Chapter 2

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

2.1 Materials Used

2.1.1 Polymers

1 Silicone rubber

Silicone rubber used in the present investigation was general-purpose silicone rubber supplied by GE Silicones, having the following specifications:

- Hardness: 40 (Shore A)
- Grade: FSE 7140
- Density, g/cm³: 1.41
- Appearance: Neutral
2 High density polyethylene (HDPE)

High-density polyethylene used was Indothene HD, supplied by Indian Petrochemical Corporation Ltd, Vadodara, which had the following properties:

Density, gm/cm$^3$ 0.957
Melt flow index (gm/10 min) 5.2

3 Nitrile rubber (NBR)

Nitrile rubber (NBR), used in the present study was supplied by Apar India, Mumbai that had the following specifications:

Grade Aparene N-553 NS
Acrylonitrile content 33%
Mooney viscosity [ML (1+4)] at 100°C 48

4 Natural rubber (NR)

Natural rubber used was solid block rubber ISNR-5 grade obtained from Rubber Research Institute of India, Kottayam, 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.

1. Dirt content, % by mass, max 0.05
2. Volatile mater, max 1.00
3. Nitrogen content, max 0.70
4. Ash content 0.60
5. Initial Plasticity, $P_0$, min 30.00
6. Plasticity retention index, PRI, min 60.00

5 Ethylene -propylene-diene rubber (EPDM)

Ethylene -propylene-diene rubber used has the following specifications:
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<table>
<thead>
<tr>
<th>Grade</th>
<th>SR EP 33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene content</td>
<td>33 mole%</td>
</tr>
<tr>
<td>Diene content</td>
<td>1 mole%</td>
</tr>
<tr>
<td>Mooney viscosity [ML (1+4)] at 100°C</td>
<td>52.</td>
</tr>
</tbody>
</table>

6 Low density polyethylene (LDPE)

Low-density polyethylene used was Indothene 24 FS 040 grade obtained from Indian Petrochemical Corporation Ltd, Vadodara, which had the following properties:

- Density, gm/cm³: 0.922
- Melting range, °C: 105-110
- Melt flow index at 190°C (gm/10 min): 6.0

7 Polyvinylchloride (PVC)

Polyvinyl chloride used was Emulsion grade having the K value 70.5, supplied by Indian Petrochemical Corporation Ltd, Vadodara.

2.1.2 Additives

1 Acetylene black (AB)

Acetylene black used in the study was supplied by Travancore Electrochemicals, Kerala, having the following specifications:

- Average EM particle diameter: 41 nm
- Dibutylphthalate (DBP) absorption: 310 mL 100g⁻¹

2 High structure ISAF black (N-234)

High structure ISAF black used was supplied by Cabot India Ltd. (Mumbai, India), having the following specifications:
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Average particle diameter 23 nm
DBP absorption 125 mL 100 g⁻¹

3 Lamp black (LB)

Lamp black used was supplied by Cabot India Ltd. (Mumbai), with an average particle diameter, 100 nm.

4 High Structure HAF black (N-339)

Improved High Structure HAF (N-339) black used was supplied by Cabot India Ltd. (Mumbai, India), having a DBP absorption of 120 mL 100 g⁻¹ and average particle diameter of 26 nm.

5 High Structure HAF black (N-347)

High Structure HAF (N-347) black used was supplied by Cabot India Ltd. (Mumbai, India), having a DBP absorption of 124 mL 100 g⁻¹ and average particle diameter of 27 nm.

6 Intermediate Super Abrasion Furnace black (ISAF, N-220)

Intermediate Super Abrasion Furnace (ISAF, N-220) black) used was supplied by Cabot India Ltd. (Mumbai, India), with a DBP absorption of 114 mL 100 g⁻¹ and average particle diameter of 21 nm.

7 Graphite powder

Graphite powder used in the study was supplied by Asian Minerals (Chennai), having the following specifications:
Density, g/cm³ 2.25
8 Copper powder

Electrolytic purpose grade copper powder supplied by E. Merck (India) Ltd., Mumbai, was used in the present study, having the following specifications:
- Density, g/cm³: 8.94
- Melting Point, °C: 1083
- Mohs' hardness: 3.0

9 40% active dicumyl peroxide (DCP)

Dicumyl peroxide used was a crystal with a purity of 99% and density, 1.02 (gm cm³). The recommended processing temperature of the material is 160-200°C.

10 Zinc Oxide (ZnO)

Zinc Oxide was supplied by M/s Meta Zinc Ltd, Mumbai, having the following specifications:
- Specific gravity: 5.5
- Zinc Oxide content: 99.5%
- Acidity: 0.4 % max
- Heat loss (2 hours at 100°C): 0.5% max

11 Stearic acid

Stearic acid used in the study was supplied by Godrej Soaps (Pvt) Ltd, Mumbai having the following specifications:
- Melting point: 50-69°C
- Acid number: 185 – 210
Iodine value

12 Dibenzthiazyl disulphide (MBTS)

Dibenzthiazyl disulphide used in the study was supplied by Bayer Chemicals, Mumbai and had the following specifications:
Specific gravity 1.34
Melting point $165^\circ$C

13 Tetramethyl thiruam disulphide (TMTD)

Tetramethylthiuram disulphide (TMTD), was supplied by ICI India Ltd., Mumbai, having the specifications:
Specific gravity 1.42
Melting point $140^\circ$C

14 Sulphur (S)

Sulphur (soluble), was supplied by Standard Chemical Company Pvt. Ltd., Chennai having the following specifications:
Specific gravity 2.05
Acidity 0.01% max
Ash 0.01% max
Solubility in CS$_2$ 98% max

15 Dioctylphthalate (DOP)

Dioctylphthalate used was commercial grade, supplied by Rubo-Synth Impex Pvt. Ltd., having the following specifications:
Specific gravity 0.986
Viscosity, cps 60
16 Magnesium oxide (MgO)

Magnesium oxide used was commercial grade calcined light magnesia with a specific gravity of 3.6, supplied by Central Drug House Pvt. Ltd., Mumbai.

2.1.3 Materials used in the synthesis

1 Para-phenylene diamine (PPD)

Para-phenylene diamine used for the synthesis was LR grade, supplied by Central Drug House (P) Ltd., Mumbai, having the following specifications:

- Melting point: 141°C
- Boiling point: 267°C

2 Glyoxal

Glyoxal used for the synthesis was of two types:

(a) Glyoxal 40% solution, supplied by Kemphasol, Mumbai, having the following specifications:
   - Density, g/cm³: 1.29
   - Boiling point: 51°C

(b) Glyoxal hydrate (trimer) for synthesis, supplied by Merck-Schuchardt, Hohenbrunn, which is colourless crystalline powder.

3 N,N-Dimethyl formamide (DMF)

N,N-Dimethyl formamide used had an assay (GC) of 99.5%, boiling point of 153°C, density of 0.9445 g/cm³ and was supplied by E. Merck (India) Ltd., Mumbai.
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4 m-Cresol

m-Cresol used was 98% pure, LR grade, supplied by Central Drug House (P) Ltd., Mumbai, having boiling point of 202°C and density of 1.034 g/cm³.

5 Toluene

Toluene used in the present study was sulphur free, LR grade, supplied by s.d. fine-CHEM Ltd., Mumbai, having boiling point of 110°C and density of 0.866 g/cm³.

6 Methanol

Methanol used in the present study was AR grade, supplied by s.d. fine-CHEM Ltd., Mumbai having boiling point of 65°C and density of 0.7866 g/cm³.

6 Tetrahydrofuran (THF)

Tetrahydrofuran used was supplied by E. Merck (India) Ltd., Mumbai, having boiling point of 66°C and density of 0.8892 g/cm³.

8 Acetone

Acetone used in the present study was LR grade, supplied by s.d. fine-CHEM Ltd., Mumbai.

9 Silica

Silica used was Ultracil VN-3, having a surface area of 170 m²g⁻¹ and particle size range 11-19 nm, supplied by United Silica Industrial Ltd., Taiwan.
10 Hydrochloric acid (HCl)

Hydrochloric acid used was LR grade, having an assay (acidimetric) of 35-38 %, supplied by E. Merck (India) Ltd., Mumbai.

11 Perchloric acid (HClO₄)

Perchloric acid used was 60 %, LR grade, supplied by Citra Diagnostics, Kochi.

12 Iodine (I₂)

Iodine used was LR grade, supplied by Qualigens fine chemicals, Mumbai.

13 Carbon tetra chloride (CCl₄)

Carbon tetra chloride used was supplied by E. Merck (India) Ltd., Mumbai.

14 Sodium hydroxide (NaOH)

Sodium hydroxide used in the present study was LR grade, supplied by s.d.fine-CHEM Ltd., Mumbai.

2.2 Experimental methods

2.2.1 Brabender Mixing

Brabender Plasticorder (a type of torque rheometer made by M/s Brabender OHG Duisburg, Germany, Model PL 3S) has been widely used for polymer blending, processability studies of polymers, modelling processes such as extrusion and evaluation of the rheological properties of the polymer melts.¹⁻⁵ The
torque rheometer is essentially a device for measuring the torque generated due to the resistance of a material being mixed or flowing under preselected conditions of shear and temperature. The heart of the torque rheometer is a jacketed mixing chamber whose volume is approximately 40 cc for the model used. Two horizontal rotors with protrusions do mixing or shearing of the material in the mixing chamber. The resistance generated by the material is made available with the help of a dynamometer. The dynamometer is attached to a precise mechanical measuring system, which indicates and records the torque. A DC thyristor controlled drive is used for speed control of the rotors (0 to 150 rpm range). Circulating hot silicone oil controls the temperature of the mixing chamber. The temperature can be varied up to $300^\circ$C. Thermocouple with a temperature recorder is used for control and measurement of temperature. Different types of rotors can be employed depending upon the nature of the polymers.

The rotors can be easily mounted and dismounted by simple fastening and coupling system. Once test conditions (rotor, type, rpm and temperature) are set, sufficient time should be given for the temperature to attain the set value and become steady, subsequently the material can be charged into the mixing chamber.

### 2.2.2 Mill Mixing and Homogenization using Mixing Mill

Mixing and homogenization of elastomers and compounding ingredients were done on a laboratory size (15 x 33 cm) two-roll mill at a friction ratio of 1:1.25. The elastomer was given one pass through the nip of (0.002 X 100")$. Then it was given two passes through the nip of (0.002 x 10)" and allowed to band at the nip of (0.002 x 55)" after the nerve had disappeared. The compounding ingredients were added as per ASTM D 3184 (1980). The band was properly cut from both sides to improve the homogeneity of the compound.
After completion of the mixing, the compound was homogenized by passing six times endwise through a tight nip and finally the batch was sheeted out as very thin sheet (2 mm thickness).

2.2.3 Cure characteristics using Goettfert Elastograph.

The cure characteristics of the compounds were determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotor less cure meter with a quick temperature control mechanism and well defined homogeneous temperature distribution in the die or test chamber. In this instrument, a specimen of definite size is kept in the lower half of the cavity, which is oscillated through a small deformation angle ($\pm 0.2^\circ$). The frequency is 50 oscillations per minute. The torque is measured on the lower oscillating die half.

The following data can be taken from the torque-time curve.

1. Minimum torque: torque obtained by the mix after homogenizing at the test temperature before the onset of cure.
2. Maximum torque: this is the torque recorded after the curing of the mix is completed.
3. Scorch time ($t_{10}$): this is the time for attaining 10% of the maximum torque.
4. Optimum cure time ($t_{90}$): This is the time taken for attaining 90% of the maximum torque.
5. Cure rate: Cure rate was determined from the following equation

   \[ \text{Cure rate (Nm/min)} = \frac{(T_{\text{max}} - T_{\text{min}})}{(t_{90} - t_{10})} \]

where $T_{\text{max}}$ and $T_{\text{min}}$ are the maximum and minimum torque respectively and $t_{90}$ and $t_{10}$ are the times corresponding the optimum cure time and scorch time respectively.

The elastograph microprocessor evaluates the vulcanization and prints out these data after each measurement.
2.2.4 Moulding of test specimens

The test specimens for determining the physical properties were molded in standard mould by compression molding in an electrically heated hydraulic press having 45 x 45 cm platens at a pressure of 200 kg/cm² in the mould. The rubber compounds were vulcanized up to their respective optimum cure times at specified temperatures. Upon completion of the required cure cycle, the pressure was released and the sheet was stripped off from the mould and suddenly cooled by plunging into cold water. After a few seconds, the samples were taken from the cold water; and stored in a cold dark place for 24 h and were used for the subsequent tests.

2.3 Physical test methods

For parameters described below, at least three specimens per sample were tested for each property and the mean values reported.

2.3.1 Tensile strength, elongation at break and modulus

These parameters were determined according to ASTM D 412 (1980) test method, using dumb bell shaped test pieces. The samples were punched out from the moulded sheets using C-type die along the mill grain direction of the vulcanized sheets. The thicknesses of the narrow portion of specimens were measured using a dial gauge. The specimens were tested on a Zwick universal testing machine (UTM) model 1445 at 28±2°C and at a crosshead speed of 500 mm per minute. The tensile strength, elongation at break and modulus were recorded on a strip chart recorder. The machine had a sensitivity of 0.5 % of full-scale load.
The ultimate tensile strength (TS) of the sample was measured as the force measured by the load cell at the time of break divided by the original cross sectional area of the sample at the point of minimum cross section.

Ultimate tensile strength = Force (N)/cross sectional Area (mm$^2$)

The elongation at break (EB %) of the sample was measured in terms of its initial length 'L$_0$' and final length 'L$_1$' as,

EB = (L$_1$ - L$_0$) x 100/L$_0$

2.3.2 Tear strength

The samples were cut from the compression-molded sheets parallel to the mill grain direction. The test was carried out on a Zwick Universal Testing Machine (UTM) as per ASTM D 624 91981) using the un nicked, 90° angle test pieces. The speed of extension was 500 mm/min and the test temperature 28±2°C.

2.3.3 Hardness

The hardness of the samples was tested using Zwick 3114 hardness tester (shore A) in accordance with ASTM D 2240 (1981). The tests were performed on mechanically unstressed samples. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens.

2.3.4 Density

The prepared polymer samples were compressed into pellets in a pelletizer. The mass of the pellet and thickness of the pellet was determined and the volume of the pellet was calculated using the equation, V = π$r^2$t, where 'V' is the volume of the pellet, 'r' is the radius of the pellet and 't' is the thickness of the pellet. The density of the sample is then calculated from the equation,
2.3.5 Measurement of D.C. conductivity

The problems due to external electrical pick-ups and varying humidity in the laboratory can be minimized by holding the samples inside a metal chamber as shown in figure 2.1. Figure 2.1 shows various parts of the conductivity cell. The chamber was well grounded and could be evacuated to $10^{-2}$ torr so that it acted as a shield to the electrical pick-ups and ambient humidity. The chamber had a metallic cylindrical body of height 30 cm and diameter of 10 cm. It also had a pumping port, which could be connected to a rotary pump. The top of the cell was closed vacuum tight using a circular metal plate, from which a sample holder was connected by welding. This holder was provided with a heater (~40W) in order to vary the temperature of the sample for measurement purposes. The heating rate of the sample can be maintained constant, throughout the experiment by carefully adjusting the voltage. All insulations of the holder were made from Teflon. The heater could go up to $-200^\circ$C. A chromel-Alumel thermocouple was used to measure the temperature. The electrodes of the holder were copper blocks mounted on Teflon strips. The electrical connections were taken out through BNCs. Shielded cables were used outside the metallic cell, to make connections to d.c. power supply and electrometer.

A steady d.c. power supply (6 V) was used as the voltage source. The current flowing through the sample was measured by a digital multimeter (APLAB model 1087). For low conductivity samples, Keithley 236 Source Measurement Unit was used for the current measurement.

Schematic diagram of experimental setup used for D.C. conductivity measurement in the present work is shown in figure 2.2. For electrical conductivity measurements the silver electrodes were deposited in the planar rubber sample with a gap in between them. The d.c. voltage was applied across
The voltage was measured using a high impedance digital voltmeter. The electrometer was connected in series with the power supply and the samples. The pressure inside was maintained constant at $10^{-2}$ torr using a Rotary pump for rubber samples. The measurements were done at atmospheric pressure for the synthesized samples in the pellet form. The temperature was noted by measuring the voltage across the thermocouple. The d.c. bias (6V) was applied as shown in Fig. 2.2. The temperature of the sample was slowly increased at a constant rate using the variable D.C. power supply. Then the current through the sample was monitored using the digital multimeter at different temperatures, from 25°C to 150°C. The electrical conductivity, $\sigma$, can be calculated using the equation,

$$\sigma = \frac{J}{E}$$

where $J$ is the current density, $E$ is the field strength, and $A$ is the area.

Resistivity is the reciprocal of conductivity.

The temperature dependence of the electrical conductivity is described by an expression of the type

$$\sigma = \sigma_0 \exp\left(-\frac{E}{kT}\right)$$

where, $\sigma$ is the conductivity of the sample at a temperature $T$, $\sigma_0$ is the constant which is characteristic of the material, $E$ is the energy of activation, and $k$ is the Boltzmann constant.

$$\log \sigma = \log \sigma_0 - \left(\frac{E}{kT}\right)$$
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Fig. 2.1 Conductivity cell

1. Metal cylinder
2. Glass window
3. B.N.C.
4. LN₂ chamber
5. Teflon blocks
6. Electrode
7. Substrate with film
8. Heater/Substrate holder
9. Electrode-LN₂ interconnections
10. Electrical connections to the heater
11. Pumping ports
12. Thermocouple
2.3.6 Measurement of microwave conductivity

The dielectric properties and conductivity of the samples were measured using cavity perturbation technique. The experimental set up consists of a HP 8510 vector network analyzer, sweep oscillator, S-parameter test set and rectangular cavity resonator. The measurements were done in S-band at 2.17GHz at room temperature (25°C).

In microwave studies the conductivity can be calculated using the equation,

\[ \text{Conductivity, } \sigma = 2\pi f_0 \varepsilon_0 \epsilon_r \]
where \( f_s \) is the resonant frequency, \( \varepsilon_0 \) is the dielectric constant of air and \( \varepsilon_r'' \) is the imaginary part of the complex permittivity, which is given by the equation,

\[
\varepsilon_r'' = \frac{(V_c/V_s)(Q_t - Q_s)}{Q_t Q_s}
\]

where, \( V_c \) is the volume of cavity, \( V_s \) is the volume of sample, \( Q_s \) is the quality factor of the cavity loaded with the sample and \( Q_t \) is the quality factor of the cavity with the empty sample holder.

The real part of the complex permittivity \( \varepsilon_r' \) is usually known as dielectric constant of the material. It can be calculated from the equation,

\[
\varepsilon_r' = 1 + \frac{(f_t - f_s)}{2f_s (V_c/V_s)}
\]

where \( f_t \) is the resonant frequency of the unloaded cavity and \( f_s \) is the resonant frequency of the cavity loaded with the sample.

The pelletized samples were inserted into the cavity and the perturbations produced at a particular microwave frequency were noted. The resonant frequency and quality factor were recorded and dielectric constant and microwave conductivity were calculated using the above equations.

2.3.7 Thermal diffusivity

Thermal properties of polymeric materials are always important and often critical in both processing stages and product uses. Thermal diffusivity is an important material property, determining the temperature distributions in nonsteady-state heat conduction. It can be defined by the mathematical expression,

\[
\alpha = \frac{\kappa}{\rho c_p},
\]

where \( \kappa \) is the thermal conductivity, \( \rho \) is the density and \( c_p \) is the specific capacity at constant pressure. In general, thermal conductivity of polymers are quite low and of the order of 0.1 –0.3 \( \times \) 10^{-6} m^2/Sec.

Thermal diffusivity was determined by photo acoustic technique.
2.3.8 Infrared spectroscopy

Infrared (IR) spectra are generated by the absorption of electromagnetic radiation in the frequency range 400 to 4000 cm\(^{-1}\) by organic molecules. Different functional groups and structural features in the molecule absorb the characteristic frequencies. The frequency and intensity of absorption are indication of the bond strengths and structural geometry in the molecule. Particles of the polymer samples were flattened by means of cold compression between two diamond windows. IR spectra of the samples were recorded with a Biorad UMA 500 infrared microscope, which is coupled to a Biorad FTS 6000 spectrometer. Spectra were recorded with a resolution of 4 cm\(^{-1}\) co-adding 100 scans.

2.3.9 Thermo gravimetric analysis (TGA)

TGA measures the change in the mass of a sample as it is heated, cooled, or held isothermally. Therefore, a TGA can detect percentage of moisture and volatiles, percentage of fillers and additives in multicomponent system, compositional difference in blends, degradation temperature and decomposition kinetics study of a sample. The two most important information that can be extracted out of the thermogram are: (a) the extrapolated onset temperature, which provides indication of the thermal stability of the specimen, and (b) the percentage weight of loss of the components present, which enables quantification of organic polymer and additives. Thermo gravimetric analysis was recorded on Perkin-Elmer TGA-7 instrument at a heating rate of 10°C/min. from 35°C to 800°C in nitrogen atmosphere.

2.3.10 Molecular weight determination

Molecular weight of the polymer was determined by Gel Permeation Chromatography. GPC (Waters WISP 710 B) equipped with PFG columns, provided by PSS polymer standard services. Measurements were conducted in
Hexa fluoro isopropanol at 25°C at a flow rate of 0.4 ml/min. using a UV detector (Waters 490).

2.3.11 UV-Visible spectroscopy

UV spectra of the palletized polymer samples were taken using HITACHI 330 spectrophotometer.
2.4 References