CHAPTER II
Experimental Methods and Characterization

The experimental procedures and analytical techniques used for the synthesis and characterization of electrically conductive composites of three different elastomeric polymers such as methyl vinyl silicone (VMQ) polymer, RTV silicone polymer and Ethylene propylene diene monomer (EPDM) polymer are described in this chapter. The various conductive fillers used for this purpose are polyaniline, steel fibers, conductive carbon, expanded graphite, TiB₂, polybutadiene rubber and alkaline earth metal doped aluminium oxides. Polyaniline doped with two different acids (Camphor sulfonic acid and Ligno sulfonic acid) were used in the composites, of which the camphor sulfonic acid doped polyaniline was synthesized in the laboratory. The alkaline earth metal doped aluminium oxides were also synthesized in the laboratory and rest all the fillers were procured and used as such.

Three types of composites have been synthesized in this work. These include the composites with single filler, hybrid composites where a combination of fillers was used and nano composites where nanofillers were used. Two roll open mixing mill method and casting method were adopted for synthesizing the composites.

The composites were analyzed using different techniques including two probe conductivity measurement of electrical resistance, Shore A hardness, tensile and tear strength, rebound impact, thermogravimetry (TG) and Scanning electron microscopy (SEM). The synthesized nano powders of doped aluminium oxides were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), SEM, Field emission scanning electron microscopy (FESEM) and Transmission electron microscopy (TEM).
2.1 Materials and Chemicals

High temperature vulcanizing (HTV) VMQ polymer (TSE 221-4-U with Shore A 40), VMQ polymer with Shore A 10, room temperature vulcanizing (liquid rubber) hydroxyl terminated poly dimethyl siloxane (RTV-7888) and vinyl terminated poly dimethyl siloxane (RTV-8001) were procured from Momentive Performance. EPDM polymer was purchased from Kuhmo Products, Taiwan. The polybutadiene rubber – Grade Cisamer – 1220 was purchased from Gujarat Apar Industries. The curing agents such as dicumyl peroxide (Dicup 40C) and 2, 5 dimethyl-2, 5 di (tert butyl peroxy) hexane (Luperox 101-45) were purchased from Arkema Inc. – India. Electrically conductive carbon - Vulcan XC-72 from Cabot Corporation - India ; Steel fibers from Bekaert, Expanded graphite from Metachem- India and Titanium diboride from Momentive Performance – India were procured and used as such. Stearic acid, mercaptobenzimidazole and triallyl cyanurate were purchased from the local market.

Conductive Ligno sulfonic acid doped Polyaniline was purchased from Aldrich. Camphor sulfonic acid doped polyaniline was synthesized in the laboratory by using aniline, ammonium per sulphate and toluene from Qualigens and CSA from Aldrich.

Two types of steel fibers with the diameter of 7–8 micron and lengths of ~ 5 mm and continuous length in several meters named as short fibers (SF) and long fibers (LF) respectively have been used. The expanded graphite as purchased has vermiciform flakes like structure with the circumference of the worm ~ ¼ to ½ inch and length up to 2-4 mm. The distance between intercalated layers of EG was ~3 to 6 Å. TiB₂ had a mean particle size of 14 μm.

Doped aluminium oxides were synthesized using AR grade Al (NO₃)₃; MgCl₂; CaCl₂; SrCl₂; BaCl₂ and Urea from Loba Chemie. Double distilled water was used as a solvent for the reactions.
2.2 Synthesis of Polyaniline

High purity of monomers, chemicals and solvents are required for obtaining good quality polymer. The polymerization conditions should be strictly controlled. Environment for polymerization should be inert and dry because a slight variation in the polymerization conditions may alter the nature of polyaniline obtained. Polyaniline should be kept in a dark, cool and dry place as it may undergo oxidation reaction under light and heat.

Interfacial polymerization method was adopted for synthesis of CSA doped polyaniline (Pani.CSA). The proposed mechanism for the synthesis of conductive polyaniline using camphor sulfonic acid as a dopant by interfacial method is given in Figure 2.1.

Two different solutions were prepared, one solution containing 0.1 M aniline in toluene and the other with 0.1 M ammonium per sulphate together with 0.01 M CSA in distilled water. The two solutions were then carefully transferred in a beaker generating an interface between the 2 layers. After 3-5 min Polyaniline is formed at the interface which gradually diffuses into the aqueous phase. After 24 h the reaction was completed. The dark green coloured product obtained was washed with water and dried in an oven to get free flowing powder. Thus, the electrically conductive CSA doped polyaniline was obtained (Figure 2.2).
**Figure 2.1:** Mechanism for polymerization of CSA doped polyaniline

**Figure 2.2:** Electrically conductive CSA doped polyaniline
2.3 Synthesis of Doped Aluminium Oxides by Microwave Combustion

The possibility to tune the physical and chemical properties of nanoscale materials through variation in the crystal size and shape is a major driving force in nanoparticle research. The synthesis of alkaline earth metals (Mg, Ca, Sr and Ba) doped aluminium oxides was carried out by microwave combustion method which is a rapid, economical and clean method giving white colored flaky and acicular rod shaped electrically conductive doped aluminium oxides. Schematic of the microwave oven is shown in Figure 2.3.

![Figure 2.3: Schematic of a microwave oven](image)

In the typical experiments, for obtaining the doped aluminium oxides, the precursor salts aluminium nitrate and alkaline earth metal chlorides such as MgCl\(_2\), CaCl\(_2\), SrCl\(_2\) and BaCl\(_2\) were microwave irradiated with urea as the fuel. The dopants were used by varying the concentration such as 0.2, 0.4, 0.6 and 1 %. The redox mixture with the stoichiometric ratio (Oxidizer / Fuel = Φ = 1) was considered for the combustion by calculating the total oxidizing and reducing valences of the components for balancing the stoichiometric numerical coefficients. This serves to get an equivalent ratio ‘Φ’ of the oxidizer to fuel to be unity and releases the maximum energy from the combustion [1]. Calculated amounts of Al(NO\(_3\))\(_3\), respective chlorides and urea, as mentioned in Table
2.1, were dissolved in a small amount of water in a beaker and heated to 70-80°C for few minutes to form a gel due to the complexing of metal ion with urea. The mixture was microwave irradiated at 60% power for 5 minutes. In the initial few seconds water starts evaporating from the gel followed by foaming and frothing of the gel forming a dry mass. This dry mass ignites spontaneously with a highly luminescent flame accompanied by evolution and expulsion of large volume of gases like NH₃, N₂, H₂O, and CO₂ etc. out of the microwave cavity. After completion of the reaction the white coloured powders of Mg, Ca, Sr and Ba doped aluminium oxides were collected, crushed, washed with double distilled water and analyzed for various properties.

**Table 2.1:** Precursors and fuel composition used for synthesis of doped aluminium oxides

<table>
<thead>
<tr>
<th>Weight of Al(NO₃)₃ (g)</th>
<th>Chemical</th>
<th>Weight in (g)</th>
<th>Weight of Urea (g)</th>
<th>Yield (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>MgCl₂</td>
<td>0.0043</td>
<td>0.808</td>
<td>0.293</td>
</tr>
<tr>
<td>2</td>
<td>CaCl₂</td>
<td>0.0031</td>
<td>0.807</td>
<td>0.280</td>
</tr>
<tr>
<td>2</td>
<td>SrCl₂</td>
<td>0.0059</td>
<td>0.849</td>
<td>0.423</td>
</tr>
<tr>
<td>2</td>
<td>BaCl₂</td>
<td>0.0052</td>
<td>0.807</td>
<td>0.308</td>
</tr>
</tbody>
</table>

**2.4 Methods used for Synthesizing Composites**

In the present work the laboratory scale - two roll open mixing mill has been used for the synthesis of the composites of VMQ and EPDM polymers which are solid in nature, however, the composites of RTV- 7888 / RTV-8001, the liquid rubbers, were synthesized.
by manual mixing followed by casting. The details of the same are given in the following section.

**2.4.1 Two Roll Open Mill Mixing**

Rubber polymer mixing mills are designed to ensure perfect and uniform blending of natural and synthetic polymers with other raw materials. These mills provide uniform mixing of the materials to the desired level. Most of the mixing mills are driven by electronic motor and different models have different outputs. A mixing mill is a machine consisting of two adjacent, heavy, hardened-steel, counter-rotating horizontal rolls used for mechanical mixing of materials. Generally, they revolve at a slightly different speed. The mill rolls are hollow and may be heated or cooled as needed.

![Figure 2.4: Schematic illustration of two-roll mill](image)

The process of mixing is carried out between two contrary rotors as shown in Figure 2.4. The wicks of both the rotors are arranged parallely which move at different speeds. Due to the difference in tangential speed and nip constriction, the polymer compound experiences displacement as well as pressure energy simultaneously during the process of mixing. The pressure energy increases the displacement energy which in turn contributes towards the polymeric bond breaking. The breakage of rubber polymer chains allows the other chemicals to be uniformly mixed with it.

The roll mills are often temperature controlled (water cooling) with the friction of about 1:1.2. The roll nip should be always adjusted in such a way as to allow the formation of a sufficient polymer bead (i.e. mixing zone) in the nip. The silicone polymer
is homogenized for 2 to 10 minutes before incorporating additives. To speed up and optimize homogenization, frequent incisions are made at the edges of the sheet, or it is rolled up and folded back into the center of the nip.

This type of mixing of VMQ normally involves the use of organic peroxides. At elevated temperatures, they decompose to form highly reactive radicals which chemically crosslink the polymer chains resulting into a highly elastic, three-dimensional network.

The composites of EPDM rubber and steel fibers were prepared by this method at a temperature of 40–45°C. Initially the EPDM rubber was masticated on the mill for 4–5 min followed by the addition of stearic acid and antioxidant mercaptobenzimidazole at an interval of few minutes. This mixture was rolled for 3 to 4 min. Further, Dicumyl peroxide-40 (Dicup 40—a curative) and Triallyl cyanurate (TAC an accelerator) were added and the whole mixture was initially roll milled for 3–6 min with 5–6 mm nip gap followed by further roll milling for 4–5 min with 2–3 mm nip gap. After assuring for the homogenization of the mixture, steel fibers were added slowly and roll milled for another 5–6 min without the use of knife cut. Sheets of the composites with a size of 150 mm*150mm*2 mm were compression molded at 170°C for 10 min in a hot compression press.

2.4.2 Casting Method

This method involves three steps i.e. mixing, deaeration and casting the reaction mass into respective moulds for curing before one obtains the composites.

- **Mixing** -

  This method has been adopted for room temperature vulcanization of silicone polymers. High temperatures (above 38°C) were avoided in the mould making area to prevent premature expiration of the working time. Surfaces and mixing containers were cleaned and dried before use. For mixing purpose, a container of ~ 4-5 times larger volume than the volume of RTV silicone polymer compound was used. RTV silicone base polymer was weighed, to this, appropriate amount of curing agent was added after shaking thoroughly prior to use. The two were mixed thoroughly with the help of clean
tools by scraping the sides and bottom of the container to produce a homogeneous mixture. Automatic dispensing machines designed to meter, mix, deaerate and dispense silicone polymer reduce the necessary preparation steps and are therefore recommended for use where volume is sufficient to justify the costs.

- **Deaeration**
  Deaeration of the polymer is necessary to remove the entrapped air. Air entrapped during mixing should be removed to eliminate voids in the cured product. The mixed material was exposed to a vacuum of about 20 mm mercury where the material expands, crests, and recedes close to the original level as the bubbles break. Degassing is usually completed in about two minutes after frothing ceases. After this step the mixture is poured into respective moulds for curing.

- **Curing Time Cycle**
  RTV-7888 and RTV-8001 silicone polymers are designed to cure at room temperature with Alkoxy silane + dibutyl tin dilaurate and Pt – complex catalysts as curing agents respectively. Curing of the compound begins immediately after the two components are blended. Moulds of the unlimited thickness usually cure in maximum 16 h. The mixed material vulcanizes at room temperature by condensation and addition reactions respectively. The systems are sensitive to changes in heat and humidity, therefore, variation in cure speed may be seen if one or both variables are changed. The cure rate is influenced by temperature. Low temperature prolongs the work life and cure time; high temperature has a reverse effect on the same.

2.5 Characterization of the Synthesized Materials

2.5.1 Characterization of Camphor Sulfonic Acid Doped Polyaniline (Pani.CSA)

The first and foremost characterization for confirmation of Emeraldine salt phase of Pani.CSA is visual inspection, which is the colour of the synthesized powder. Dark green colour of the powder confirms the phase formation.
The electrical conductivity measurement of Pani.CSA proves the formation of Emeraldine salt phase of polyaniline. For this purpose, the dried powder of Pani.CSA was transferred into a pellet forming mould and pressed under a pressure of 5 ton in a hydraulic press. The electrical resistance of the pellet was measured using ‘Agilent’ multimeter with two probes.

2.5.2 Characterization of Alkaline Earth Metal Doped Aluminium Oxide Powders

The confirmation of the product formation by FTIR, phase formation by XRD and morphology of the synthesized alkaline earth metal doped aluminium oxide powders by SEM, FESEM and TEM techniques were carried out.

- **Fourier Transform Infra Red Spectroscopy**

An FT-IR spectrometer is an instrument which acquires broadband NIR to FIR spectra. Unlike a dispersive instrument, i.e. grating monochromator or spectrograph, FT-IR spectrometers collect all wavelengths simultaneously. An FT-IR is typically based on Interferometer experimental setup as is shown in Figure 2.5. The interferometer consists of a beam splitter, a fixed mirror and a mirror that translates back and forth very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source [2].

The range of infrared region is 12800 ~ 10 cm\(^{-1}\). It can be divided into near-infrared region (12800 ~ 4000 cm\(^{-1}\)), mid-infrared region (4000 ~ 200 cm\(^{-1}\)) and far-infrared region (50 ~ 1000 cm\(^{-1}\)). Infrared absorption spectroscopy is the method which is used to determine the structures of molecules with the characteristic absorption of infrared radiation. Infrared spectrum is the molecular vibrational spectrum. When exposed to infrared radiation, sample molecules selectively absorb radiation of specific wavelengths
which causes the change of dipole moment of sample molecules. Consequently, the vibrational energy levels of sample molecules transfer from ground state to excited state. The frequency of the absorption peak is determined by the vibrational energy gap. The number of absorption peaks is related to the number of vibrational freedom of the molecule. The intensity of absorption peaks is related to the change of dipole moment and the possibility of the transition of energy levels. Therefore, by analyzing the infrared spectrum, one can readily obtain abundant structure information regarding the molecule.

FTIR spectra of the freshly prepared doped aluminium oxides were recorded on a Shimadzu 8400S FT-IR spectrophotometer and scanned over the range of 4000 - 450 cm$^{-1}$. The solid samples were crushed with anhydrous KBr powder and loaded on the instrument. Background scan was performed prior to running the spectrum of samples and deducted appropriately.

Figure 2.5: Schematic of FTIR: A = mid-IR source, B = aperture wheel, C = filter wheel, D = exit port, E = beam splitter, F = switch mirror, G = sample compartment window (KBr), G' = optional window, H = sample cell, I = detector.
X-Ray Diffraction

Max von Laue, in 1912, discovered that the crystalline substances act as three-dimensional diffraction gratings for X-ray wavelengths similar to the spacing of planes in a crystal lattice. X-ray diffraction is now a common technique for the study of crystal structures and atomic spacing. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays (Figure 2.6) with the sample produces constructive interference (and a diffracted ray) when conditions satisfy the Bragg's Law \( n\lambda=2d \sin \theta \). Where, \( d \) is the spacing between two adjacent lattice planes, \( \lambda \) is the wavelength of the X-ray radiation, \( n \) is an integer and \( \theta \) is known as the diffraction angle or Bragg's angle. This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By changing the geometry of the incident rays, the orientation of the centered crystal and the detector, all possible diffraction directions of the lattice are attained. All diffraction methods are based on generation of X-rays in an X-ray tube. These X-rays are directed at the sample and the diffracted rays are collected. A key component of all the diffractions is the angle between the incident and diffracted rays [3]. Powder diffraction caters to the identification of phases in the solid state mixtures. The mean crystallite sizes (\( D \)) of the particles can be determined from XRD line-broadening measurement from the Scherrer equation (2.1)

\[
D = \frac{K\lambda}{\beta \cos \theta}
\]

Equation 2.1

Where, \( D \) is the crystallite size, \( K \) is the shape factor (0.94); \( \lambda \) is the wavelength (Cu K\( \alpha \)), \( \beta \) the full width at the half maximum in radians, and \( \theta \) the Bragg’s diffraction angle. Figure 2.7 shows the schematic of the X-ray diffractometer. In this work, the phase analysis of the samples was carried out using Bruker–X-ray diffractometer with monochromatic CuK\( \alpha \) radiation (\( \lambda=1.5406\text{Å} \)) with the scan rate of 0.1° min\(^{-1} \). Silicon was used as an external standard for correction due to instrumental broadening. The diffractogram shows 2\( \theta \) on the X-axis and X-ray intensity on the Y-axis. The results of
the synthesized alkaline earth metal doped aluminium oxide powders were compared with the indexes for manual searching of PDF file (Joint Committee for Powder Diffraction Systems).

**Figure 2.6:** Verification of Bragg’s law

**Picture 2.7:** Schematic of X-Ray diffractometer
• **Scanning Electron Microscopy**

The scanning electron microscope comprises of two main parts: an electron column and an electron detector as can be seen from Figure 2.8. In the electron column, an electron cathode generates an electron beam, which is then collimated by electromagnetic condenser lenses focused by an objective lens and finally raster across the sample surface by the scanning coils. Secondary electrons and backscattered electrons are emitted from the specimen at the irradiated spot of the primary electron beam, and they are collected by the detector and form the specimen image in the microscope. The most common thermionic electron source consists of three components: a tungsten wire filament, the Wehnelt cylinder (or grid cap), and the anode. Thermionic emission occurs when sufficient heat is supplied to the emitter so that electrons can overcome the energy barrier of the filament to escape from it. Electrons emitted from the heated filament travel in all directions. The grid cap is maintained at a slightly more negative potential than the filament to extract the electrons to the specimen. The anode accelerates electrons; a hole in the anode allows only a fraction of these electrons to continue down the column towards the lenses. Most of the electrons emitted from the filament are captured by the anode and return to the high voltage supply and are measured as the “emission current”. The light flashes are then detected and amplified by a photomultiplier tube [4].

For the characterization of the doped aluminium oxides, the freshly synthesized samples were drop-coated on a glass slide and air dried. These were then coated by ~15 nm thick coating of Pt with JEOL JFC 1600 auto fine coater and placed on the sample stub using JEOL JSM 6360-A SEM analyzer.

• **Field Emission Scanning Electron Microscopy**

This technique enables one to study the surface morphology of materials. It is a microscope that uses a beam of electrons instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons in a raster mode. Electrons liberated from the field emission source are accelerated under a high electrical field gradient.
Figure 2.8: Schematic diagram of scanning electron microscope

Figure 2.9: Schematic of detectors (SE, CL and in lens) positioning in FESEM
These primary electrons are focused within the high vacuum column and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result, secondary electrons are emitted from echo spot on the object. The angle and velocity of these secondary electrons relates to the surface structure of the object. A detector traps the secondary electrons and produces an electronic signal. This signal is amplified and transformed to a video scan-image that can be seen on a monitor or to a digital image that can be saved and processed further.

As shown in the schematic of the instrument (Figure 2.9), the field-emission cathode in the electron gun of a scanning electron microscope provides narrower probing beams at low as well as high electron energy, resulting in both improved spatial resolution and minimized sample charging and damage. FE-SEM produces clearer, less electrostatically distorted images with spatial resolution down to 1.5 nm. This is 3 to 6 times better than conventional SEM.

The morphologies of the doped aluminium oxides were studied on model Hitachi S-4800 II operating at an accelerating voltage of 10 kV, after coating the specimens with platinum.

- **Transmission Electron Microscopy**

  In transmission electron microscopy, the electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when being heated. A condenser directs the electrons into a loosely focused beam (Figure 2.10). The beam is then accelerated towards the specimen by the positive anode. Electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube. After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system allows electrons only within a small energy range to pass through, so that the electrons in the electron beam will have a well-defined energy [5].

  The magnetic lens, which is a circular electro-magnet, is capable of generating a precise circular magnetic field. The field acts like an optical lens to focus the electrons. An aperture is a thin disk with a small (2-100 μm) circular through-hole. It is used to
restrict the electron beam and filter out unwanted electrons before hitting the specimen. TEM works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus, the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen.

The morphology of the samples was studied on a Philips CM200 transmission electron microscope operating at an accelerating voltage of 200 kV. The doped aluminium oxide samples were dispersed in isopropanol by sonication for 1 – 2 minutes and loaded on carbon coated grids of 200 mesh size. The grids were viewed under the microscope after drying under IR lamp.

![Schematic diagram of transmission electron microscope](image)

**Figure 2.10:** Schematic diagram of transmission electron microscope
2.5.3 Characterization of the Composites

The elastomeric polymers used in this work (VMQ, EPDM and RTV-SI polymers) have properties that are drastically different from other engineering materials. Consequently, the testing procedures for these polymers are unique. It has both, elastic and viscous properties. The physical tests vary as a function of time. Crosslinking does not stop precisely at the time the polymer is taken from the mold. It continues as the polymer cools to room temperature and even proceeds slowly at room temperature. Changes are most rapid initially, and it is a standard practice not to test rubbers within 16 h of vulcanization [6, 7]. The composites were cured by compression moulding in appropriate moulds at 170ºC for 10 min under a pressure of 10.34 MPa to prepare the specimens according to the ASTM standards for various characterizations.

- Electrical Resistance

The electrical resistance of the composites was measured on ‘Agilent U 1252 A’ two probe multimeter from Germany as shown in Figure 2.11. Multimeter places a voltage at the two probes which causes a current to flow in the sample and the resulting resistance is then measured. Sample buttons of 4 mm thickness and 6 mm diameter were used for this purpose. As the electrical resistance is higher at surface in case of elastomeric polymers [8, 9], the surface resistance was measured keeping the probes 1 cm apart. Resistance was measured before and after curing as well as heat ageing of the samples at 90ºC for 50 to 100 h.

![Multimeter](image)

**Figure 2.11: Multimeter**
ASTM D 573-88 describes the standard test method for deterioration of elastomeric polymers in an air oven due to the combined effects of oxidative and thermal aging. The basic principle of the test is to expose the test piece to air at an elevated temperature for specified periods of time. After aging, the electrical properties are measured and compared with the properties of the original test pieces. It is important to avoid the simultaneous aging of materials that are markedly different. This is because some of the chemicals being volatile migrate from one specimen to other in an aging oven, invalidating the results. An oven design that divides the available capacity into a number of aging cells is recommended to segregate the test pieces. The specimens of composites were analyzed after the heat ageing at 90°C for 100 h.

- **Rheometry**

  The preparation of rubber compound is influenced by several factors that affect the results obtained including the variability in the quality of the ingredients such as polymer, vulcanizing agent, cure activator, cure accelerator, fillers etc. Normally, a test of the compound made with a Rheometer permits to identify most of the possible problems in a rubber compound. The test takes only a few minutes. One can measure the change in the properties of a rubber compound during the course of vulcanization using this instrument. Rheometer measures the force associated with the cyclic strain which is applied to a test piece by the machine. The test is carried out at a predetermined constant temperature and the measure of stiffness is recorded continuously as a function of time [10].

  Oscillating Disk Rheometer (Figure 2.12) is the most ‘traditional’ kind of rheometer. A circular piece of the composite in raw state, with diameter of ~ 15 mm and thickness of about 6 mm, is placed between the two dies. A rotor, placed in the middle of the dies oscillates with ± 3 degrees (or ± 1 degree). The rotor is connected to a torque sensor to measure the torque response of the rubber at the deformation. Typically, the working temperature is set between 170°C and 190°C. When different kinds of rubbers are used, a ‘blank’ test to clean the rotor is required. The processing phase, during which the viscous (plastic) behavior of the compound is dominating shows rubber processability and therefore furnish useful indications about the fluency in the moulds.
The meaningful results are least torque (ML); Scorch time (tS1, tS2) which is the time required for the increase of 1 (ts1) or 2 (ts2) points from Minimum Torque. This number is an indication of the time required for the beginning of the process of cross linking. During the curing phase of the curve the cross-linking process evolves. The Rheometric study is very important since it gives an idea about the curing time required for the completion of curing and also the degree of cross linking can be understood. Typical data that can be obtained from the curve are 1) t’10: time corresponding to 10% curing; 2) t’50: time corresponding to 50% curing; 3) t’90: time corresponding to 90% curing. This result is considered as the optimum vulcanization time. The maximum value of torque obtained is related to the final level of cross-linking, the quality of the polymer used, the filler used, the compounding process and the sum of this result is maximum.

**Figure 2.12:** Oscillating disc rheometer
torque (MH). After the Maximum Torque has been reached, the degradation of the compound can be measured.

The rheological properties were measured according to ASTM D 02084, on Future Foundation - Oscillating Disc Rheometer, which is a shearing disk (rotor) rheometer. The instrument depicted in Figure 2.12 consists of a rotor (Biconical disc) embedded in the test piece between a sealed die cavity which is made to oscillate through a small specified rotary amplitude. This action exerts a shear strain on the test piece. The torque (force) required to oscillate the disc depends upon stiffness (shear modulus) of the compound. Thus, these studies represent a fingerprint of the composite’s vulcanization and processing character.

- **Morphology of the Composites**

  The homogeneity of the composites was characterized by scanning the specimens of the composites under electron microscope. For SEM analysis, samples of the composites were prepared by pressing the sheets in a hydraulic press and cutting pieces of 0.5 * 0.5 cm size. These were then coated by ~15 nm thick coating of Pt with JEOL JFC 1600 auto fine coater and placed on the sample stub using JEOL JSM 6360-A SEM analyzer.

- **Thermogravimetric Analysis**

  Thermogravimetric Analysis is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Figure 2.13 shows a schematic diagram of a thermogravimetric analyzer. The sample is heated in a furnace at a constant heating rate and the sample mass undergoes changes which refer either to desorption of volatile components from the sample (negative weight change) or to absorption of gaseous components from the atmosphere surrounding the sample (positive weight change).

  Thus, weight loss of a polymer as a function of temperature was determined by the Thermogravimetric analysis (TG) with an accuracy of ±1 µg. Thermogravimetric analyzer model TA-60 WS of Shimadzu – Japan was used for TGA analysis. TGA were
recorded in the range between RT and 1000°C at a scanning rate of 10°C min⁻¹ under nitrogen atmosphere with a flow rate of 50 ml min⁻¹.

![Figure 2.13: Schematic of TGA](image)

- **Physical Properties**

- **Specific Gravity**
  Specific gravity of the samples was determined by using the hydrostatic weighing method as per the ASTM standard D297–93. Weighing balance from Contech Instruments was used for specific gravity measurement. Testing was done at room temperature. This method directly gives the specific gravity value, which is the ratio of mass of a unit volume of composite to the mass of a unit volume of water [11].

- **Hardness**
  Hardness is defined as the resistance to indentation. The indentor is a calibrated spring needle [12, 13]. The durometer (Figure 2.14) is an instrument that measures the penetration of a stress-loaded metal sphere into the polymer. Hardness measurements in
rubber polymer are expressed in Shore A or Shore D units according to ASTM-D 2240 test procedures. Due to the viscoelastic nature of elastomeric polymer, a durometer reading reaches a maximum value as soon as the metal sphere reaches maximum penetration into the specimen and then decreases within the next 5 to 15 sec. Hand-held spring-loaded durometers are commonly used but are subject to operator error. Bench-top dead-weight-loaded instruments reduce the error to a minimum. The specimens of thickness and diameter of 6 mm each were loaded on Type–2 durometer Shore A operating stand and tested on GSE Testing Instrument - Mumbai with an indenter of type “A” for the hardness.

![Figure 2.14: Durometer](image)

- **Mechanical Properties** -

- **Tensile Strength**

  Although silicone polymer is rarely used in simple extension, tensile properties are the most measured parameters after hardness. This is in part attributable to the use of tensile strength as a general measure of quality. Tensile properties are sensitive to errors in processing as inadequate dispersion of fillers during mixing and incorrect vulcanization conditions can affect the property, it is merely the sum of every component in the composite [14]. ASTM standard D-412 was followed for testing the tensile strength of the samples. A sheet of size 150 * 150 * 2 mm\(^3\) was used to prepare the specimens. Five dumb belled shaped specimens with ASTM standard dimensions were punched in a
Die–C. Punching machine was used to get a single impact stroke to achieve sharp, smoothly cut edges of the specimens. Computerized Tensile Testing machine by Star Testing Systems (shown in Figure 2.15) was used for measuring the tensile strength. Before testing, the thickness was measured at three points along the center straight portion of the dumb bell and averaged. The width of the test piece is not measured; by convention, it is taken as the width of the die. The specimens were held in the tensile testing machine by self tightening grips, which distribute the clamping pressure evenly over the width of the tab.

![Tensile and tear testing machine](image)

**Figure 2.15:** Tensile and tear testing machine

Extension of the test piece was measured by a clip-on extensometer attached to the central portion of the specimen. The extensometer was carefully checked to grip the specimen with sufficient force to prevent slippage. The strengths of all five specimens were measured, the extreme high and extreme low readings were discarded and average of three specimens was taken.
• **Tear Strength**

Vibration isolators and dampers that are subjected to cyclical loads frequently fail due to the fracturing of the rubber components. As shown in the specimen in (Figure 2.14) for tear testing, a fracture may initiate in an area where stress concentration is at a maximum. After initiation, the fracture increases in size and progresses into a tearing action. Tear properties are therefore important in some applications. Tensile tests are run on dumb bell-shaped samples containing no flaws. The stress is therefore evenly distributed across the sample. Tear-testing procedures concentrate the stress in one area, either through sample design or by cutting a nick in the sample.

The peak force and sample thickness are recorded. Tear strength testing was done with reference to ASTM standard D-624. Three dumb bells were punched from the sheet of size 150 * 150 * 2 mm³. Punching machine with a single impact stroke was used to ensure smooth cut surfaces in Die-C with dimensions as per ASTM standard D-624. These specimens were tested and average of the three was taken. Tear strength was measured on Star Testing Systems machine from India.

• **Dynamic stress and strain properties - Rebound resilience**

Resilience, measured by several relatively simple tests, is sometimes used for estimating the dynamic properties of a rubber compound. As shown in Figure 2.16, in these test methods, a strain is applied to a rubber test sample by a free-falling indentor.
Figure 2.16: Vertical rebound resilience tester

Resilience is defined as the ratio of the energy of the indentor after impact to its energy before impact (expressed as a percentage) [15]. The ratio of the energy dissipated in overcoming internal friction to the energy stored is a function of the viscoelasticity of the rubber. Two widely used methods include the pendulum and the falling weight methods. Although, resilience is a crude measurement of the dynamic properties of rubber, it is attractive because of its simplicity and low cost. This test was performed using ASTM standard D 2632-01. The specimen of 12 mm thickness and 6 mm diameter was used. Impact resilience was measured by Vertical Rebound Resiliometer by the ‘Shore Instrument and Manufacturing Co’, Mumbai- India.
References