surface crystallinity, surface chemical nature etc. Each of these parameters has its own importance on rubber compound properties [36].

2.3.2.1 Carbon black particle size and surface area

In the commercial manufacturing of carbon black, it is produced in the form of fine particles. The size of the same lie in between 5 nm to 500 nm. Particle size is unique property of carbon black which defines its applications and determines the gradation of carbon black as per ASTM D1765. The size of the particles is visually analyzed by microscopic analysis and several studies were carried out to characterize the particle size of carbon black. Burgess et al [37], determined particle size of carbon by automated electron microscopy while later Hess and McDonald [38] measured the same by a feature specific Quantimet 720 system with online data recording and processing system, which has linked with a transition electron microscopy. This method of particle size measurement of carbon black is a very useful technique for classification of carbon black based on absolute particle size. The measurement of particle size by electron microscopy is a tedious process, time consuming, involves costly testing apparatus and equipment and needs specialized skilled analyst. To simplify the measurement of particle size, the concept of surface area measurement was drawn which is a function of particle size. Parkinson [39] established this feature and showed a linear relationship between reciprocal of particle diameter with specific surface area of carbon black as shown in Fig-1.11, which demonstrates lower particle size results high surface area of carbon black, which is measured by nitrogen surface area measurement.

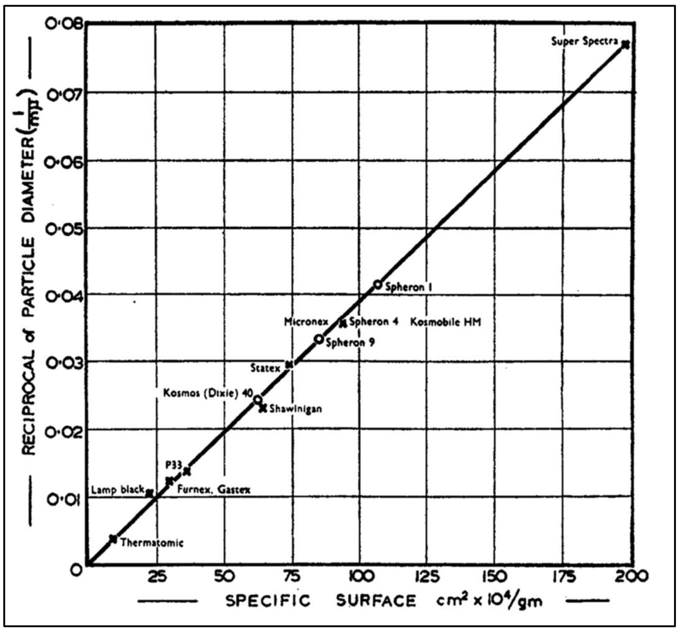


Fig-2.11: Correlation of particle size in term of its reciprocal with surface area of carbon black

As stated, the carbon black nomenclature is based on its particle size and standard form of carbon black nomenclature consists of three digits, which start with letter 'N' or 'S' which signifies the curing characteristics of carbon black in rubber compound. 'N' denotes normal curing while 'S' denotes slow curing characteristics. In an example of ASTM grade carbon black, N330, where the first digit '3' signifies the particle size of carbon black and the last two digits provides ideation about the structure properties of carbon black. A table for carbon black gradation, and significance of first digit with particle size of ASTM grade carbon black is shown in Table-2.1 where typical value of surface area and particle size of corresponding carbon black grade are shown.

Table-2.1: Gradation of ASTM grade carbon black.

First Digit Number	Surface Area (m2/g)	Particle Size (nm)
1	121-150	Nov-19
2	100-120	20-25
3	70-99	26-30
5	40-49	40-48
6	33-39	49-60
7	21-32	61-100
9	0-10	201-500

2.3.2.2 Carbon black structure:

It was assumed that carbon black particles are discreate unit of carbon black, however, later study suggested that in the commercial manufacturing of carbon black by furnace process, the produced carbon black no longer remain as single discrete unit. At the very high process temperature the carbon black particles formed, are fused together, and form branched units. Hence, carbon black particles exist as branched type and cluster forms microstructure, called aggregates, and is the basic and discrete unit of carbon black, which was first investigated by Ladd and Wiegand [40] and later the same was confirmed by Hess and Ford [41]. The aggregated feature of carbon black is termed as carbon black structure and bigger size of aggregates are called high structure carbon black. The aggregates further clustered together form higher branched complexes due to the Van der Waals force of interaction. These structures formed by clustering of aggregates is called agglomerates. The formation of carbon black aggregates and agglomerates from carbon black particles is schematically represented in Fig-2.12.

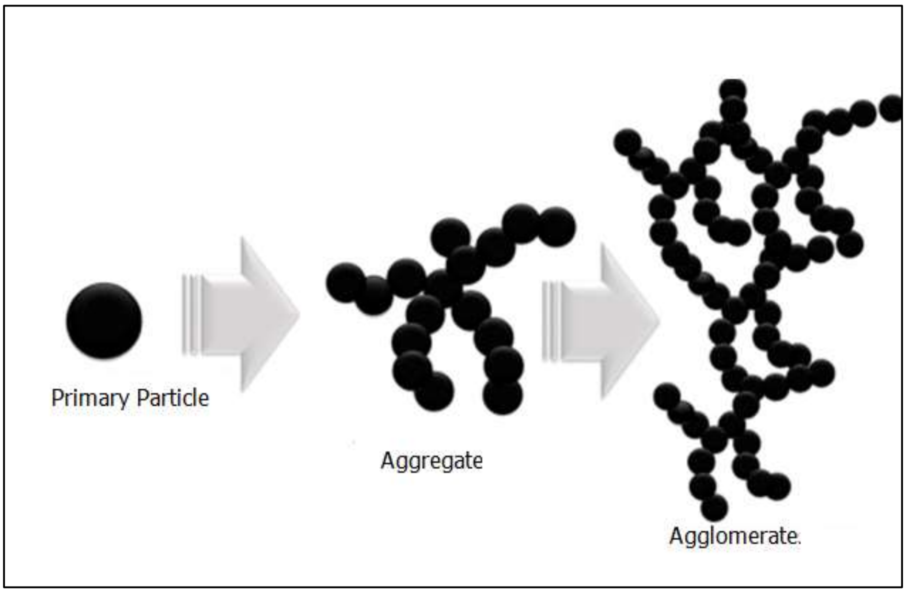


Fig-2.12: *Schematic representation of carbon black particle and formation of structure*

The void volume of carbon black is measured by oil absorption number (OAN) which is defined as the volume (ml) of oil consumed per 100 g of carbon black. Higher OAN value indicates presence of higher void volume in the carbon black structure and resembles high structure carbon black. The secondary structure of carbon black which is due to the presence of carbon black agglomerates is expressed by OAN whereas the primary structure due to the aggregate is expressed by compressed OAN of carbon black [42-43].

Such highly branched carbon black aggregates and agglomerates are termed as high structure carbon black and the same leads to high internal void space, which is schematically in the Fig-2.13 where it is seen that carbon black aggregates with low branched structure provides lower void space compared to carbon black with high branched structure. Hence, measure of void volume of carbon black represents the structure of carbon black [44].

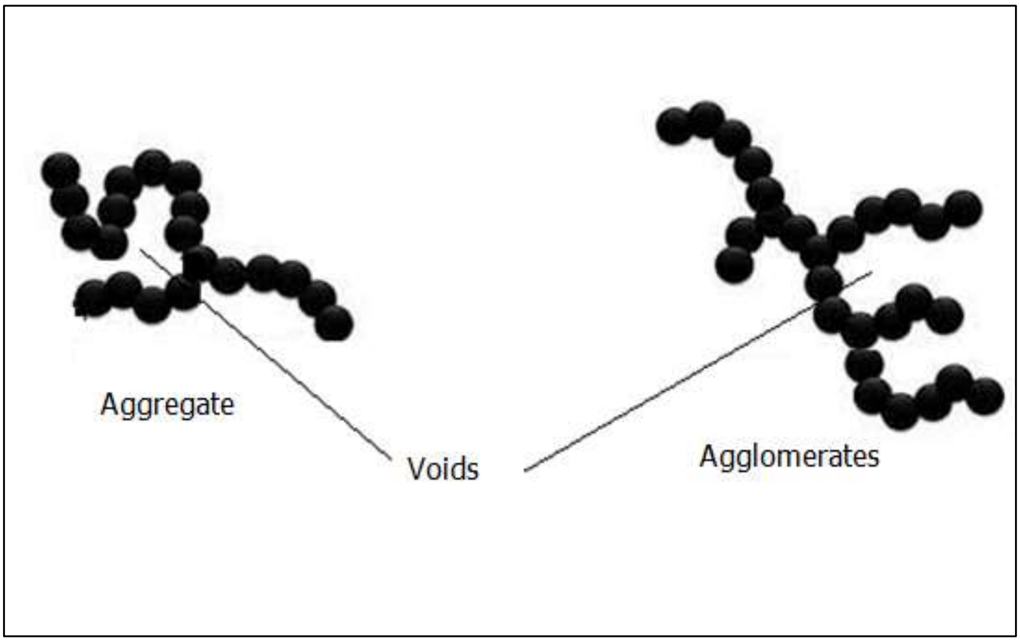


Fig-2.13: *Schematic representation of void volume and structure of carbon black*

Particles size and structure properties of carbon black are the key characteristics which determines the performance of carbon black in the end applications such as tyre tread compounds. Carbon black with smaller particle size boosts the tensile strength, abrasion resistance, tear strength of rubber compound compared to the same with relatively higher particle size. Carbon black with smallest particle size is characterized with high particle surface area and provides increased physical contact area with rubber molecules, leads to increased reinforcement with the rubber.

While carbon black particles are in contact with rubber molecules, they get adsorbed on carbon black surface as a result the rubber molecular chains becomes immobilized, which hinder the mobility of rubber molecules and as a result the viscosity of rubber compound becomes high with increase of carbon black surface area or reduction of particle size.

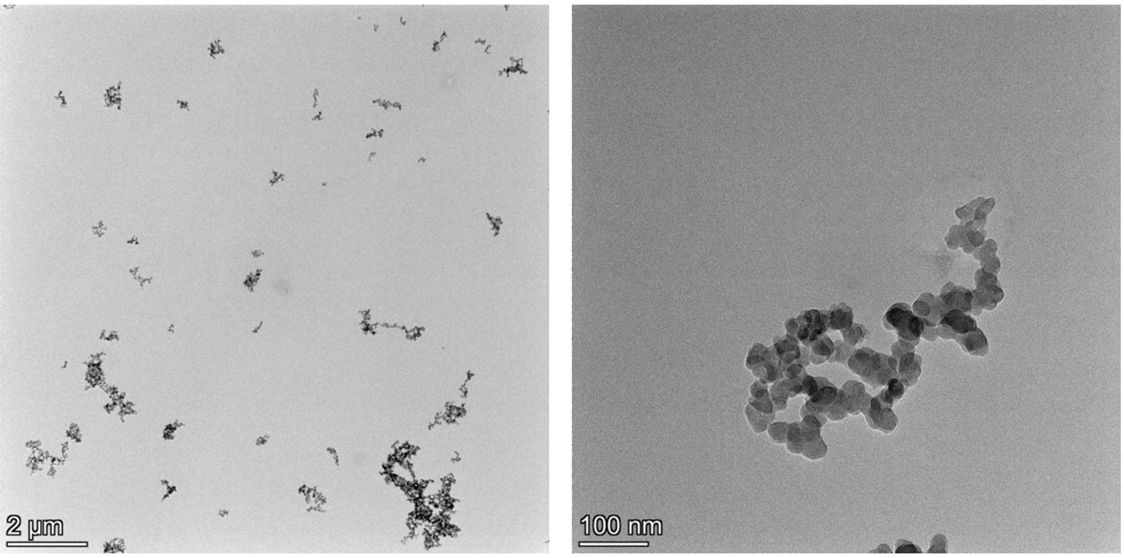
Extensively studied carried out on the effect of carbon black particle size and surface area on rubber performance properties and observed an increase in Mooney viscosity, wear resistance property, increase in hysteresis energy loss, increase heat generation, increase tensile strength, tear strength of rubber compound with increase in surface area and reduction in particle size of carbon black [39, 45].

In rubber compounding process, during mixing, the rubber molecular chains get adsorbed on carbon black surface and at the same time the ends of rubber chains penetrate into the voids of carbon black and resulting strong physical attachment of carbon black with rubber molecules which generates modulus and reinforcement in the rubber compound. Thus, carbon black with high structure value results higher modulus in the rubber compound due to higher propensity of carbon black physical interaction as caused by higher penetration of rubber molecule chain ends into the carbon black voids. Several literatures demonstrate that carbon black with high structure property results in high modulus, high hardness, high heat build-up, high tensile strength, high compound Mooney viscosity in the rubber compounds [46-47].

In the reinforcement of rubber compound, carbon black particles interact with each other to form filler-filler interactions and the same leads to Payne effect in rubber compound as stated above. Carbon black characteristics such as particle size, surface area and the structure play significant role on the network formation in the rubber matrix. In general carbon black with high surface area and high structure leads to greater extent of filler-filler interaction and thereby provides higher Payne effect in rubber compound [18].

2.3.2.3 Aggregate Size Distribution

Aggregates are the discrete and primary unit of carbon black; hence, their size and size distribution are important parameters of carbon black, these features depend on manufacturing conditions, process inputs, and the reactor design [35]. Aggregates are characterized by visualization through TEM analysis which shows that different size of aggregates are scattered in the system. TEM analysis at high resolution and higher magnification shows that each of the aggregates are formed by the fusion of carbon black particles as shown in Fig-2.14.



(a) (b)

Fig-2.14: *(a) TEM analysis of aggregates shows different size of aggregates present in carbon black. (b) A discrete aggregate of carbon black formed by fused of carbon particles as shown in higher magnification of TEM analysis (Current Investigation)*

One of the potential methods to determine aggregate size distribution of carbon black is disc centrifuged sedimentation method where the size of aggregate is represented by the aggregate diameter, assuming spherical shape of the same. The pattern of size distribution is characterized with statistical distribution parameters such as mean, mode, full width half maximum (FWHM) value, 'dn' values [48]. In this method, aggregate size distribution is characterized by graphical technique where the different size of aggregates is plotted in X-axis and in the Y-axis the relative concentration of individual aggregates are plotted in term of differential volume (dV/dD). A model aggregate size distribution of carbon black is shown in Fig-2.15 where the pattern of aggregate size distribution is expressed by FWHM value, which is defined as the width of distribution plot at the 50% height of distribution graph. Higher value FWHM value signifies a broad aggregate size distribution while lower value of the same represents narrow aggregate size distribution. The 'mean' value of aggregates is defined as the arithmetic average of different size aggregates presents in carbon black while 'mode' value of aggregate size distribution described the maximum occurrence of aggregate present in the carbon black. The 'd_n' value is defined as the limit of the aggregate size, which occupy 'n%' of total aggregate volume in the carbon black, where 'n' is an integer. The aggregate size distribution plot is further characterized by cumulative distribution curve which represents the cumulative volume of aggregates at the respective aggregate size. Thus, aggregate size distribution parameter d_{10}, is the aggregate size which corresponds to 10% volume fraction of aggregates. It is determined from the cumulative curve, and which is the aggregate size at 10% of cumulative curve. The d_{10} value as well as the d_{90} of aggregate size are demonstrated graphically in the ploy as shown in Fig-2.15.

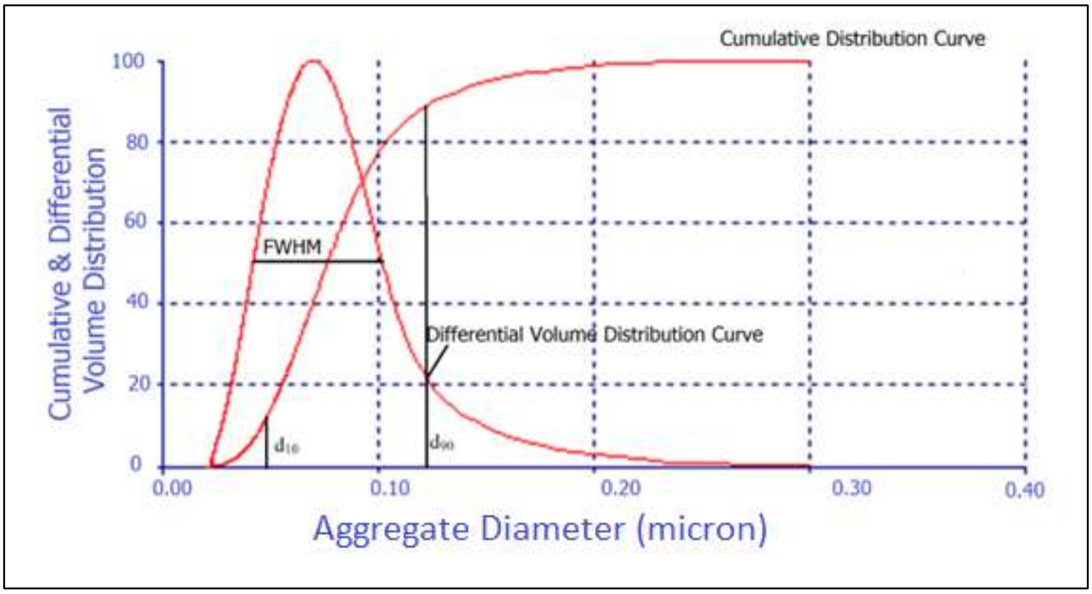


Fig-2.15: *A typical aggregate size distribution and cumulative distribution of carbon black*

Aggregate size distribution of carbon black plays a significant role in defining the dynamic properties as well as the physical properties of rubber compound. Stacy et al. [49] and Wang et al [50] showed that carbon black characterized with broad aggregate size distribution provides low hysteresis in rubber compounds in comparison to the narrow aggregate size distribution carbon black. Hironori et al. [51] explained that while carbon black is characterized with broad aggregate size distribution, which leads to higher inter-aggregate distance in rubber matrix and consequently results in lower hysteresis loss of the compound, where the hysteresis loss of the rubber compound is expressed by $\tan\delta$ value as measured by dynamic mechanical analysis. Pattern of aggregate size distribution also affects the physical properties of rubber compound as demonstrated by Diehl et al [52], where they showed that carbon black with narrow aggregate size distribution results superior abrasion resistance performance in rubber compound for truck tyre tread application.

2.3.2.4 Surface chemical property of carbon black

Surface Morphology of carbon black is also characterized with surface chemical nature of carbon black. It consists of several organic functional groups which are generated in carbon black during the manufacturing process. The surface chemistry of carbon black was characterized by XPS study, and it reveals the functional groups present in carbon black are oxygen rich and they are generated during manufacturing process due to the presence of air. The oxygen atoms are present in carbon black as surface functional groups as well as the heteroatoms within the ring structure. The different oxygen containing functional groups are aldehydes, ketones, lactones, carboxylic acid, hydroxides, quinones, phenols, anhydrides etc [53]. A schematic representation of surface functional groups of carbon black in in Fig-2.16.

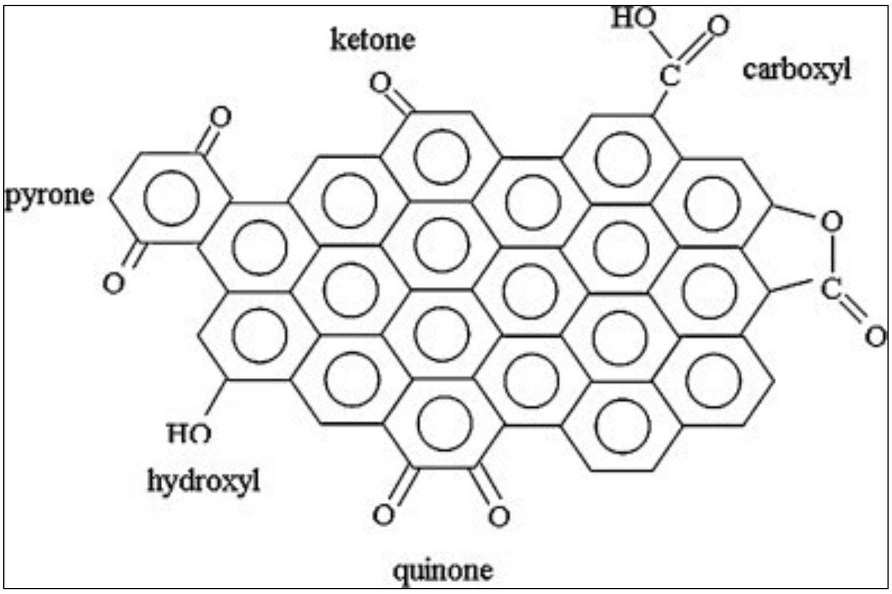


Fig-2.16: *Schematic representation of carbon black surface chemistry*

Carbon black surface functional groups assist in interaction with rubber molecules and can lead to increase filler-polymer interaction and reduce filler-filler interaction in the rubber matrix depending on the chemical nature of rubber molecules. Carbon black surface functional groups are the chemical reactive sites, which take part in reaction with different chemical, functionalizing and grafting agent and change the surface chemical nature of the carbon black. To enhance the compatibility between carbon black and rubber, a good number of studies were conducted either on modification of rubber or in modification of carbon black surface chemistry or both by the chemical treatment, which results in increased filler dispersion, increased filler-polymer interaction, and reduced filler-filler interaction in the rubber matrix [54].

2.4 Carbon Black Development/ Modification for Tyre Tread Compound

One promising method for enhancing tyre tread performance is to design the tread compound, by optimizing dose of compounding ingredient, using modified or superior compounding ingredients, incorporating innovative raw materials into the compound formulation. In order to achieve optimum properties of tyre compound, different raw material manufactures are continuously improving the quality of material, modifying the same and have introduced innovative material which can boost the performance of tread compound [35, 50].

Carbon black is the major filler used in tyre tread compound though use of silica in presence of coupling agent is also common in tyre tread compound applications, particularly for the passenger car tyre application. In the recent development of tyre tread compound, it has been demonstrated in literatures that introduction of nano-fillers such as graphene, carbon nanotube, nano-clay provides superior performance in end uses however due to its difficulties in handling, mixing and other processing challenged, the uses of these fillers are very limited in the field of tyre tread compound.

There is consistent improvement and development of carbon black though carbon black manufacturing process modification, raw material modification, optimizing carbon black morphological characteristics, post treatment of carbon black, hybrid filler technology etc. Improvement in the basic carbon black properties such as particle size, surface area, structure, aggregate size distribution, surface porosity, crystallinity, and surface chemistry etc, could lead to enhancement of tyre tread properties.

Martin (55) showed that carbon black with optimized combination of surface area and structure lead to optimized rubber compound performance and benefits different in parts of tyres. He patented the concept on the effect of high agglomeration of carbon black on rubber compound and established that carbon black with high ratio of secondary structure value to primary structure value provides high reinforcement in rubber matrix and increase the physical strength into the same. He further demonstrated that carbon black with increase difference in NSA-STSA value causes high wear resistance for the rubber compound, which benefits tyre tread performance, where NSA represents nitrogen surface area and STSA represents statistical thickness surface area.

Branan et al [56] introduced the concept of "Skewness" in carbon black and it is defined as the degree of asymmetry of carbon black mean aggregate size. According to the definition of skewness, a skewness value closed to zero signifies symmetrical distribution of aggregates and while larger value indicates spread out of the aggregates with an asymmetric distribution of aggregates where the size of the aggregates was measured by electron microscopy. They demonstrated that modification of carbon black with high skewness value of greater than 1.5 benefits toward high resilience of rubber compound and which could benefit in low rolling resistance for tyre tread compound.

Carbon black with tailor made aggregate size distribution play significant roles in rolling resistance of tyre tread compound. Broad aggregate size distribution signifies higher inter-aggregate distance as compared to carbon black having narrow aggregates size distribution for an equivalent particle size of the carbon black [57]. Thus, broad aggregate size distribution carbon black has a scope of lowering tendency of re-agglomeration in rubber compound and hence provides rubber compound with improved filler dispersion and lower hysteresis loss. Earlier described that Wang et al. developed carbon black with broad aggregate size distribution and observed significant filler dispersion in the rubber matrix with increased performance properties.

Carbon black particles with roughness on surface results in higher contact area with rubber molecules. As higher surface roughness increases the contact of polymer molecules with carbon black the filler-polymer interaction also increases. Vogler et al [58] manufactured carbon black in furnace reactor where carbon black with rough surface characteristics was produced and termed as inversion carbon black, a schematic representation of the same is portrayed in Fig-2.17, where it is demonstrated that inversion carbon black surface with high irregularity in comparison with conventional ASTM grade furnace carbon black and the irregular shape of the same causes potentially high interaction with larger part of rubber molecules and consequently it leads to enhance rubber compound properties for tyre tread compound such as lower hysteresis loss to lower Payne effect and reduced rolling resistance etc.

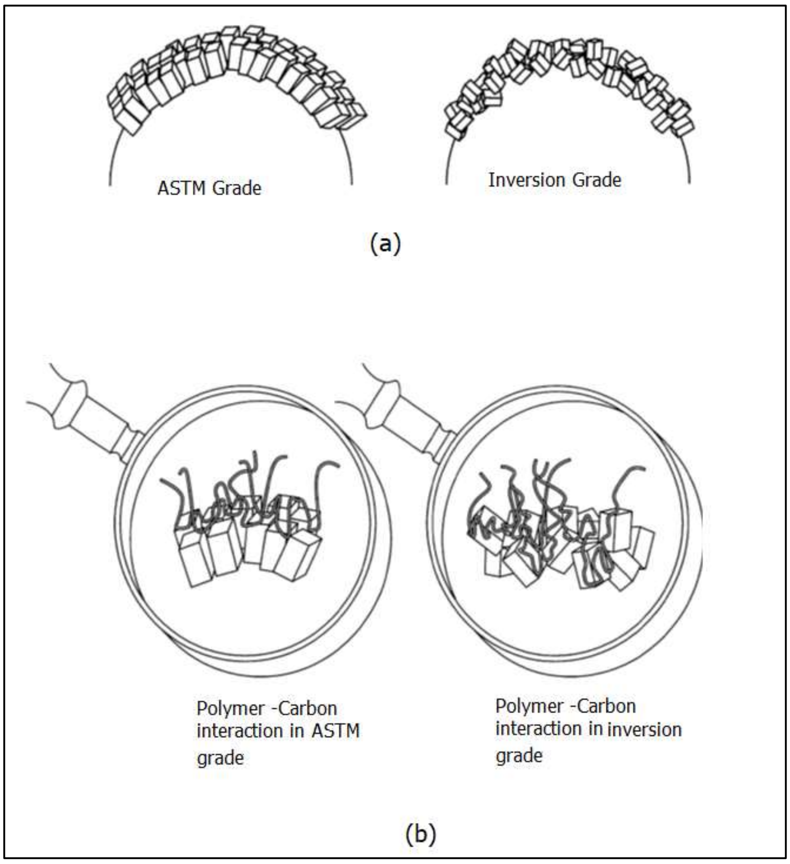


Fig-2.17: *(a)Surface phenomenon of ASTM grade carbon black and Inversion carbon black, (b) Concept of high molecular intact with inversion carbon bon black surface compared to ASTM grade carbon black.*

Plasma treatment of carbon black changes carbon black crystallinity and surface chemical characteristics. There are several methods for plasma treatment of carbon black, Tricas et al [59] treated carbon black in a atmospheric plasma reactor where carbon black was treated with air plasma and nitrogen plasma at different condition of treatment. Earlier Johnson et al [60] treated carbon black with plasma of helium gas using a plasma torch with a varied current flow of 20 to 2000 Amperes. The extent of plasma treatment was characterized by XRD, XPS, pH, microscopic analysis etc. Plasma treatment on carbon black increases its polarity which increase carbon black interaction with rubber molecules with increased polarity and it effects on mechanical a s well as dynamic property of rubber compound.

Oxidation of carbon black by different methods have been introduced such as acid treatment, air treatment at high temperature, Ozone treatment, hydrogen peroxide treatment, plasma treatment etc [61-62]. It has been seen on oxidation, carbon black leads to change its surface porosity, change in crystallinity, surface roughness, surface chemistry etc. The extent of carbon black characteristics modification truly depends on the route of oxidation as well as on the extent of the oxidation. Kamegawa et al [63] described that on oxidation of carbon black with nitric acid treatment, large numbers of porosities are generated on carbon black surface. The oxidation further leads to change in carbon black morphology by destruction of crystalline arrangement on the carbon black surface, which causes change in resultant surface area of carbon black. The change in carbon black morphology and surface chemistry, thus, effect rubber compound properties based on the method of oxidation.

Literature survey suggests that increased functional groups on the carbon black surface exert a noticeable effect on interaction of carbon black and rubber molecules. Wu et al. [64] modified rubber molecules with dimethyl amino multi functionalization to increase the compatibility of rubber molecules with carbon black and observed improvement of carbon black dispersion in the modified rubber matrix, which caused enhanced tensile strength, elongation at break, and the skid resistance properties of rubber compounds. Kirino [65] modified carbon black surface chemistry with a silane compound having an amino group and used the same in a rubber blend system consisting of a second rubber modified with maleic anhydride. The combined modification of carbon black and rubber resulted in improvement of filler dispersion and distribution in the rubber matrix, which resulted improvement of abrasion resistance and reduction of heat buildup property. Herd et al. [66] functionalized carbon black by using ozone, peroxide, amine treatment and studied the effect of those functionalized carbon black with functionalized rubber system where the rubber molecules are functionalized along the polymer chains. It had been shown the functionalization of carbon black with ozone, peroxide, and amine the hysteresis energy loss, abrasion loss of rubber compounds was reduced substantially in the functionalized rubber system. Thus, the functionalization of carbon black or rubber or both is a potential way of improving rubber compound properties by enhancing the filler-polymer interactions, reducing the filler-filler interaction, and improving the filler dispersion in the rubber matrix.

2.5 Research Scope

Carbon black is the most important filler in tyre application, which provides reinforcement, wear resistance and mechanical strength in tyre tread compounds. However, on incorporation of carbon black in rubber compound there are few detrimental effects that appeared in rubber compound such as heat buildup, hysteresis energy loss, Payne effect etc which practically play contrary roles in tyre tread compound performance. Hence several research activities were adopted to improve carbon black characteristics such as surface chemistry modification, change in carbon black morphology, structure, aggregate size, aggregate size distribution etc. to counter the detrimental effects and provides a balanced properties of tyre tread compounds.

Though considerable research work is carried out on carbon black modification to improve its performance in tyre application, there are still plenty of scope available for further modification and development of carbon black based on its morphology, surface characteristics and colloidal parameters which can enhance tyre tread compound properties. In the present research attempts have been made to modify carbon black characteristics for improvement of rubber compound performance for the tyre tread application.

Objective of the research work is to improve the tyre tread compound performance by modifying carbon black characteristics. To achieve the same, different approaches were adopted to modify the carbon black characteristics. Attempts were made to induce changes in carbon black surface and structural morphology to make it not only more compatible with rubber but also to reduce the tendency of inter-particle network formation owing to low hysteresis, low heat buildup, low Payne effect, enhanced abrasion resistance etc in tyre tread compound. The same were achieved by different methods involving optimization of aggregate size distribution of carbon black, ozone treatment of carbon black to change carbon black morphology and functionalization of carbon black by chemical treatment. All these modifications were encouraging as they resulted in a significant reduction of the rolling resistance of the tyre tread compounds.

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