CHAPTER II

EXPERIMENTAL TECHNIQUES
The materials used and the experimental procedures adopted in the present investigations are described in this chapter.

II.1 MATERIALS

II.1.1 Centrifuged Natural Rubber Latex

High ammonia type 60 per cent centrifuged latex conforming to the specifications of the Bureau of Indian Standards: BIS 5430-1981 obtained from the Pilot Latex Processing Centre of Rubber Board was used in this study. The properties of the latex estimated by us are as follows.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dry rubber content, % by mass</td>
<td>60.00</td>
</tr>
<tr>
<td>2</td>
<td>Non-rubber solids, % by mass</td>
<td>1.50</td>
</tr>
<tr>
<td>3</td>
<td>Coagulam content, % by mass</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>Sludge content, % by mass</td>
<td>0.007</td>
</tr>
<tr>
<td>5</td>
<td>Alkalinity as ammonia, % by mass</td>
<td>0.75</td>
</tr>
<tr>
<td>6</td>
<td>KOH number</td>
<td>0.65</td>
</tr>
<tr>
<td>7</td>
<td>Mechanical stability time, seconds</td>
<td>1075</td>
</tr>
<tr>
<td>8</td>
<td>Volatile fatty acid number</td>
<td>0.04</td>
</tr>
<tr>
<td>9</td>
<td>Copper content, ppm on total solids</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Manganese content, ppm on total solids</td>
<td>2</td>
</tr>
</tbody>
</table>
II.1.2 Modified Natural Rubber Latices

II.1.2.a Epoxidised natural rubber latex (ENR)

High ammonia type centrifuged NR latex (deammoniated to 0.3% ammonia) was used. Formic acid (98%), hydrogen peroxide (30%), formalin (40%), sodium bicarbonate, and methanol were of laboratory reagent grade. Spectroscopically pure toluene was used for IR studies. The non-ionic stabiliser used was Vulcastab VL, the active ingredient of which is an ethylene oxide condensate, supplied by ICI (India) Ltd. The reaction recipe used is given below.¹

1) Reaction Recipe

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rubber Hydrocarbon</td>
<td>2.94 moles of isoprene units dm⁻³</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.955 moles dm⁻³</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>3.75 moles dm⁻³</td>
</tr>
<tr>
<td>Non ionic stabiliser</td>
<td>3 phr</td>
</tr>
</tbody>
</table>

2) Preparation of epoxidised natural rubber (ENR) latex

100ml of NR latex was taken in a three necked RB flask equipped with a stirrer, thermometer and a condenser. The latex was stabilised by adding 11ml of Vulcastab VL (20% W/V). It was placed in a constant temperature bath. The ammonia in the latex was neutralised by adding
quantitative amounts of formalin. The latex was diluted with water and the required amount of formic acid was added followed by hydrogen peroxide and the DRC was adjusted at 20%. The temperature of bath was maintained at 40 ± 0.1°C. The reaction was allowed to continue for 24 hours. At the end of the reaction, the acid was neutralised with saturated sodium bicarbonate solution and then with ammonia solution. The latex was used for further blending studies by keeping it in a closed container. The ENR latex obtained was of 50 mole% epoxy content and known as ENR-50.

II.1.2.b Graft co-polymers of natural rubber latex

1) Radiation induced graft copolymerisation of methylmethacrylate in natural rubber latex

a) Materials

High ammonia preserved centrifuged natural rubber latex conforming to BIS 5430-1981 was used for grafting reactions. Methyl methacrylate was freed from inhibitor by washing first with 10% solution of sodium hydroxide and then with distilled water and finally dried over anhydrous sodium sulphate.

b) Graft Copolymerisation

A gamma chamber model 5000 supplied by the Bhabha Atomic Research Centre, Mumbai was used as the source for γ-radiation. The dose rate was 0.1 Mrad./h.
A 50% emulsion of methyl methacrylate was prepared by mixing monomer under stirring with equal weight of water containing vulcastab VL as the emulsifying agent. It was then mixed with high ammonia preserved centrifuged latex in the ratio of 1:1 by dry weight. The mixture was then subjected to a total irradiation dose of 0.5 Mrad. The percentage yield of the product which was a mixture of graft copolymer, free poly methyl methacrylate and unreacted rubber was determined, after FTIR characterisation. The obtained methyl methacrylate grafted NR latex known as MGNR 50 was kept in sealed containers for blending studies after making the ammonia concentration to 0.7%.

c) Recipe for 50% MMA emulsion preparation

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by (Wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Methacrylate (Washed)</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>95</td>
</tr>
<tr>
<td>Vulcastab VL (20%)</td>
<td>5</td>
</tr>
</tbody>
</table>

II.1.2.b 2) Radiation induced graft copolymerisation of styrene in natural rubber latex

a) Materials

High ammonia preserved centrifuged natural rubber latex conforming to BIS-5430, 1981 was used. Styrene was washed first with 10% sodium hydroxide solution to free it from inhibitor and then with distilled water.
b) **Graft Copolymerisation**

A gamma chamber model 5000 supplied by the Bhabha atomic research centre, Mumbai was used as the radiation source. The dose rate was 0.1 Mrad/h. Centrifuged latex (preserved with 0.7% ammonia) and styrene as 50% emulsion were mixed in the ratio 1:1. The latex mixture was then irradiated to a total dose of 0.75 Mrad.\(^3\) The percentage yield of the product which was a mixture of graft copolymer, free polystyrene, and free NR was determined, after FTIR characterisation. The obtained styrene grafted NR latex (SGNR-50) was kept in closed container after making the ammonia concentration to 0.7% for further blending studies.

c) **Recipe for 50% Styrene emulsion**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Parts by (Wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene (Washed)</td>
<td>100</td>
</tr>
<tr>
<td>Water</td>
<td>85</td>
</tr>
<tr>
<td>Vulcastab VL (20%)</td>
<td>15</td>
</tr>
</tbody>
</table>

II.1.2.c **Preparation of radiation prevulcanized natural rubber latex: (RVNRL)**

A gamma chamber model 5000 supplied by the Bhabha Atomic Research Centre, Mumbai, was used as the radiation source. High ammonia preserved centrifuged natural rubber latex stabilised with a solution of KOH (0.2phr) was used for radiation vulcanization. The
radiation sensitiser n-butyl acrylate (n-BA), 5phr was added to the stabilised NR latex while stirring. Stirring was continued for 1h and the mixture was then irradiated with gamma rays from the C0-60 source at a total dose of 1.5 Mrad. The irradiation was conducted at a constant dose rate of 0.1 Mrad/h at room temperature. The radiation prevulcanized natural rubber latex (RVNRL) thus obtained was kept at room temperature tightly covered to prevent any loss of volatile materials such as ammonia.

1) **Recipe for radiation prevulcanized NR latex (preparation)**

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Weight (gms.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60% centrifuged NR latex</td>
<td>167</td>
</tr>
<tr>
<td>10% KOH solution</td>
<td>2</td>
</tr>
<tr>
<td>n-butyl acrylate (n-BA)</td>
<td>5</td>
</tr>
</tbody>
</table>

Total dose 1.5 Mrad at a dose rate of 0.1 Mrad/h

The specifications of Gamma chamber 5000 is given below.

Gamma chamber 5000 is a compact self shielded Cobalt-60 gamma irradiator providing an irradiation volume of 5000c.c. The materials for irradiation is placed in an irradiation chamber located in the vertical drawer inside the lead flask. The drawer can be moved up and down with the help of a system of motorised drive which enables precise positioning of the irradiation chamber at the centre of the radiation field.
The photograph showing the instrument is given in Figure II.1.

2) **Specifications**

Minimum Co-60 source capacity : 444 TBq (12,000 Ci)

Dose rate at maximum capacity : 9kGy/h (0.9 Mrad/h) at the centre of sample chamber

Dose rate uniformity : +25% or better radially

-25% or better axially

Irradiation volume : 5000 c.c. approx

Size of sample chamber : 17.5 c.m (dia) x 21.0 cm (ht)

Shielding material : Lead and stainless steel

Weight of the units : 5000 Kg approx.

Size of the unit : 125c.m (l) x 106.5c.m.(w) x 150cm (ht)

Timer range : 6 seconds onwards

### II.1.3 SYNTHETIC LATTICES

a) Carboxylated styrene butadiene rubber (XSBR) latex

   Total Solid Content (TSC) = 50%

   Carboxyl content = 3%, Grade Powerene PLX-802

   Source – Apar Ltd, Gujarat, India

b) Acrylonitrile-butadine rubber (NBR) latex

   Total solid content (TSC) = 41%

   Acrylonitrile content = 28%. Grade Perbunan N 2890

   Source- Bayer AG, W. Germany
II.2 RUBBER CHEMICALS

II.2.1 Accelerators

The accelerators used in this study were obtained from M/S Indian Explosives Limited (IEL), Culcutta. A short description of the important accelerators used given below:

a) Zinc diethyl dithiocarbamate (ZDEC)

This ultra accelerator is a cream white powder of density 1.47 g/cm$^3$, m.p $175^\circ$C; soluble in carbon disulphide, benzene and chloroform and is non-toxic. It ensures rapid low temperature vulcanization in the presence of a small amount of sulphur and is active in latex mixes even in the absence of zinc oxide.

b) Zinc salt of 2-mercapto benzothiazole (ZMBT)

A light yellow powder, density 1.63 g/cm$^3$, m.p $145^\circ$C, non-toxic, soluble in benzene, ethanol and chloroform. It is a slow accelerator and it can not be used alone in latex work.

c) Tetramethyl thiuram disulphide (TMTD)

A white powder, density 1.29g/cm$^3$, m.p $165^\circ$C, soluble in chloroform, benzene and hot alcohol and is an ultra accelerator.
d) Zinc dibutyl dithiocarbamate (ZDBC)

This ultra accelerator is a white yellow powder of density 1.26g/cm$^3$, m.p 104$^\circ$C, Zinc content 15%, soluble in chloroform, it is more active than zinc diethyl dithiocarbamate accelerator in latex mixes and providing higher modulus for vulcanizates.

II.2.2 Fillers and Pigments

Anatase form of titanium dioxide (TiO$_2$) was obtained from M/S Travancore Titanium Products, Trivandrum, precipitated calcium carbonate, china clay and barium sulphate (barytes) used in this study were of commercial grade obtained locally.

II.2.3 Antioxidants

a) Antioxidant SP

This is styrenated phenol and was obtained from M/S Indian Explosives Limited, Culcutta.

b) Wingstay-L

This is chemically butylated reaction product of p-cresol and cyclopentadiene. It is a cream coloured powder of density 1.1g/cm$^3$, melting range 100$^\circ$C minimum. It is a non-staining substituted phenolic type antioxidant widely used in latex for high temperature protection.
Manufactured by Vanderbilt rubber chemical company. CT, USA in the trade name Vanox L.

The structure is given below

```
[OH
  |  
  CH₃
  |  
  X
```

**c) Antioxidant HS**

This is chemically 1,2-dihydro 2,2,4-trimethyl quinoline. It is obtained as brown solid flakes of density 1.08 g/cm³ with m.p 90⁰C. It is a staining type amine antioxidant. It is insoluble in water but soluble in benzene. The structure is given as

```
[CH₃
  |  
  CH₃
  |  
  CH₃
  |  
  N
  |  
  H
```

**d) Crystol EPR 3400**

Molecular Weight = 689. It is chemically Tris (nonyl phenyl) phosphite. It is a non-staining phosphite type antioxidant. It is a
colourless viscous liquid used widely in SBR formulations. The structure is given as,

\[
\left(\begin{array}{c}
C_9H_{19} \\
\end{array}\right) \overset{O}{\underset{P}{\bigcirc}} \overset{O}{\underset{P}{\bigcirc}} \overset{O}{\underset{P}{\bigcirc}}
\]

II.2.4 UV-stabilisers

The Lowilite class of UV-stabilisers used in this study were obtained from M/S Great Lakes Chemicals, W. Lafayette, IN, USA.

a) Lowilite 20

It is a benzophenone class UV-stabiliser. It is chemically 2-hydroxy, 4-methoxy benzophenone. It is a creamy powder of molecule weight 228, m.p 62°C, TGA (at 214°C, 50% mass loss), insoluble in water but soluble in acetone and ethyl acetate.

The structure is

\[
\begin{array}{c}
\text{O} \\
\text{OH} \\
\text{OCH}_3 \\
\text{O} \\
\end{array}
\]

b) Lowilite 55

It is a benzotriazole class UV-stabiliser and is chemically 2-(2\text{H-hydroxy-5\text{H-methyl phenyl}) benzotriazole. It is a creamy powder of molecular weight 225, m.p 128°C, TGA (at 213°C, 50% mass loss).
insoluble in water but sparingly soluble in acetone and ethyl acetate. The structure is

\[ \text{Structure Image} \]

c) **Lowilite 76**

It is a hindered amine class light stabiliser (HALS). It is chemically Bis (1,2,2,6,6 penta methyl-4-piperidinyl) sebacate. It is an amber liquid of molecular weight 509, m.p 31°C, TGA (at 323°C, 50% mass loss), insoluble in water, acetone and ethyl acetate. The structure is

\[ \text{Structure Image} \]

The first two were added as aqueous dispersions while third one was made into emulsion with oleic acid and ammonia and administered into latex compound.
II.2.5 Other Chemicals

Thiourea, oleic acid, zinc oxide ($\rho=5.5$) and elemental sulphur ($\rho=2.05$) were of commercial grade.

II.2.6 Special Chemicals

Propane-2-thiol and piperidine were of analytical grade and were obtained from Fluke A.G West Germany. n-butyl acrylate was obtained from IPCL Chennai.

II.2.7 Solvents

Benzene, toluene, n-heptane, petroleum ether were of analytical grade.

II.2.8 Surface Active Agents

a) Dispersol F

It is sodium salt of a sulphonic acid manufactured by M/S Indian Explosives Limited, Culcutta. It was used as a dispersing agent in the preparation of dispersion of solid ingredients.

b) Potassium laurate

It is an anionic soap, soluble in water and is used as a stabilising agent in latex. This was prepared from chemically pure lauric acid and potassium hydroxide.
II.3 LATEX COMPOUNDING

II.3.1 Preparation of Dispersions

The solid ingredients were added into latex as dispersions. The materials were made to dispersion in water by grinding action and the dispersing agents prevent the dispersed particles from reaggregating. The quantity of dispersing agent to be used for preparing dispersions depends on the nature of materials to be dispersed. For very fine particle size ingredients like zinc oxide, the quantity of dispersing agent required is about 1 per cent by weight whereas for materials like sulphur, 2 to 2.5 per cent 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 container rotates and 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 ball mill depends on speed of rotation of the container, size and material of the ball, viscosity of the slurry, period of ball milling etc.

Formulations of the dispersions used in this study are given below.
a) **Sulphur dispersion (50%)**

Sulphur : 100
Dispersol F : 3
Deionised water : 97
Ball milled for 72 hours

b) **ZDEC Dispersion (50%)**

ZDEC : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 48 hours

c) **ZMBT dispersion (50 %)**

ZMBT : 100
Dispersol F : 2
KOH : Trace
Deionised water : 98
Ball milled for 24 hours

d) **ZDBC dispersion (50%)**

ZDBC : 100
Dispersol F : 2
Deionised water : 98
Ball milled for 48 hours

e) **TMTD dispersion (50%)**

TMTD : 100
Dispersol F : 2
10% ammonium caseinate : 5
Deionised water : 93
Ball milled for 48 hours
f) **ZnO dispersion (50%)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>1</td>
</tr>
<tr>
<td>Deionised water</td>
<td>99</td>
</tr>
</tbody>
</table>

Ball milled for 48 hours

g) **Titanium dioxide dispersion (33%)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>2</td>
</tr>
<tr>
<td>Deionised water</td>
<td>198</td>
</tr>
</tbody>
</table>

Ball milled for 48 hours

h) **Precipitated calcium carbonate dispersion (50%)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precipitated calcium carbonate</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>2</td>
</tr>
<tr>
<td>Deionised water</td>
<td>98</td>
</tr>
</tbody>
</table>

Ball milled for 24 hours

i) **China clay dispersion (50%)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>China clay</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>2</td>
</tr>
<tr>
<td>KOH</td>
<td>Trace</td>
</tr>
<tr>
<td>Deionised water</td>
<td>98</td>
</tr>
</tbody>
</table>

Ball milled for 24 hours

j) **Barium sulphate (Barytes) dispersion (50%)**

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium sulphate</td>
<td>100</td>
</tr>
<tr>
<td>Dispersol F</td>
<td>2</td>
</tr>
<tr>
<td>Deionised water</td>
<td>98</td>
</tr>
</tbody>
</table>

Ball milled for 24 hours
k) Wingstay-L dispersion (50%)
Wingstay-L 100
Dispersol F 2
Deionised water 98
Ball milled for 24 hours

l) Antioxidant HS dispersion (50%)
Antioxidant HS 100
Dispersol F 2
Deionised water 98
Ball milled for 24 hours

m) Lowilite 20 dispersion (50%)
Lowilite 20 100
Dispersol F 2
Deionised water 98
Ball milled for 24 hours

n) Lowilite 55 dispersion (50%)
Lowilite 55 100
Dispersol F 2
Deionised water 98
Ball milled for 24 hours

II.3.2 Preparation of Emulsions

The liquid antioxidant SP and Crystol EPR 3400 are immiscible with water and added into latex compound as emulsions. The following recipe was used for preparing emulsions:
a) **Antioxidant SP emulsion (50%)**

Part A

- Antioxidant SP 100
- Oleic acid 3

Part B

- Liquor ammonia 3
- Deionised water 94

Part A was warmed and added to B in small quantities under high speed stirring.

b) **Crystol EPR 3400 emulsion (50%)**

Part A

- Crystol EPR 3400 100
- Oleic acid 3

Part B

- Liquor ammonia 3
- Deionised water 94

Part A was warmed and added to B in small quantities under high speed stirring.

c) **Lowilite 76 emulsion (50%)**

Part A

- Lowilite 76 100
- Oleic acid 3

Part B

- Liquor ammonia 3
- Deionised water 94

Part A was warmed and added to B in small quantities under high speed stirring.
II.3.3 De ammoniation of Latex

As High Ammonia type concentrated latex was used, it was
de-ammoniated to 0.3 per cent by stirring in a laboratory type de-ammoniation
tank for 3 hours. The high ammonia content in latex will create problems
in its conversion to solid products or in the stability of the latex
compound in the presence of zinc oxide. The concentration of ammonia
in latex was estimated as per BIS 3708-Part I 1966.

II.3.4 Compounding

The mixing of the ingredients was done as per the order given in the
compound formulations given in the respective chapters. 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
in order to prevent settling of the ingredients.

II.3.5 Maturation

The latex compound was matured at ambient temperature for
24 hours. This was done with the following objectives:

a) To equilibrate the added surface active agents and those naturally
   present between the aqueous and interfacial phases.

b) To remove the air bubbles introduced in the compounds while
   compounding.
c) To dissolve the vulcanizing agents in the aqueous phase and make them migrate into rubber particles which can offer better technological properties.

d) To obtain a certain degree of prevulcanization to the latex.

e) To allow time for the reaction of ammoniated latex with zinc oxide for getting uniform physico chemical properties.

II.4 PREPARATION OF TEST SAMPLES

II.4.1 Latex Film

Latex films were cast on glass cells using the latex compounds as described by Flint and Naunton. Cellophane adhesive tapes were stuck to the edges of the glass plates to form the cells. The size of the glass cells was 6"x6" and about 10-15 ml of the latex compound was poured and distributed so that a film of thickness 0.3-1 mm was obtained upon drying. The glass cells with the latex compound were placed on leveled table and dried overnight at ambient temperature.

II.4.2 Latex Thread

Latex thread was prepared by extruding the latex compounds through a glass capillary tube into an acid bath (20 per cent formic acid). As the latex filaments passed through the bath, acid diffused into the centre of the thread and total gelation occurred. The thread was then
washed, dried and vulcanized. The diameter of the latex thread was controlled by adjusting the following factors.

a) Hydrostatic pressure on the latex compound in the capillaries.

b) The internal diameter of the capillaries.

c) The rubber content and viscosity of the latex compound.

d) The rate at which the transfer rollers remove the thread from the acid bath.

A schematic diagram of the latex thread plant used in this experiment is given in Figure II.2. The plant consisted of a header tank, constant pressure head device, coagulant bath, washing bath, drying chamber and the talc dusting system. Constancy of the extrusion pressure was ensured by feeding the nozzles through a manifold which was connected to the constant pressure head. The level of this head may be altered within limits if desired.

The compounded latex after maturation was stored in the header tank. From the header tank the latex passed to a manifold extruding head which distributed the compound to the capillaries through flexible tubes. Glass nozzles of 0.6mm diameter were used and immersed in a bath of 20 per cent formic acid. The length of the acid bath was 10 feet. The coagulated thread was transferred to the washing bath of 6 feet length containing water at 70°C. After washing the thread entered the air drying oven of 12 feet
length set at 100°C, where it was dried. Talc powder was then applied over the thread to remove tackiness and the thread was wound on wooden frames. The drying was completed at ambient temperature.

II.5 VULCANIZATION OF TEST SAMPLES

II.5.1 Latex Films

Dried latex film was used for preparation of vulcanized dumbbell samples. Latex films under conventional vulcanization system were cured for 60 minutes in boiling water while those in efficient vulcanization system were cured for 90 minutes.

II.5.2 Vulcanization of Latex Threads

The threads were vulcanized in boiling water. The threads with conventional vulcanizing system (CV) were vulcanized for 60 minutes and threads with efficient vulcanizing system (EV) were vulcanized for 90 minutes.

II.6 DEGRADATION STUDIES

The latex films prepared using different accelerator combinations and various fillers were cut into dumbbells conforming to ASTM D-412 after proper vulcanization. The dumbbell film samples and thread samples were UV-irradiated for different durations and also heat aged at 100°C for 22 hours. These were then used for chemical and physical testing.
II.6.1 Heat Ageing

Heat ageing studies were conducted in an air circulating multicellular hot air oven (TEMPO). The ageing was conducted at 100°C for 22 hours.

II.6.2 UV-Irradiation Chamber

It is a metallic chamber of 86 x 30 x 58 cm dimensions. The UV-light sources are fitted at the top and bottom parts of the chamber in a face to face manner. A plain glass sheet of area 2580cm² is fitted inside the middle of the chamber and it holds the samples for irradiation. Both the surfaces of the latex test specimens were simultaneously exposed to UV-radiation for fixed durations. The chamber has holes at the base, so that air can freely pass through the chamber. The UV-source was two 15W capacity fluorescent tubes. It was reported that fluorescent UV-sources are most effective for exposure studies.\textsuperscript{7,8,9}

The photograph showing the instrument is given in Figure II.3.

II.7 PHYSICAL TESTS

II.7.1 Mechanical Stability Time (MST)

The mechanical stability of latex means the ability of latex to withstand the colloidal destabilisative effects of mechanical origin such as shearing and agitation. 80gm latex (compounded) of 55% total solid content, after reaching 35°C temperature was subjected to mechanical
agitation in a KLAXON (UK) MST tester at 14000rpm. The time elapses before gross colloidal destabilisation appearance was denoted as MST in seconds.

II.7.2 Viscosity of Latex Compounds

Many methods are used for this. Brookfield (LVT model) is a technical viscometer and is used for determining the viscosity of latex compound. It consists of a rotating member which is usually a cylinder driven by a synchronous motor through a beryllium-copper torque spring. The viscous drag on cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The torque and therefore the viscosity is indicated by means of the pointer and scale. A range of speed of the discs and cylinders are available so that a wide range of viscosity may be covered. Natural rubber latex is non-Newtonian fluid and its viscosity decreases with increasing shear rate. In the present study the viscosity of the latices was measured at ambient temperature at 60 rpm (using spindle No.2).

II.7.3 Modulus, Tensile Strength and Elongation at Break

At least three specimens per sample were tested for each property and the mean values reported.
In the present work these tests were carried out using an Instron Universal Testing Machine (UTM) model D 4411. The machine consisted of load frame and an electronic control unit. Load measuring device is a load cell fixed at the top of the load frame. Below the load cell is a moving platform driven by continuously variable speed motor. Grips suitable for dumb bell specimens are fixed on to the load cell and moving platform. During testing the specimen is subjected to stretching at constant speed. Force and elongation are continuously monitored by the electronic unit. As soon as the test specimen breaks test results are displayed in the electronic unit.

All the tests were carried out at ambient temperature (30°C). Specimens were cut from the cast vulcanized films. The thickness was measured by bench thickness gauge. The moving cross head was adjusted by operating the switch. The velocity of the moving cross head was adjusted to be 500mm/min.

The specimen was elongated and the values corresponding to ultimate tensile strength, elongation and modulus were obtained.
II.8 CHEMICAL TESTS

II.8.1 pH

The pH of rubber latices was measured with a glass electrode and saturated calomel cell after standardising the pH metre.

II.8.2 Determination of Swell Index and Volume Fraction of Rubber

Samples of approximately 1cm diameter, 0.25cm thickness and 0.3g weight were punched from the central portion of the vulcanized latex film and allowed to swell in thiophane free benzene containing 0.5 per cent phenyl β naphthylamine at 35°C in a thermostatically controlled water bath. Swollen samples taken after 48 hours were blotted with filter paper and weighed quickly in a stoppered weighing bottle. For natural rubber vulcanizates, the 36h was found to be sufficient for attaining equilibrium. Samples were dried in an oven for 24h at 70°C, and then in vacuum and finally weighed after allowing them to cool in a desiccator. Duplicate readings were taken for each sample. Swell index was the weight of benzene absorbed per gram of sample. The volume fraction of rubber "$V_r$" was calculated by the method reported by Ellis and Welding,\textsuperscript{10} which takes into account the correction of swelling increment with duration of immersion after the equilibrium is attained.

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}}$$ II(1)
Where $T$ is the weight of test specimen, $D$ its deswollen weight, $F$, the weight fraction of insoluble components, and $A_0$ is the weight of the absorbed solvent, corrected for the swelling increment $\rho_r$ and $\rho_s$ are the densities of rubber and solvent respectively.

$$\rho_r \text{(NR)} = 0.92$$

$$\rho_s \text{(benzene)} = 0.875$$

From the collected data, the value of $A_0$ was calculated. The value of “$V_r$” can be taken as a measure of crosslink density.

II.8.3 Ammonia-modified Swelling

The samples of the vulcanized latex films containing different filler contents were swollen for 48h in flat dishes containing benzene in ammonia atmosphere.\textsuperscript{11} For this the samples were put in a desiccator the bottom of which contained liquor ammonia. After swelling in ammonia atmosphere the samples were thoroughly washed with benzene and dried in a vacuum desiccator at room temperature ($30^\circ$C) and tested for $V_r$ by swelling in benzene. The difference in chemical crosslink density as obtained by swelling in benzene of the original vulcanizate and the same after ammonia treatment gives a measure of rubber-filler attachment or coupling bond. In this, the ammonia permeates the benzene solvent and preferentially cleaves the rubber-filler attachment.
II.8.4 Determination of Concentration of Different Types of Crosslinks

The concentration of polysulphidic crosslinks (-Sx-) was estimated from the determination of chemical crosslinks of the vulcanizate before and after treatment with thiolamine. Treatment of the vulcanizate with propane-2-thiol (0.4m) and piperidine (0.4m) in n-heptane at room temperature for 2h cleaves the polysulphidic crosslinks in the network. The experimental method used is as described in detail by Campbell.\textsuperscript{12,13} Action of propane 2-thiol is based on nucleophilic displacement reactions by alkane thiols on sulphur atoms of polysulphides to cleave the sulphur bonds as shown below. They depend on the relative rates of the two displacement reactions and high resistance of the carbon-sulphur linkage in monosulphides to such nucleophilic displacement.

\[
\begin{align*}
R-S: + S-S_x &\longrightarrow R-S-S-R^l + H-S_x-S-R^l \\
R-S: + S-S-R^l &\longrightarrow R-S-S-R^l + R^l-SH \\
R-S: + R^l-S-R^l &\longrightarrow R-S-R^l + R^l-SH
\end{align*}
\]

Scheme II.1
II.8.5 Treatment with Propane-2-thiol

The samples (1mm thick and 0.3g weight) were placed in a cylindrical tube 30cm long and 3cm in diameter, clamped horizontally and purged with nitrogen. The specimens were well covered with 100ml of the thiol-amine reagent (prepared by dissolving in n-heptane, and making up to one litre with further pure heptane). The gas tap was closed to maintain the nitrogen blanket in the tube. The solution was agitated occasionally during the two hour period. After renewing the stream of nitrogen through the apparatus the reagent was run off and replaced by 100ml of petroleum ether (b.P 40-60°C) and the apparatus was agitated occasionally during one hour. This cold extraction was repeated with fresh petroleum ether every hour until four such extractions were made under nitrogen. The specimens were then removed and dried overnight in vacuum to constant weight. Then the chemical crosslink density, was measured by equilibrium swelling method as described earlier. When the sample thickness was more than 1mm, the specimens were swollen in n-heptane overnight at room temperature under nitrogen and sufficient propane-2-thiol and piperidine were added to give concentrations of 0.4m for each reagent in the final solution. The cleavage reaction in the presence of propane-2-thiol, piperidine and n-heptane is exemplified for trisulphide in the following equation.
\[ \text{Pr}^i \text{SH} + \text{RSSR} \rightarrow \text{Pr}^i \text{SS Pr}^i + \text{RSSPr}^i + \text{RSH} + \text{HS}^+ \text{H}_2 \text{N}^+ \]

where \( \text{Pr}^i = \text{isopropyl} \)

**Scheme II.2**

The thiol-amine combination gives an associate possibly piperidinium propane-2-thiolate in ion pair, in which the sulphur atom has enhanced nucleophilic properties\(^{15}\) which is capable of cleaving organic trisulphides and higher polysulphides within 30 minutes at 20\(^\circ\)C, while reacting with corresponding disulphides at about one thousandth of this rate. The favoured polysulphide cleavage is due to delocalisation of the displaced 6-electron pair of \( \text{RSS}^- \) shown in following equation.

\[ \begin{align*}
\text{RS}^- + \text{S}^- + \text{SR} & \rightarrow \text{Pr}^i \text{SSR}^- + \text{S}^- + \text{SR} \\
\text{Pr}^i \text{S}^- & \rightarrow \text{Pr}^i \text{SSR}^- + \text{S}^+ + \text{SR}^- \\
\text{Pr}^i \text{S}^- & \rightarrow \text{Pr}^i \text{SSR}^- + \text{S}^- \text{R} \\
\end{align*} \]

**Scheme II.3**

\( \text{Pr}^i \text{S}^- \) is used to represent the nucleophilic thiol-amine associate.
The difference in the Vr values of the sample before and after thiol-amine chemical probe gives the polysulphidic crosslink content in the vulcanizate.

**II.8.6 Determination of Sol Content**

The extent of chain scission in a vulcanizate was estimated by determining its sol content. The estimation was done by the method described by Bristow\(^\text{16}\) in which the samples were extracted with cold acetone in the dark for 8 to 10 days, the acetone being replenished four times during this period. This samples were then dried to constant weight in vacuum at room temperature. Weighed samples were extracted with cold benzene in the dark for 8 to 10 days, the benzene being replenished four times during this period. After benzene extraction, the samples were dried to constant weight in vacuo. The sol content is the weight loss during benzene extraction.

**II.9 CHARACTERISATION**

Infrared studies were carried out using SHIMADZU 8101M (JAPAN) FTIR spectrometer. The graft co polymer purified by solvent extraction was used in each case for taking the IR spectrum. The copolymer was dissolved in toluene and cast into a film on a sodium chloride cell and the IR spectrum was taken in the frequency range of 4000-400 cm\(^{-1}\). Epoxidised NR also was dissolved in spectroscopically pure toluene and absorption spectra was recorded.
II.10 MORPHOLOGICAL STUDIES

II.10.1 Optical Microscope

Test samples of gum latex vulcanizates of NR which were unexposed and exposed to UV-radiation were examined for morphological changes. Photomicrographs were taken on Leica Wild M8 Zoom stereo Microscope and wild MPS 46/52 photoautomate using Kodak max 400 films.

II.10.2 Scanning Electron Microscope

The surface of the unexposed and UV-exposed cast latex film with and without UV stabiliser was sputter coated with gold and photomicrographs were taken using a JEOL JSM-5600 LV model scanning electron microscope.

II.11 DISCOLOURATION

The colour changes of the UV exposed and unexposed samples were photographed using Kodak max 400 films.
Figure II.1 Gamma Chamber 5000
Figure II.2 Schematic diagram of latex thread plant
Fig. II.3: UV-Irradiation chamber
REFERENCES


