CHAPTER 2

LITERATURE SURVEY

2.1 BACKGROUND

Tires are the most prominent rubber articles both with respect to importance as well as volume of production. Tire acts as a rubber spring that provides riding comfort, steering response, traction and braking. More than half of the natural and synthetic rubbers and 90% of the worldwide productions of carbon black are used in the tire industry.

Reduction of green house gas emission is a major challenge to all vehicle manufacturers in the world and to address this concern, they are designing their automobiles to make them more fuel efficient. Tire industries are also working on new compounds and tire design to bring down tire rolling resistance for greater fuel efficiency. A global effort is on the way to put legislations on critical tire performance related to environment and safety. European Union proposed tire labeling from 2012 where tire would be given rating based on wet traction, rolling resistance and noise.

It is well established that fillers influence the hysteresis loss in the rubber which is mainly responsible for tire rolling resistance. In the last 20 years, almost 20% reduction of rolling resistance has been achieved by introducing silica technology in passenger car tire. However, only silica technology is not sufficient to meet the present tire labeling requirement that demands 20-30% reduction in rolling resistance from the present level. New technology is the need of the day that will be able to provide such a decline of the rolling resistance (20 to 30%) without affecting wet grip and wear.

There is a continuous search for new fillers and new materials to reduce the hysteresis loss of tread rubber, which accounts for ~40% rolling loss. In this journey, scientists have identified nanoclay as potential filler for rubber reinforcement and modified the clay to make it compatible with rubber. Rubber nanocomposites showed remarkable improvement of properties like strength and elongation but is still far behind to meet the properties required for tire tread application.

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This investigation is aimed to continue this search with the target of development of low rolling resistance nanocomposite based tread compounds for passenger car radial (PCR) tires as well as truck bus radial (TBR) tires. Further it was aimed to develop software for the prediction of rolling resistance of tire with nanocomposite tread using finite element simulation.

2.2 TIRE TECHNOLOGY

2.2.1 History

Sumerians invented the wheel 5000 years ago. The world's first pneumatic tire was invented by Scottish engineer, Robert William Thomson in 1845. Forty years later, in 1888 John Boyd Dunlop revived the pneumatic tire. The first commercially available pneumatic tire consisted of an inner-tube surrounded by a "cover" made up of several layers of rubber coated woven canvas-type fabric which was much thicker in the area that touches the ground this rubber mass that comes in contact with the surface is called tread. The first application of this invention was in bicycle tires (Blow 1986). The present radial tire was first developed and patented by Michelin in 1948.

2.2.2 Definition

A tire is a much more complex object than it looks. Actually a tire is many things: geometrically, it is a torus; mechanically, a flexible-membrane pressure container; structurally, a high-performance composite; and chemically, a tire consists of materials made up from long chain macromolecules (Mark 1994).

2.2.3 Functions

The functions of a tire can be considered in relation to three basic roles: (a) vehicle mobility, (b) performance and integrity, and (c) comfort. Performance, including driving and braking torque and rolling resistance, exerts or transfers forces or moments in forward direction. Vehicle mobility, including cornering, steering response, and abrasion, acts in the lateral direction, and the forces involved in comfort act vertically (Mark 1994).

To describe the characteristics of a tire and the forces and moments acting on it, it is necessary to define an axis system that serves as a reference for the definition of various parameters as shown in Fig. 2.1.
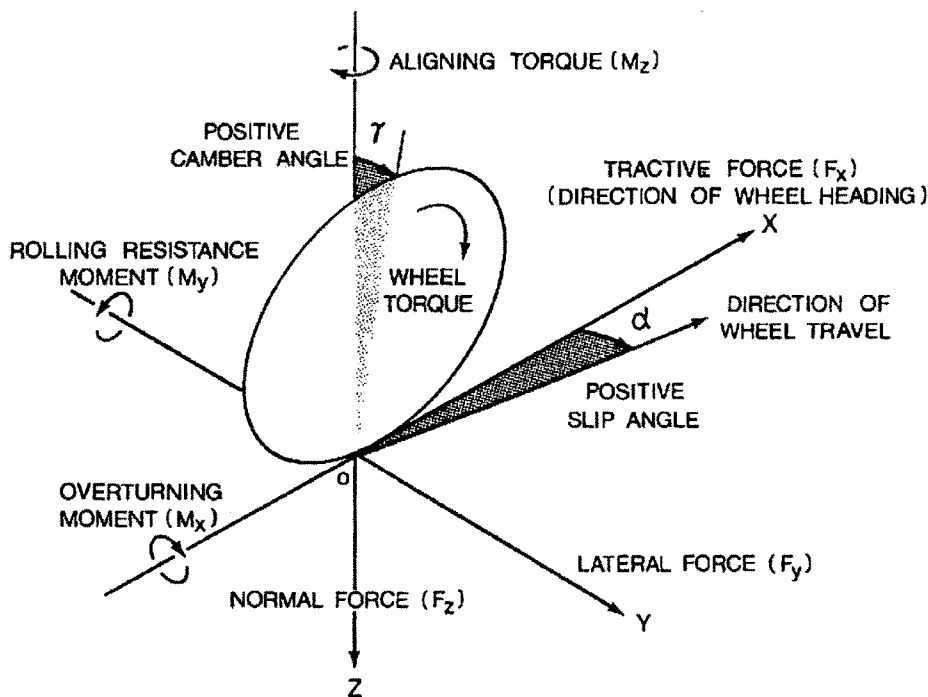

Fig. 2.1-Tire axis system and characteristics

2.2.4 Tire components

Typically a passenger car radial tire comprises of different components which includes tread, sidewall, steel belts, fabric body ply, apex, rim strip, inner liner, fabric cap ply and metal bead as shown in the Fig. 2.2. While in truck bus radial tires fabric body is replaced by steel body and additionally, shoulder cushions and belt edge filler are also included and as shown in Fig. 2.3.

Tread is the top most abrasion resistant rubber component of tire with different pattern which comes in contact with road; it forms the protective coating for the carcass. It is the most important component responsible for the main tire performance indicators like traction, breaking, handling, wear and rolling resistance.
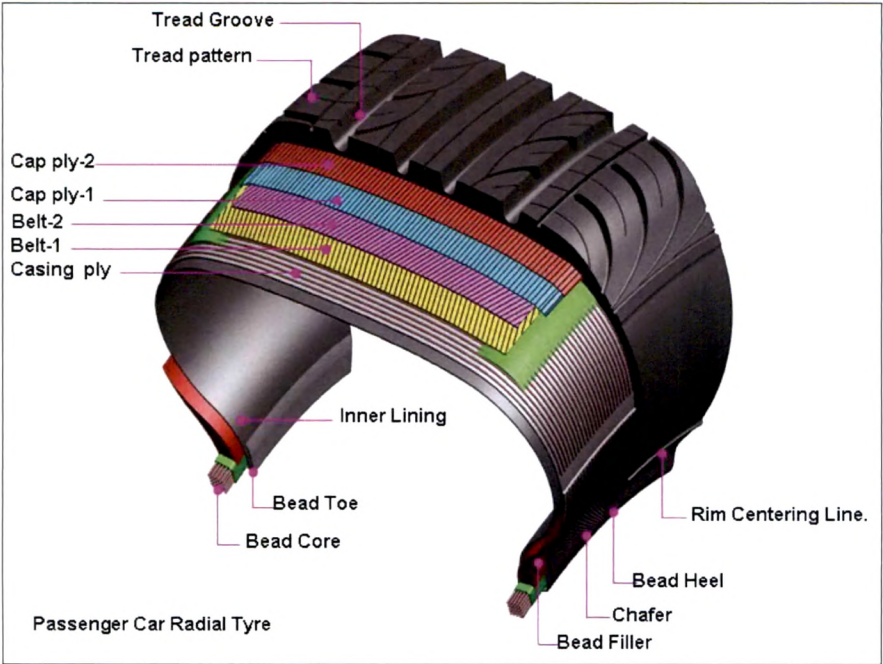
Tread Groove
Tread pattern
Cap ply-2
Cap ply-1
Belt-2
Belt-1
Casing ply
Inner Lining
Bead Toe
Bead Core
Rim Centering Line.
Bead Heel
Chafer
Bead Filler
Passenger Car Radial Tyre

Fig. 2.2- Passenger car radial (PCR) tire construction

PROTECTOR BELT
BELT EDGE STRIP
WORKING BELT- II
WORKING BELT- I
TRANSITION BELT
BODY PLY
Truck Bus Radial Tire
TREAD CAP
TREAD BASE
TREAD CUSHION
BELT EDGE FILLER
SHOULDER CUSHION
SHOULDER COVER STRIP
SOFT APEX
SIDEWALL
BEAD BUNDLE
INNER LINER
BEAD CUSHION
RIM STRIP
STEEL CHAFER
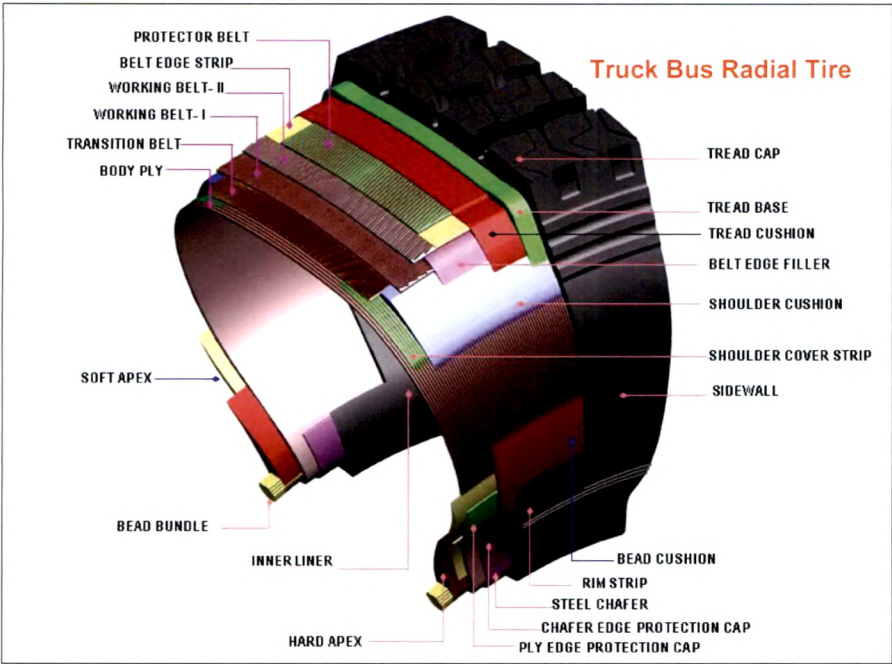CHAFER EDGE PROTECTION CAP
PLY EDGE PROTECTION CAP
HARD APEX

Fig. 2.3- Truck bus radial (TBR) tire construction

2.2.5 Tire nomenclature

The tire designation system is written on the tire sidewall, it is as described below. If the marking reads 205/65R15 V it implies the following

- 205 is section width in mm
- 65 is the tire aspect ration (Aspect ratio= Section height/section width)
- R represents radial construction
- 15 is nominal rim diameter in inch
- V denote speed rating of the tire

2.2.6 Application of tire

The different types of tire applications are shown below (Fig. 2.4);

Fig. 2.4- Tire applications in different areas

2.3 TIRE ROLLING RESISTANCE

Tire rolling resistance is defined as the energy consumed per unit distance of travel as a tire rolls under load. The energy consumed by the tire is converted into heat. The proper unit of rolling resistance is J/m, which equals to N, the unit of force.

Thus, the rolling resistance, F_{RR} is given by the equation:

$$F_{RR} = \mathcal{H}/V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (2.1)$$

Where the rate of heat development $\mathcal{H}$ and ($\equiv dH/dt$) is often termed power loss $\mathcal{P}_R$ and V is the road speed of the tire,

$$F_{RR} = \mathcal{P}_R/V = [P_{in} - P_{out}] / V \dots\dots\dots\dots\dots (2.2)$$

Where, P_{in} is the tire input power provided by the motor, and P_{out} is the tire output power supplied to traction of the car.

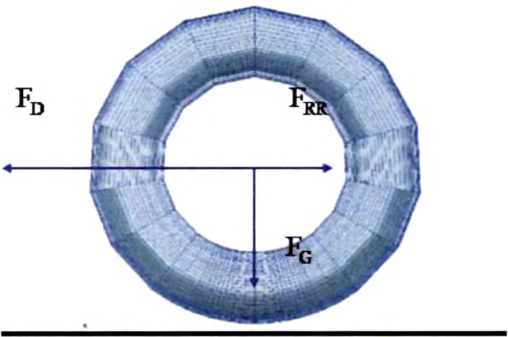Rolling resistance is force acting in the opposite direction to the driving force (Fig. 2.5).

Fig. 2.5- forces acting on tires

Where; F_D - Driving force

F_G - Contact force

F_{RR} – Rolling Resistance force

The rolling resistance coefficient (C_R) of a tire is expressed by;

$$C_R \,[\%] = [\text{Rolling Resistance (N)} / \text{Wheel Load (kg)} \times g \,(m/s^2)] \times 100 \dots\dots\dots (2.3)$$

## 2.4 TIRE TREAD

2.4.1 Performance

Tire tread is top most circumferential rubber layer with pattern that touches the ground. The characteristics of a good tire are (a) it should generate the highest possible traction force between tire and road (b) the steering characteristics should be exact and predictable under all handling situations (c) it should have the lowest possible rolling resistance and (d) give the highest possible mileage. In all these requirements the tire tread compound plays a major role viz.

a) The tire traction is determined by the friction properties of the tread compound.

b) The steering characteristics depend, apart from constructional features, on the stiffness of the tread compound, i.e. on its dynamic modulus and again on the friction properties.

c) The rolling resistance of the tire depends largely on the loss modulus of the tread compound

d) The mileage a tire depends on the abrasion resistance of the tread compound (Grosch,1996).

2.4.2 Tread compound design

The three important properties such as rolling resistance tread wear and wet grip form the so called "magic triangle" of tire properties, which means that a balance must be found between these properties. These requirements are conflicting, as it is impossible to improve all three characteristics at the same time. A compromise between these characteristics should always be achieved.

The "magic triangle of tire technology" is a principle in the tire world that says improvement to rolling resistance has to come at the expense of wet-road grip and durability (Fig. 2.6). Introduction of silica/silane technology coupled with invention of high vinyl solution styrene butadiene rubber (SSBR), made it possible to enhance the magic triangle thereby reducing the rolling resistance without sacrificing grip and wear. This technology was used to develop the "GREEN TIRE" i.e. energy efficient tire.
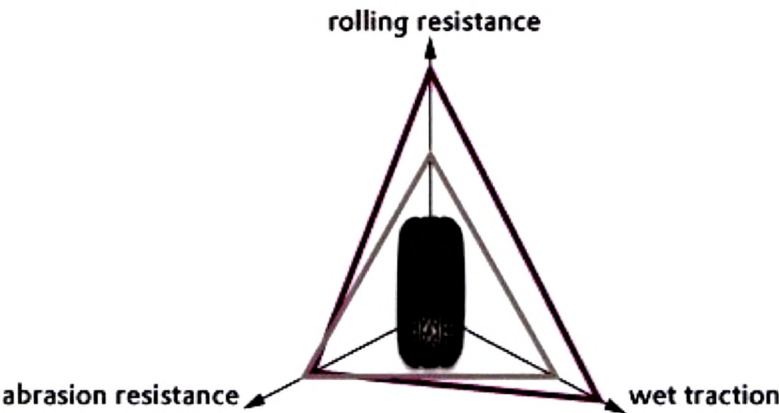
Fig. 2.6- Magic triangle of PCR tread compound

2.4.3 Requirements

The contributions of different tire components on rolling resistance of a passenger car are shown in Fig. 2.7. The contribution of tread rubber on rolling resistance is the highest and accounts for 39% of the total losses in PCR tire. While in TBR tires the tread alone accounts for 40% of the losses as shown Fig. 2.8.

A major problem facing tire designers has traditionally been to achieve a compromise between low rolling resistance, high wet grip and high wear resistance in passenger car tire. The lower is the rolling resistance; the less fuel is required to propel the vehicle forward. Lowering the rolling resistance, however, commonly results in a reduction in wet grip performance, which of course is unacceptable (Freund, 1998; Brinke, 2002).

A major step in solving this problem can be achieved by the replacement of (part or all) carbon black by silica in the tire's tread compound. This has enabled manufacturers to produce tires which provide improved wet grip properties, better winter performance and lower rolling resistance all at the same time (Freund, 1998; Brinke, 2002). Therefore silica based tread is considered to be a revolutionary in tire technology.

Grip is best served by rubber compounds, which absorb high levels of energy. Rolling resistance, on the other hand, is affected by low frequency distortion – the deflection of the tire as it

revolves, low rolling resistance requires compounds that absorb low quantities of energy. With the addition of silica, it was possible to produce compounds, which provide higher hysteresis at high frequencies (higher traction) as well as lower hysteresis at low frequencies (lower RR) than what was achievable with carbon black (Meneghetti, 2005).
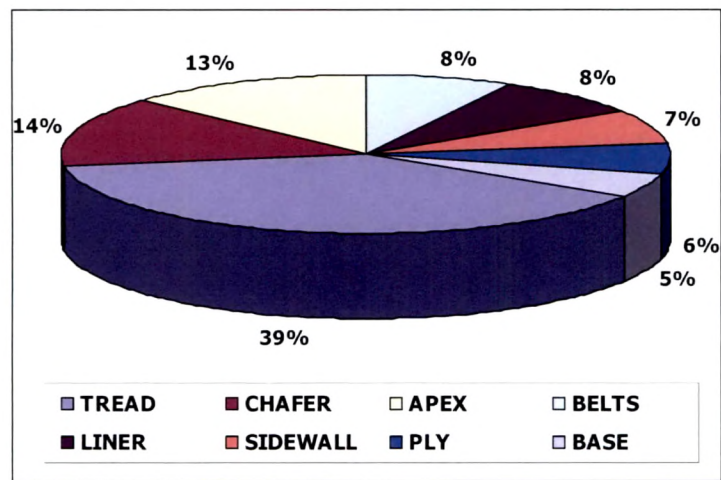

Fig. 2.7- Contribution of tire components towards rolling resistance in PCR tire
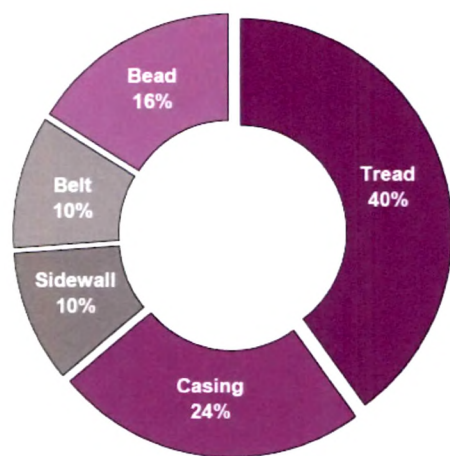

Fig. 2.8- Contribution of tire components towards rolling resistance in TBR tire

The increased concern of protecting the environment gives rise to a demand for tires which can combine a long service life, driving safety and low fuel consumption. World wide vehicle manufacturers and tire industries are working on to reduce rolling resistance to increase fuel efficiency of vehicle and reduce green house gas emission. European Union (EU) has made

legislation on tire labeling implementable by 2012 where tire will be rated based on tire rolling resistance, wet traction and noise (Fig. 2.9 to 2.11)
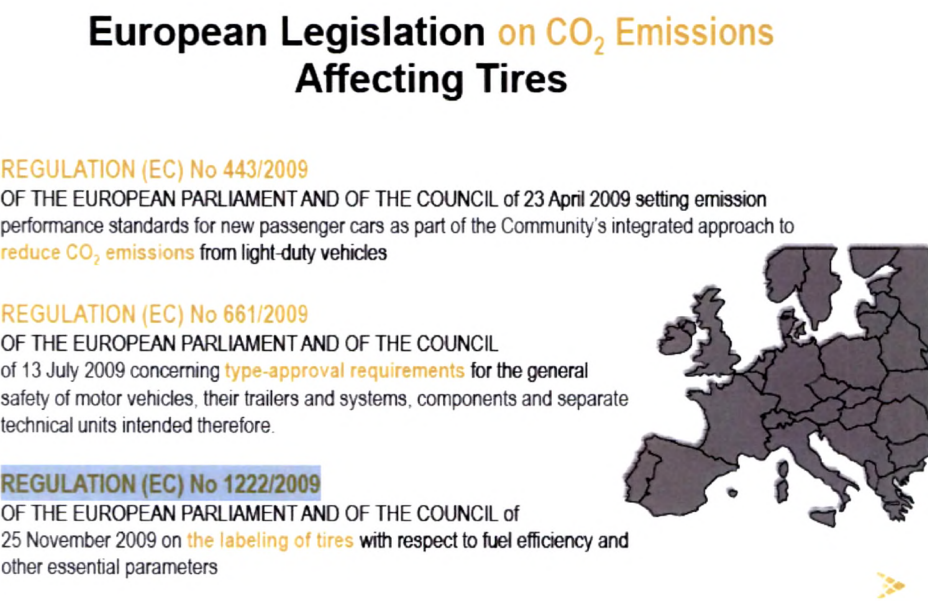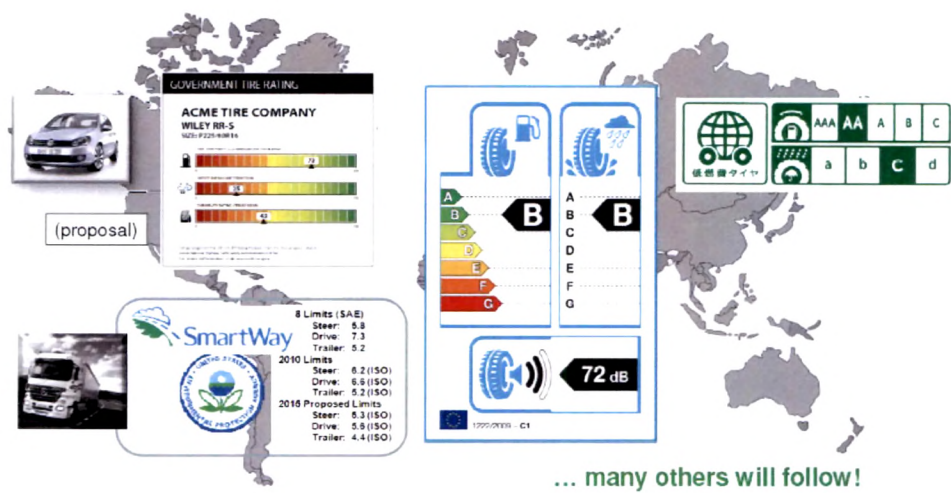

Fig. 2.9- EU legislation on tire labeling

Fig. 2.10- The world wide tire labeling

Rolling Resistance Coefficient
単位 (N/kN)

転がり抵抗係数 (RRC) ISO28580	等級 Grade	EU Classifi-cation
RRC ≦ 6.5	AAA	A
6.6 ≦ RRC ≦ 7.7	AA	B
7.8 ≦ RRC ≦ 9.0	A	C
9.1 ≦ RRC ≦ 10.5	B	E
10.6 ≦ RRC ≦ 12.0	C	F

Fig. 2.11- EU classification for PCR tire rolling resistance

2.4.4 Tread compound formulations

The general raw materials used in a tire tread compound formulations are Rubber (Natural Rubber; Emulsion and Solution Styrene Butadiene rubber; Polybutadiene rubber), fillers (carbon black and silica), petroleum oils (TDAE, RAE, MES and Naphthenic), sulphur, accelerator (Sulphenamide; thiuram; guanidine), accelerator activator (zinc oxide and stearic acid), antidegradants (diphenyl diamines; substituted phenols), wax, resins and zinc salt of fatty acids as process aids.

The rubbers used in a typical passenger car radial (PCR) tire tread compound are emulsion SBR / solution SBR blended with BR. Filler used are silica, carbon black and silica and carbon black combination with higher dosages of process oil (10 – 15%).

In truck bus tire (TBR) tread, blend of Natural rubber and Polybutadiene rubber is widely used. The main filler for TBR tread is highly reinforcing carbon black and generally no process oil is used.

2.5 FILLERS AND REINFORCEMENT

2.5.1 Reinforcement

The reinforcement improves the critical properties of rubber compounds like hardness, modulus, tensile strength, elongation, tear strength and abrasion resistance. Carbon black and silica are mainly used as reinforcing filler in tire tread compounds. The reinforcing effect depends on several parameters such as filler particle size and its structure, surface energy and morphology; and volume fraction of filler. Lower filler-filler interaction and better filler-rubber interaction are desirable for lower hysteresis loss in rubber compounds.

The filler-filler interaction was first measured by Payne and is termed as Payne's effect. The Payne effect is the drop of the shear modulus (G') with increasing strain amplitude. It corresponds to a gel-sol transition of the filler network at moderate strain and a breakdown of remaining sub-clusters at large strain. The dependence of the shear modulus (G') on strain for a reinforced rubber vulcanizate is shown in Fig. 2.12. The Shear modulus (G') of a filled rubber compound is built-up of the following:

i.   A strain-independent contribution of the rubber network, which is the result of the proportionality of the G'-modulus to νRT, where ν is the number of moles of elastically effective network chains per unit volume (cross-link density).

ii.   A strain-independent hydrodynamic effect of the filler, which was first derived by Albert Einstein and later exemplified for rubber by Guth and Gold (1938) and Smallwood (1944) and presented in Equ.2.4.

$$G = Go \ (1+ 2.5\varphi + 14.1\varphi^2)\ldots\ldots\ldots\ldots (2.4)$$

Where, G and Go are the moduli of the filled and unfilled system respectively and φ is the volume fraction of the filler

iii.   A strain-independent effect due to chemical/physical rubber to filler interactions

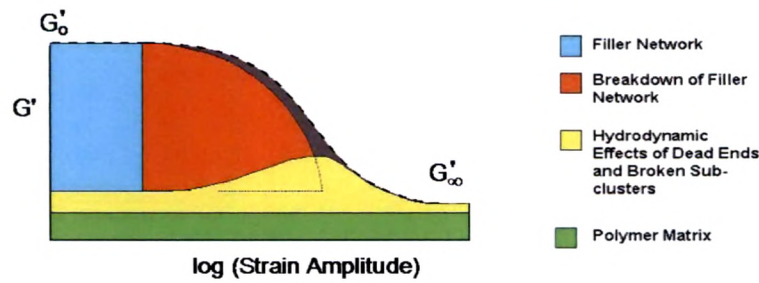iv.   A strain-dependent contribution of the filler (Payne 1965, 1971)

Fig. 2.12- Payne's effect: the shear modulus (G) as a function of strain for a reinforced rubber compound

2.5.2 Characterization of rubber filler systems- surface, inter phase and interface.

In elastomeric nano-composite, interfacial interactions between filler particles and polymer matrix affect the following parameters;

- dispersibility of the nano-fillers in the polymer
- adhesion properties of fillers and polymer and
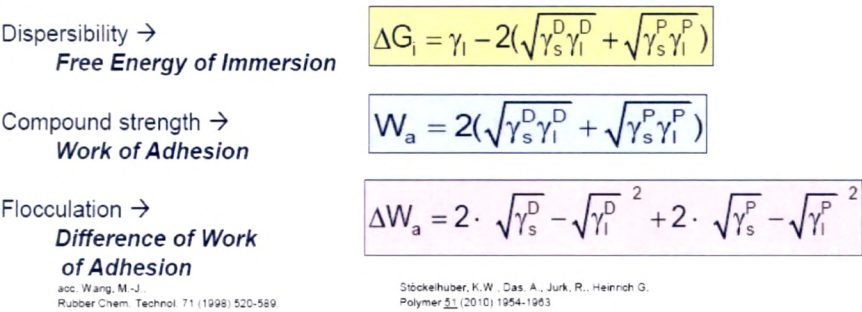- Flocculation (re-agglomeration) of fillers in polymer matrix.

Dispersibility →
Free Energy of Immersion

$$\Delta G_i = \gamma_l - 2\left(\sqrt{\gamma_s^D \gamma_l^D} + \sqrt{\gamma_s^P \gamma_l^P}\right)$$

Compound strength →
Work of Adhesion

$$W_a = 2\left(\sqrt{\gamma_s^D \gamma_l^D} + \sqrt{\gamma_s^P \gamma_l^P}\right)$$

Flocculation →
Difference of Work of Adhesion

acc. Wang, M.-J.
Rubber Chem. Technol. 71 (1998) 520-589.

$$\Delta W_a = 2 \cdot \left(\sqrt{\gamma_s^D} - \sqrt{\gamma_l^D}\right)^2 + 2 \cdot \left(\sqrt{\gamma_s^P} - \sqrt{\gamma_l^P}\right)^2$$

Stöckelhuber, K.W., Das, A., Jurk, R., Heinrich G.
Polymer 51 (2010) 1954-1963

Fig. 2.13- Calculation of free energy, work of adhesion and filler flocculation

These interfacial interactions primarily depend on surface energies and polarities of filler and polymer. From the surface energetic values, the thermodynamic predictors for dispersibility, filler-polymer adhesion and filler flocculation can be derived by the equations shown in Fig. 2.13. The dispersibility of fillers in polymers matrix depends on free energy of immersion

of fillers as well as rubbers. Free energy of immersion (ΔG_i) for rubber / filler combination can be calculated by the following equation;

$$\Delta G_i = \gamma_l - 2(\sqrt{\gamma_s^D \gamma_l^D} + \sqrt{\gamma_s^P \gamma_l^P})$$

With knowledge of the dispersive and polar components of surface energy of both

of filler (γ_s^D, γ_s^P), and

of rubber (γ_l^D, γ_l^P)

predictions of dispersibility are possible

Calculation of surface energy by fitting equations of a set of contact angle measurements of test liquids with different surface tension and polarity are shown in Fig. 2.14;
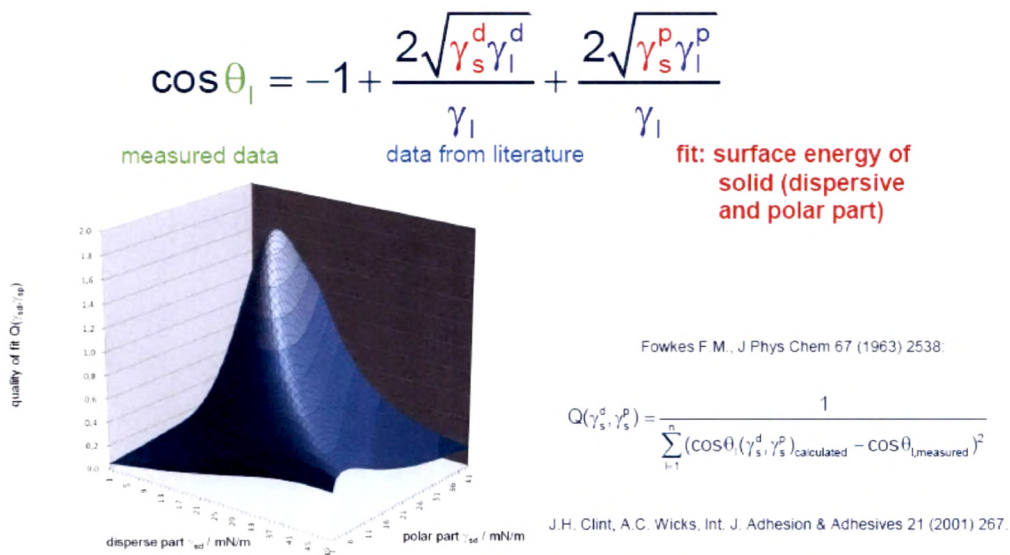

Fig. 2.14- Calculation of surface energy

Surface energy of different fillers and polymers are presented in Fig. 2.15 and 2.16 respectively.
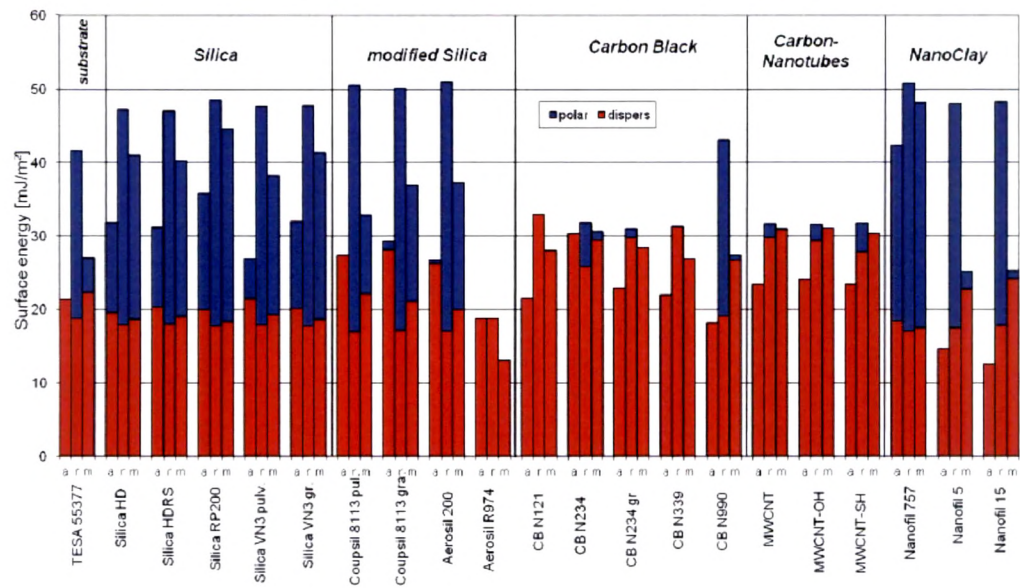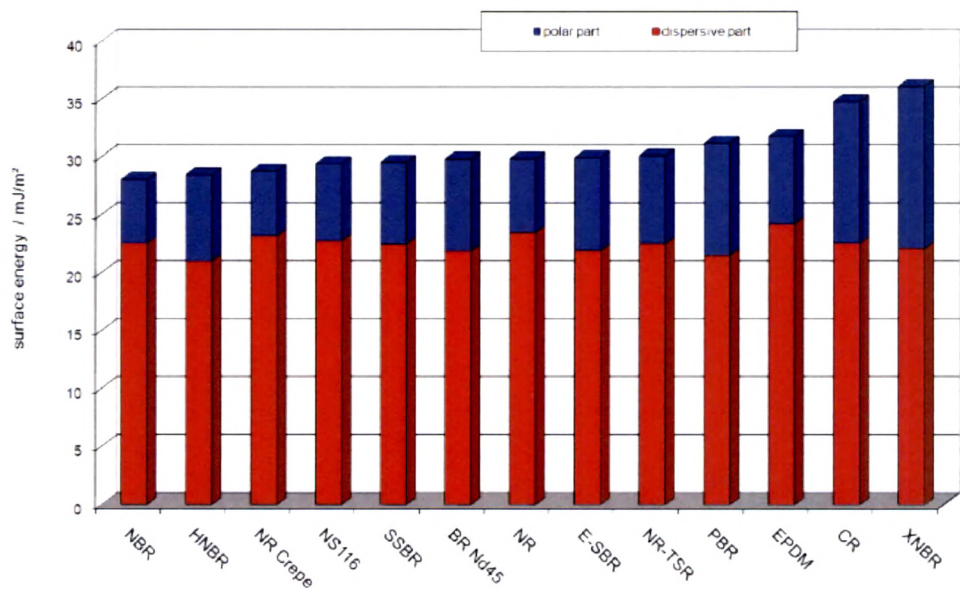

Fig. 2.15- Surface energy of fillers

Fig. 2.16- Surface energy of rubbers

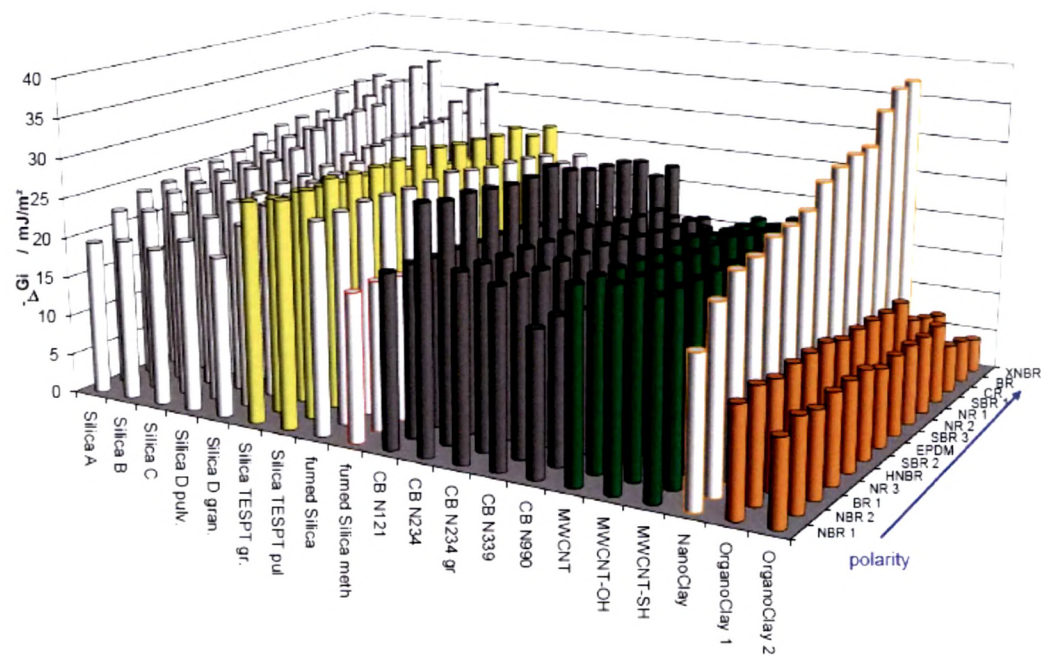Free energy of immersion (ΔG_i) of different fillers polymers are shown in Fig. 2.17.

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Fig. 2.17- Free energy of immersion of rubbers and fillers

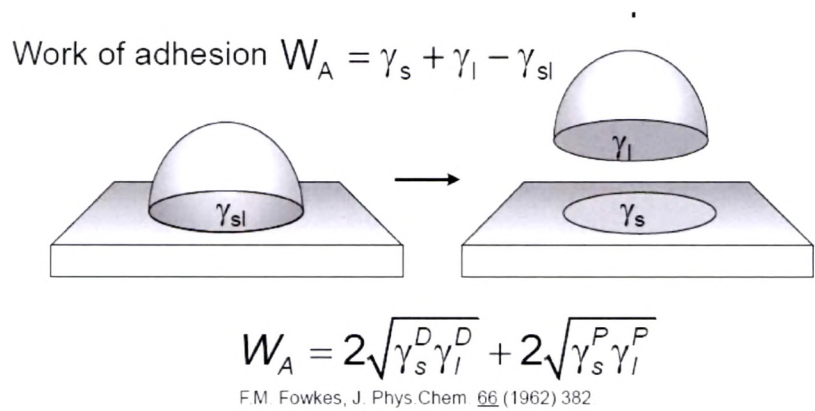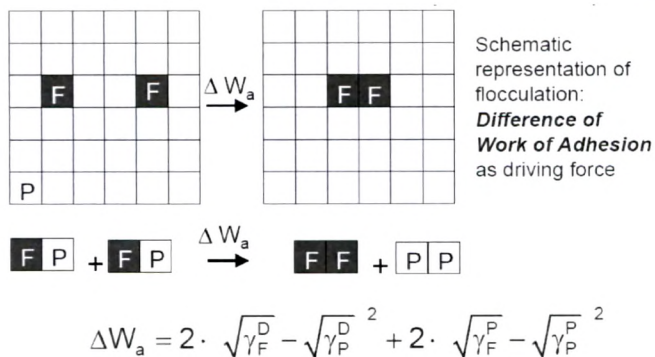The work of adhesion as calculated by Fowkes (1962) based on thermodynamic approach is shown in Fig. 2.18.

Work of adhesion $W_A = \gamma_s + \gamma_l - \gamma_{sl}$

$$W_A = 2\sqrt{\gamma_s^D \gamma_l^D} + 2\sqrt{\gamma_s^P \gamma_l^P}$$

F.M. Fowkes, J. Phys.Chem 66 (1962) 382

Fig. 2.18- Calculation of work of adhesion

Thermodynamics of filler flocculation is shown in Fig.2.19.

$$\Delta W_a = 2 \cdot \left(\sqrt{\gamma_F^D} - \sqrt{\gamma_P^D} \right)^2 + 2 \cdot \left(\sqrt{\gamma_F^P} - \sqrt{\gamma_P^P} \right)^2$$

M- J. Wang Rubber Chem. Techn. 71 (1998) 520.

Fig. 2.19- Calculation of filler flocculation

2.5.3 Carbon black filler

Carbon black is the most important filler obtained till date for reinforcing rubber. Application of carbon black results in an increase in strength properties, wear resistance and fatigue resistance. In addition, due to its colour it is an excellent absorber of light. It therefore absorbs most of the ultraviolet components of sunlight, which can otherwise initiate oxidative degradation of the rubber. Carbon black is produced by thermal cracking of petroleum oil called carbon black feed stock. Carbon black is classified based on particle size and structure. Carbon black particle have diameter in nm range but they remain as aggregates state primary structure. Carbon black structure; SEM picture of carbon black; carbon black structures in filled rubbers on different length scales and nano structure surface carbon black are shown in Fig. 2.20 to 2.23 respectively.
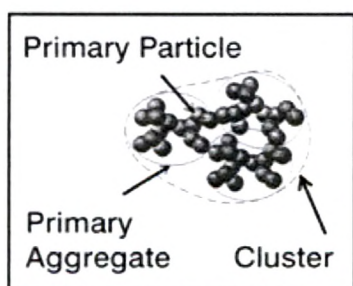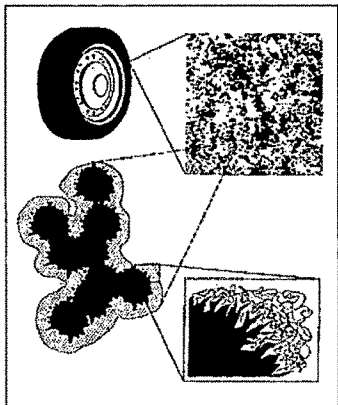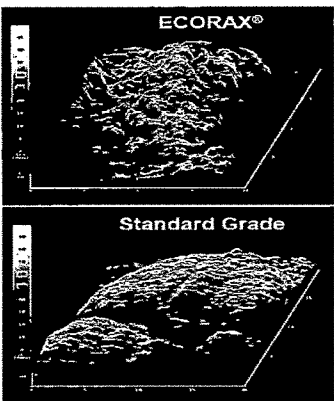

Fig. 2.20- Carbon black structure
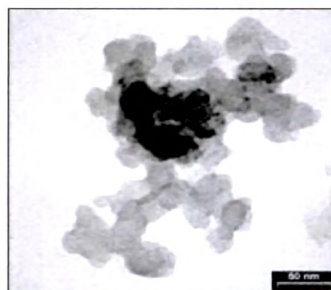
Fig.2.21- SEM image of carbon black

Fig. 2.22- Structures in filled rubbers on different length

Fig.2.23- ECOREX, Nano structures CB and standard CB
(Evonic Industries)

Carbon black was introduced as a reinforcing agent in rubber in year 1904 and since then it is being used as main reinforcing filler for rubber and tire compounds. Reinforcing fillers such as carbon black and silica are added to rubber compounds to improve their mechanical and dynamical properties required for the different diversified applications.

The reinforcement is governed by hydrodynamic effects and physical/chemical interactions of the filler surface with rubber matrix (Payne 1965; Donnet 1993). The reinforcing effect depends on several parameters such as filler particle size and their structure, surface energy, morphology and volume fraction of filler. However, filler-filler interaction also plays major role in rubber hysteresis behavior (Fro¨hlich, 2005). It is well established that lower filler-filler interaction leads to lower hysteresis loss of the compounds (Wang,1998).

2.5.4 Silica fillers

Silica occurs commonly in nature as sandstone, silica sand or quartzite. It is the starting material for the production of silicate glasses and ceramics. Silica is one of the most abundant oxide materials in the earth's crust. It can exist in an amorphous form (vitreous silica) or in a variety of crystalline forms. Often it will occur as a non-crystalline oxidation product on the surface of silicon or silicon compounds. Silica is inorganic filler and widely used as reinforcing filler in rubber compounds.

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The reinforcing effect of silica is related to its morphology. The morphology study of silica shows that it consists of three characteristic structures, namely primary particles, aggregates and agglomerates. A primary particle has cross-sectional dimensions of 5 – 100 nm. Aggregates of multiple primary particles are formed by chemical and physical-chemical interactions which has dimensions about 100 – 500 nm. The aggregate can be quantified by the size of the primary particles as expressed in their specific surface area, the number of primary particles and their geometrical arrangement in the aggregate. The term "structure" encompasses all these three parameters to give a general measure of the aggregate. The aggregates are then condensed into agglomerates by Van der Waals forces. Typical dimensions of agglomerates are in the order of magnitude of 1 – 40 µm. Silica agglomerates are disintegrated during rubber mixing, more or less to the size of aggregates or even primary particles. Thus precipitated silica has 0.02 micron in average particle size and an average surface area of 150-175 square meters per gram.

Silica aggregates are comparable to those of carbon blacks, but have a larger structure. This structure accounts for the greater reinforcing power relative to carbon black. Because of its high specific component of surface energy, silica has a strong tendency to agglomerate, and is difficult to disperse in rubber and rapidly re-agglomerates after mixing. Most often silica is used along with silane coupling agents when more than 5% silica is present in the rubber compound. Development of silane, bis (triethoxysilylpropyl)-tetrasulfan (TESPT), and based coupling agents changed the chemistry of silica reinforcement. The hydroxyl groups present in the silica surface react with silane coupling agent and form chemical bonds between silica and silane and this takes place during silica mixing process, thereafter, it forms bond with rubber during vulcanization. Silane acts as a chemical bridge between inorganic silica filler and organic rubber (Fig. 2.24). Silica filler particles form strong filler network because of hydrogen bonding of surface hydroxyl groups, thus giving rise to high filler-filler interaction. Higher filler-filler interaction results in higher hysteresis loss in the rubber.

Silane reacts with surface hydroxyl group of silica and results in substantial reduction in the filler-filler interaction. Silica filler along with silane when mixed in the rubber matrix under specific conditions offers high reinforcement with lower hysteresis loss. It is well established that lower filler-filler interaction leads to lower hysteresis loss of the compounds (Huber, 1999; Schon, 2003).
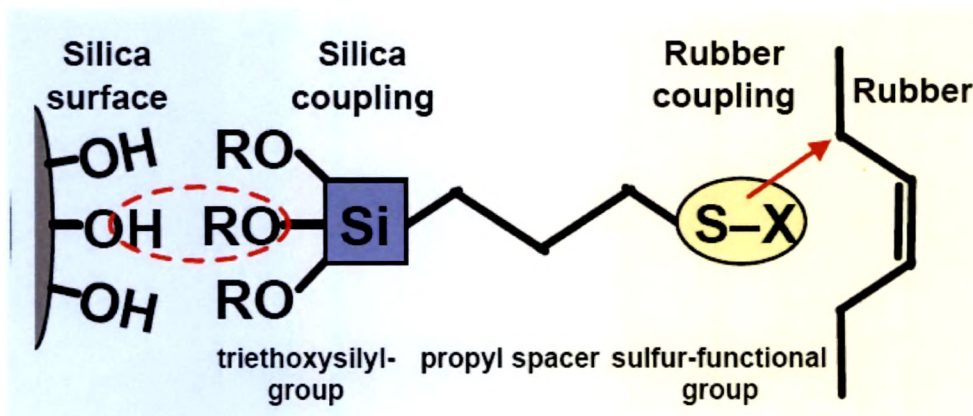
Fig.2.24- Silica-silane reaction

The use of silica (SiO_2) as reinforcing filler, in place of conventional carbon black (CB), has become popular in the last two decades (Ansarifar, 2003) after the introduction of silane coupling agent. Tire industries were successful to develop low rolling resistance passenger tread compound without sacrificing traction by using precipitated silica and silane and solution SBR. Such tires can reduce fuel consumption by approximately 6% and reduce emission of pollutants.

Due to the increasing demand for fuel economy and environmental concern, replacement of carbon black by silica and clay is gaining potential although silica is very successful in passenger tire for lower of rolling resistance but it is not so successful in the truck bus radial tire segment owing to its relatively poor bonding with natural rubber (Wang, 2000; Schon, 2003).
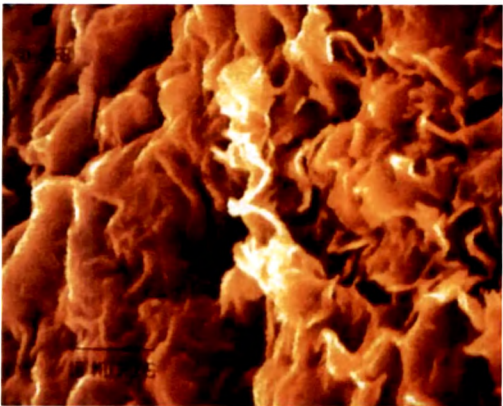
2.5.5 Nanoclay (Na-montmorilonite: Na-MMT)

Clays are naturally occurring minerals with variability in their constitution depending on their groups and sources. The essential nanoclay raw material is montmorillonite (MMT); a 2-to-1 layered smectite clay mineral with a layered structure. Individual layer thicknesses are just one nanometer, but surface dimensions are generally 300 to more than 600 nanometers, resulting in an unusually high aspect ratio. The clays used for the preparation of nanoclays belong to smectite group clays which are also known as 2 : 1 phyllosilicates, the most common of which are montmorillonite {Si4[Al1×67Mg0×33]O10(OH)2×nH2O×X0×33 = Na, K or Ca} where octahedral site is isomorphically substituted as shown in Fig. 2.25.
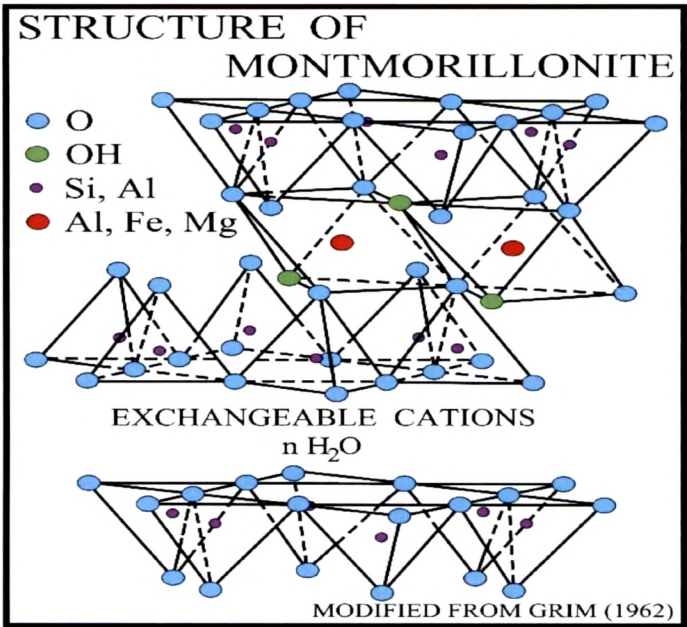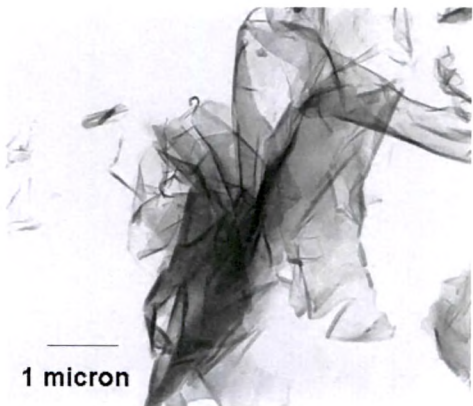
Fig. 2.25- Structure of montmorillonite (MMT) nanoclay

Microscopy image of smectite bentonite clays rock and montmorillonite are shown in the Fig. 2.26 and 2.27)

Fig. 2.26- SEM image of bentonite clay

Fig. 2.27- TEM image of MMT

2.5.6 Organoclay (organic layer silicate)

Nanoclay (Na-MMT) has layer silicate structure and organically modified Nanoclay is known as organoclay. This is natural montmorillonite modified with a quaternary ammonium salt and its trade name is Cloisite® 15A produced by Southern Clay Products, USA. Cloisite® 15A is off white power material.

Kim el al (2006) investigated the X-ray diffraction patterns of the Na-MMT and the organoclay (Cloisite® 15A, Southern Clay Products, USA). The Na-MMT shows a diffraction pattern peak at $2\theta=7.2°$, which corresponds to the average basal spacing (d-spacing) of 12.3 Å. In the organoclay, two peaks are shown. The first peak, which is the major peak, moved to lower angles, i.e., $2\theta=2.8°$. The basal spacing increased from 12.3 to 31.5 Å. This spacing indicates that long alkyl (dimethyl dihydrogenatetallow) ammonium ions were inserted into the gallery of Na-MMT, as a result, an intercalated structure formed as shown in Fig. 2.28. The inserted long alkyl chains caused the hydrophilic nature of the clay to decrease, and this effect improved the dispersion of silicates in the rubber matrix. The second peak is shown at $2\theta=7.2°$, which is same as the peak of the Na-MMT. This result indicates that some amounts of Na-MMT were not modified with alkyl ammonium ions.
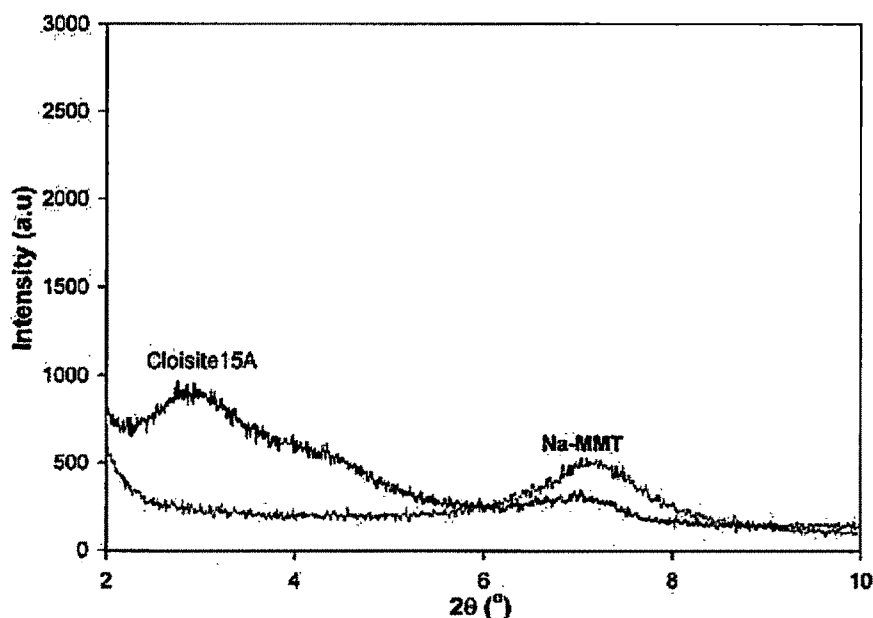
Fig. 2.28- XRD patterns of organoclay (Cloisite 15A®) and Na-MMT

2.6 NANOCOMPOSITES

2.6.1 Nano materials

Chemical structure or images of commonly investigated nano particles are shown below (Fig.2.29);

POSS

Layered Silicate

Carbon Nanofiber

Single Wall Carbon Nanotube, needs reference

Expanded Graphite Nanoplatelets
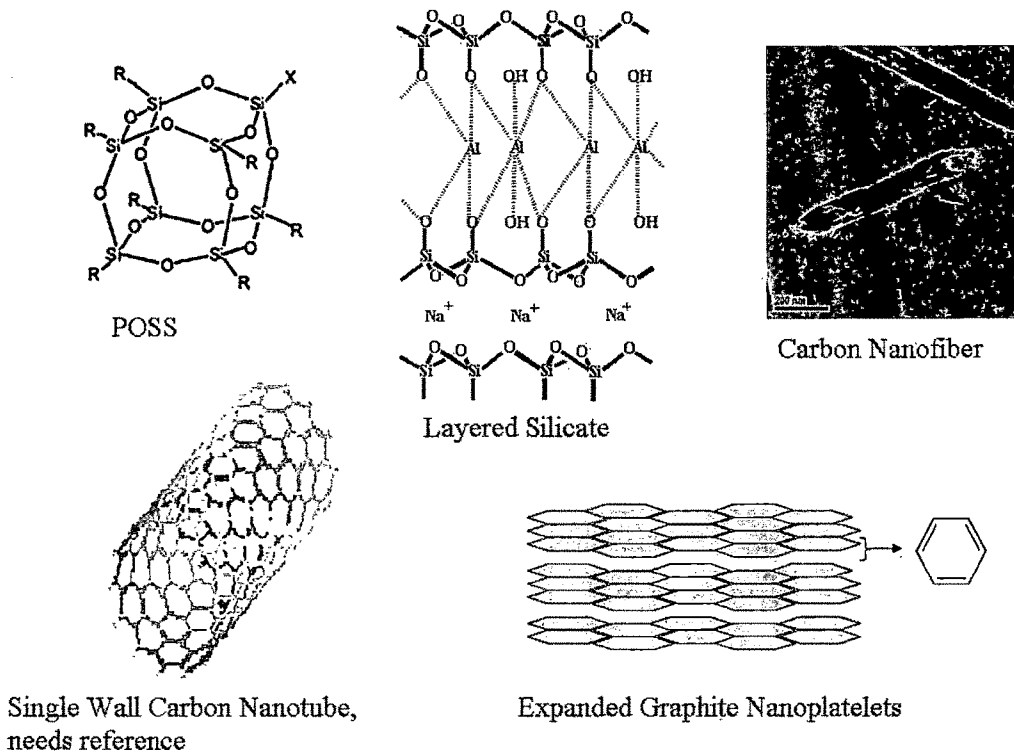
Fig. 2.29- Chemical structure of different nano particles

2.6.2 Polymer and rubber nanocomposites

The term "polymer nanocomposite" broadly describes any number of multi component systems, where the primary component is the polymer and the filler material has at least one dimension below 100nm. Rubbers are generally organophilic and naturally occurring montmorillonite is hydrophilic, hence unmodified nanoclay disperses in rubbers with great difficulty. Through clay

surface modification, montmorillonite can be made organophilic and, therefore, compatible with conventional organic polymers.

Polymer/clay nanocomposites are being extensively investigated because these nanocomposites have enormous potential for commercial utilization in diverse areas such as coating, flame-retarding, barrier, electronic materials and composite. Polymer nanocomposites were developed in late 1980's in both co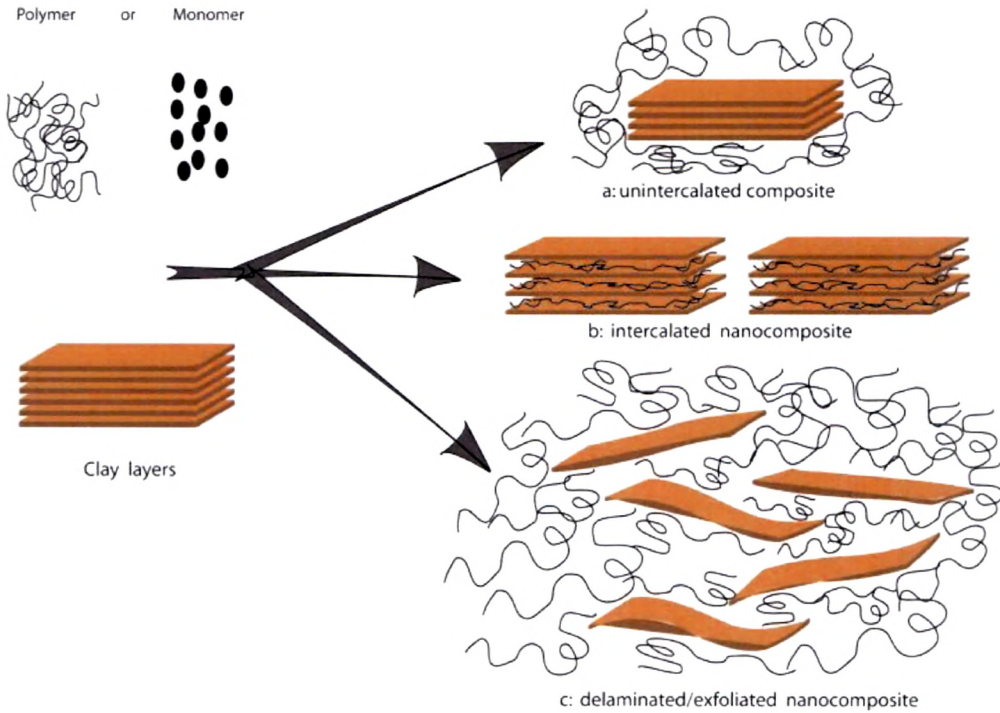mmercial research and academic laboratories. Toyota was the first company that synthesized clay-polyamide nanocomposite and used the same as structural components in their automobiles (Usuki,1993). Intercalated and exfoliated structure of rubber nanocomposite is shown in Fig. 2.30.

Polymer   or   Monomer

a: unintercalated composite

b: intercalated nanocomposite

Clay layers

c: delaminated/exfoliated nanocomposite

Fig. 2.30- Intercalated and exfoliated structure of rubber nanocomposite

A good number of research papers are available on polymer/clay nanocomposites (Usuki,1993). Literature survey shows that a fair amount of interesting work has been published with organic layered silicate and different thermoplastics polymers like Nylon (Kojima,1993), polystyrene (Qutubuddin,2001) and polyethylene oxide (Vaia,1997). A number of interesting investigations

has been reported in the field of rubber nanocomposite using organic layer silicate (OLS) and different rubbers like EVA (Alexandre, 2000), ENR (Bandyopadhyay, 2000; Mark, 2001; Ray 2003) and Thermo Plastic Elastomer (TPE) (Ray 2001).

Varghese and Karger-Kocsis (2003) mixed NR latex with organoclay forming NR nanocomposites of high stiffness and low damping characteristics. Most of the NR nanocomposites however are derived from high molecular weight Natural rubber. NR-clay (10 phr) nanocomposites have also demonstrated comparable mechanical properties to NR filled with 40 phr carbon black (Arroyo, 2003). The clay improved the strength without reducing elasticity of the material. Gatner *et al.* (2001) prepared rubber nanocomposite based on BR and NR with OLS (Organic layered silicate) swollen in toluene and obtained very good tensile strength and elongation.

Organically modified montmorillonite (organoclay) is usually employed to prepare nanocomposites possessing much higher mechanical properties and gas barrier properties (Kojima, 1993). Preparation, structure, and properties of rubber/organoclay nanocomposites have been investigated for a number of rubber matrices, e.g., natural rubber, NR (Ganter, 2001; Joly, 2002; Varghese, 2003; Varghese, 2004), butadiene rubber ,BR (Ganter, 2001).

Some rubber/clay nanocomposites reported in the literature have mechanical properties similar to or better than rubber filled with carbon black. Arroyo *et al.* (2003) prepared natural rubber nanocomposites with 10 phr organoclay with similar modulus, tensile strength and hardness as natural rubber with 40 phr carbon black. Magaraphan *et al.* (2003) also prepared natural rubber nanocomposites with 7 phr of MMT functionalized with octadecylamine which presented higher tensile strength and elongation than NR with 20 phr carbon black.

Emulsion styrene butadiene rubber nanocomposite based on organic layered silicate has been investigated by a number of investigators (Zhang 2000, Wang 2000, Sadhu, 2003).

If properly dispersed, about 5-6 phr nano filler loaded rubber composites would provide properties equivalent to that of 40-50 phr carbon black or silica filled composites. However, the major challenge is to disperse the nano filler in polymer matrix. Over the years different techniques were applied to prepare the nanoclay composite with layered silicate structure in the

nano scale dispersion. The different mixing technique commonly used are melt intercalation (LeBaron, 1999; Usuki, 2002), reactive mixing (Liu, 2006), latex coagulation (Zhang, 2000) and solution method (Giannelis,1998). Mousa and Karger-Kocsis (2001) also prepared nanocomposites of SBR and organoclay mixed in two-roll mill. These nanocomposites showed very good tensile strength but supporting evidence like X-ray diffraction or TEM were not provided.

Giannelis and co-workers (1996) have found a way to alter non-reinforcing clay to very effective-reinforcing clay. Studies have been reported on clay reinforcement of emulsion SBR (Wang, 2000; Zhang, 2000; Fu, 2001; Ganter, 2001; Sadhu, 2003), however, the mechanical properties obtained render them unsuitable for practical applications.

Schon *et al.* (2003) prepared rubber compounds based on butadiene rubber (BR) and styrene butadiene rubber (SBR) containing organophilic layered silicates; they reported excellent dispersion of organoclay nano fillers in the rubber matrix by matrix–filler reactive bonding using bis(triethoxysilylpropyl)-tetrasulfan (TESPT).

Das *et al.* (Heinrich, 2008) developed a novel method to prepare nano composite comprising SSBR and organic layer silicate and obtained very good strength. Earlier workers have reported the properties of CB filled rubber vulcanizates. It has been amply demonstrated that the structure, particle size, and functional groups on the surface influence the critical performance properties.

Jia *et al.* (2005) reported a very high reinforcement and stiffening effect of nanoclay in nanoclay-carbon black filled rubber composites having 10, 20, 30 phr of total filler loading. Combined effect of nanoclay and nanoclay-carbon black on properties of natural rubber (NR) nanocomposites was evaluated, it was found that nanocomposites based on NR and nanoclay-carbon black retained advantages from both the fillers.

Meneghetti (2005) studied the effects of carbon black on SBR and on SBR/clay nanocomposites. While carbon black alone (40 phr) offered great improvement in the mechanical properties of the rubber, the synergism of organoclay and carbon black brought similar property enhancements but at half the total filler loading (10 phr each filler).

2.7 FINITE ELEMENT TIRE SIMULATION AND ROLLING RESISTANCE PREDICTION OF TIRE

Lou *et al.* (1978) studied the relationship of tire rolling resistance to the viscoelastic properties of the tread rubber. They have found the rolling resistance force was nearly a linear function of the tread material loss ratio (fractional hysteresis) measured at either constant strain or constant stress. They have calculated loss ratio as the ratio of energy loss (hysteresis) to total energy input obtained from constant crosshead speed loading cycles on an Instron UTM. Good correlation was also observed between rolling resistance force and a viscoelastic index (loss tangent) obtained from sinusoidal strain cycles on a Rheovibron instrument.

Although several factors, including tire-road friction and aerodynamic drag are known to contribute to tire rolling loss, it is generally agreed that hysteresis losses are dominant. Approximately 90% of tire rolling loss is attributed to viscoelastic behaviour of the rubber and cord component for a typical passenger car tire (Willett, 1973; Willett, 1974), of which hysteresis loss of tread rubber alone accounts for ~40% of total tire rolling resistance.

Glaeser (2005) of Federal Highway Research Institute, Germany reports that

1. At a constant speed of 100 km/h a passenger car needs ~50% of its fuel to overcome rolling resistance and the rest of the fuel is used to overcome air drag.

2. At a constant speed of 80 km/h a truck needs ~40% of his fuel to overcome rolling resistance

3. In all driving conditions an average of 25% of the fuel consumption of a passenger car is due to rolling resistance (75% air drag and acceleration)

4. Energy efficient tires having 20% less rolling resistance in comparison to conventional tires reduces the fuel consumption of a car by ~5%

Although the above mentioned figures are very impressive but much more needs to be attained. The challenge for further reduction of rolling resistance of tire from the present level are (a)

development of low hysteresis tread compound, (b) low weight optimized tire design and (c) prediction of the tire rolling resistance in the design stage. The recent development of rubber nanocomposites offers the opportunity to reduce hysteresis loss further and this could be used to develop low rolling resistance tire.

Measurement of tire rolling resistance using either a pulley wheel or flat track tire testing machine is time consuming as well as expensive because it requires a test tire to be prepared, hence to speed up the development process and to reduce testing costs, prediction of tire rolling resistance using simulation techniques has received considerable importance (Kobayashi, 1987; Warholic, 1987; Luchini, 1994; Park, 1997).

The method for the evaluation of energy dissipation in a tire using finite element analysis to prediction rolling resistance has been studied by many investigators. Kobayashi *et al.* (1987) evaluated the energy dissipation using the product of elastic strain energy obtained from structural simulation and the loss tangent of materials. Using finite element simulation Nakajima (1966) and Abe (1996) showed that tire structure and compound properties could be optimized to reduce rolling resistance.

Shida *et al.* have used a static finite element method for tire rolling resistance simulation (Shida 1999). The method implements a static deflection analysis first and the stress and strain thus obtained, together with the loss factors of the materials determined separately, are used to estimate the energy dissipation of a rolling tire. The loss factors of the rubber materials are experimentally obtained and the effective loss tangents of the fiber-reinforced rubber are determined by the homogenization theory of dynamic viscoelasticity. The rolling resistance simulation of a passenger car radial tire using this approach accurately captures the trends of an actual tire.

Ebbott *et al.* (1999) used a finite element-based method to predict tire rolling resistance and temperature distributions. The particular attention was given to the material properties and constitutive modeling as these have a significant effect on the predictions. A coupled thermo-mechanical method is described where both the stiffness and the loss properties are updated as a function of strain, temperature, and frequency. The simulation results for rolling resistance and steady state temperature distribution were compared with experiments for passenger and radial medium truck tires.

Pillai and Fielding-Russell (1992) proposed a simple predictive equation for tire rolling resistance that involves the concept of whole tire hysteresis ratio. Rubber is a highly non-linear viscoelastic material however; this method uses linear viscoelastic properties defined by Prony series.

Most of the above methods used non linear static simulation but uses linear viscoelastic approach for energy dissipation calculation to predict rolling resistance. However, rubbers are a highly non-linear viscoelastic material and hence require non linear viscoelastic simulation. The viscoelastic simulation implemented in ABAQUS uses linear viscoelastic properties defined by Prony series (Abaqus, Example Problem manual, Version 6.7, Vol II and III). A software program is required to capture non linear viscoelastic characteristics of rubber from non linear viscoelastic material properties to evaluate energy dissipation for rolling resistance prediction.

2.8 SCOPE OF THE WORK

Although considerable amount of work has been done on SBR-clay and BR-clay nanocomposites but there is almost a total lack of literature on SBR/BR-clay nanocomposite. In the tire industry, SBR/BR blend is of considerable importance as it is widely used in passenger car tire tread compound. Hence, investigation of nanocomposite based on SBR/BR blends and organoclay would not only be interesting but also have wide applications.

Clay dispersion in SBR rubber is very difficult and when dispersed it still does not show much improvement in modulus, tensile strength, elongation at break, tear strength and tear and breaking energy. Uses of compatibilizer in SBR rubber has shown better clay dispersion and correspondingly improvement in mechanical properties compared to nanocomposite not using compatibilizer. Thus it is necessary important to study the effect of compatibilizer having different polarity on clay dispersion, mechanical properties and nanocomposite morphology.

CHAPTER 2: LITERATURE SURVEY

Different mixing techniques have been used by different researchers to prepare nanocomposite but comparison of the different mixing techniques with respect to clay dispersion and subsequent properties of nanocomposites is not reported in the literature this aspect also needs to be addressed.

Literature is available on clay dosages in different rubbers such as NR, SBR, BR, NBR, etc. but optimum dosages for SBR/BR was not found. To achieve the appropriate clay dispersion and nanocomposite properties, study on dosages of clay as well as compatibilizer is required and the optimum loading of clay and compatibilizer needs to be identified.

Hence the investigation on the effect of carrier polymer, mixing techniques, dosages of compatibilizer and organoclay in SBR/BR blends has immense importance for the development of nanocomposite for tread compounds that would result in desirable properties with low hysteresis losses.

Literature survey shows that some papers are available where nanocomposites were projected for tire tread application but properties reported are far from actual requirement. They have only focused on tensile strength and elongation at break of nanocomposite but for tire tread application the most important properties are hardness, low strain modulus, tear strength and abrasion resistance, wet grip and rolling resistance.

In the existing literature there is no report on rubber clay nanocomposite that can meet the properties required for tread application. Some literature was obtained where carbon black was introduced in SBR/clay nanocomposite and found synergistic effect but not aimed for any specific application.

In this investigatation, dual filler system comprising of organic layer silicate (organoclay) and conventional filler like carbon black or silica is introduced to prepare the nanocomposites based on SBR/BR blend. The three different SBR rubbers ESBR, SSBR and F-SSBR are incorporated in this study for comparison purposes. The objective of this investigation was to improve the

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performance properties e.g. hardness, low strain modulus, tear strength, viscoelastic properties and abrasion resistance of the nanocomposites and, simultaneously, to minimize the hysteresis loss (rolling resistance).

Although, there exists a fair amount of literature on NR and BR and clay nanocomposite, but there is no literature on NR/BR blend and clay nanocomposite. For many practical applications NR/BR blends are used and especially in the automotive tire, NR/BR blends are used in truck bus radial tread and sidewall compounds. Therefore it is quite interesting and appropriate to investigate nanocomposite based on NR/BR blend and clay and the effect of carrier polymer, mixing technique, filler dosages etc.

Literature survey revealed that most of the works on NR nanocomposite were with nanoclay. Some investigators reported use of carbon black with clay to prepare nanocomposite. These nanocomposites were projected for tread application but the properties reported were far from the specified critical performance properties for tread applications.

In this investigation a dual filler system comprising of organoclay and conventional filler like carbon black or silica, was investigated to prepare the nanocomposite based on NR/BR blend. The aim of this investigation was to achieve performance properties e.g. hardness, low strain modulus, tear strength and abrasion resistance of nanocomposite that are comparable to commercial tread compound whereas to minimize the hysteresis loss (rolling resistance).

Development of low hysteresis PCR and TBR tread compounds based on nanocomposites and prediction of rolling resistance in tire would not only be highly interesting but also very much useful to improve fuel efficiency and thereby reduce the CO_2 emission. In this investigation, passenger car radial (PCR) and truck bus radial (TBR) tread compounds based on different nanocomposites were studied for rolling resistance and compared with respective standard tread compounds using simulation technique.

CHAPTER 2: LITERATURE SURVEY

A steady state rolling resistance simulation was done and the strain energy and principal strains were extracted from the result file using an internal developed program (Rolling resistance code). Energy dissipation was evaluated using the product of elastic strain energy and the loss tangent of materials through post processing using Rolling resistance code (RR code). The post processing approach was adopted. The non-linear viscoelastic behavior was incorporated by providing strain and temperature dependent dynamic viscoelastic properties of rubber.

The work address the primary objective of development of nanocomposites that can match the prevalent tire tread compounds in term of physical properties while returning much lower rolling resistance without sacrificing other requirements viz. Wet traction, Dry traction, Wear, etc.

It also addresses the secondary objective of prediction of rolling resistance during the design stage through finite element simulation.