CHAPTER 3

MATERIALS AND METHODS

This Chapter describes materials, experimental methods and analytical techniques used in this investigation.

3.0 RAW MATERIALS

3.1.1 Raw material description

The rubbers, fillers and other compounding materials used in this investigation are presented in this section which includes brief material descriptions, grade, supplier and technical specification data of raw materials. Detailed information is presented in subsequent sections.

Table 3.1-Raw material summary

MATERIALS	GRADE	SUPPLIER	TECHNICAL DETAILS
Natural Rubber, (NR)	SMR 20	Hock Hin, Malaysia	Mooney viscosity (MV): 87
Emulsion styrene butadiene rubber (E-SBR)	SBR1502	Kumho Petrochemical, South Korea.	23.5% styrene; MV: 50
Solution styrene butadiene rubber (S-SBR)	Buna VSL 5025-0 HM	Lanxess A.G, Germany	25% styrene; 50% Vinyl, MV: 70
Functionalized SSBR (FS-SBR)	Nipol NS 116R	Zeon Corporation, Japan	MV: 45; 21% Styrene, 50% Vinyl; Sn coupled, chain end modified,
Polybutadiene rubber, BR	Cisamer 1220	Reliance Industries Ltd (IPCL), India	MV: 44; Cis content: 96%
Carboxylated nitrile rubber (XNBR)	Chemigum. XNBR146 and 750	Eliokem India Pvt. Ltd.	Carboxylation 1 and 7%;
Organoclay	Cloisite®15A	Southern clay products, Inc, USA	Montmorillonite (MMT) modified with a quaternary ammonium salt. Basal spacing of this organoclay is reported to be 3.15 nm.
Highly Dispersable Silica; Amorphous Precipitated Silica (10 SiO2, 1 H2O)	Ultrasil®7000GR	Evonic Degussa A.G, Germany	N_2 Surface Area (BET)-170 m^2/g; DBP (structure): 198

Table 3.1-Raw material summary (contd.)

MATERIALS	GRADE	SUPPLIER	TECHNICAL DETAILS
Silane coupling agent, Bis(triethoxysilylpropyl)-tetrasulfan	Si 69 (TESPT)	Evonic Degussa A.G, Germany	100% liquid silane, Sulfur content 22.5%
Silane coupling agent	X-50S	Evonic Degussa A.G, Germany	%50 TESPT and 50% Carbon black.
Carbon Black	ISAF, N220	PCBL, India	N_2 Surface Area (BET):121 m^2/g DBP No.:114
N-(1,3-dimethyl-butyl)-N'-phenyl-P-Phenylenediamine	6PPD	NOCIL, India	Molecular wt.: 268; M.P : 48-51°C
N-Tertiarybutyl-2-benzothiazole-sulfenamide	TBBS	NOCIL, India	Molecular wt.: 238 ; M.P : 104°C
Diphenyl guanidine	DPG	Hindustan Chemicals, India	Molecular wt.: 211; M.P : 142°C
Zinc Oxide	ZnO	Upper, India	Density: 5.6 g/cc ZnO content: 99%
Stearic acid	Fatty acid (C18)	Palm Oleo, Malaysia	Solidification point 50-60 °C
Soluble Sulfur	Rhombic Sulfur (S_8)	Solar, India	Total Sulfur 99%

3.1.2 Natural Rubber (NR)

Natural rubber is one of nature's unique materials. Crude rubber is primarily hydrocarbon in nature. In 1826 English chemist Michael Faraday (1791–1867) analyzed natural rubber and found it to have the empirical formula C5H8, along with 2 to 4 percent protein and 1 to 4 percent acetone-soluble materials (resins, fatty acids, and sterols). Samuel Shrowder Pickles (1878–1962) proposed in 1910 that rubber is a linear polymer of isoprene. Natural rubber is produced commercially from the latex of *Hevea Brasiliensis*.

The natural rubber consists of Cis-1,4-Polyisoprene molecules and the molecular weights of rubber molecules range from 50,000 to 3,000,000. The latex has approximately the following composition (%): Water 55-70, Rubber 30-40, Resins 1.5-2, Protein1.5-3, Ash, 0.5-1, Sugar 1-2. The It is far more common to filter the harvested latex, dilute it with water and then to cause it to coagulate using substances such as acetic acid or formic acid or by means of electrophoresis.

The chemical structure of NR is shown in Fig. 3.1. The natural rubber trees and tapping and latex collection are shown in Fig. 3.2.

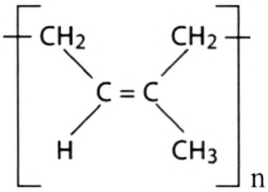


Fig. 3.1- Chemical structure of NR

Fig. 3.2- *Heavea Brasiliensis* tree and tapping

Standard international grades of NR;

- Sheets Rubber - Ribbed Smoked Sheet (RSS)
- Block rubber, Technically Specified Rubber (TSR)
- Latex Concentration
- Crepes rubber - Estate Brown Crepe (EBC)

In this investigation, SMR 20 (Standard Malaysian Rubber 20) was used. It was received from M/s Hock Hin (HR), Malaysia and its specification is shown in Table 3.2.

Table 3.2-Technical specifications of SMR 20

Parameters	***Values***
Dirt (max) %wt	0.20
Nitrogen (max) % wt	0.60
Mooney viscosity (ML, 1+4, 100°C), MU	80±7

3.1.3 Emulsion styrene butadiene rubber (ESBR)

Styrene butadiene rubber (SBR) is a synthetic rubber copolymer consisting of styrene and butadiene. It was originally developed prior to World War II in Germany. It has good abrasion resistance and good aging stability when protected by additives, and is widely used in car tire where it may be blended with natural rubber and polybutadiene rubber. SBR can be produced by two basically different processes; (a) from solution or (b) as emulsion. SBR–1502 used in this investigation is a cold polymerized by emulsion method. It is a high molecular weight styrene butadiene rubber combining good extrusion behavior and superior compound properties. It has relatively wide molecular weight distribution and the butadiene component has an average about 9% Cis-1,4, 54.5% trans and 13% 1,2 vinyl structure.

The chemical structure of SBR 1502 is shown in Fig.3.3.

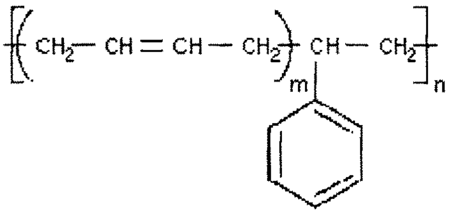


Fig. 3.3- Chemical structure of SBR

The rubber samples were received from M/s. Kumho Petrochemical, South Korea. The technical specification of SBR1502 is presented in Table 3.3.

Table 3.3-Technical specification of SBR 1502

Parameters	***Values***
Mooney viscosity (ML 1+4 AT 100°C	50 +/- 6
Antioxidant (wt %)	1.00 - 1.40
Specific gravity	0,92
Bound styrene (wt %)	22.5 - 24.5
Free organic acids (wt %)	5.00 - 6.50

3.1.4 Solution styrene butadiene rubber (SSBR)

Solution polymerized styrene-butadiene rubber (S-SBR) is an elastomer synthesized from styrene and butadiene via anionic random copolymerization process. S-SBR is mainly used in automobile tire with characteristics of energy saving and high wet skid resistance. The solution SSBR BUNA VSL 5025-0 HM was received from Lanxess, Germany and the detail technical specifications and microstructure are specified in Table 3.4 and 3.5.

Table 3.4-Technical specification of SSBR BUNA VSL 5025-0

Parameters	***Values***
Mooney viscosity (ML 1+4 AT 100°C	70 +/- 4
Bound styrene (wt %)	25 - 27
Polydispersity Index, Mw/Mn	2.64
Specific gravity	0.92

Table 3.5-Microstructure and macrostructure of S-SBR

S-SBR	Styrene,%	1.2 butadiene,%	1.4 butadiene, %	Tg, °C
BUNA VSL 5025-0	25	50	25	-13.2

3.1.5 Functionalized solution SBR (FSSBR)

Functionalized S-SBR is synthesized via anionic living polymerization process from styrene and butadiene in low carbon aliphatic hydrocarbon and/or naphthenic hydrocarbon in the presence of organic lithium compound as initiator. Functionalized S-SBR is mainly used in automobile tire with characteristics of energy saving and high wet skid resistance.

Nipol NS 116R of Zeon Corporation, Japan is a functionalized solution styrene butadiene rubber (FSSBR) with Sn coupled and chain ends modified COOH-groups was used in this investigation. The Sn coupling and chain end modification enhanced adhesion between the polymer chain and the silica. The details technical specification are provided in Table-3.6

Table 3.6-Technical specification of functionalized SSBR

Parameters	***Values***
Mooney viscosity (ML 1+4 AT 100°C	45.0
Vinyl Content (wt%)	50.0
Bound styrene (wt %)	21.0

3.1.6 Polybutadiene rubber (BR)

Polybutadiene (BR) is the second largest volume synthetic rubber produced, next to styrene-butadiene rubber (SBR). Consumption was about 1,953,000 metric tons worldwide in 1999. The major use of BR is in tires with over 70% of the polymer produced going into treads and sidewalls. Cured BR imparts excellent abrasion resistance (good tread wear), and low rolling resistance (good fuel economy) due to its low glass transition temperature (T_g <–90°C).

Butadiene rubbers are produced by the solution polymerization process of monomer 1,3-butadiene with the aid of organometallic catalysts such as neodymium, cobalt, lithium or titanium based which influences the microstructure and macrostructure of the polymers and therefore its properties.

The macrostructure of Co-BR is distinguished by a moderately broad molecular weight distribution and medium degree of branching. The micro and macrostructure of Co BR is shown in Table 3.7 and Fig. 3.4. The Co-BR (Cisamer 1220) used in this study was received from Reliance Industries Limited, India and its technical specification are provided in Table 3.8.

Table 3.7-Polybutadiene rubber – micro and macrostructures

Catalyst	**cis 1,4**	**trans 1,4**	**vinyl 1,2**	**Tg (DSC)**
Co	96	2	2	-107

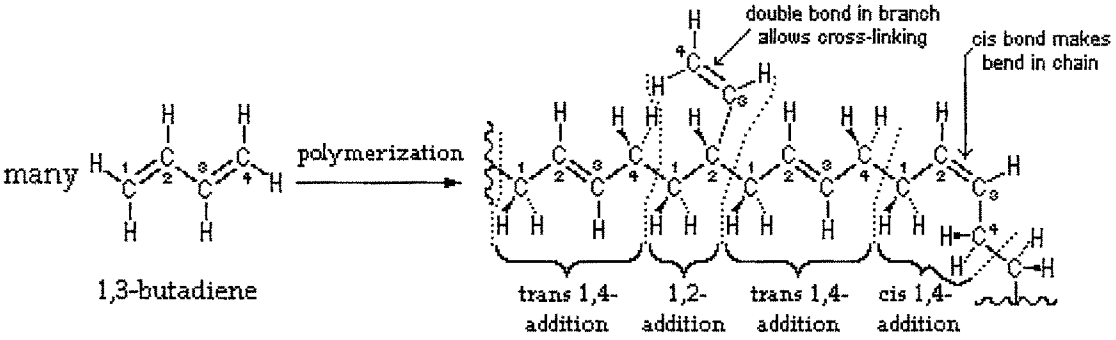


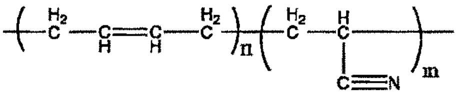
Fig. 3.4-Micro and macrostructure of BR

Table 3.8-Technical specification of BR

Parameters	***Values***
1,4-Cis content, %	96.0
Specific gravity	0.91
Mooney viscosity (ML 1+4 at 100°C)	44.0

3.1.7 Nitrile rubber (NBR) and carboxylated NBR (XNBR)

Nitrile butadiene rubber (NBR) is a family of unsaturated copolymers of 2-propenenitrile and various butadiene monomers (1,2-butadiene and 1,3-butadiene). Although its physical and chemical properties vary depending on the polymer's composition of nitrile, this form of synthetic rubber is generally resistant to oil, fuel, and other chemicals (the more nitrile within the polymer, the higher the resistance to oils but the lower the flexibility of the material). The chemical structure of Nitrile rubber is shown in Fig.3.5.



$$\left(\overset{H_2}{C}-\underset{H}{C}=\underset{H}{C}-\overset{H_2}{C}\right)_n\left(\overset{H_2}{C}-\overset{H}{\underset{C\equiv N}{C}}\right)_m$$

Fig. 3.5- Chemical structure of NBR

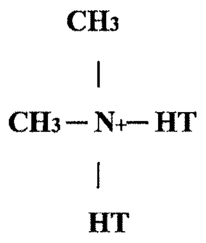
Chemigum® NX146 and NX 750 is a cold polymerized, medium ACN terpolymer based on acrylonitrile, butadiene and carboxylic acid, and emulsified with synthetic soap(s). The technical specifications are shown in Table 3.9.

Table 3.9-Technical specification of NBR/XNBR

	XNBR-0 (NBR)	XNBR-1	XNBR-7
Bound Acrylonitrile, %	32.0	33	32.5
Carboxylation, %	0	1.0	7.0
MV, ML (1+4) at 100°C	51.0	47.0	52.0
Specific gravity	0.99	0.98	0.98

3.1.8 Organoclay (Cloisite®15A)

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. The chemical structure of quaternary ammonium salt used to modify nanoclay is shown in Fig. 3.6. The typical properties of Cloisite® 15A is given in Table 3.10.



$$\begin{array}{c} CH_3 \\ | \\ CH_3-N^{+}-HT \\ | \\ HT \end{array}$$

Fig. 3.6- Chemical structure of organoclay

The organic modifier 2M2HT is dimethyl, dihydrogenatedtallow, quaternary ammonium; where HT is Hydrogenated Tallow (~65% C18; ~30% C16; ~5% C14) and anion is chloride.

Table 3.10-treatment/properties of clay

	Organic Modifier (1)	Modifier Concentration	% Moisture	% Weight Loss on Ignition
Cloisite® 15A	2M2HT	125 meq/100g clay	< 2%	43%

Table 3.11-Typical dry particle sizes: (microns, by volume)

10% less than:	50% less than:	90% less than:
2μm	6μm	13μm

3.1.9 Carbon black (ISAF-N220)

Carbon black is a material produced by the incomplete combustion of heavy petroleum products such as FCC tar, coal tar, ethylene cracking, and a small amount from vegetable oil. Carbon black is a form of amorphous carbon that has high surface-area-to-volume ratio. Carbon black is used as a pigment and reinforcement in rubber and plastic products. The most common use (70%) of carbon black is as a pigment and reinforcing phase in automobile tires. Carbon black also helps conduct heat away from the tread and belt area of the tire, reducing thermal damage and increasing tire life.

Carbon black is a reinforcing filler and imparts reinforcing strength properties to rubber in a similar way an iron rod embedded in a cement matrix provides strength to the concrete. The carbon black produced through the furnace process has a small granular form and is easily incorporated and dispersed in a rubber matrix. The carbon black ISAF (N220) used in the investigation was received from M/s. Phillips Carbon Black Ltd., India and properties are presented in Table 3.12.

Table 3.12-Grades and properties of Carbon Black

Parameters	**Values**
Name /ASTM No.	ISAF (N220)
Iodine Adsorption (mg/g)	121.0
CTAB Surface Area (m^2/g)	111.0
BET, N_2SA (m^2/g)	119.0
DBP Absorption	114.0
Compressed DBP (ml/100g)	100.0
Tint (%ITRB)	115.0

3.1.10 Highly dispersible silica (HDS)

Silica or silicon dioxide (SiO2) in its pure form is colorless to white. Highly dispersible Silica's (HDS) are precipitated synthetic amorphous silica obtained from a process essentially using sand, which is the most abundant mineral present in the earth's crust. Precipitated silica is used as reinforcement filler in the rubber industry.

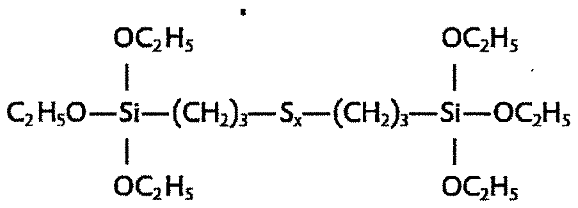
ULTRASIL® 7000 GR from Evonic Industries is highly reinforcing silica which was especially developed for application in low rolling resistant passenger car tire tread compounds, so called "Green Tire". HD silica in combination with bifunctional silanes imparts to tread compounds high abrasion resistance combined with excellent rolling resistance and wet traction. The technical specification of Ultasil® 7000GR is shown in Table 3.13

Table 3.13-Physico-chemical properties of ULTRASIL 7000GR

Parameters	**Units**	**Values**
Density	g/cm^3	2.1
Specific surface area (N_2)	m^2 / g	170
DBP Absorption	Nos.	198
Heating loss	%	5.2

3.1.11 Silane coupling agent

Si 69® is a bifunctional, sulfur-containing organosilane used in the rubber industry in combination with white fillers that carry silanol groups and this is a treade name of Evonic Industries. Si 69® reacts with fillers containing silanol groups during mixing and with the polymer during the vulcanization process with formation of covalent chemical bonds. This imparts better tensile strength, higher modus, reduced compression set, increased abrasion resistance and optimized dynamic properties. It is widely used in low rolling resistance tires tread production with silica filler and solution SBR. The chemical structure is presented in Fig. 3.7 and physico-chemical properties are given in Table 3.14.



Bis(triethoxysilylpropyl) polysulfide, $\bar{x} = 3.70$

Fig. 3.7- Chemical structure of Si 69®

Table 3.14-Physico-chemical properties of Si 69®

Parameters	**unit**	**values**
Density	g/cm^3	1.10
Average molecular weight	g / mol	532
Sulfur content	%	22.5
Average Sulfur chain length, HPLC		3.70

3.1.12 Antidegradant

The most widely used antidegradant in the rubber industry is 6PPD that has a generic name N-(1, 3-dimethylbutyl)-N'-phenyl-p-phenylenediamine. It's chemical structure is given below:

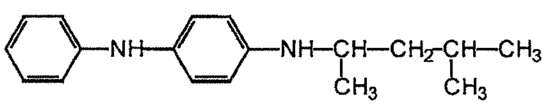


Fig 3.8- Chemical structure of 6PPD

6PPD acts as strong anti-ozonant as well as antioxidant. Technical specification of 6PPD is shown in Table 3.15.

Table 3.15- Properties of 6PPD

Parameters	**Values**
Molecular Weight	268
Melting Point (Final), °C	48-51
Specific Gravity @ 60°C	0.986-1.00

Pilflex® 13 is trade name of 6PPP of NOCIL India Ltd. 6PPD offers excellent resistance to rubber vulcanizates against degradative factors such as ozone (static and dynamic), flex cracking and fatigue, oxidative heat aging, metal-ion catalyzed oxidative aging, UV light and weathering. Pilflex® 13 is the most suitable PPD antidegradant for NR, NR-BR, SBR, SBR-BR and NBR based compounds.

3.1.13 Sulfenamide accelerator (TBBS)

TBBS (N-tert-butyl-2-benzothiazolesulfenamide) is a ultra fast delayed action sulfenamide accelerator for NR, SBR, BR, NBR and other sulfur cured diene rubbers. TBBS exhibits very good storage stability as compared to other sulfeamide accelerators. TBBS pellets disperse easily in rubber. The normal dosage of TBBS is in the range of 0.5-1.5. For TBBS normal dosages of zinc oxide and stearic acid are necessary for cure activation.

TBBS alone or in combination with secondary accelerators is widely used in NR, SBR, NR-SBR/BR blend, SBR/BR blend, NBR and other synthetic rubber based compounds for the manufacture of auto tires, NR-auto tubes, tire retreading materials and Molded and Extruded rubber products. Technical specification of TBBS is shown in Table 3.16 and chemical structure in Fig. 3.9.

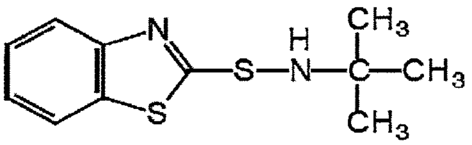


Fig. 3.9- Chemical structure of TBBS

Table 3.16-Properties of TBBS

Parameters	Values
Molecular Weight	238
Assay (Titration), % (min)	96.0
Melting Point (Initial), °C (min)	104
Specific Gravity @ 25°C	1.280

3.1.14 Diphenyl guanidine (DPG)

Guanidine, is called carbamidine. Diphenylguanidine is one of common accelerators for the vulcanization of rubber in combination with thiazoles and sulfenamides. Though it does not show better activity than thiuram and dithiocarbamates, it has better stability. It is used as a complexing agent for the detection of metals and organic bases.

DPG can be used for NR, IR, SBR, NBR and CR. Very useful basic accelerator that can be used in combination with acidic accelerators, it is very seldom used alone. It can be used as secondary accelerator with thiazoles and sulphenamides in NR and SBR compounds, giving good physical properties.

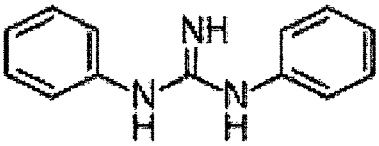


Fig. 3.10- Chemical structure of 1, 3-Diphenylguanidine (DPG)

Table 3.17-Properties of DPG

Parameters	**Values**
Product Name	1, 3-Diphenylguanidine
Molecular Formula	C13H13N3
Molecular Weight	211.26
Initial melting point °C	142

3.1.15 Rhombic sulfur

Sulfur is the chemical element with atomic number 16, represented by the symbol S. It is an abundant, multivalent non-metal. At normal conditions, sulfur atoms form cyclic octatomic molecules with chemical formula S_8. Elemental sulfur is a bright yellow crystalline solid. Chemically, sulfur can react as either an oxidant or reducing agent. Amorphous or "plastic" sulfur is produced by rapid cooling of molten sulfur—for example, by pouring it into cold water.

X-ray crystallography studies show that the amorphous form may have a helical structure with eight atoms per turn.

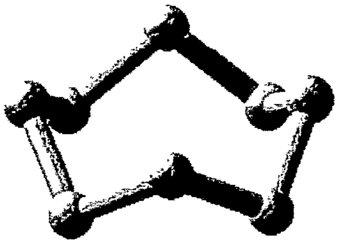


Fig. 3.11- Chemical structure of rhombic Sulfur (S_8)

Table 3.18-Technical specifications of rhombic sulfur

Parameters	**Values**
Name, symbol, number	Sulfur, S, 16
Density at 25.0°C	2.07 $g{\cdot}cm^{-3}$
Total sulfur content	99%
Melting point	115.2 °C

3.1.16 Zinc oxide

Zinc Oxide is used as activator in rubber compounds. Zinc Oxide is manufactured using a physical vapour synthesis process. In this process, zinc metal is vaporized. This vapour is rapidly cooled in the presence of oxygen, causing nucleation and condensation of nano crystalline zinc oxide particles. The particles are non-porous and their surfaces are free of residual chemical contaminants. The TEM images of Zinc oxide particle size and morphology are shown in Fig. 3.12 and 3.13 respectively.

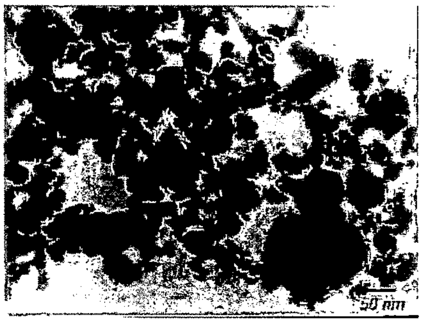


Fig. 3.12- Particle size distribution

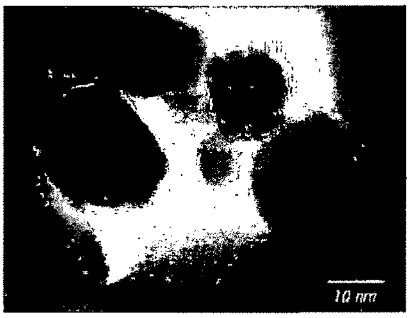


Fig. 3.13- Particle morphology

During the process, the particles form weak agglomerates up to tens of microns in size. These agglomerates can be reduced with suitable dispersion techniques, providing a typical particle size distribution ranging from a few nano meters to a few hundred nano meters. The technical specification of rubber grade Zinc oxide is presented in Table 3.19.

Table 3.19-Technical specifications of zinc oxide

Parameters	**Value**
ZnO content	99.0 %
Density	5.6 g/cm^3 at 25°C
Nitrogen surface area (BET)	4.0 m^2/g

3.1.17 Stearic acid

Stearic acid is a saturated fatty acid with 18 carbon chain and has the IUPAC name octadecanoic acid. It is a waxy solid, and its chemical formula is $C_{18}H_{36}O_2$, or $CH_3(CH_2)_{16}COOH$. The chemical structure is shown in Fig. 3.14.

Table 3.20-Technical specifications of stearic acid

Parameters	**Values**
Chemical composition	Mixture of predominantly saturated fatty acids
Solidification point	50.0 - 60
Fatty acid fractions, C16-C20)	90.0 % min
Acid number	195.0 mg KOH/g

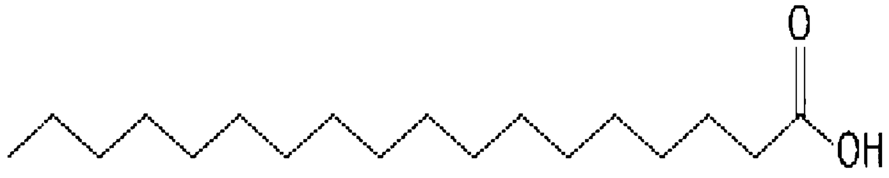


Fig. 3.14- Chemical structure of stearic acid

3.2 MIXING AND PREPARATION OF NANOCOMPOSITES

3.2.1 Mixing equipments

The mixing equipment used in the investigations to prepare nanocomposite and rubber compounds are described below.

(a) Brabender Plasticorder

Brabender Plasticorder PL 2000E was used to mix rubber-clay master batch. It has 70 cc chambers for mixing and was heated with oil. It has variable rotor speed and temperature. A load is applied on the ram to apply pressure during mixing.

(b) Laboratory Banbury

This has capacity of 3.2 liters. It has four wing rotors with variable speed from 0 to 150 rpm. It has temperature control unit (TCU) temperature range 40 to 80^{o}C. It has timer and temperature controller to record mixing time and temperature and release batches as per set points. The Banbury had PLC control and had software that provided important information on mixing like batch temperature, mixing time, power and total input energy.

(C) Two roll Mill

This the oldest rubber mixing equipment and even today is widely used in the laboratory as well small scale industry. It has two rolls rotating in the opposite direction with different speed so that in-between rolls, a shear force is generated which helps to masticate rubber and subsequently incorporates ingredients into rubber to make compound.

The friction ratio varies from 1.1 to 1.3 and the back roll moves faster than front roll. The rolls have inside core through which cold water or steam can pass for cooling or heating. Both the rolls have same dimension, 6'' diameter and 13'' length. The rubber band is formed in the front roll where the mixing takes place.

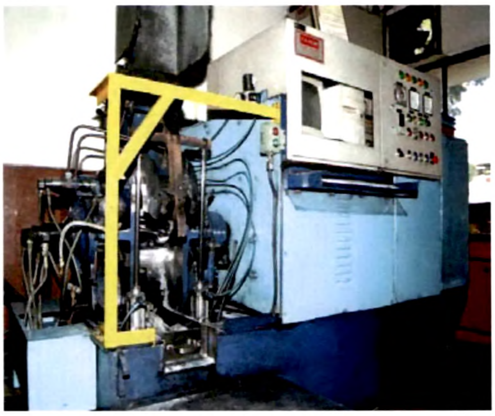


Fig. 3.15- Laboratory Banbury

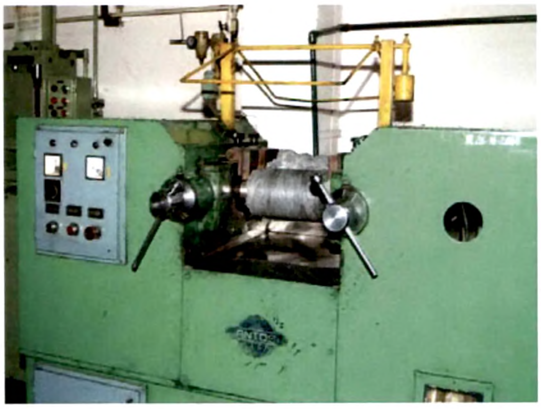


Fig. 3.16- Two rolls mill.

3.2.2 Preparation of organoclay-XNBR master batch

Three different mixing techniques were employed to prepare Organoclay and XNBR (carboxylated nitrile rubber) master batches;

1. **Two-roll mixing:** In this technique, a uniform band of XNBR was made and filler was incorporated. The mixing was carried out for 10 minutes.
2. **Solution mixing:** XNBR was dissolved in an equi-volume solution of MEK and Toluene and kept for 24 hours. Organoclay was mixed in ethanol and gradually poured into the rubber solution with constant stirring for 4 hours. The solvent was removed by air drying and finally by drying in a vacuum oven at $60^{o}C$ for 8 hours.
3. **Internal mixer:** In this process the master batch was prepared in an internal mixer (Brabender Plasticorder PL2000E, Brabender A.G, Germany) at $160^{0}C$ with rotor speed of 50 rpm for mixing time of 10 minutes.

3.2.3 Preparation of SBR/BR and NR/BR-organoclay nanocomposites

Rubber nanocomposites were prepared in a two-step method;

Step I: Preparation of clay-XNBR master batch.

Step II: Mixing of the master batch prepared in step-I with SBR/BR or NR/BR blends in a two-roll mixing mill and then all other ingredients such as zinc oxide, stearic acid, 6PPD, Sulfur, TBBS and DPG were added and mixed thoroughly.

3.2.4 Preparation on SBR/BR and NR/BR-dual fillers nanocomposites

The dual filler rubber nanocomposites were prepared in three steps;

Step A: Preparation of clay-XNBR (7%) master batch in internal mixer.

Step B: Preparation of SBR/BR and NR/BR master batches with carbon black or silica-silane in a laboratory Banbury mixer at 40 rpm for 6 minutes and dumped at 150°C.

Step C: Master batches prepared in Step A and B were mixed in a two roll mixing mill and, subsequently, all additives such as zinc oxide, stearic acid, antioxidant (6PPD), Sulfur and accelerators (TBBS and DPG) were added and mixed thoroughly.

3.3 EXPERIMENTAL DESIGN

3.3.1 SBR/BR-organoclay nanocomposites

The entire experimental investigation was conducted in four different stages as shown in schematic diagram (Fig. 3.17).

Stage-I: Effect of carboxyl group % in carrier polymer

The effect of carboxyl group % in carrier polymer (XNBR) on clay dispersion and properties of nanocomposite based on FS-SBR/BR and organoclay were investigated. The dosages of carrier polymer and organoclay were 10 and 6 phr respectively and the carboxyl group in XNBR was varied from 0 to 7%. In this case the master batch used was prepared by internal mixing process.

Stage-II: Influence of different mixing techniques

The influence of different mixing techniques like 2-roll mixing, solution mixing and internal mixing method used for the preparation of nanocomposite was investigated. The dosages of carrier polymer (7% Carboxylated nitrile rubber; XNBR-7) and organoclay were 10 and 6 phr respectively in FSSBR/BR and organoclay nanocomposite.

Stage-III: Types of SBR rubber

The mechanical and viscoelastic properties of different type of SBR (ESBR, SSBR and FSSBR)/BR based nanocomposites were evaluated. XRD and TEM characterization of some selected nanocomposites were also done. The dosages of carrier polymer (XNBR-7) and organoclay were kept 10 and 6 phr respectively.

Stage-IV: Dosage optimization of Clay and XNBR

The dosage optimization of carrier polymer (XNBR-7) and organoclay in ESBR-clay nanocomposite was carried out. Clay dosages varied from 3.8 to 9.8 phr where as XNBR dosages were from 6.3 to 13.8 phr.

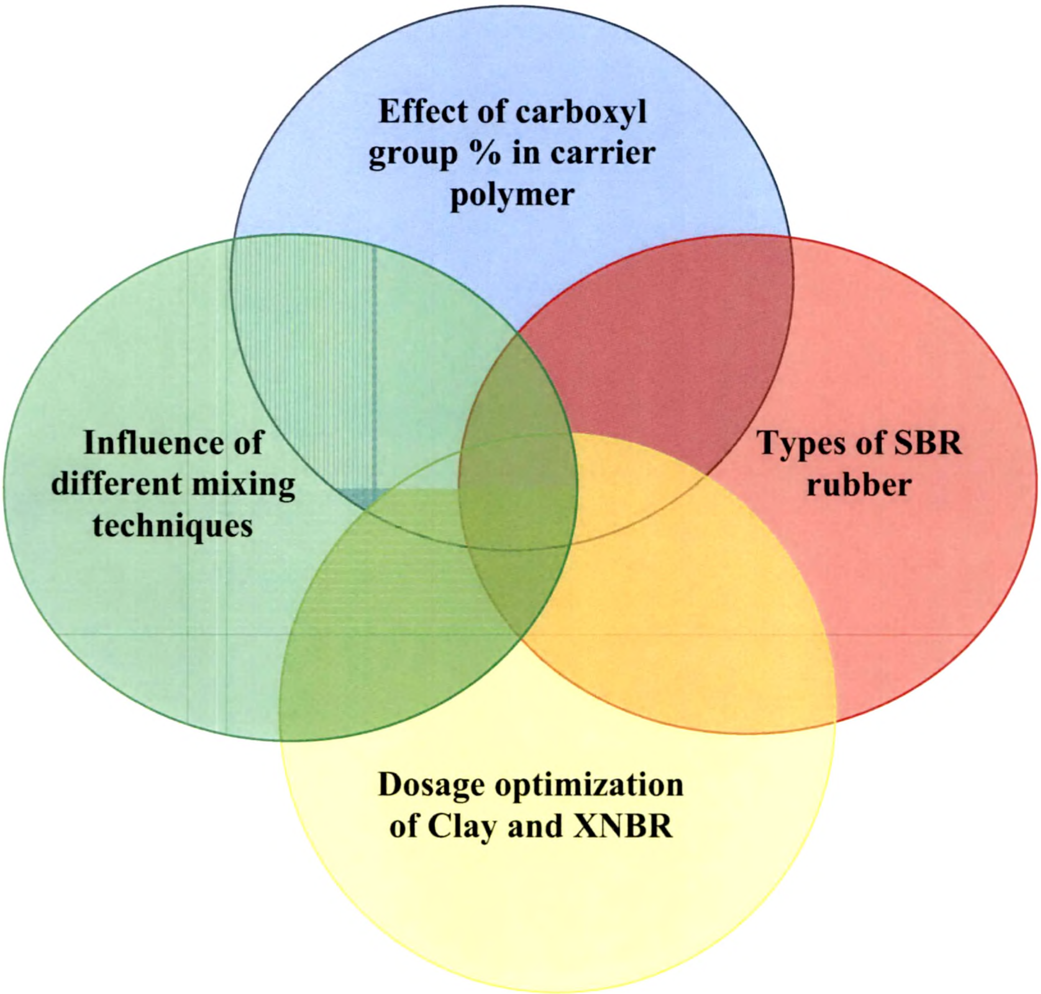


Fig. 3.17- Schematic diagram of experimental design of SBR/BR and clay nanocomposite

3.3.2 NR/BR - organoclay nanocomposites

The entire investigation was conducted in three parts as shown in schematic diagram (Fig. 3.18).

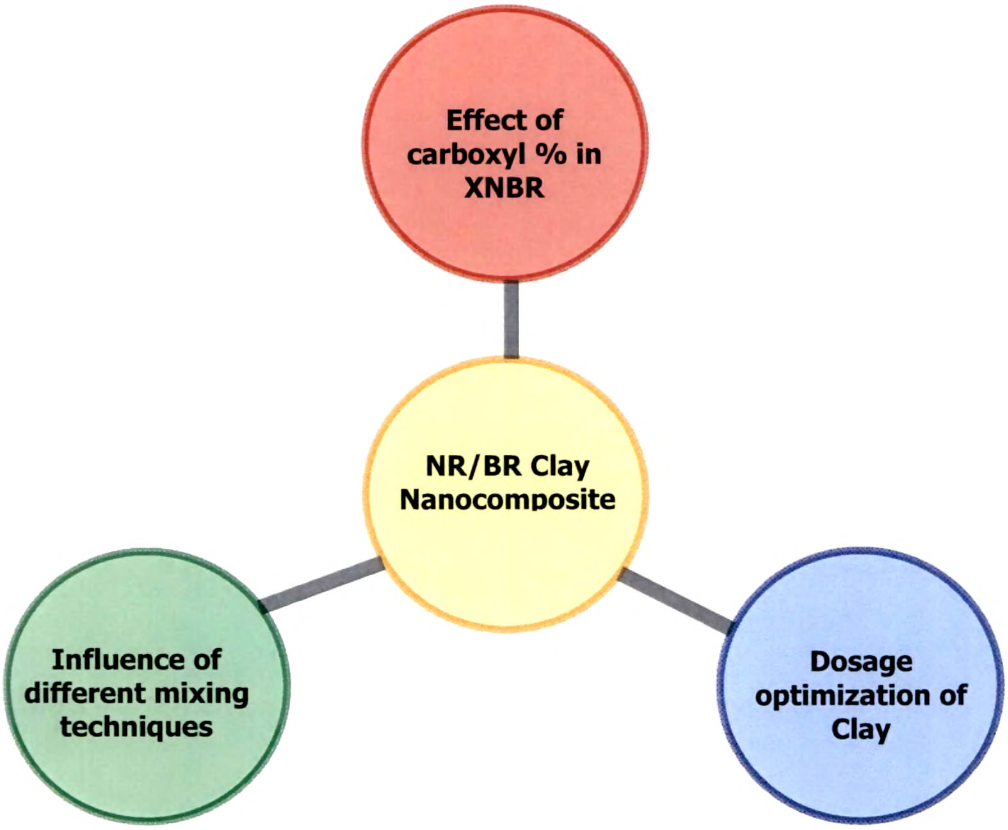


Fig. 3.18- Schematic diagram of experimental design of "NR/BR and clay" nanocomposite

Part I: Effect of carboxyl % in XNBR

The effect of carboxyl group % of carrier polymer on clay dispersion and properties nanocomposite based on NR/BR and organoclay were investigated. The dosages of carrier polymer and organoclay were 10 and 7 phr respectively and the carboxyl group in XNBR was varied from 1 to 7%. In this case the master batch used was prepared by internal mixing process.

Part-II: Influence of different mixing techniques

The influence of different mixing techniques like 2-roll mixing, solution mixing and internal mixing method used for the preparation of nanocomposite was investigated. The dosages of carrier polymer (7% Carboxylated nitrile rubber; XNBR-7) and organoclay were 10 and 7 phr respectively in NR/BR nanocomposite.

Part-III: Dosage optimization of Clay

The dosage optimization of organoclay in NR-clay nanocomposite was done. Clay dosages vary from 4.0 to 10 phr whereas XNBR was kept constant at 10 phr.

3.4 COMPOUND FORMULATIONS

3.4.1 SBR/BR- organoclay nanocomposites formulations

All the formulations were based on SBR/BR rubber blends and the detailed compound recipes used in this investigation are presented in Table 3.21 to 3.24.

Table 3.21-SBR/BR nanocomposite formulation-variation carboxyl group in XNBR

Compound ref.	C-0	C-1	C-4	C-7
Carboxyl group (%) in XNBR	0	1	4	7
Formulations *, phr	FSSBR 70.0, BR 30.0, XNBR 10.0, Clay 6.0, ZnO 3.0, stearic acid 2.0, 6PPD 1.0, Sulpfur 1.6, TBBS 1.7, DPG 1.8.			

Table 3.22-SBR/BR nanocomposite formulation - different mixing method

Compound ref.	M-1	M-2	M-3
Mixing Technique	2-roll Mill	Solution	Internal mixer
Formulations , phr	FSSBR 70.0, BR 30.0, XNBR (7%) 10.0, MMT 6.0, ZnO 3.0, Stearic Acid 2.0, 6PPD 1.0, Sulfur 1.6, TBBS 1.7, DPG 1.8.		

Table 3.23-SBR/BR gum vulcanizates and nanocomposite formulations

Formulations*	FSSBR: BR (70:30)		SSBR: BR (70:30)		ESBR: BR (70:30)	
	Gum (G1)	filled (R1)	Gum (G2)	filled (R2)	Gum (G3)	filled (R3)
XNBR (7%)	0	10.0	0	10.0	0	10.0
Clay	0	6.0	0	6.0	0	6.0

* Other common ingredients are ZnO 3.0, Stearic Acid 2.0, 6PPD 1.0, Sulfur 1.6, TBBS 1.7, DPG 1.8.

Table 3.24-SBR/BR nanocomposite formulation-clay and XNBR dosages optimization

Compound code	D0	D1	D2	D3	D4	D5	D6
Organoclay ,Phr*	0.0	3.8	6.0	8.3	4.4	7.1	9.8
XNBR (7%),phr	0.0	6.3	10.0	13.8	5.6	8.9	12.2

* Common ingredients: ESBR 70, BR 30, ZnO 3, Stearic Acid 2, 6PPD 1, Sulfur 1.6, TBBS 1.70, DPG 1.8.

3.4.2 Compound formulations of SBR/BR-dual fillers nanocomposites

The compound formulations of different nanocomposites and Control compounds (standard passenger car radial tread recipes) are shown in Tables 3.25 and 3.26.

Table 3.25-SBR/BR compound formulations- "dual filler" nanocomposites (phr) [a]

	ESBR	**SSBR**	**FSSBR**	**PBR**	**XNBR**	**MMT**	**CB**	**Silica**	**TDESP**
EG	70.0			30.0					
SG		70.0		30.0					
EOC-6	70.0			30.0	10.0	6.0			
SOC-6		70.0		30.0	10.0	6.0			
EC-5	70.0			30.0	10.0	4.0	5.0		
EC-15	70.0			30.0	10.0	4.0	15.0		
EC-25	70.0			30.0	10.0	4.0	25.0		
SC-25		70.0		30.0	10.0	4.0	25.0		
FC-25			70.0	30.0	10.0	4.0	25.0		
ES-5	70.0			30.0	10.0	4.0		5.0	2.0
ES-15	70.0			30.0	10.0	4.0		15.0	2.0
ES-25	70.0			30.0	10.0	4.0		25.0	2.0
SS-25		70.0		30.0	10.0	4.0		25.0	2.0
FS-25			70.0	30.0	10.0	4.0		25.0	2.0

[a] other common ingredients: ZnO 3.0, Stearic Acid 2.0, 6PPD 1.0, Sulfur 1.6, TBBS 1.70, DPG 1.8

Table 3.26-Control compound formulations (phr)

	ESBR	SSBR	BR	Carbon Black N220	Silica 7000GR	TDESP Si-69
Control-1	70.0	-	30.0	70.0	-	-
Control-2	-	70.0	30.0	-	70.0	7.0

3.4.3 NR/BR-organoclay nanocomposites formulations

The detailed compound formulations (phr) are presented in Table 3.27.

Table 3.27-NR/BR clay nanocomposites formulations* (phr)

			NR	BR	XNBR	Clay
Effect of carboxyl %	NBG	Gum	70.0	30.0	0.0	0.0
	NB1	1% carboxyl	70.0	30.0	10.0	7.0
	NB4	4% carboxyl	70.0	30.0	10.0	7.0
	NB7	7% carboxyl	70.0	30.0	10.0	7.0
Effect of mixing methods	OM	2 rolls mill	70.0	30.0	10.0	7.0
	SM	Solution	70.0	30.0	10.0	7.0
	IM	Internal Mixer	70.0	30.0	10.0	7.0
Clay dosages variation	F0	Gum	70.0	30.0	0.0	0.0
	F4		70.0	30.0	10.0	4.0
	F7		70.0	30.0	10.0	7.0
	F10		70.0	30.0	10.0	10.0

* Common ingredients: Zinc Oxide 5.0, Stearic acid 2.5, 6PPD 1.0, Sulfur 1.5, TBBS 1.3, and DPG 0.5.

3.4.3 Compound formulations of NR/BR-dual fillers nanocomposites

The compound formulations of NR/BR dual filler nanocomposites are presented in Table 3.28 and the formulation (phr) of Control compounds are as follows;

A. Control 3: NR 70.0, BR 30.0, Carbon Black (N220) 50 and Sulfur/accelerator = 1.5
B. Control 4: NR 70.0, BR 30.0, HD silica 45.0, X 50-S 10.0 and Sulfur/accelerator = 1.0

Table 3.28-Compound formations: NR/BR "dual filler" nanocomposites

Formulations*	NM-7	NC-10	NC-15	NC-20	NS-10	NS-15	*NS-20*
NR	70.0	70.0	70.0	70.0	70.0	70.0	*70.0*
BR	30.0	30.0	30.0	30.0	30.0	30.0	*30*
XNBR	10.0	10.0	10.0	10.0	10.0	10.0	*10.0*
Clay	7.0	5.0	5.0	5.0	5.0	5.0	*5.0*
Carbon Black		10.0	15.0	20.0			
Silica					10.0	15.0	*20.0*
Silane, X 50S					*2.0*	*3.0*	*4.0*

*Common ingredients: Zinc Oxide 5.0, Stearic acid 2.5, 6PPD 1.0, Sulfur 1.5, TBBS 1.3, DPG 0.5

3.5 MATERIAL TESTING AND CHARACTERIZATION

3.5.1 Rheological properties

The cure characteristic of the rubber nanocomposites was studied using a moving die rheometer (MDR 2000E, Alpha Technology, USA). This rheometer is capable of measuring rubber compound cure under isothermal test conditions at constant strain and frequency. Temperature range is ambient to 200°C. The oscillation frequency is 1.667 Hz and strain 0.5, 1.0 or 3.0 degrees (2.8%, 7%, 14% or 42%).

Fig. 3.19- MDR 2000E

Rheometric studies were carried out with 0.5° torque for 30 minutes at 160°C for all SBR/BR compounds and 150°C for all NR/BR compounds including nanocomposites.

3.5.2 Sample preparation

Rubber samples were prepared in compression mould under pressure at temperature and time mentioned in Table 3.29.

Table 3.29-Rubber sample vulcanization conditions

Compound	Samples	Temperature	Time
SBR/BR	Rubber sheet of 2±0.1 mm thickness(6''X6'')	160°C	Tc90 + 3 minutes
	Abrasion and Heat build Up	160°C	Tc90 + 10 minutes
NR/BR	Rubber sheet of 2±0.1 mm thickness(6''X6'')	150°C	Tc90 + 3 minutes
	Abrasion and Heat build Up	150°C	Tc90 + 10 minutes

The sample was cured in hydraulic presses of 100 tons having and 50 tons (M/s.Santosh, India) as shown in the Fig. 3.20. Different samples specimens were cut from tensile rubber sheet using pneumatic hollow die punch of M/s.Ceast, Italy (Fig. 3.21).

Fig. 3.20- Hydraulic curing press

Fig. 3.21- Hollow die punch

3.5.3 Rubber specimens for mechanical and dynamic test

The rubber samples used for mechanical and dynamic mechanical testing are presented in Fig.3.22.

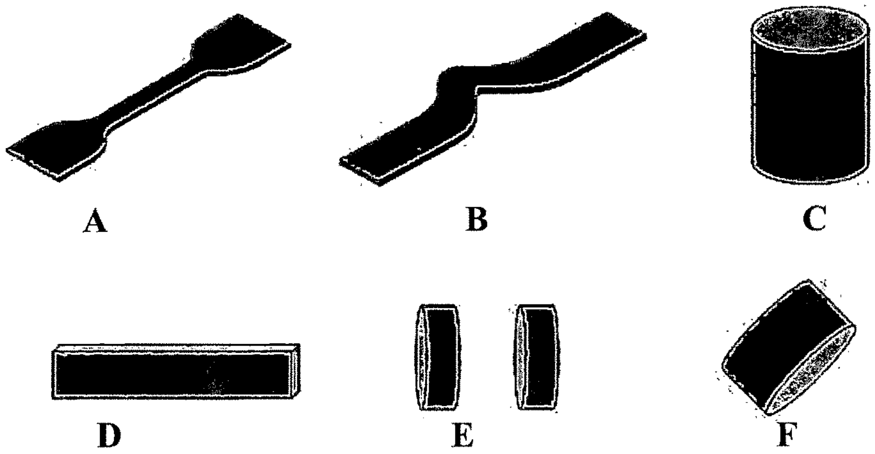


Fig. 3.22 - Rubber specimens (A) Tensile dumbbell (B) Angle tear specimen (C) HBU specimen (D) DMA Tension- compression (E) DMA Shear (F) DIN abrasion specimen

3.5.5 Stress-Strain properties

Stress-Strain properties (modulus, tensile strength, elongation at break and breaking energy) were measured using a universal tensile testing machine (Zwick Z010, Zwick, Germany) using 2.5 kN load cell. Test was done with a cross head speed of 200 mm/min as per ISO 527. The extensometer gauge length was 25 mm, sample width was 6 mm and thickness was 2.0±0.2 mm.

3.5.6. Tear properties

Tear strength and tear energy were measured by using Zwick UTM as per ASTM D-624 using angle tear specimen. The test speed was 200 mm/min and load cell used was 2.5 kN and temperature was 25°C.

3.5.7 Hardness test

The rubber hardness was measured using a circular sample of 30 mm diameter and 6 mm thickness. Measurement was carried out using Automatic Hardness Tester (Ceast, Italy) with fixed load as per ASTM D2230.The rubber hardness was expressed in Shore-A.

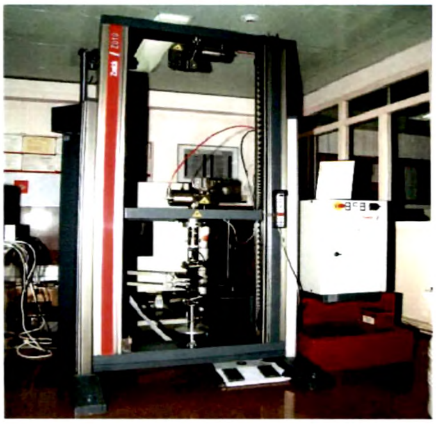


Fig. 3.23- Zwick UTM

Fig. 3.24- Hardness tester

3.5.8 DIN abrasion test

Abrasion loss was determined using Zwick Abrader Zwick 6012 (Zwick, Germany) as per DIN 53516. The circular rubber sample fitted the holder in the abrader against rotation drum while sample is moving from one end to other end. The path length was 40 meter. The load on the sample was 10 N.

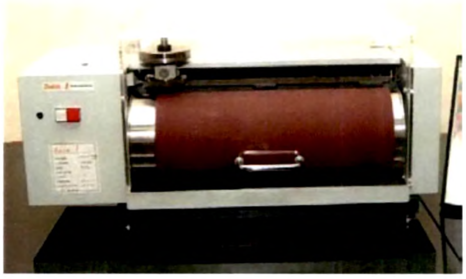


Fig. 3.25- Zwick DIN abrader

The volume loss of rubber sample is calculated using the following formula;

$$\text{Volume loss (mm}^3\text{)} = \frac{\text{Weight loss of sample X 200}}{\text{Density of sample X Weight loss of standard sample}}$$

3.5.9 Heat build up test

Heat development was measured using BF Goodrich Flexometer Model II from BF Goodrich, USA as per ASTM D623. The sample was cylindrical having height 25 mm and diameter 17 mm. The sample is vibrating with frequency of 10 Hz and strain 17.5% with 55 lbs load on the sample. The test time was 25 minutes and preheat time was 60 minutes. The initial base temperature PCR and TBR are 50°C and 100°C respectively. The increase in temperature measured after 25 minutes was the heat build up in the sample.

Fig. 3.26- BF Goodrich Flexometer

Fig. 3.27- Viscoanalyse VA 400

3.5.10 Dynamic mechanical test

The viscoelastic properties of rubber compounds were determined by dynamic-mechanical analysis using Viscoanalyzer VA4000 (Metravib RDS, France). The temperature sweep was done in tension compression mode from –30 °C to 80 °C with a heating rate of 2°C/min at 10 Hz and 0.25 % single strain amplitude (SSA) for SBR/BR blend. For NR/BR blends temperature sweep was done in tension compression mode from –110 °C to 80 °C with a heating rate of 2 °C/min at 3 Hz and 0.1 % single strain amplitude (SSA)

3.5.11 Filler characterization

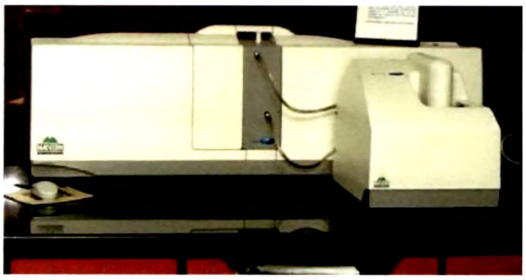


Fig. 3.28- Particle size analyzer

The particle size distribution of all the fillers carbon black, silica and nanoclay were measured by Particle Size Analyzer- Master Sizer 2000 (Malvern Instruments , UK). The test conditions were Stirrer rpm: 750; Pump rpm: 1250; Sonication: 50% for 10 min and obscuration around 5%.

BET Nitrogen surface area of carbon black and silica were measured by Nitrogen Surface Area Analyzer- Nova 1200 (Quantachrome, USA). The drying condition for silica was 1 hour at 160°C and for carbon black 30 minutes at 300°C and partial pressure was maintained at 0.05 to 0.3 and Nitrogen flow rate was at 15 psi. Structure of carbon black and silica was measured by Brabender

Carbon black structure is determined by DBP absorption method using DBP (Dibutylphthalate) Absorpto meter (Brabender A.G, Germany). Test conditions are sample weight is 20 gm, drying at 125°C for 1 hour and rotor speed is 125 rpm.

3.5.12 X-ray diffraction (XRD)

The nanocomposites were also characterized by X-ray diffraction and transmission electron microscopy (TEM). The basal spacing of the organoclay was evaluated by means of wide-angle X-ray diffraction in a Phillips X-pert Pro diffractometer (PANalytical, Eindhoven, NL) at narrow angular range of 2^0–10^0 using Cu K_α-radiation ($k = 0.154$ nm).

In these studies acceleration voltages of 40 kV and beam current of 30 mA were used. The scanning rate was maintained at 1.5^0/min. The d-spacing of the particles were calculated using the Bragg's law.

3.5.13 Transmission electron microscopy (TEM)

The microstructure of nanocomposite was imaged using Transmission Electron Microscopy. Ultra-thin sections of nanocomposite were cut by microtome at about -100°C (below glass transition temperature, Tg of rubber), and the images were taken by JEM 2010 with an acceleration voltage of 200 kV.

3.6 MATERIAL PARAMETER IDENTIFICATION FOR TIRE SIMULATION

A tire is a composite material and consists of different materials such as rubber compounds, textile fabrics, steel cords and bead wire; however for different tire components different rubber compounds are used. For structural simulation stress-strain properties of all these materials in uniaxial tension and compression mode are required and were measured in the laboratory using Zwick UTM.

The rubber samples were subjected to repeated cyclic stress-strain cycle before testing to remove the Mullins effect. Test speed was kept low 5 mm/ minute to capture equilibrium stress-strain data. Stress-strain properties of fabrics (polyester and nylon) and steel cords were also determined by Zwick UTM and test speed were 50 mm/min in tension mode.

Viscoelastic properties of rubber (tanδ) were measured using dynamic mechanical thermal analyzer (VA 4000) from Metravib, France by strain sweep which was carried out in a simple shear mode at two different temperatures 30° and 60°C at 10 Hz and double strain amplitude was varied from 0.02 % to 80% .

3.7 ROLLING RESISTANCE EXPERIMENT

The rolling resistance computed through finite element tire simulation was validated by indoor rolling resistance measurement using drum type pulley wheel machine attached with rolling resistance measurement kits.

3.8.1 Passenger car radial (PCR) tire

Rolling resistance test of 205/60R15 and 155/70R14 PCR tires with Control (standard) tread compounds were carried out on Pulley Wheel (drum type) machine attached with rolling resistance measurement kits as per SAE test standard. Two numbers of tires in each category were tested and average rolling resistance value was taken for validation. The test conditions are described in Table 3.26.

3.8.2 Truck bus radial (TBR) tires

Rolling resistance test of 10.00R20 , 295/80R22.5 and 315/80R22.5 TBR with Control carbon black tread compounds (standard tread) were carried out on Pulley Wheel (drum type) machine as per ISO 18164 test standard. Average results of two tires in each category were used for validation. The test conditions are described in Table 3.30.

Table 3.30- Rolling resistance (RR) test conditions

Parameters	**PCR**	***TBR***
Test Standard	SAE J 1269	*ISO 18164*
Wheel Speed	80 kmph	*80 kmph*
Room Temperature	25 ± 2 °C	*25 ± 2 °C*
Inflation Pressure (I.P)	35 psi	*Rated Inflation*
Load	80% rated load	*85% of Rated Load*
Conditioning	*30 min warm up at rated load and rated inflation*	*90 min warm up at rated load and rated inflation*

The standard tire rolling resistance measurement equipment is shown in the Fig. 3.29.

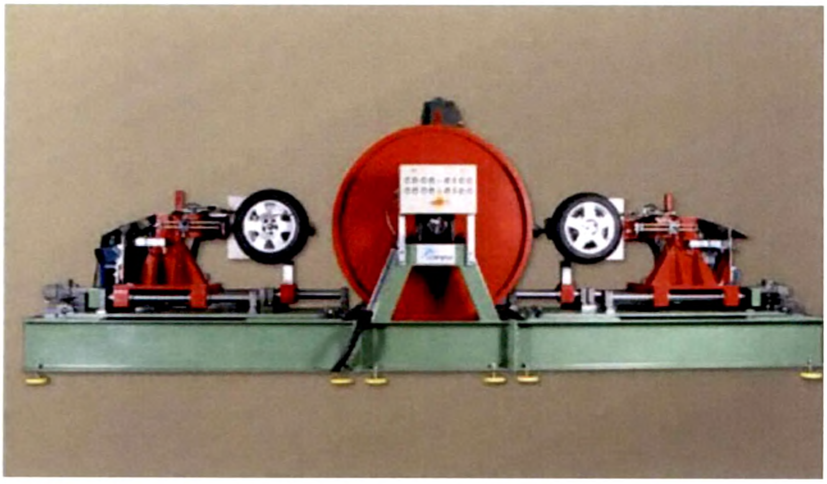


Fig. 3.29- Tire rolling resistance measurement equipment