CHAPTER II

MATERIALS AND EXPERIMENTAL

The details of the materials used and experimental techniques adopted in the present investigation are given in this chapter.
II.1. Materials used

II.1.1. Natural rubber

The natural rubber (NR) used for the study was technically specified form of rubber, obtained from the Rubber Research Institute of India, Kottayam. This rubber satisfied the Bureau of Indian Standards specifications for ISNR-5 grade natural rubber. The specification parameters and their limits for the ISNR-5 grade NR are given in Table II.1. The rubber from the same lot has been used in a particular experiment, since the basic properties such as molecular weight, molecular weight distribution and the contents of non-rubber constituents of NR are affected by clonal variation, season, use of yield stimulants and methods of preparation[1,2].

II.1.2. Sisal fibre

Sisal fibre (Agave sisalana) was obtained from local sources. The sisal fibre is extracted from the plant Agave sisalana which is available in plenty in the southern parts of India. The chemical constitution of sisal fibre is given in Table II.2. The fibre was washed thoroughly with water and dried in an air oven at 80°C for 4 - 6 h., before being chopped into the desired length for fibre treatment and composite preparation.
II.1.3. Rubber chemicals

Commercial grade accelerator N-cyclohexyl benzthiazyl sulphenamide (CBS) and antioxidant 2,2,4-trimethyl 1,2 dihydroquinoline polymerised (TDQ) used for the study were obtained from the Alkali and Chemical Corporation of India Ltd., Rishra.

II.1.4. Other chemicals

Zinc oxide (specific gravity - 5.5), stearic acid (specific gravity 0.92) and elemental sulphur (specific gravity - 1.9) used in the study were chemically pure grades.

II.1.5. Special chemicals

Resorcinol (specific gravity - 2.36) and hexamethylenetetramine (specific gravity 1.33) were of chemically pure grades and were obtained from Aldrich Chemical Company.

II.1.6. Solvents

Benzene, pentane, hexane, heptane and octane were of analytical grade.

II.2. Chemical treatment of fibre

Sisal fibre chopped to a length of 10 mm when used as such is designated as the untreated fibre. Acetylated
fibre was prepared from the raw sisal fibre as per the methods reported by Chand et al.[3] by immersing the chopped fibre (10 mm) in 18% aqueous sodium hydroxide solution at 35°C for 1 h. It was washed with water several times and then dried. This fibre was soaked in glacial acetic acid for 1 h. at 35°C, decanted and then soaked in acetic anhydride containing two drops of concentrated sulphuric acid for five minutes. The fibre was filtered through a Buchner funnel, washed with water and freed from acid and then dried in an oven at 70°C for 24 h. The acetylated fibre was kept in polythene bags to prevent moisture absorption.

II.3. Preparation of compounds
II.3.1. Composite preparation

The composites were prepared in a two-roll laboratory model open mixing mill (150 x 300 mm) at a nip gap of 1.3 mm and at a friction ratio of 1:1.25. Nip gap, mill roll speed ratio, time of mixing and temperature of the rolls were kept the same for all mixes. In order to disperse resorcinol homogeneously in the mixes, it was added in molten state[4]. Similarly finely powdered hexamethylenetetramine was used for the purpose of homogeneous mixing. Orientation of the fibre in the mill grain direction was achieved by repeated passing of the uncured compound through a tight nip[5].
II.3.2. Time of optimum cure

Optimum cure times at 150°C were determined by using Monsanto rheometer (model R-100). The optimum cure time corresponds to the time to achieve 90 per cent \( t_{90} \) of the cure calculated from the formula,

\[
\text{Optimum cure} = [0.9 (L_f - L_i) + L_i] \quad \text{.....(II.1)}
\]

In the cases where the rheographs show maximum or plateau, \( L_f \) and \( L_i \) are the maximum and minimum torques respectively. But in the case of rheographs showing marching modulus, optimum cure time was calculated as follows. Two tangents AC and BC were drawn on the rheograph as shown in Figure II.1. They meet each other at point C. The points of contact (A and B) of the tangents and rheograph were connected by a straight line AB. The middle point O of the straight line was connected with point C (point of interaction of the two tangents). The line CO cuts the rheograph at point T. The time corresponding to the modulus at point T of the rheograph was taken as the optimum cure time.

II.3.3. Moulding of test samples

Blanks cut from the uncured sheet were marked with the direction of the mill grain and were vulcanized at 150°C in a hydraulic press having steam heated platens to their respective cure times, as obtained from Monsanto rheometer. Test pieces were punched out from the moulded
sheet along and across the direction of fibre orientation for tensile and tear tests. The orientations of fibres along and across the grain direction are shown in Figure II.2. Test samples for other tests such as abrasion resistance, compression set, ozone resistance etc. were directly moulded out.

II.3.4. Fibre breakage

Shear forces during mixing cause breakage of the fibres. Extent of fibre breakage and the fall in the mean aspect ratio (average length to diameter ratio) of the fibres from its original value (before mixing) was determined by dissolution of the mixes in benzene, followed by extraction of the fibres and examination of length and diameter of the extracted fibres by a polarizing microscope under reflected light. A batch size of 200 fibres was taken and the distribution of fibre length was assessed using an optical microscope.

II.4. Physical tests

At least three specimens per sample were tested for each property and the mean of these values was reported. Excepting hardness, resilience and abrasion in the Du Pont abrasion tester, the other tests were carried out both along (longitudinally oriented fibres) and across (transversely oriented fibres) the grain direction. In
the case of hardness and compression set the direction of fibre alignment is normal to the direction of application of load.

11.4.1. Modulus, tensile strength and elongation at break

In the present work, these tests were carried out using a Zwick Universal Testing Machine model 1474 according to ASTM test method D 412 - 51 T. Samples were punched out from vulcanized sheets both along and across the grain directions using a dumb-bell die (C-type). The thickness of the narrow portion was measured by a bench thickness gauge. The above tests were carried out at room temperature (28 \( \pm \) 2°C) and at a cross-head speed of 500 mm per minute.

11.4.2. Tear resistance

This property was tested as per ASTM D 624-81 test method, using unnicked 90° angle test specimens which were punched out from the moulded sheets, along the mill grain direction. This test was also carried out in the Zwick UTM, at a cross-head speed of 500 mm per minute and at 28 \( \pm \) 2°C. The tear strength values are reported in kN/m.

11.4.3. Hardness

As per ASTM D-2240-81 test method, the hardness of the samples was measured 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 reading was taken immediately after the establishment of firm contact.

II.4.4. Abrasion resistance

The abrasion resistance of the samples was tested using a Du pont abrader. In this machine, two test pieces, each having 2 cm square surface, are simultaneously held against an abrasive paper disc which rotates at a speed of 40 rpm. The normal load on the samples was 3.26 Kg and the silicon carbide abrasive paper used for the test was of grain size 320. The samples were abraded for 10 min. after an initial conditioning period of 5 min. Separate abrasive discs were used for each sample. The abrasion loss of the samples was calculated and expressed as volume loss in cm$^3$ h$^{-1}$.

II.4.5. 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 per cent 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. The compression set was calculated using the equation
compression set (%) = \frac{t_o - t_f}{t_o - t_s} \times 100 \quad \ldots (II.2)

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

II.4.6. 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,

\[
\text{Rebound resilience (\%) = } \frac{1 - \cos \Theta_2}{1 - \cos \Theta_1} \times 100 \quad \ldots (II.3)
\]

where \( \Theta_1 \) and \( \Theta_2 \) are the initial and rebound angles respectively. \( \Theta_1 \) was 45° in all cases.

II.5. Melt flow studies

II.5.1 Equipment details

A capillary rheometer attached to a Zwick UTM model 1474 was used to carry out the melt flow studies. The extrusion assembly consisted of a barrel, made of hardened steel, mounted on a special support, underneath the moving cross-head of the Zwick UTM. A hardened steel plunger,
which is accurately ground to fit inside the barrel is held to the load cell extension. An insulating ring thermally isolates the barrel from the rest of the machine and prevents heat losses due to conduction. The capillary is inserted at the bottom of the barrel and is locked using a clamping device. The capillary is made of tungsten carbide. The barrel was heated using a three zone temperature control system. The difference between the successive temperature zones in the barrel was kept at 5°C and the temperature of the lower zone, where the capillary is located, is taken as the test temperature.

The moving cross-head of the Zwick UTM runs the barrel at a constant speed irrespective of the load on the melt, maintaining constant volumetric flow rate through the capillary. The cross-head speed can be varied from 0.5 mm/min. to 500 mm/min. giving shear rates ranging from 3 s⁻¹ to 3000 s⁻¹ for a capillary of l/d = 40. Forces corresponding to specific plunger speeds were recorded on a strip chart recorder. These values were converted into shear stresses.

II.5.2. Test procedure

The sample to be tested was placed inside the barrel which was maintained at the test temperature. The sample was forced down to the capillary using the plunger attached to the cross-head. After a warming up period of
three minutes, the melt was extruded through the capillary at pre-selected speeds of the cross-head. The melt height in the barrel before extrusion was kept the same in all experiments and the machine was operated to give ten different plunger speeds. Each plunger speed was continued until the recorded force was stabilized, before changing to the next speed. Forces corresponding to specific plunger speeds were recorded. The force and cross-head speed were converted into apparent shear stress ($\tau_w$) and shear rate ($\dot{\gamma}_w$) at the wall by using the following equations [6].

$$\tau_w = \frac{F}{4 \lambda_p (l_c/d_c)} \quad \ldots \quad \text{(II.4)}$$

$$\dot{\gamma}_w = \frac{(3n' + 1)}{4n'} \frac{32Q}{\lambda d_c^3} \quad \ldots \quad \text{(II.5)}$$

where

- $F$ = Force applied at a particular shear rate
- $A_p$ = Cross sectional area of the plunger
- $l_c$ = Length of the capillary
- $d_c$ = Diameter of the capillary
- $Q$ = Volume flow rate
- $n'$ = Flow behaviour index, defined by $\frac{d (\log \tau_w)}{d (\log \dot{\gamma}_w)}$
- $\dot{\gamma}_{wa}$ = Apparent wall shear rate
- $\dot{\gamma}_w$ = Actual shear rate at wall
'n' is determined by regression analysis of the values of $f_w$ and $\dot{\gamma}_{wa}$ obtained from the experimental data. The shear viscosity $\eta$ was calculated as

$$\eta = \frac{f_w}{\dot{\gamma}_{wa}}$$

..... (11.6)

The shear stress at the wall requires correction as suggested by Bagely[7]. But the correction factor diminishes as the length to diameter ratio increases. For a capillary having $\frac{L}{d}$ ratio 40, it is assumed that the correction factor is negligible. For the analysis of the data, the following assumptions were also made:

1. There is no slip at the capillary wall.
2. The material is incompressible.
3. The fluid is time independent.
4. The flow pattern is constant along the capillary.
5. The flow is isothermal.
6. The flow properties are independent of hydrostatic pressure.

II.5.3. Extrudate swell

It is expressed as the diameter of the extrudate to that of the capillary used. The extrudate emerging from the capillary was collected without any deformation. The diameter of the extrudate was measured after 24 h. rest period using a WILD Stereomicroscope model M 650 at several points on the extrudate. The average value of 10 readings was taken as diameter ($d_e$) of the extrudate and
swelling index was calculated as \( \frac{d_e}{d_c} \) where \( d_c \) is the diameter of the capillary. For each sample, the extrudate swell at two different shear rates was determined.

II.6. Degradation studies

II.6.1. 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 pphm which is generated by an UV quartz lamp. The test was carried out as per ASTM D-1149-81 specification. The test was conducted at 38°C.

II.6.2. Radiation studies

Test samples (2 ± 0.2 mm thick) were irradiated with \( \gamma \)-rays from a \(^{60}\)Co source in a gamma chamber. The samples were irradiated for different radiation doses at a dose rate of 0.321 Mrad/h in air at room temperature. The mechanical properties were measured before and after irradiation.

II.6.3. Thermal ageing

Test samples (2 ± 0.2 mm thick) were aged at 100°C for three and five days in an oven. The tensile and
tensile strengths were measured before and after ageing. The percentage retention of properties after ageing was calculated.

II.7. Scanning electron microscopy studies

The scanning electron microscopy (SEM) photomicrographs given in this work were obtained using JEOL 35 C model scanning electron microscope, the principle of which is given in Figure II.3 [8]. 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 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[9]. The operating conditions of the SEM are summarised in Table II.3.

II.8. Dynamic mechanical properties

The dynamic mechanical properties of NR-Sisal composites were measured using a dynamic mechanical analyser (Polymer Laboratories DMTA MK-II), consisting 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 strain amplitude of 64 μm and a frequency of 10 Hz. The heating rate of the samples was 1°C/min. Liquid nitrogen was used to achieve sub ambient temperature. The mechanical loss factor tanδ and dynamic moduli (E' and E'') were calculated with a micro computer.

II.9. Stress relaxation

The stress relaxation measurements were carried out in a Zwick Universal Testing Machine model 1474. The dumbbell shaped test specimen was pulled to desired strain level (20-70%) at fixed strain rate of 0.016 s⁻¹. The test was carried out at room temperature. The stress was recorded as a function of time on a chart paper initially at a higher speed and later at a lower speed. The ratio \( \sigma_t / \sigma_0 \) is plotted against logarithm of time, \( \sigma_t \) and \( \sigma_0 \) being stresses at time \( t \) and that at zero time, respectively.

II.10. Swelling studies

For swelling studies, vulcanized composites were cut circularly (diameter 1.94 cm). The thickness of the composite was measured using a micrometer screw gauge. Dry weights of the cut samples were taken before immersion in the liquid contained in air tight weighing bottles. The samples were removed from the bottles at periodic intervals, the wet surface was quickly dried using a
piece of blotting paper and weighed immediately in air tight weighing bottles. During swelling any change in the diameter and thickness of the sample was determined by means of a vernier calipzer and a micrometer, respectively.

The uptake of the liquid by the polymer during swelling was expressed as moles of liquid sorbed by 100 g. of the polymer. This method was found to be more convenient for comparison of sorption data and was adopted by many researchers[10,11].

To determine the volume fraction of rubber in the unswollen vulcanizate, the test specimen was weighed both in air and water. The difference between the two weights gave the volume of the samples. Using the base formulation, the amount of rubber present in the weighed sample of each specimen and its volume were calculated. From these data the volume fraction of rubber present in dry specimen was calculated and it is denoted as $V_I$. These dry specimens were then swollen in solvents upto equilibrium swelling volume. Volume of swollen samples was determined by hexane displacement method. The displaced volume of hexane was corrected for actual volume of swollen samples by multiplying them with density of hexane. From this, the volume fraction of rubber in the swollen sample was calculated.
References


Table II.1. Specifications for ISNR-5 grade natural rubber

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Limit</th>
<th>Actual value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dirt content, % by mass, max</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>Volatile matter, % by mass, max</td>
<td>0.80</td>
<td>0.50</td>
</tr>
<tr>
<td>Nitrogen, % by mass, max</td>
<td>0.60</td>
<td>0.30</td>
</tr>
<tr>
<td>Ash, % by mass, max</td>
<td>0.50</td>
<td>0.40</td>
</tr>
<tr>
<td>Initial plasticity, P_o, min.</td>
<td>30</td>
<td>38</td>
</tr>
<tr>
<td>Plasticity retention index PRI, min.</td>
<td>60</td>
<td>78</td>
</tr>
</tbody>
</table>

Table II.2. Chemical constitution of sisal fibre

- Cellulose - 78%
- Hemi cellulose - 10%
- Lignin - 8%
- Waxes - 2%
- Ash - 1%
Table II.3. Operating conditions of the SEM

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specimen position, tilt, degree</td>
<td>adjustable</td>
</tr>
<tr>
<td>Maximum resolution, nm</td>
<td>0.5</td>
</tr>
<tr>
<td>Spot size, angstrom</td>
<td>640</td>
</tr>
<tr>
<td>Emission current, amp.</td>
<td>26</td>
</tr>
<tr>
<td>Aperture, microns</td>
<td>200</td>
</tr>
<tr>
<td>H.T., Kv</td>
<td>25</td>
</tr>
<tr>
<td>Depth of focus</td>
<td>high</td>
</tr>
</tbody>
</table>
Figure II.1. Determination of optimum cure time by modified tangent method.
Figure 11.2. Longitudinal and transverse orientation of the fibre.