Chapter 2

MATERIALS AND EXPERIMENTAL METHODS

Abstract

The materials used for the study are given in this chapter. The synthesis and characterization of the new accelerators 1-phenyl 5- (ortho, meta and para)-tolyl 2, 4 dithiobiurets (o-DTB, p-DTB and m-DTB) are described in this chapter. The experimental techniques used for compounding, curing and the measurements of physical and mechanical properties are discussed. The procedures for the analysis of the various parameters and properties are given in this chapter.
2.1. **Materials**

Natural rubber, (poly cis 2-methyl butadiene) used was ISNR5 obtained from the Rubber Research Institute, Kottayam, Kerala, India. The characteristics of ISNR5 are given in Table 2.1.

The structure of natural rubber is

\[
\text{CH}_3\left(\text{CH}_2\right)\text{C} = \text{C} = \text{H} \left(\text{CH}_2\right)_n
\]

<table>
<thead>
<tr>
<th>Property</th>
<th>Approximate values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen content (%)</td>
<td>0.6</td>
</tr>
<tr>
<td>Dirt (%)</td>
<td>0.05</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>0.80</td>
</tr>
<tr>
<td>Ash content (%)</td>
<td>0.60</td>
</tr>
<tr>
<td>Plasticity (P_0)</td>
<td>30</td>
</tr>
<tr>
<td>Plasticity retention index (PRI)</td>
<td>60</td>
</tr>
</tbody>
</table>

Styrene Butadiene Rubber (SBR) was obtained from Japan synthetics Rubber Japan. The structure of SBR is given below.
Experimental

The chemical constituents of SBR are given in Table 2.2.

**Table 2.2. Properties of SBR**

<table>
<thead>
<tr>
<th>Chemical constituent (%)</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene content</td>
<td>21.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>-</td>
<td>0.75</td>
</tr>
<tr>
<td>Organic acid</td>
<td>4.75</td>
<td>7</td>
</tr>
<tr>
<td>Soap</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Ash</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td>Antioxidant</td>
<td>0.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>

Natural rubber latex

High ammonia type 60% centrifuged natural rubber latex confirming to the specifications of the Bureau of Indian Standards (BIS 5430-1981) was used in this study. The properties of the latex used are given below.

- Dry rubber content, % by mass: 60.0
- Total solid content, % by mass: 61.050
- Coagulum content, % by mass: 0.05
Sludge content, % by mass 0.10
Alkalinity as ammonia, % by mass 0.60
Mechanical stability time in minutes 475
KOH number 1.0
Copper, max ppm 8
Manganese, max ppm 8

N-Cyclohexyl benzothiazyl sulphenamide used in the study was Santocure CBS supplied by Polyolefines Industries, Mumbai.

Thiourea (TU) used in the present study was supplied by Sisco Research Laboratories, Mumbai. The accelerators, DCBS (Vulcacit DZ), MBS (Vulcacit MZ) were obtained from Bayer-AG, Germany.

Aromatic oil (Process oil)
Supplied by Hindustan Organic Chemicals, Cochin.

Naphthenic oil (Process oil)
Supplied by Hindustan Petroleum Corporation Ltd., Mumbai

Dispersol F

The dispersing agent used in the preparation of dispersions of solid ingredients is dispersol F. It was supplied by Indian Explosives Ltd., Kolkata.

Potassium oleate

It is the soap used as a stabilising agent in latex. This was prepared by reacting chemically pure oleic acid and potassium hydroxide. A 10% solution...
Experimental

of potassium oleate was prepared by warming a mixture of 28.2 g oleic acid and 5.6 g potassium hydroxide in 270 ml water.

Other rubber chemicals such as zinc oxide, stearic acid and sulphur were all commercial grades obtained from Ranbaxy Ltd. Bombay, India. Propane-2-thiol, 1-hexanethiol and piperidine, analytical grade were supplied by E-Merck, Germany. Aniline, carbon disulphide, ammonia, thiourea, NaOH, HCl etc. used were laboratory grade. HAF Black (N330) was obtained from United Carbon India Limited, Bombay, India. The structures of the accelerators used are

DCBS (N-dicyclohexyl benzothiazole 2-sulphenamide)

MBS (2-morpholinothio benzothiazole)

N-cyclohexyl benzothiazole 2- sulphenamide (CBS)
2.2. Synthesis of 1-phenyl 5-(ortho, para and meta) tolyl – 2, 4 dithio biuret (o-, p- and m- DTB)

Dithiobiurets were prepared by the reaction between the three different tolyl thioureas with phenyl isothiocyanate [1]. Ortho, para and meta, tolyl thioureas were prepared by the interaction of the three different toluidines (o-, p- and m-) with ammonium thiocyanate in hydrochloric acid.

Ammonium phenyl dithiocarbamate was prepared by the interaction of carbon disulfide and aniline in ammoniacal medium at 0°C. Ammonium phenyl dithiocarbamate thus obtained was steam distilled with lead nitrate to obtain phenyl isothiocyanate. Phenyl isothiocyanate (0.025 mol) was added dropwise to a stirred solution of tolyl thiourea (0.025 mol) and powdered sodium hydroxide (0.025 mol) in acetonitrile (15ml) and the reaction mixture was heated at 60°C for 0.5 hour when a clear solution resulted. This was then diluted with water (150ml), filtered and the filtrate acidified with con. hydrochloric acid (4ml. 33%).
Experimental

Scheme 2.1. Reaction route for the preparation of o-DTB.

The crude DTB obtained was dissolved in minimum quantity of 4% aqueous sodium hydroxide to remove any unreacted thiourea and filtered. The alkaline filtrate on acidification at 0°C afforded DTB, which was re-crystallised from ethanol. Ortho, para and meta dithiobiurets were prepared by the reaction of the three different tolyl thioureas with phenyl isothiocyanate separately. The reaction pathway is shown in Scheme 2.1
Yield of o-DTB = 78%  Melting point-151°C
Yield of p-DTB = 81%  Melting point-147°C
Yield of m-DTB = 71%  Melting point-142°C

2.2. Characterization of o- p- and m-DTBs

The crude DTB is purified by recrystallising it in ethanol. Pure samples were analyzed using infra-red spectroscopy and H-NMR spectra.

2.2.1. IR-Spectra

I.R. spectra of the samples were taken on a FTIR impact 410 spectrometer. About 5mg of pure DTB was pelletised with KBr and the IR spectrum was taken using FTIR impact 410 Spectrophotometer. The spectra for o- p- and m- DTBs are given in Figures 2.1, 2.2 and 2.3 respectively.

Figure 2.1. IR-spectrum of o-DTB
**o-DTB**

Characteristic absorbance peaks obtained are 3170 cm\(^{-1}\) (NH-str), 1595 cm\(^{-1}\) (NH-def), 1195 cm\(^{-1}\) (CS-str), 2915 cm\(^{-1}\) (methyl CH-str), 3028 cm\(^{-1}\) (aromatic CH-str). This confirms the presence of -NH\(_2\), -CH\(_2\), -CS- and phenyl ring structure present in DTB. The characteristic group frequency for o-substituted derivative is 747 cm\(^{-1}\)

**Figure 2.2.** IR-spectrum of p-DTB
p-DTB

Characteristic absorbance peaks obtained are 3171 cm\(^{-1}\) (NH-str), 1600 cm\(^{-1}\) (NH-def), 1175 cm\(^{-1}\) (CS-str), 3020 cm\(^{-1}\) (aromatic CH-str). This confirms the presence of -NH\(_2\), -CH\(_2\), -CS- and phenyl ring structure present in DTB. The characteristic group frequency for p-substituted derivative is 818 cm\(^{-1}\).

Figure 2.3. IR-spectrum of m-DTB
**m-DTB**

Characteristic absorbance peaks obtained are $3159 \text{ cm}^{-1}$ (NH-str), $1595 \text{ cm}^{-1}$ (NH-def), $2917 \text{ cm}^{-1}$ (methyl CH-str), $3027 \text{ cm}^{-1}$ (aromatic CH-str). This confirms the presence of -NH$_2$-, -CH-, -CS- and phenyl ring structure present in DTB. The characteristic group frequencies for m-substituted derivative are $814.9$, $754.07$, and $691.72 \text{ cm}^{-1}$ respectively.

2.2.2. **H-NMR Spectra**

The proton NMR spectrum of the newly synthesised compound is given in Figures 2.4, 2.5 and 2.6 respectively. The spectra were taken on Brucker WM 300 MHz and the chemical shifts values are reported in parts per million (ppm) relative to tetra methyl silane ($0.00 \text{ ppm}$). The spectrum was taken by dissolving the purified compound in DMSO-D6 solvent. Characteristic peaks corresponding to protons of different environment were obtained. The aromatic protons are found downfield because of the ring current effect. In the case of ortho, meta and para DTBs the characteristic peaks for phenyl and tolyl groups are in between 7 and 8 ppm. Protons on the nitrogen atom are seen as a broad peak downfield in between 8 and 8.5 ppm. The protons of the methyl group in tolyl group are seen up in between 2 and 3 ppm. In the case of ortho and para tolyl groups the methyl protons are at 2.3 ppm and for meta tolyl methyl protons peaks are at 2.1 ppm.
The peak at 2.5 ppm corresponds to the solvent DMSO and that corresponding to absorbed moisture is observed at 3.5 ppm. This spectrum confirms the structure of DTB.
Figure 2.5. H-NMR of p-DTB
2.4. Compounding of Rubber

Compounding of rubber was carried out on a two roll open mill (300 x 150mm) at a friction ratio 1:1.14 according to ASTM-D-3182-94. First the rubber was masticated in the mill in order to lower its viscosity. After lowering the viscosity, ingredients like zinc oxide, stearic acid, accelerators, sulphur and fillers were added. After incorporating the ingredients, the batch was homogenised by passing it in single direction in order to ensure the orientation of chains and to preserve the mill direction.
before moulding. The total time of mixing and roll temperature were kept constant through out the study.

2.5. Cure Characteristics

Monsanto Rheometer R-100 was used to measure the curing behaviour of the rubber compounds. In this instrument, the compound rubber is placed in a cylindrical cavity (50mm x 10mm) and a biconical rotor of diameter 37 mm is embedded in it, which is oscillated sinusoidally through a small arc amplitude (1 to 3 degree). The cavity and specimen are maintained to within 150± 0.5 °C and the force required to oscillate the disc is measured. A typical torque-time curve (vulcanisation curve) also known as rheograph is shown in Figure 2.7

![Figure 2.7](image)

**Figure 2.7.** A typical rheograph from Monsanto Rheometer (R-100).
The relevant data that could be taken from the torque-time curve are:

a) **Minimum torque** ($M_L$): This is the torque attained by the mix after homogenising at the test temperature before the onset of cure.

b) **Maximum Torque** ($M_H$): This is the torque recorded after the curing of the mix is completed

c) **Induction time** ($T_{5}$): This is the time taken for attaining 5% of the maximum torque (5% vulcanisation).

d) **Scorch time** ($T_{10}$): This is the time taken for two units (0.2Nm) rise above the minimum torque (about 10% vulcanisation).

**Optimum cure time** ($T_{90}$): This is the time taken for attaining 90% of the maximum torque (90% vulcanisation) and can be calculated according to the equation 2.1.

$$T_{90} = \left[ \frac{M_H - M_L}{100} \right] \times M_L + M_L \quad (2.1)$$

Where $M_H$ and $M_L$ are maximum and minimum torque respectively.

**Cure rate index (CRI)**: Cure rate index was determined from the rheographs of the respective mixes.

$$\text{Cure rate index} = \frac{100}{T_{90} - T_{10}} \quad (2.2)$$

where $T_{90}$ and $T_{10}$ are times corresponding to optimum cure and scorch time respectively.
2.6. **Vulcanisation**

Vulcanisation of the samples was carried out in an electrically heated hydraulic press at 150°C at a pressure of 120 kg/cm² in a mould for optimum cure time. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hours, and were used for subsequent physical tests and chemical analysis. For samples having thickness more than 6 mm (for compression set) additional timings based on the sample thickness were used to obtain satisfactory mouldings.

2.7. **Preparation of Double Networks**

Curing of the compounds was done in two steps. In the first step the rubber compound was cured for $T_{50}$ (50% of the optimum cure time) at 120°C in a hydraulic press at 120 kg/cm² pressure. In the second step, partially crosslinked rubber was extended uniaxially to various desired lengths using a metal holder. The extended rubber, placed in between the metallic holder was kept in an air oven at 100°C in order to complete the cure. Lower temperature was used for completing the cure, in order to minimize the degradation during curing under tension, necessary to produce double networks.
The experimental set up for the preparation of double networks is shown in Figure 2.8. The set up (a) represents the rubber specimen kept within holders. The extended rubber, (b) placed in between the metallic holder was kept in an air oven at 100°C in order to complete the cure. After completing the cure, (c) the force with which the sample extended is released.
2.8. Mechanical Properties

2.8.1. Tensile Strength, Modulus and Elongation at Break

Tensile testing of the samples was performed according to ASTM D 412-80 test method using dumb-bell shaped test specimens at a crosshead speed of 50 mm/min and a gauge length of 30mm using Zwick Universal testing machine (model 1465) with a load cell of 5kN. Modulus at 300 % elongation was measured from the load displacement curves. The tensile strength and modulus are reported in MPa and elongation at break in percentage. At least five concordant measurements are taken to represent each data point.

\[
\text{Tensile strength (N/mm}^2\text{)} = \frac{\text{Force at break (N)}}{\text{Area of cross section (mm}^2\text{)}}
\]  

(2.3)

2.8.2. Tear Resistance

The test was carried out as per ASTM method D 624-98; unnicked, 90° angle test pieces were used. The samples were cut from the vulcanised sheets parallel to the grain direction. The test was carried out on universal testing machine (TNE series 5T). The speed of extension was 500 mm / minute and the temperature of testing was 28 ± 2°C. Tear resistance has been reported in N/mm.

\[
\text{Tear strength (N/mm)} = \frac{\text{Ultimate load (N)}}{\text{Thickness (mm)}}
\]

(2.4)
2.8.3. Compression Set

The samples (1.25 cm thick and 2.8 cm diameter) in duplicate compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C (ASTM D 396-98). After the heating period, the samples were taken out, cooled to room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows.

\[
\text{Compression set (\%)} = \frac{t_0 - t_1}{t_0 - t_s} \times 100 \quad (2.5)
\]

where \(t_0\) and \(t_1\) are the initial and final thickness of the specimen and \(t_s\) is the thickness of the space bar used.

2.8.4. Rebound Resilience

Dunlop Tripsometer (ASTM D 2632-96) was used to measure rebound resilience. The sample was held in position by suction. It was conditioned by striking with the indentor six times. The temperature of the specimen holder and sample was kept constant at 35°C.

Rebound resilience was calculated as follows.

\[
\text{Rebound resilience (\%)} = \frac{1 - \cos \theta_2}{1 - \cos \theta_1} \times 100 \quad (2.6)
\]

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

Shore A type Durometer was employed to find out the hardness of the vulcanisates. A calibrated spring is used in the instrument to provide the indenting force. Readings were taken after 15 seconds of the indentation when firm contact has been established with the specimens. The method employed is the same as that in ASTM D 2240-97.

2.8.6. Heat Build-up

The heat build-up was measured using the Goodrich flexometer conforming to ASTM D 623-78 (Method A). Cylindrical samples of height 25 mm and 19 mm diameter were used to carry out the test. The oven temperature was kept constant at 50°C. The stroke was adjusted to 4.45 mm and the load to 10.9 kg. The sample was pre-conditioned to the oven temperature for 20 minutes. The heat development at the base of the sample was sensed by a thermocouple and relayed to a digital temperature indicator. The temperature rise ($\Delta T$°C) at the end of 20 minutes was taken as the heat-build up.

2.8.7. Ageing

Dumb-bell shaped tensile test samples were prepared and kept in an air oven at pre-determined temperature (70°C) for specified periods as per ASTM D 572-99. Mechanical properties were measured before and after ageing.

2.8.8. Swelling Measurement

Gravimetric sorption method was used to determine the swelling behaviour of the vulcanisates, this being expressed as the mole percent uptake of toluene by 100 g of rubber at 25°C. Samples of approximately 1 cm
diameter and 0.2 cm thickness, and 0.2 g weight were punched out from the vulcanisate. Measurement of weight of samples was carried out before and after swelling in toluene solvent. The mole percent uptake of solvent at time \( t \), \( (Q_t) \) was calculated from the equation 2.7

\[
Q_t = \frac{W_t - W_o}{W_o} \times 100 \quad \ldots \quad (2.7)
\]

where \( W_o \) and \( W_t \) are the weights of dry and swollen samples, respectively. \( M_w \) is the molar mass of toluene (92.14 g mol\(^{-1}\)).

### 2.8.9. Anisotropic Swelling

The anisotropic swelling studies provide an idea about the extent of hydrocarbon chain alignment. Rectangular test pieces of length 25 mm and breadth 10 mm were cut from double-networked samples of varying residual extension ratios for various angles of orientation like 0\(^o\), 45\(^o\), 90\(^o\) etc. The length, breadth and thickness of the samples were measured before and after swelling. The longitudinal and transverse swelling ratios \( a_L \) and \( a_T \) were then calculated.

\[
a_L = \frac{\text{New length}}{\text{Original length}} \quad \ldots \quad (2.8)
\]

\[
a_T = \frac{\text{New breadth}}{\text{Original breadth}} \quad \ldots \quad (2.9)
\]

The swelling ratio \( a^2\theta \) in any direction forming an angle \( \theta \) with chain orientation is calculated using the expression 2.10
\[ a^2 \theta = (a_r^2 - a_L^2)^2 \sin^2 \theta + a_L^2 \] \hspace{1cm} \text{(2.10)}

A plot of \( a^2 \theta \) against \( \sin^2 \theta \) is a straight line of slope \((a_L - a_r)\) and intercept \(a_L^2\).

### 2.9. Network Characterisation

#### 2.9.1. Determination of Total Crosslink Density

A circular test piece with 2cm diameter, weighing about 0.2g was cut from the compression-molded rubber sample using a steel edged die. The sample was immersed in pure toluene at room temperature to allow the swelling to reach diffusion equilibrium [2]. At the end of this period the test piece was taken out and the adhered liquid was rapidly removed by blotting with filter paper and the swollen weight was immediately measured. The samples were dried in vacuum to constant weight and the desorbed weight was taken.

The chemical cross-link density (1/2M_c) was calculated using the Flory-Rehner equation (2,11) [3].

\[ -\ln(1-V_r) + V_r + \chi V_r^2 = \frac{\rho_r V_s (V_r)^{1/3}}{M_c} \] \hspace{1cm} \text{(2.11)}

where \( \rho_r \) = density of test specimen (0.921g/cm\(^3\)); \( V_s \) = molar volume of solvent \([V_s \text{ (toluene)} = 106.2 \text{ cm}^3/\text{mol}]\); \( \chi \) = the parameter characteristic of the interaction between rubber and solvent \([\chi_{\text{NR-toluene}} = 0.42]\); \( M_c \) = number average molecular weight of the rubber chains between cross-links; and \( V_r \) = volume fraction of rubber in the swollen net work. Samples of approximately 1 cm diameter and 0.2 cm thickness, and 0.2 g weight were
punched out from the central portion of the vulcanisate. These were then allowed to swell in toluene for 48 hrs. The swollen samples were taken out and weighed. The solvent was removed in vacuum and the samples weighed again. The $V_r$ in the swollen network was then calculated by the method reported by Ellis and welding from the equation (2,12) [5].

$$V_r = \frac{(D - FT)\rho_r^{-1}}{(D - FT)\rho_r^{-1} + A_0\rho_s^{-1}} \quad \ldots (2.12)$$

where $T$ = weight of the test specimen

$D$ = weight of the deswollen test specimen

$F$ = weight fraction of insoluble components

$A_0$ = weight of the absorbed solvent corrected for the swelling increment.

$\rho_r$ = density of test specimen (0.921 g/cm$^3$)

$\rho_s$ = density of solvent (0.886 g/cm$^3$)

2.9.2. Determination of Mono, Di and Polysulphidic Linkages

a) Concentration of Polysulphidic linkages

The concentration of polysulphidic crosslinks was estimated from the change in the crosslink density of the vulcanisates before and after treatment with propane thiol and piperidine, which cleave the polysulphidic crosslinks in the network [6].
Vulcanisate sample weighing about 0.2-0.3 g was allowed to stand in excess of solvent (toluene) containing 0.1 % PBN for 24 hours at room temperature. Then the solvent was replaced by a solution (100ml) of 0.4 M propane thiol and piperidine in toluene containing 0.5% PBN for two hours. On completion of reaction, the sample was removed from the reagent solution washed with petroleum ether (four times), surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. The specimen was kept in excess of the solvent with 0.1% PBN for 24 hours, and finally extracted for two hours in pure solvent. The swollen sample was weighed, solvent removed in vacuum and the sample weighed again. The volume fraction of rubber (\(V_r\)) was then determined.

b) **Concentration of Disulphidic and Monosulphidic Linkages**

Both polysulphidic and disulphidic crosslinks in the vulcanisates could be cleaved by treatment with 1-hexane-thiol in piperidine. The determination of crosslink density before and after this treatment gives the concentration of monosulphidic linkages, assuming carbon-carbon linkages to be negligible. Since the concentration of polysulphidic linkages was determined before, the concentration of disulphidic linkages was also estimated [7].

Vulcanisate sample weighing about 0.2-0.3g was allowed to stand in 100 ml of 1-hexane thiol in piperidine (1M solution) containing 0.5% PBN for 48 hours at room temperature. The mixture was agitated occasionally. On completion of reaction the sample was removed from the reagent solution, washed with petroleum ether (four times) surface dried on filter paper as quickly as possible and dried in vacuum to constant weight at room temperature. Then the specimen was kept in excess solvent (toluene) containing 0.1% PBN for 24 hours. Finally the specimen was kept in pure
solvent for 2 hours and weighed. The solvent was removed in vacuum and the de-swollen sample was weighed. The volume fraction of rubber in the swollen network was then determined as before and the crosslink density was calculated.

2.10. Compounding of Latex

2.10.1. Preparation of dispersions

The soluble compounding ingredients are added to the latex as aqueous solutions, and water insoluble or water immiscible liquids as dispersion or emulsion. The materials were made to disperse in water by grinding action and the dispersing agent prevents the dispersed particles from re-aggregating. The quantity of dispersing agent to be used for preparing dispersions depends on the nature of materials to be dispersed. For very fine particles like ZnO the quantity of dispersing agent required is about 1% by weight whereas for materials like sulphur, 2-2.5% is required. A ball mill is used for making the dispersions of the ingredients. A ball mill consists of a cylindrical container in which the slurry is placed together with porcelain 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 the slurry to be pulverised. The efficiency of the ball mill depends on the speed of rotation of jar, size and material of ball, viscosity of slurry, period of ball milling etc.

For the present study the following dispersions were made using a ball mill. Dispersol F (sodium salt of a sulphonic acid) is used as the dispersing agent. DTB and thiourea are added to latex as 10% aqueous solutions.
Experimental

50% zinc oxide dispersion:

Zinc oxide ... 100.0
Dispersol F ... 2.0
Water (de-ionised) ... 98.0
Ball milled for 48 hrs

33% TMTD dispersion:

TMTD ... 100.0
Dispersol F ... 2.5
Water (de-ionised) ... 197.5
Ball milled for 48 hrs

50% ZDC dispersion:

ZDC ... 100.0
Dispersol F ... 2.5
Water (de-ionised) ... 97.5
Ball milled for 48 hrs

50% sulphur dispersion:

Sulphur ... 100.0
Dispersol F ... 3.0
Water (de-ionised) ... 97.0
Ball milled for 48 hrs
50% CaCO$_3$ dispersion

Sulphur ... 100.0
Dispersol F ... 2.0
Water (de-ionised) ... 98.0

Ball milled for 48 hrs

50% Silica dispersion

Silica 100.0
Dispersol F ... 2.0
Water (de-ionised) ... 97.0

Ball milled for 48 hrs

2.10.2. Compounding of latex

High ammonia type concentrated latex was used for the present study. It was de-ammoniated to 0.3% by stirring in a laboratory type de-ammoniation tank for 3 hrs. The high ammonia content in latex will affect the stability of latex compound in presence of zinc oxide. The total alkalinity of latex was estimated according to ASTM D 1076-88 as percentage of ammonia. Mixing of ingredients to natural rubber latex was in the following order stabilising agents, sulphur, accelerators and zinc oxide. All the ingredients were added with slow and thorough stirring. After the addition of ingredients, the compounds were kept for maturation at room temperature for 24 hours.

2.10.3. Vulcanisation and testing

Latex films were prepared by casting the matured compound in shallow glass dishes according to ASTM D 412-80. The film thickness was
controlled in the range of 1 to 1.25 mm. The films were then vulcanised at 120 °C for specific time intervals in an air oven. The tensile strength of the vulcanised latex film was then determined both before and after ageing. The specimens for ageing were kept in an air oven at 70°C for 7 days. The total chemical crosslink density and polysulphidic linkages were determined by equilibrium swelling method. For latex compounds, the optimum cure time was found out from the tensile strength-time graph. Tensile strength values were plotted against time of vulcanisation. From the graph, the time taken for attaining the optimum property is taken as the optimum cure time.

2.11. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA tests were conducted on an Eplexor™ 150 N (Gabo Qualimeter, Ahlden, Germany). Viscoelastic material parameters such as storage modulus and loss modulus (E' and E" respectively) were measured over a broad temperature range (-90 to +40°C) at a heating rate of 2°C/min. Rectangular specimens 60mm x 10mm x 6mm (length x width x thickness) were subjected to tensile loading consisting of a static preload of 3±1 N at frequency of 1Hz.
2.12. References


