This chapter deals with the description of the materials used, the methods of sample preparation and the experimental techniques adopted in the present investigations.

2.1 Materials

2.1.1 Natural rubber

Natural rubber (NR) used for the study was solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam, Kerala, having the Mooney viscosity (ML (1+4)) at 100 °C = 85.3. The Bureau of Indian standard (BIS) specifications for this grade of rubber is given below.

<table>
<thead>
<tr>
<th>Table 2.1: Specification for ISNR-5 rubber</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt content</td>
</tr>
<tr>
<td>Volatile matter</td>
</tr>
<tr>
<td>Nitrogen</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Initial plasticity number, P₀, min</td>
</tr>
<tr>
<td>Plasticity retention index, PRI, min</td>
</tr>
</tbody>
</table>
2.1.2 Coir

Coir is an important lignocellulosic fiber obtained from the fibrous mesocarp of coconut, the fruit of coconut trees (*cocos nucifera*), which is cultivated extensively in Kerala, the southern state of India. The chemical composition of the coir fiber is given below. Coir fibers procured locally were chopped to approximately 6 mm and used.

Table 2.2: Chemical composition of Coir

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>32–43%</td>
</tr>
<tr>
<td>Lignin</td>
<td>40–45%</td>
</tr>
<tr>
<td>Hemi-cellulose</td>
<td>0.15–0.25%</td>
</tr>
<tr>
<td>Pectins and related compounds</td>
<td>3–4%</td>
</tr>
<tr>
<td>Moisture content</td>
<td>8</td>
</tr>
</tbody>
</table>

2.1.3 Chemicals

Table 2.3: Details of chemicals used

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemical</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ferric chloride (FeCl₃)</td>
<td>E- Merck Mumbai., India., Purity - 97%, Melting point &lt;270°C</td>
</tr>
<tr>
<td>2</td>
<td>Ferrous sulphate (FeSO₄)</td>
<td>E- Merck Mumbai., India., Purity - 99%, Melting point &lt;70°C</td>
</tr>
<tr>
<td>3</td>
<td>Ammonium hydroxide (NH₄OH)</td>
<td>E- Merck Mumbai., India., Purity – 25-29%, Boiling point&gt; 24°C</td>
</tr>
<tr>
<td>4</td>
<td>Acetone (C₃H₆O)</td>
<td>E- Merck Mumbai., India., Purity - 99%, Boiling point &gt;56°C</td>
</tr>
<tr>
<td>5</td>
<td>Aniline (C₆H₅-NH₂)</td>
<td>E- Merck Mumbai., India., Purity - 97%, Melting point - 196-198 °C</td>
</tr>
<tr>
<td>6</td>
<td>Hydrochloric acid (HCl)</td>
<td>E-Merck Mumbai., India., Purity - 37%, Density - 1.2 g/mL at 25 °C, Boiling point &gt; 100 °C</td>
</tr>
<tr>
<td>7</td>
<td>Sulphuric acid (H₂SO₄)</td>
<td>E-Merck Mumbai., India., Assay - 95.0-98.0%, Boiling point - 337°C, Residue on ignition ≤5 ppm</td>
</tr>
</tbody>
</table>
### Materials and Methods

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Chemical</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>Sodium hydroxide (NaOH)</td>
<td>E-Merck Mumbai., India., Purity ≥97.0%, Melting point - 318 °C</td>
</tr>
<tr>
<td>9</td>
<td>Ammonium persulphate ((NH₄)₂S₂O₈)</td>
<td>E-Merck Mumbai., India., Assay ≥ 98.0%, Residue on ignition ≤0.05%</td>
</tr>
<tr>
<td>10</td>
<td>Sodium chlorite (NaClO₂)</td>
<td>E-Merck Mumbai., India., Assay - 80%</td>
</tr>
<tr>
<td>11</td>
<td>Acetic acid (CH₃COOH)</td>
<td>E-Merck Mumbai., India., Density - 1.049 g/mL at 25 °C, Boiling point - 117-118 °C, Melting point - 16.2 °C</td>
</tr>
<tr>
<td>12</td>
<td>Zinc oxide (ZnO)</td>
<td>Meta Zinc Ltd. Mumbai., Specific gravity - 5.5, Zinc oxide content - 98%, Heat loss (2 hours at 100°C) -0.5% maximum</td>
</tr>
<tr>
<td>13</td>
<td>Stearic acid (C₁₇H₃₅CO₂H)</td>
<td>Godrej Soaps (P) Ltd, Mumbai., Melting point - 50-69 °C, Acid number -185-210</td>
</tr>
<tr>
<td>14</td>
<td>1,2-dihydro-2,2,4-trimethylquinoline (TQ)</td>
<td>Bayer India Ltd, Mumbai., Appearance - Amber to brown granules, Melting point - 80-100°C, Loss on drying (Max) % - 0.30, Ash (Max) % - 0.30</td>
</tr>
<tr>
<td>15</td>
<td>Zinc di-butyl dithiocarbamate (ZDBC)</td>
<td>Merchem Ltd, Kerala., Appearance -White powder, Density - 1.270 g/cc, pH value -neutral</td>
</tr>
<tr>
<td>16</td>
<td>Sulphur (S)</td>
<td>Standard Chemical Company Pvt. Ltd., Chennai, India., Purity - 99.0 to 99.5%, Specific gravity - 2.05, Acidity - 0.01, Ash - 0.01 % (max), Melting Point - 115-125 °C, Moisture Content - 0.15% (max)</td>
</tr>
</tbody>
</table>

### 2.2 Processing

#### 2.2.1 Compounding

The mixing and homogenization of elastomers and the compounding ingredients were done as per ASTM D 3182 on a two roll laboratory size mixing mill (150 x 330 mm²) at a friction ratio of 1:1.25. Once a smooth band of elastomer was formed on the roll, the ingredients were added in the following order: activators, fillers, anti-oxidant, accelerator and finally sulphur. After complete mixing the stock was passed six times through the tight nip and finally sheeted out at a fixed nip gap so as to orient the fillers
preferentially in one direction. The sheets were kept for a 24 hour maturation period before testing.

### 2.2.2 Cure characteristics

Cure characteristics of the vulcanizates were determined at 90 °C for 2 hours as per the ASTM D 2084-01 by using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) which is a computer controlled moving die rheometer with a unique test gap design, an advanced temperature control system and fully automated operation modes. The machine has two directly heated, opposed biconical dies that are designed to achieve a constant shear gradient over the entire sample chamber. To determine the cure characteristics of the rubber compound, approximately 5 g of the sample was kept in the lower die, which was oscillating through a small deformation angle (± 0.2°) at a frequency of 50 cpm. The torque transducer on the upper die senses the force being transmitted through the rubber. A typical cure curve is shown in Fig. 2.1.

![Fig. 2.1: A typical cure curve](image-url)
The following data can be obtained from the cure curve.

**Minimum torque** (\(T_{\text{min}}\)): It is the lowest torque shown by the mix at the test temperature before the onset of cure.

**Maximum torque** (\(T_{\text{max}}\)): It is the maximum torque recorded when curing of the mix is completed.

**Differential (Maximum – Minimum) torque**: It is the difference between maximum torque and minimum torque during vulcanization. It represents improvement in the degree of cross-linking on vulcanization, i.e. it is a measure of final cross link density of the vulcanizate.

**Scorch time** (\(T_{10}\)): It is taken as the time for 10% rise in torque from the minimum torque.

The optimum cure time (\(T_{90}\)): Corresponds to the time to achieve 90% of maximum cure which was calculated using the formula

\[
\text{Torque at optimum cure} = 0.9 \ (T_{\text{max}} - T_{\text{min}}) + T_{\text{min}}
\]

Time required to achieve torque at optimum cure is taken as \(T_{90}\).

### 2.2.3 Vulcanization

Test specimens marked with the mill grain direction were vulcanized at 90 ± 2 °C and at a pressure of 180 kg/cm² in an electrically heated hydraulic press to their respective cure times. At the end of curing cycle, the pressure was released, the sheets were stripped off from the mould and were cooled quickly by plunging into water and stored in a cold dark place for 24 hours and were used for subsequent property measurements.
2.3 Experimental methods

2.3.1 Mechanical properties

The vulcanizates were tested for different mechanical properties like tensile strength, tear strength, modulus and elongation at break according to relevant ASTM standards. The properties were measured after a conditioning period of 24 hours.

2.3.2 Tensile Properties

Tensile properties were measured using Shimadzu Universal Testing Machine Model AG-I 10 kN according to ASTM D412. Samples were punched out from the moulded sheets along the grain direction with a dumb-bell die (die E). The grip separation speed was 500 mm/min. The strength and percentage elongation were evaluated after each measurement automatically by the microprocessor and presented on a visual display. Averages of at least five sample measurements were taken to represent each data point. The ultimate strength, modulus at 300% elongation and elongation at break of the samples were noted.

2.3.3 Tear Strength

The tear strength was determined using Shimadzu Universal Testing Machine Model AG-I 10 KN according to ASTM D624 (die C). The samples were punched out from the moulded sheets along the direction of filler orientation. The test speed was 500 mm/min.

2.3.4 Dynamic mechanical analysis (DMA)

TA Instruments DMA Q800 was used to conduct dynamic mechanical analysis. Test specimens having a dimension of 30 mm x 3 mm x 2 mm were used in tension mode. Frequency sweep experiments were conducted over a frequency range of 1Hz to 30 Hz at 40 °C. The amplitude was fixed at 15 μm.
2.3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analyses of the fillers, gum and composites were carried out on TA Instruments TGA Q50 with a heating rate of 20 °C/min under nitrogen atmosphere. The rate of flow of nitrogen through the furnace was kept at 40 ml/min.

2.3.6 Scanning electron microscopy (SEM)

Scanning electron microscope studies were carried out using SEM model 6390LA JEOL instrument. To find the morphology and size of fillers (polyaniline, Fe₃O₄, cellulose), the samples were placed on the carbon tape and gold plated to suppress specimen charging. To study the morphology of composite cross sections, the cut surfaces were sputter coated with gold.

2.3.7 Transmission electron microscopy (TEM)

Transmission electron micrographs of Fe₃O₄ powders were recorded using JEOL: JEM 1400, operating at 120 kV.

2.3.8 X-ray diffraction (XRD)

X-ray diffractograms of the fillers were recorded using a Bruker AXS D8 Advance Diffractometer using CuK radiation (λ = 1.54 Å) at 35 kV and 25 mA with a smallest addressable increment of 0.001 °. XRD results were obtained in the range 2θ = 10 ° to 80 ° at a scan rate of 4 °/min.

2.3.9 Fourier transform infrared spectroscopy (FTIR)

Infrared spectra were recorded on a Bruker FTIR spectrophotometer model Tensor 27 (spectral range of 4000 cm⁻¹ to 600 cm⁻¹ with standard KBr beam splitter) in attenuated total reflectance (ATR) mode. It uses zinc selenide as the crystal material with high sensitivity DLATGS detector with KBr window.
2.3.10 DC electrical conductivity

2.3.10.1 Pelletization of PANi and PANi coated cellulose

For electrical measurements bulk sample of PANi and PANi coated cellulose are to be obtained in the form of pellets. Pellets of diameter 12 mm and thickness around 2 mm were prepared by compressing the powders under a load of 6 tonnes in a pelletizer.

2.3.10.2 Conductivity measurements

The DC electrical conductivity of the PANi pellets, PANi coated cellulose pellets and the conducting elastomer composites were measured by a two-probe method using a Keithley 2400 source-measure unit, which is a fully programmable instrument capable of sourcing and measuring voltage or current simultaneously with accuracy. A constant current source was used to pass a steady current through one of the probes and the voltage across the other was measured. The samples were placed between two electrodes through which current was passed and the resistance was measured directly from the instrument. The measurements were done at room temperature. The conductivity of the sample was calculated by the following formula:

$$\sigma = \left( \frac{1}{R} \right) \frac{l}{A}$$

where, $\sigma$ is the electrical conductivity, $R$ is the resistance in ohm, $l$ is the spacing between the probes in centimetres and $A$ is the area of contact of the probes with the sample in centimetre square.

2.3.11 Vibrating sample magnetometer (VSM)

Magnetic measurements of the pristine Fe$_3$O$_4$ nanoparticles and the magnetic composites were made at room temperature using a PAR
Materials and Methods

EG&G 4500 Vibrating sample magnetometer. Magnetization was measured as a function of applied field in the range ±15,000 Oe.

2.3.12 Dielectric measurements

The dielectric measurements were carried out at frequencies ranging from 0.1 MHz to 5 MHz using an Impedance analyzer, Agilent E 4980 A Precision LCR Meter. Disc shaped samples having diameter 12 mm and thickness 2 mm were used for the measurements. The samples were mounted in between the disc electrodes. Dielectric constant ($\varepsilon'$), Dielectric loss ($\varepsilon''$) and the AC conductivity ($\sigma_{AC}$) were obtained from the instrument.

2.3.13 Microwave properties

The microwave characteristics of the prepared conducting polymer composites were studied using cavity perturbation technique. The experimental set up consists of a ZVB20 vector network analyzer, sweep oscillator, S-parameter test set and rectangular cavity resonator. The measurements were done in S (2.5–4 GHz) and X (7–12 GHz) band frequencies at room temperature (25 °C). The dimensions of X band rectangular wave-guide used in the measurements were 14.1 × 2.3 × 1 cm and that of S band were 34.5 cm × 7.2 cm × 3.4 cm respectively.

For a rectangular cavity, real part of the dielectric permittivity can be calculated from the relation

$$\frac{\Delta f}{f_s} = 2\frac{V_s}{V_c}(\varepsilon' - 1)$$

where $\Delta f$ is the shift in resonance frequency on introduction of the sample into the cavity and $V_s$ and $V_c$ are the volume of the sample and cavity respectively.
The imaginary part of the dielectric permittivity is given as

$$\left[ \frac{1}{2Q_s} - \frac{1}{2Q_c} \right] = 2\frac{V_s}{V_c} \epsilon'$$

$Q_s$ and $Q_c$ are the quality factors of the cavity with and without sample, given by

$$Q_s = \frac{f_s}{\Delta f}, Q_c = \frac{f_c}{\Delta f}$$

Magnetic permeability was measured by perturbing the cavity by the samples at positions where the electric field is zero. The real and imaginary parts of the complex permeability of composite samples were determined using the relations

$$\mu' - 1 = \frac{1}{8a^2}\left( \frac{\Delta f}{f_s} \right) \frac{V_c}{V_s}$$
and

$$\mu'' = \frac{1}{16a^2} \left[ \frac{1}{Q_s} - \frac{1}{Q_c} \right] \frac{V_c}{V_s}$$
respectively.

$$\lambda_p = \frac{2\lambda}{P}$$

where $p$ is the number of modes in which the cavity is excited for a particular measurement.

### 2.3.14 Electro magnetic interference (EMI) shielding

EMI shielding measurements were carried out in S (2-4 GHz) band and X (7-12 GHz) band frequencies using wave-guides coupled to a ZVB20 vector network analyzer. The wave-guides were of dimensions $2.3 \times 1 \times 14.1$ cm for X band and $7.2 \times 3.4 \times 34.5$ cm for S band. The two test port cables of the network analyzer were connected via two wave-guide to coaxial adapters.
The sample was placed between the two sections of the waveguide and the output recorded. The output from the vector network analyzer is in terms of scattering parameters, $S_{xy}$. The first number in the suffix refers to what port the output is measured at and the second number refers to where the signal originate from. Hence $S_{11}$ is the reflected signal and $S_{21}$ is the transmitted signal. Shielding efficiency of the sample can be calculated from $S_{21}$.

### 2.3.15 Lignin content

0.5g of the sample was weighed ($W_1$) and 7.5 ml 72 % $H_2SO_4$ added. Kept at room temperature for 2 hours by stirring at every 15 minutes. Transferred the contents to a 500 ml RB flask and diluted with 280 ml of deionised water. Heated the liquid to a gentle boil and refluxed for 4 hours. Filtered the solution through previously ignited filtering crucible. Dried the crucible and contents at 105 ± 3 °C for 2 hours. Cooled in a desiccator and weighed ($W_2$). Placed the crucible and contents in the muffle furnace and ignited at 575 ± 25 °C for 3 hours. Cooled in a desiccator and weighed ($W_3$).

\[
\% \text{lignin} = \left( \frac{W_2 - W_3}{W_1} \right) \times 100
\]