A detailed description of the experimental procedures adopted and the materials used in the present study is given in this chapter.

2.1. MATERIALS USED

2.1.1 Elastomers

2.1.1.A. Natural Rubber (NR)

Natural rubber confirming to ISNR-5 grade of Mooney viscosity (M<sub>L</sub> 1+4, 100°C) equal to 85, used in the present study, is obtained from Rubber Research Institute of India, Kottayam. For a particular experiment rubber from the same lot has been used because the molecular weight, molecular distribution and non rubber constituents of natural rubber are known to be affected by clonal variation, season, use of yield stimulant and method of preparation<sup>1,2</sup>. Specification of the ISNR-5 grade rubber is given below.
Chapter 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt content, % by mass, max.</td>
<td>0.05</td>
</tr>
<tr>
<td>Volatile matter, % by mass, max.</td>
<td>1.00</td>
</tr>
<tr>
<td>Nitrogen, % by mass, max.</td>
<td>0.70</td>
</tr>
<tr>
<td>Ash, % by mass, max.</td>
<td>0.60</td>
</tr>
<tr>
<td>Initial plasticity, P_o, min.</td>
<td>30.00</td>
</tr>
<tr>
<td>Plasticity retention index</td>
<td>60.00</td>
</tr>
</tbody>
</table>

2.1.1.B. Natural Rubber Latex

High ammonia type 60% centrifuged natural rubber latex confirming to the specifications of the bureau of Indian standards, (BIS 5430-1981) used in this study. It was obtained from M/s Harrison Malayalam Ltd., Kochi. The properties of the latex used are given below.

- Dry rubber content, % by mass: 60.04
- Total solid content, % by mass: 61.05
- Coagulum content, % by mass: 0.03
- Sludge content, % by mass: 0.004
- Alkalinity as ammonia, % by mass: 0.73
- KOH number: 0.65
- Mechanical stability time, sec: 1075
- Volatile fatty acid number: 0.04
- Copper content: Traces
- Manganese content: Traces

2.1.1.C. Styrene Butadiene Rubber (SBR)

Styrene butadiene rubber used was Synaprene 1502 grade, obtained from Synthetics and Chemicals Ltd., Bareilly, U P, India. The Mooney viscosity (M<sub>L</sub>, 1+4, 100° C) was 52. Other specifications are given below.

- Volatile matter, % by mass: 0.23
- Ash, % by mass: 0.24
- Organic acid, %: 5.53
Soap  Traces
Bound styrene  24.3

2.1.1.D. Chloroprene Rubber (CR)

Chloroprene rubber used in this study was W type (CR B 30) with Mooney viscosity \([M_L (1+4), 100^\circ C] 47\). Du Pont, USA, supplied the rubber.

2.1.2 Other Ingredients
2.1.2.A. Zinc Oxide (activator)

Zinc oxide supplied by M/s Meta Zinc Ltd. Mumbai, was having the specifications given below.

Specific gravity  5.7
Zinc oxide content, (%)  98
Acidity (%) max.  0.4
Heat loss (2hrs. at 100°C) (%) max.  0.5

2.1.2.B. Stearic Acid (Co-activator)

Stearic acid was supplied by Godrej Soap (P) Ltd. Mumbai and had the following specifications.

Melting point  50-69°C
Acid number  185-210
Iodine number (max)  9.05
Specific gravity,  0.85
Ash (%) max.  0.10

2.1.2.C. Tetra methyl thiuram disulphide (TMTD) (Accelerator)

TMTD supplied by Rubochem. Industries, Kottayam had the following specifications.

Melting point  138°C
Specific gravity  1.405 ± 0.025
Ash (%) max  0.5
Moisture (%) max  1
2.1.2.D. Mercaptobenzthiazyl disulphide (MBTS) (Accelerator)

Bayer Chemicals Mumbai, supplied MBTS required in the present study. It had the following specifications:

- Specific gravity: 1.51
- Melting point: 165°C

2.1.2.E. Cyclohexyl Benzothiazyl Sulphenamide (CBS) (Accelerator)

CBS used in the study was Santocure CBS supplied by Polyolefins Industries, Mumbai having the following specifications:

- Ash (%): max. 0.5
- Moisture (%): max. 0.5
- Specific gravity: 1.27

2.1.2.F. Thiourea (TU) (Accelerator)

Thiourea used for this study was of analytical grade supplied by Sisco Research Laboratory, Mumbai

- Purity (%): 99.5
- Sulphurated ash (max): 0.1

2.1.2.G. Ethylene Thiourea (NA22) (Accelerator)

Ethylene thiourea was obtained from National Physical and Oceanographic Laboratory, Cochin, India and was of commercial grade.

2.1.2.H. Sulphur (Cross linking agent)

Standard Chemical Co. Pvt. Ltd Chennai supplied sulphur and had the following specifications:

- Specific gravity: 2.05
- Acidity (%): max. 0.01
- Ash (%): max. 0.1
- Solubility in CS₂ (%): max. 98

2.1.2.I. Magnesium Oxide (Cross linking agent)

Magnesium oxide used in the study was calcined light magnesia with specific gravity of 3.6, supplied by Central Drug house (P) Ltd., Mumbai.
2.1.2.J. Fillers

(a) High Abration Furnace Black (N 330) used in the study was supplied by M/s. Carbon and Chemicals India Ltd., Cochin. It had the following specifications:

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>black granules</td>
</tr>
<tr>
<td>DBP absorption</td>
<td>102 ± 5 cc/100g</td>
</tr>
<tr>
<td>Pour density</td>
<td>376.0 Kg/m³</td>
</tr>
<tr>
<td>Iodine number</td>
<td>82</td>
</tr>
<tr>
<td>Loss on heating (100°C, 1 hr) (%) max.</td>
<td>2.5</td>
</tr>
</tbody>
</table>

(b) Precipitated silica used was of commercial grade supplied by Rubo-Chem Industries Pvt. Ltd., Mumbai. The specifications of this are given below:

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH (5% aqueous solution)</td>
<td>6.3</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.03</td>
</tr>
<tr>
<td>SiO₂ hydrate on dried sample, min</td>
<td>90%</td>
</tr>
<tr>
<td>Loss on heating (105°C, 2 hrs.)</td>
<td>5.5%</td>
</tr>
</tbody>
</table>

2.1.2.K. Process Oils

(a) Aromatic oil

Supplied by Hindustan Organic Chemicals Ltd., Kochi. It had the following specifications:

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.98</td>
</tr>
<tr>
<td>Aniline point (°C)</td>
<td>43.00</td>
</tr>
<tr>
<td>Ash content % by mass</td>
<td>0.01</td>
</tr>
<tr>
<td>Viscosity gravity constant</td>
<td>0.96</td>
</tr>
</tbody>
</table>

(b) Naphthenic oil

Naphthenic oil was supplied by Indian Oil Corporation. It had the following specifications.

<table>
<thead>
<tr>
<th>Property</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Light</td>
</tr>
<tr>
<td>Pour point (°C)</td>
<td>-20</td>
</tr>
</tbody>
</table>
Chapter 2

Aniline point (°C) 78
Viscosity gravity constant (VGC) 0.85-0.9
Aromaticity 10-30

2.1.2.L. Dispersol F (Dispersing agent)

Dispersol F was used as the dispersing agent in the preparation of dispersions of solid ingredients. It was supplied by M/s. Indian Explosives Ltd., Kolkotta

2.1.2.M. Potassium Oleate (Stabilising agent)

It is an anionic soap soluble in water and is used as a stabilizing agent in latex. This was prepared from chemically pure oleic acid and potassium hydroxide. A 10% solution of potassium oleate is prepared by warming a mixture of 28.2g oleic acid and 5.6g potassium hydroxide with 270 ml water.

2.1.2.N. Other Chemicals Used

Other reagents such as toluene and benzene used for swelling studies, guanidine carbonate, phenyl isothiocyanate, sodium hydroxide, ethylene glycol etc. were all of analar grade.

2.2 EXPERIMENTAL METHODS

2.2.1 Compounding

Mixes were prepared on a laboratory size two roll-mixing mill (15 x 33 cm) as per ASTM designation D 3182-89. The mixing was carried out at a friction ratio of 1:1.22 for natural rubber 1:1.1 for styrene butadiene rubber and 1:1.25 for chloroprene rubber. The mill opening was set at 0.2 mm and the elastomer was passed through the rolls twice without banding. This was then banded on the slow roll with mill opening at 1.4 mm and was increased to 1.9 mm as the band become smooth. The temperature of the rolls was maintained at 70±5° C. The compounding ingredients were added as per procedure given in ASTM D 3184-89 and ASTM D 3182-89 in the following order: activator, filler, accelerator and
curing agents. Before the addition of accelerator and sulphur the batch was thoroughly cooled.

After the completion of mixing, homogenisation of the compound was carried out by passing the rolled stock endwise six times at a mill opening of 0.8 mm. The mill is opened to give a minimum stock thickness of 6mm and the stock was passed through the rolls four times folding it back on itself each time.

2.2.2 Determination of Cure Characteristics

The cure characteristics of the mixes were determined using Goettfert elastograph model 67.85. It is a microprocessor controlled 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 (±0.2). The frequency of oscillation is 50 per minute. The torque is measured on the lower oscillating die half. The following data can be obtained from a typical elastograph cure curve shown below:
### Chapter 2

<table>
<thead>
<tr>
<th>i.</th>
<th>Minimum torque, $M_L$</th>
<th>Torque obtained by the mix after homogenizing at the test temperature before the onset of cure.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ii.</td>
<td>Maximum torque, $M_{II}$</td>
<td>This is the torque recorded after the curing of the mix is completed.</td>
</tr>
<tr>
<td>iii.</td>
<td>Torque, $M_T$</td>
<td>Torque at any time $T$</td>
</tr>
<tr>
<td>iv.</td>
<td>Optimum cure time, $T_{90}$</td>
<td>It is the time taken for obtaining 90% of the maximum torque.</td>
</tr>
<tr>
<td>v.</td>
<td>Scorch time, $T_{10}$</td>
<td>This is the time for attaining 10% of the maximum torque.</td>
</tr>
<tr>
<td>vi.</td>
<td>Induction time, $T_5$</td>
<td>It is the time taken for 5% vulcanisation.</td>
</tr>
<tr>
<td>vii.</td>
<td>Cure rate index: CRI</td>
<td>It is calculated as: $100/(T_{90} - T_{10})$ where $T_{90}$ and $T_{10}$ are the time corresponding to optimum cure time and scorch time respectively.</td>
</tr>
</tbody>
</table>

#### 2.2.3 Moulding of Test Specimens

For determining the physical properties, the test specimens were moulded in standard moulds by compression moulding in an electrically heated hydraulic press having $30 \times 30$cm platens at a pressure of 11.764 MPa on the mould. The rubber compounds were vulcanised upto their optimum cure times and at specified temperatures. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cool and dark place for 24 hours and were used for subsequent physical tests. Additional curing time based on the sample thickness for samples having thickness higher than 6mm (compression set, abrasion resistance etc.) was given to obtain satisfactory mouldings.

#### 2.2.4 Physical Tests on Vulcanisates

Physical tests carried out on vulcanisates such as tensile strength, tear strength, hardness, compression set, abrasion resistance etc. have been standardised in the rubber industry to design compounds to meet service conditions, to investigate product or process failures and to ascertain quality.
assurance for a quicker prediction of quality. The most commonly sought physical property of any rubber vulcanisate is its tensile strength and it is defined as the force per unit area of cross section which is required to break the test specimen, the condition being such that the stress is substantially uniform over whole of the cross section. The elongation at break (EB) is the maximum value of elongation expressed as a percentage of the original length. The value of tensile stress (force/unit area) required to stretch the test piece from the unstrained condition to a given elongation is called modulus or more accurately 'tensile stress at a given strain'.

Tensile strength in itself bears little relation to product service. But it is extremely useful for many comparative studies. High tensile strength coupled with a reasonable EB can be obtained with quality rubber mixes. They are also useful in the determination of cure properties of compounds. The cure conditions giving the highest tensile strength being widely adopted as optimum cure. Deterioration on ageing can be followed by the drop in the tensile strength. Effect of many compounding ingredients can be decided by tensile property studies. Finally, as a control test, it is valuable since any mistake in mixing or processing giving inferior product is indicated by a drop in tensile strength. For parameters described below, at least three specimens per sample were tested for each property and the mean values are reported.

(A) Tensile Properties: Modulus, tensile strength, and elongation at break

The tensile properties of the vulcanisates were determined on a Zwick universal testing machine, model1445, using a crosshead speed of 500mm/min as per ASTM D 412-87 (method A). All the tests were carried out at 28 ± 2°C. Dumbbell specimens for the test were punched out of the moulded sheet along the mill grain direction using a dumbbell die (C-type). The thickness of the narrow portion was measured using a bench thickness gauge. The sample was held tight by the two grips, the upper grip being fixed. The tensile strength, elongation at break and modulus were evaluated and printed out after each measurement by the microprocessor.
(B) Tear Resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples were cut from the compression moulded sheets parallel to the mill grain direction. The test was carried out on the ‘Zwick’ universal testing machine. The speed of extension was 500mm/min and the test temperature 28 ± 2°C.

(C) Hardness

The hardness (Shore A) of the moulded samples was determined using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1986). The tests were performed on unstressed samples of 30mm diameter and 6 mm thickness. 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 specimen.

(D) Compression Set

The samples (6.25mm thick and 18mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C. After the heating period, the samples were taken out, cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

\[
\text{Compression set (\%)} = 100 \times \frac{t_0 - t_1}{t_0 - t_s}
\]

Where \(t_0\) and \(t_1\) are the initial and final thickness of the specimen respectively and \(t_s\) the thickness of the spacer bar used. The procedure used was ASTM D 395 (1982 method B)

(E) Abrasion Resistance

The abrasion resistance of the samples was determined using a DIN abrader (DIN 53516). Sample having a diameter of 6±0.2 mm and a thickness of 6mm 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 taken. The weight after the final run was also noted. The difference in weight is
the abrasion loss. It is expressed as the volume of the test piece abraded by its travel through 42 m on a standard abrasive surface. The abrasion loss was calculated as follows:

\[ V = \frac{\Delta M}{\rho} \]

Where \( \Delta M \) = mass loss, \( \rho \) = density of the sample and \( V \) = abrasion loss. The result is expressed in cm\(^3\)/hr.

**F) Rebound Resilience**

Rebound resilience is measured using a vertical rebound resilience tester as per ASTM D 2632-88. A plunger weighing 28 ± 0.5 g is dropped from a height of 40 cm to the sample of thickness 12.5 mm and the rebound height is measured.

**G) Density**

Density of the samples was determined as per ASTM D 297 (1981). In this method the weight of the specimen in air was first noted and then specimen was immersed in water and its loss of weight in water was determined. The density of the sample was calculated as:

\[ \text{Density} = \frac{\text{Weight of specimen in air} \times \text{density of water}}{\text{Loss of weight of specimen in water}} \]

Density of water is taken as 1 g / cm\(^3\).

**H) Ageing Studies**

Ageing studies were carried out according to ASTM D 573-88. Dumbbell samples were punched out from the vulcanised sheets and kept in air oven at predetermined temperatures for specified periods. Physical properties like tensile strength, elongation at break, modulus etc. were determined after ageing. Knowing the values of these tests before ageing, the retention of these properties was calculated for assessing the effect of ageing.
2.2.5 Chemical Test Methods

Determination of Chemical Crosslinks of the Vulcanisates

The crosslink density of the vulcanisates was determined from the equilibrium swelling data as follows:

Approximately 0.2 gm of sample was punched out from the central portion of the vulcanisate and the accurately weighed sample was allowed to swell in suitable solvent for 24 hrs. The outer portion of the swollen sample was then dried using a filter paper and then weighed. The solvent was removed in vacuum by placing in an oven at 50°C for 22 hrs. The deswollen weight was determined. The volume fraction of rubber, in the deswollen network was then calculated by the method reported by Ellis and Welding\textsuperscript{3,4} from the following equation.

\[ V_r = \frac{(D - FT) \rho_r^{-1}}{(D - FT) \rho_r^{-1} + A_0 \rho_s^{-1}} \]

Where \(T\) is the weight of the test specimen, \(D\) the deswollen weight, \(F\) the weight fraction of the insoluble components of the vulcanisates, \(A_0\) the weight of the absorbed solvent corrected for the swelling increment; \(\rho_r\) and \(\rho_s\) are the density of rubber and solvent respectively. Knowing the value of \(V_r\) the total cross-link density, \(1/2M_c\) was calculated using Flory-Rehner equation\textsuperscript{5,6}.

\[-[\ln(1-V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (V_r)^{1/3}}{M_c} \]

Where \(V_s = \) molar volume of solvent, \(\chi = \) the parameter characteristic of the interaction between rubber and solvent, \(M_c = \) the number average molecular weight of the rubber chains between crosslinks.

The values of the parameter \(\chi\) taken for calculation were the following\textsuperscript{7}:

For  
NR-toluene \hspace{1cm} = \hspace{1cm} 0.42  
SBR-toluene \hspace{1cm} = \hspace{1cm} 0.32  
CR-benzene \hspace{1cm} = \hspace{1cm} 0.26
Although natural rubber gum vulcanisates have received much attention, fewer details are available on network structure of filled vulcanisates. This is because of the uncertainties introduced by the filler – rubber interactions. The volume fraction of rubber ($V_r$) here is calculated assuming that the filler does not swell. It is then converted to $V_{r0}$ (the value $V_r$ would have had in the absence of filler) according to Cunneen and Russell\textsuperscript{8} as:

$$\frac{V_{r0}}{V_r} = ae^z + b$$

Here $a$ & $b$ are constants characteristic of the system and $z$ is the weight fraction of the filler in the vulcanisate. The values for $a$ and $b$ for HAF black filled systems are $a = 0.56$ and $b = 0.44$. The corresponding values for silica filled system are $a = 1.41$ and $b = -0.41$. The values of $V_{r0}$ were then substituted in the Flory-Rehner equation in place of $V_r$ to obtain the crosslink density.

2.2.6 Compounding of Latex

**Preparation of Dispersions**

The solid ingredients were added into latex as solutions/dispersions. The materials are made to disperse in water by grinding action and the dispersing agents prevent the dispersed particles from reaggregating. The quantity of the dispersing agent to be used for preparing dispersions depends on the nature of the materials to be dispersed. For very fine particle size ingredients the quantity of dispersing agent required is about 1% by weight whereas for materials like sulphur 2 to 3 % is required. There are different types of grinding equipments like ball mill, ultrasonic mill and attrition mill. In the present study a ball mill was used for making the dispersions of the ingredients.

A ball mill consists of a cylindrical container in which the slurry is placed together with a charge of balls. When the mill is working the balls are carried round with the container a short way and then cascade. It is this process of cascading which causes the particles of slurry to be comminuted. The efficiency of the mill depends on the speed of rotation of the jar, size and material of the ball, viscosity of the slurry, period of ball milling, etc.
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The formulations of the dispersions used in this study are given below:

(i) Sulphur dispersion (50%)

Sulphur 100
Dispersol F 3
Deionised water 97

Ball milled for 72 hours

(ii) ZnO dispersion (50%)

ZnO 100
Dispersol F 3
Deionised water 97

Ball milled for 24 hours

(iii) APT dispersion (10%)

APT 10.00
Dispersol F 0.15
Water (deionised) 89.85

Ball milled for 24 hrs.

(iv) TMTD dispersion (33%)

TMTD 100.00
Dispersol F 1.50
Water (deionised) 198.50

Ball milled for 24 hrs.

(v) CBS dispersion (33%)

CBS 100.00
Dispersol F 2.5
Water (deionised) 197.50

Ball milled for 24 hrs.

De-ammoniation of Latex

High ammonia (HA) type concentrated latex was de-ammoniated to 0.23% by stirring in a laboratory type de-ammoniation tank for 3 hours.
Otherwise the high ammonia content in latex will create problems during conversion to solid products or in the stability of the latex compound in presence of zinc oxide\textsuperscript{10}. The concentration of ammonia in latex was estimated as per ASTM D 1076-88.

**Compounding**

The mixing of ingredients was done as per the order given in the respective chapter. The stabilisers were first added as solutions, followed by the other ingredients. Mixing was done in a glass vessel and stirring for homogenisation was done using a laboratory stirrer at 10-20 rpm. It was occasionally stirred during storage also in order to prevent settling of the ingredients.

**Maturation**

The latex compound was matured at ambient temperature for 24 hours. This ensures the compound to free itself of air entrained during the preparation and allows the stabilisers to distribute themselves uniformly throughout the aqueous and dispersed medium. During this maturation period important changes takes place\textsuperscript{11}. Absorption of vulcanisation ingredients into the rubber particle surface commences and becomes a continuous process with time and temperature. Further it allows time for the reaction of ammoniated latex with zinc oxide for getting uniform physico-chemical properties.

**Preparation of Latex Films**

Latex films were cast on glass dishes using the latex compound as described by Flint and Naunton\textsuperscript{12}. The size of the glass dishes was $6'' \times 6''$ and about 25 ml of the latex compound was poured and uniformly distributed so that a film of thickness 1-1.25mm was obtained upon drying. These glass dishes with the latex compound were placed on levelled tables and dried overnight.

**Vulcanisation of Latex Films**

The vulcanisation of latex films was carried out in a laboratory type air oven at 120 and at 100°C. The time for optimum cure was determined by
vulcanising the film for different duration of time and determining the tensile strength of the vulcanisate in each case. The optimum cure time was taken as the time for attaining maximum tensile strength.

2.2.7 Rheological Study of Latex

A Haake viscometer VT550 was used to study the effect of temperature and shear rate on viscosity. This has been designed to meet the most sophisticated requirements of continuous shear rheometry with 60 different rotational speed steps covering a wide range from 0.5 rpm to 800 rpm. The functional units consist of viscotester, power supply unit, temperature control vessel, sensor system and Pt 100 temperature sensor. The equipment operates over a temperature range from -30 to 150°C. Thirty different sensor systems are available. Sensor system NV was used for this study.

Latex is located in the measuring gap of the sensor system. Rotational speed, measuring time, number of measuring points and measuring temperature are preset. The rotor is rotated at the preset speed range. The latex exert a resistance to the rotational movement due to its viscosity which become apparent as a torque value applied on the measuring shaft of the VT550. The computer attached to the system calculates the relevant values for the following factors from the measured variables of speed, torque and sensor geometry.

- Viscosity $\eta$ in mPa.s
- Shear rate $\gamma$ in s$^{-1}$
- Shear stress $\tau$ in Pa

The temperature T is also measured in °C. In the present study measurements were taken at 25, 35 and 45°C at shear rates ranging from 1 to 150 s$^{-1}$. The rheological behaviour of the latex has been analysed using Power law equation.

$$\tau = Ky^n$$

where $\tau$ = shear stress (Pa)
$K$ = viscosity index
$\gamma$ = Shear rate (s$^{-1}$)
$n$ = flow index
REFERENCES


