CHAPTER 2

MATERIALS AND EXPERIMENTAL TECHNIQUES
2.1 Materials

2.1.1 Styrene butadiene rubber (SBR)

Styrene butadiene rubber (Synaprene 1502) was obtained from Synthetics and Chemicals Ltd., Bareilly, U. P., India. The basic characteristics of SBR are given in Table 2.1.

<table>
<thead>
<tr>
<th>Table 2.1. Basic characteristics of SBR</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>21.5-25.5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>0.75</td>
</tr>
<tr>
<td>Soap</td>
<td>0.70</td>
</tr>
<tr>
<td>Ash</td>
<td>0.5</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.5-1.5</td>
</tr>
<tr>
<td>Cis-1,4</td>
<td>18</td>
</tr>
<tr>
<td>Trans-1,4</td>
<td>65</td>
</tr>
<tr>
<td>1,2(vinyl)</td>
<td>17</td>
</tr>
</tbody>
</table>

2.1.2 Polychloroprene rubber (CR)

Neoprene (W type) was obtained from DuPont de Nemours and Company. The structural units in the neoprene polymer chain are in Table 2.2.
Table 2.2.  Structural changes in the neoprene polymer chain

<table>
<thead>
<tr>
<th>Type of addition</th>
<th>Formula</th>
<th>Approximate per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tran-1,4</td>
<td>[\text{-H}<em>2\text{C}</em>\text{C}=\text{C}_\text{H}_2-\text{Cl}]</td>
<td>85</td>
</tr>
<tr>
<td>Cis-1,4</td>
<td>[\text{-H}<em>2\text{C}</em>\text{C}=\text{C}_\text{H}_2\text{-Cl}]</td>
<td>10</td>
</tr>
<tr>
<td>1,2</td>
<td>[\text{-CH}<em>2\text{-C}</em>\text{H}\text{-CH}_2\text{CH}_2]</td>
<td>1.5</td>
</tr>
<tr>
<td>3,4</td>
<td>[\text{-CH}<em>2\text{-C}</em>\text{Cl}_\text{H}_2]</td>
<td>1.0</td>
</tr>
</tbody>
</table>

2.1.3 *Nitrile rubber (NBR)*

Butadiene acrylonitrile copolymer of medium acrylonitrile content, Chemaprene N-3309 supplied by Synthetics and Chemicals Ltd., Bareilly, U.P., India. The detailed specifications of this rubber are given in Table 2.3.
### Table 2.3. Specification of nitrile rubber

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volatile matter (% max)</td>
<td>0.75</td>
</tr>
<tr>
<td>Ash (% max)</td>
<td>1.0</td>
</tr>
<tr>
<td>Antioxidants (%)</td>
<td>1.0</td>
</tr>
<tr>
<td>Bound acrylonitrile content (%)</td>
<td>31-35</td>
</tr>
<tr>
<td>Mooney viscosity M_{L(1+4)} at 100°C</td>
<td>40-60</td>
</tr>
<tr>
<td>Soap (%)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

2.1.4 *Natural rubber (NR)*

Natural rubber (ISNR 5, Indian Standard Natural Rubber-5) was obtained from Rubber Research Institute of India, Kottayam, Kerala, India. The specification parameters for ISNR-5 grade natural rubber is given in Table 2.4.

### Table 2.4. Specification of ISNR-5 grade NR

<table>
<thead>
<tr>
<th>Parameters</th>
<th>%/Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt content</td>
<td>0.5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>0.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.3</td>
</tr>
<tr>
<td>Ash</td>
<td>0.4</td>
</tr>
<tr>
<td>Initial Plasticity $P_0$</td>
<td>38</td>
</tr>
<tr>
<td>Plasticity Retention Index PRI</td>
<td>78</td>
</tr>
</tbody>
</table>

2.1.5 *Solvents*

Toluene, chloroform, isopropyl alcohol, n-heptane were of reagent grade and supplied by Merck India Ltd., Mumbai.
2.1.6 Chemicals and fillers

Cetyl trimethyl ammonium bromide was obtained from E-Merk India Ltd., Mumbai. All the chemicals used for the preparation of rubber compounds were of industrial purity, sodium hydroxide, dicumyl peroxide (40% active), zinc oxide, stearic acid, N-cyclohexyl-2-benzothiazyl sulphenamide, ethylene thiourea, tetramethyl thiuram disulphide, 2,2,4-trimethyl 1,2-dihydroquinoline and sulphur were supplied by Bayer (India) Ltd., Mumbai.

Fillers

HAF: High abrasion furnace black (N220) was obtained from Philips Carbon Black Ltd., Durgapur.

Silica: Precipitated silica was supplied by Bayer (India) Ltd., Mumbai.

2.2 Preparation of dichlorocarbene modified styrene butadiene rubber (DCSBR)

Addition of dichlorocarbene to SBR was carried out by the alkaline hydrolysis of CHCl₃ using phase transfer catalyst, according to the method by Makosza¹ and later developed by Joshi.² SBR was dissolved in toluene, the phase transfer catalyst was added to this and the mixture was stirred. To this, CHCl₃ was added drop wise followed by NaOH solution (50%). The reaction product was separated from the solution and washed with hot water and cold water, until free of chlorine. The product was coagulated with isopropyl alcohol and reprecipitated from toluene solution. The modification was monitored by the determination of chlorine percentage at different times using the method of chemical analysis.
2.3 Estimation of chlorine content of the polymer

About 2 g of rubber is accurately weighed and embedded in about 2 g of fusion mixture prepared by mixing equal proposition of sodium carbonate and potassium carbonate in a platinum crucible. The contents of the crucible are fused at 900°C in a muffle furnace. The fused material is extracted in about 100 ml of distilled water and acidified with concentrated HNO₃ till liberation of carbon dioxide stop and the solution is neutral. About 5 ml more of concentrated HNO₃ is added and the solution is boiled. 40 ml of standard silver nitrate is added to the hot solution. After precipitation of the chloride, the solution is filtered and washed down with distilled water. The filtered solution is titrated with standard ammonium thiocyanate using ferric alum as indicator, to estimate the unreacted silver nitrate. The end point is the formation of a faint red colour. A blank determination is also carried out simultaneously.

\[
\text{% of chlorine} = \frac{(B - V) \times N \times 35.5}{W} \times 100
\]

where B is the volume of NH₄CNS required for the blanks,

V is the volume of NH₄CNS required for the sample, and

W is the weight of sample.

2.4 Preparation of elastomers and elastomer blends

The mixes were prepared on a laboratory size two roll mixing mill (325 x 150 mm) at a friction ratio of 1:1.5 according to ASTM D3182-74 by careful control of temperature, nip gap, time of mixing and by uniform cutting operation. The compounding ingredients were added in the following order after mastication of rubber, ZnO, stearic acid, antioxidant, filler, plasticiser and finally curatives.
2.4.a NR/DCSBR blends

Separate master batches of NR and DCSBR were prepared with all compounding ingredients without accelerator and sulphur. The master batches were blended at 70/30, 50/50 and 30/70 compositions and finalised with curatives on a two roll mixing mill. The compatibilised blends were prepared by adding the required concentration of compatibiliser to the blended master batches, before the addition of curatives.

DCSBR was vulcanised at 150°C in a hydraulic press by either sulphur vulcanisation system or peroxide vulcanising system.

2.4.b SBR/NBR blends

Master batches of SBR, NBR (without accelerator and sulphur) were prepared separately and then blended at different compositions of 70/30, 50/50 and 30/70. DCSBR, used as the compatibiliser with varying chlorine content from 15 to 35% was added to the preblended SBR/NBR blends at a constant dosage of 5 phr and compatibiliser having 25% chlorine content was added at various concentrations of 1-10 phr. The required quantity of curatives were then added and mixed properly with the pre-blended mixes. The effect of loading of fillers such as carbon black and silica (10-40 phr) on 50/50 blend compatibilised by 5 phr DCSBR containing 25% chlorine are prepared. The effect of loading of carbon black and silica on SBR/NBR blend with different composition (70/30, 50/50, 30/70) in the presence (5 phr compatibiliser) and absence of DCSBR were carried out in a two roll mixing mill. In the case of filled mixes the fillers such as carbon black and silica were added after blending the rubbers. The curatives were added after addition of fillers.
2.4.2 SBR/CR blends

Master batches of SBR and CR (without accelerator and sulphur) were prepared separately and then blended at different compositions (70/30, 50/50 and 30/70). The compatibiliser (DCSBR) with varying chlorine content from 15 to 35% were added to the preblended SBR/CR at a constant dosage of 5 phr and DCSBR having 25% chlorine content was added at various dosage of 1-10 phr on 50/50 preblend compositions. The effect of loading of fillers such as carbon black and precipitated silica (10-40 phr) on 50/50 blend compatibilised by 5 phr DCSBR containing 25% chlorine. The effect of loading of carbon black and precipitated silica of 50/50 SBR/NBR blend in the presence (5 phr) and absence of DCSBR.

2.5 Processing characteristics

2.5.1 Monsanto rheometer

The cure characteristics were determined using a Monsanto rheometric model R-100. Optimum cure time ($t_{90}$) is the time for the development of 90% of maximum rheometric torque. It is calculated using the equation,

$$t_{90} = 90 \left( \frac{M_h - M_n}{100} \right) + M_n$$

where $M_h$ and $M_n$ are the maximum and minimum rheometric torque respectively.

Rheometric scorch time is the time required for the torque value to increase by two units above the minimum torque at 150°C, denoted as $t_2$. Rheometric induction time (time required for the torque value to increase by one unit above the minimum torque at 150°C) denoted as $t_1$. 
2.6 Preparation of vulcanised samples

Samples were cured to the optimum cure time in a hydraulic press using a pressure of 300 kg/cm². The samples were immediately cooled after removed from the mould.

2.7 Characterisation studies

2.7.1 $^1H$ FTNMR studies

SBR and modified SBR was dissolved in a proton-free solvent such as CCl₄ or DCCl₃ (Although deuterium is NMR active, it does not interfere because it does not absorb in the frequency range set in instrument for $^1H$). If a more polar solvent is needed, dry (CD₃)₂S=O (perdeuterodimethyl sulfoxide) issued. The solution is placed in a long thin glass tube which is spun in the magnetic field so that all the molecules are exposed to a uniform magnetic field. A small amount of a reference compound, tetramethyl silane (CH₃)₄Si is added to the sample. The spectrum is taken with a 90 MHz JEOL EX90 FTNMR and when the $H_0$ value is reached-enabling the proton to be in resonance at the resonance at the set frequency, a signal (peak) is traced on a calibrated chart paper that plots transmittance vs. $H_0$.

2.7.2 FTIR

IR spectra of samples were recorded with a Shimadzu-8101 M Fourier transform infrared spectrophotometer, using thin films and pyrolysate of polymer. The thin film was prepared by dissolving the polymer in chloroform and then the concentrated solution (5%) was directly caste on a levelled glass plate. The light source (an electrically heated solid, e.g., a nichrome wire) produces a beam of infrared radiation which is divided (by a system of mirrors) into two parallel beams of equal intensity radiation. The sample is in
the path of one beam and the other may be used as a reference beam when a solution is to be analysed. A slowly rotating diffraction grating or prism varies the wavelength of radiation reaching the sample and then the detector. The detector records the difference in intensity between the two beams on a recorder chart as percentage transmittance. Maximum transmittance is at the top of the vertical scale, so absorbance is observed as a minimum on the chart even though it is called a peak.

2.7.3 Gel permeation chromatography

Molecular weight determination was carried out by a Waters 510 gel permeation chromatography (GPC) instrument attached to a 410 diffraction refractometer. HPLC-grade toluene was used as a solvent with a flow rate set to 1 ml/min. The GPC columns were calibrated with polystyrene standards.

2.8 Thermal analysis

Thermal analysis was carried out using a differential scanning calorimeter (DSC) and a thermogravimetric analyser (TGA) and dynamic mechanical analysis (DMA).

2.8.1 Differential scanning calorimeter

Direct calorimetric measurements, characterisation and analysis of thermal properties of the sample were made using a Perkin Elmer 7 series differential scanning calorimeter. Sub-ambient operation was carried out by cooling the specimen and the specimen holder with liquid nitrogen. Exactly weighed (about 5 mg) of sample was used for the studies. Samples were encapsulated in standard aluminium pans and covers and sealed by crimping. For purging the sample holders pure dry nitrogen gas (99.99%) was used.
The inlet gas pressure was adjusted at 2 kg/cm² to attain a flow rate of about 25 ml/min. Scanning rate was 15°C/min.

2.8.2 Thermogravimetry

A Perkin Elmer make thermogravimetric analyser was used for the studies. It is a computer controlled instrument that permits the measurement of weight changes in the sample as a function of temperature or time. It is programmed in the required temperature range to measure the weight change resulting from chemical reaction, decomposition, solvent and water evolution, curie point transitions and oxidation of the sample materials. The temperature is scanned at a linear rate. The instrument supplied by Perkin Elmer had two components, an ultrasensitive micro balance and a furnace element. The balance is sensitive to 0.1 microgram and the furnace could be heated from ambient to 1000°C at rates of 0.1 to 200°C per min. For purging the sample holder, gases commonly used are oxygen, air (a mixture of 80% nitrogen and 20% oxygen) or nitrogen so as to study the oxidation, burning and thermal stability of the materials. The purge gas flows directly over the sample. The recommended flow rate of the sample purge was kept less than the flow rate of the balance purge at all times.

2.8.3 Dynamic mechanical thermal analysis

The dynamic mechanical properties of the blends were measured using a dynamic mechanical analyser (Polymer Laboratories DMTA MK-II), consist of a temperature programmer and a controller. It measures dynamic moduli (both storage and loss) and damping of the specimen under oscillatory load as a function of temperature. The experiment was conducted at a dynamic strain of 4% at a frequency of 0.1 Hz. Liquid nitrogen was used to achieve subambient temperature and a programmed heating rate of 1°C min⁻¹ was
used. Mechanical loss factor tan δ and the dynamic moduli (E' and E'') were calculated with a microcomputer. Samples of dimension 70 x 10 x 2.5 mm were prepared for testing.

2.9 Flammability behaviour

2.9.1 Limiting oxygen index

The above test was carried out using a Limiting Oxygen Index (LOI) apparatus manufactured by Appireillage Industrial Scientific Company, France. Both oxygen and nitrogen were connected to the equipment through pressure regulators (about 2 bars). The flow of gases was regulated at 17 litres per minute by adjusting the flow speed to 4 cm per minute on the glass tube.

Test specimens of 70 to 150 mm long, 6.5 mm wide and 3 mm thick were cut from vulcanised sheets and clamped in the specimen holder vertically in the approximate centre of the column with the top of the specimen at least 100 mm below the top of the open column.

A concentration of oxygen in the mixture was selected and the flow valves were adjusted so as to read the oxygen concentration. The test chamber was purged with the mixture for 30 seconds and the specimen was ignited with the ignition flame so that it was well lit and the entire top was burning. Subsequent trials were carried out with new specimens with varying concentration of oxygen. The level of oxygen flow was adjusted to the minimum at which the specimen burned for 3 minutes or more than 30 mm length, whichever is earlier. The test specimen was changed after each trial and the test continued until reaching the minimum oxygen concentration with a precision of at least 0.2%.
2.10 Scanning electron microscopy studies

The scanning electron microscopy (SEM) photomicrographs given in this work were obtained using JEOL 35C model scanning electron microscope. The fracture surfaces were carefully cut from the failed test specimens without touching the surface and were sputter-coated with gold within 24 h of testing. The SEM observations were made within 24 h of gold coating. The fractured test specimens and the gold coated samples were stored in a desiccator till the SEM observations were made. There should not be any change in the fracture pattern when the SEM observations were made one month after gold coating.6

2.11 Crosslink density determination

2.11.a From mechanical measurements

The extent of physical crosslinks in an elastomer vulcanisate can be understood by the use of Mooney-Rivlin equation.7

\[ F = 2A_0(\lambda-\lambda^{-1}) (C_1 + \lambda^{-2} C_2) \]  

where \( F \) is the extension force required to stretch a piece of rubber vulcanisate of cross-section area \( A_0 \), to an extension ratio \( \lambda \). A plot of \( F/2A_0 (\lambda-\lambda^{-1}) V_s \lambda^{-1} \) gives a straight line whose \( \lambda \) intercept \( C_1 \) is directly related to the physically effective crosslink density \( \langle \rho_{phys} \rangle \) by the equation,

\[ C_1 = \rho R T \langle \rho_{phys} \rangle \]  

2.11.b From solvent swelling

The crosslink density of the samples was determined by the swelling method. The samples were allowed to swell in toluene and the equilibrium uptake is noted. The molecular weight between crosslinks \( M_c \) is calculated using Flory-Rehner equation.8
\[
\frac{1}{2M_c} = \left[ \frac{\rho_r V_s (V_f)^{1/3}}{\ln(1 - V_r) + V_r + \chi^2 V_r^2} \right]
\]

where \(M_c\) = molecular weight of polymer between two crosslinks
\(\rho_r\) = density of polymer
\(V_s\) = molar volume of solvent
\(V_r\) = volume fraction of polymer in swollen mass

The method of Ellis and Welding\(^9\) is given by

\[
V_r = \frac{(d-fw)\rho_r^{-1}}{(d-fw)\rho_r^{-1} + A_s \rho_s^{-1}}
\]

where \(A_s\) = amount of solvent absorbed
\(\rho_r\) = density of rubber
\(\rho_s\) = density of solvent
\(d\) = deswollen weight of the sample
\(fw\) = fraction of insoluble components
\(\chi\) = interaction parameter which is given by Hildebrand\(^{10}\) equation as

\[
\chi = \beta + \frac{V_s}{RT} (\delta_s - \delta_p)^2
\]

where \(\beta\) = lattice constant; \(V_s\) = molar volume; \(R\) = universal gas constant; \(T\) = absolute temperature; \(\delta_s\) = solubility parameter of solvent; \(\delta_p\) = solubility parameter of polymer.

From molecular weight between crosslinks \(M_c\), the crosslink density \(v\) was calculated using the following equation.

\[
v = 1/2M_c
\]
2.12 Physical test methods

2.12.1 Modulus, tensile strength and elongation at break

These three parameters were determined according to ASTM D412-92, using dumbbell specimens. The test specimens were punched out from moulded sheets using the C-type die, along the mill grain direction. The thickness of the specimen within the gauge length of the test specimen was measured using a dial gauge of accuracy 0.001 mm. The specimens were tested on a Zwick Universal Testing Machine (UTM) model 1474 at ambient temperature and at a crosshead speed of 500 mm per minute. The elongation at break, modulus and tensile strength were obtained as a print out.

2.12.2 Tear resistance

Tear resistance of the samples was tested as per ASTM-D-624-81, using unnicked 90° angle test specimens that were punched out from moulded sheets, along the mill grain direction. This test was also carried out on a Zwick UTM, at a crosshead speed of 500 mm per minute. The tear strength was reported in kN/m.

2.12.3 Hardness

Hardness of the samples was measured according to ASTM D-2240-81 using a Shore A type durometer which employed a calibrated spring to provide the indenting force. Since the hardness reading decreased with time after firm contact between the indentor and the sample, the recordings immediately after establishment of firm contact were taken.
2.12.4 Abrasion resistance

The abrasion resistance of the samples was tested using a DIN abrader according to DIN No. 5351 test method. Circular sample having a diameter of 6 ± 0.2 mm and a thickness of 6-10 mm was kept on a rotating sample holder and 10 N load was applied. Initially a pre-run was given for the sample and its weight was taken. The weight after the final run was also noted. The difference in weight is the abrasion loss.

DIN abrasion loss of specimens in mm³

= DIN abrasion loss x abrasion index of standard specimen (2.7)

where

Abrasion index of standard specimen

\[
= \frac{200}{\text{Loss of weight in gm for the standard specimen} \times 1000}
\] (2.8)

DIN abrasion loss

= Loss of weight in gm of the rubber vulcanizate

\[\times 1000 / \text{specific gravity of specimen}\] (2.9)

2.12.5 Compression set

The compression set was measured according to ASTM D 395-71 (Method B). The samples (1.25 cm thickness and 2.8 cm diameter) in duplicate, compressed to give 25% deflection, were kept in an air oven at 70°C for 22 h. After the heating period, the compression was released, the samples were cooled to room temperature for half an hour and final thickness was measured. Compression set was calculated using the equation,

\[
\text{Compression set (\%)} = \frac{t_0 - t_f}{t_0 - t_s} \times 100
\] (2.10)

where \( t_0 \) and \( t_f \) are the initial and final thickness of the specimen, respectively and \( t_s \), the thickness of the spacer bar used.
2.12.6 Rebound resilience

The rebound resilience of the composites was measured using Dunlop Tripsometer (BS 903, Part 22, 1950). The sample was held in position by applying vacuum. It was conditioned by striking the indentor six times. The temperature of the specimen holder and the sample was kept constant at 35°C. Rebound resilience was calculated as

\[ \text{Rebound resilience (\%)} = \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \times 100 \]  

(2.11)

where \(\theta_1\) and \(\theta_2\) are the initial and rebound angles respectively. \(\theta_1\) was 45° in all cases.

2.13 Degradation studies

2.13.1 Ozone cracking

The ozone test chamber manufactured by MAST Development Company, USA, was used to study ozone cracking. The chamber provided an atmosphere with a controlled concentration of ozone and temperature. Ozone concentration used was 50 ppm which is generated by a UV quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38.5°C. Ozone determination was evaluated by determining the amount of cracks obtained in the specimen after exposure to ozone for a definite period.

2.13.2 Thermal ageing

Test samples (2 ± 0.2 mm thick) were aged at 70°C for 96 h in an ageing oven. The tensile strength, elongation at break were measured before and after ageing. The percentage retention of properties after ageing was calculated.
2.13.3 Oil ageing

Oil ageing was carried out by immersing the test specimen about 2 cm x 1 cm in ASTM oils 1, 2 and 3. The weight of oil uptake was evaluated by measuring the swollen weight of samples after a specific time. The swollen samples were immersed in acetone wiped with filter paper, and transferred to weighed bottle and the final weight of the sample were taken.

\[
\text{Weight of oil absorbed} = \frac{M_2}{M_1} \times 100
\]  

(2.12)

References