Chapter 2
Materials and Experimental Techniques

2.1 Materials

2.1.1 Pineapple leaf fibre

The pineapple leaf fibre (PALF) is obtained from the leaves of the plant, *Ananas comosus* belonging to the Bromeliaceae family which is available in plenty in Kerala and Tamil Nadu. The leaves of the plant produce strong, white, fine, silky fibres. Philippines and Taiwan are the chief producers of the fibre. It is also available in Brazil, Hawai, Indonesia and West Indies. The physical and mechanical properties of PALF are given in Table 2.1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre tenacity (g/tex)</td>
<td>30.0-51.0</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>2.50-3.50</td>
</tr>
<tr>
<td>Moisture regain (%)</td>
<td>11.5-12.0</td>
</tr>
<tr>
<td>Water swelling (%)</td>
<td>49.0</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.526</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>9.0</td>
</tr>
</tbody>
</table>

Source: Ref. 1.
The fibres are extracted mechanically as well as by a process of water retting and scraping. The fibre is multicellular and the major chemical constituents are given in Table 2.2. In the present study, pineapple leaf fibre (PALF) supplied by South India Textile Research Association, Coimbatore has been used.

Table 2.2. Chemical constituents of PALF.

<table>
<thead>
<tr>
<th>Chemical constituent</th>
<th>Range in per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alpha cellulose</td>
<td>61.3–69.6</td>
</tr>
<tr>
<td>Beta cellulose</td>
<td>4.40–12.5</td>
</tr>
<tr>
<td>Gamma cellulose</td>
<td>3.30–11.5</td>
</tr>
<tr>
<td>Residual gum</td>
<td>27.2–36.0</td>
</tr>
<tr>
<td>Fat and wax</td>
<td>0.98</td>
</tr>
<tr>
<td>Ash</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Source: Ref. 1.

2.1.2 Polyethylene

Low density polyethylene (LDPE) [16MA 400] was obtained from Indian Petrochemicals Corporation Ltd., Vadodara. The physical and mechanical properties of LDPE are given in Table 2.3.

Table 2.3. Physical and mechanical properties of LDPE.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt flow index (g/10 min)</td>
<td>40.0</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>0.918</td>
</tr>
<tr>
<td>Vicat softening point (°C)</td>
<td>85.0</td>
</tr>
<tr>
<td>Crystalline point (°C)</td>
<td>104</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>8.50</td>
</tr>
<tr>
<td>Modulus of elasticity (MPa)</td>
<td>130</td>
</tr>
<tr>
<td>Elongation at break (%)</td>
<td>110</td>
</tr>
</tbody>
</table>
2.1.3 Chemicals

Poly(methylene) poly(phenyl) isocyanate (PMPPIC), supplied by Poly Sciences, USA, vinyl tri(2-ethoxy methoxy) silane [Silane A 172] and γ-amino propyl tri(methoxy) silane [Silane A 1100] supplied by Union Carbide Co., Montreal, Canada were used as coupling agents.

Benzoyl peroxide (BPO), dicumyl peroxide (DCP), potassium permanganate (KMnO₄) and NaOH [Reagent grade] were used as surface modifiers to improve the adhesion between fibre and matrix. Toluene and carbon tetrachloride used as solvents were of analytical grade.

2.2 Fibre treatment

2.2.1 Alkali treatment

Fibres were immersed in NaOH solution at different concentrations (0.5, 1 and 5%) for half an hour. Later they were washed several times using cold water and finally in acidified water (HCl 0.1 N). These fibres were then dried in an air oven at 60°C for 24 h.

2.2.2 Silane treatment

(a) Silane A 172 [Vinyl tri(2-ethoxy methoxy) silane]

A mixture of oven dried fibres, carbon tetrachloride, dicumyl peroxide (2% by weight of fibre) and vinyl tri(2-ethoxy methoxy) silane (4% by weight of fibre) was heated under reflux for 2 h. Finally, the mixture was filtered and dried.

(b) Silane A 1100 [γ-amino propyl tri(methoxy) silane]

Silane (5%) were added to a solution of acetone acidified water (95:5) to form a hydrolysed silane solution. Fibres (5 g) were dipped in this solution for
1.5 h. The fibres became yellow after the treatment. They were finally dried in an air oven at 60°C.

2.2.3 Isocyanate treatment (PMPPIC)

Fibres were dipped in toluene solution containing PMPPIC (5, 8 and 10% by weight of fibre) for half an hour at 50°C. The fibres were then decanted and dried in an oven at 60°C for 2 h. Later they were mixed with polyethylene using toluene as the solvent containing PMPPIC (6% by weight of fibre) at a temperature of 120°C.

2.2.4 Permanganate treatment (KMnO₄)

The fibres were soaked in KMnO₄ solution in acetone having different concentration (0.005, 0.01, 0.015, 0.02 and 0.05%) for 1 min. This was then decanted and the fibres were dried in an air oven.

2.2.5 Peroxide treatment

Benzoyl peroxide (1% by weight of polymer) and dicumyl peroxide (0.5% by weight of polymer) were added to the melt of polyethylene before being mixed with fibres.

2.3 Characterisation

2.3.1 IR spectroscopy

The chemically modified fibres were characterised by IR spectroscopy using Shimadzu IR 470 infrared spectrometer, Japan.
2.3.2 Scanning electron microscopy

The surface of the specimens was examined using a JEOL JSM 35C model scanning electron microscope.

2.3.3 Optical microscopy

An optical stereo microscope was used for observing the fibre orientation and also to study the fibre length distribution in LDPE matrix.

2.4 Preparation of composites

Fibres were separated from undesirable foreign matter and pith and manually chopped to different lengths of 2 mm, 6 mm and 10 mm. The chopped fibres were washed in water and dried in an air oven at 70°C for 24 h before being mixed with polyethylene. Composites of PALF/LDPE were prepared by two different methods—solution mixing and melt mixing.

In solution mixing method, fibres were added to a viscous slurry of polyethylene in toluene which was prepared by adding toluene to a melt of polyethylene at a temperature of 120°C. The solvent was then evaporated off by keeping it in a vacuum oven. Randomly oriented composites were prepared by direct injection of molten mix through a ram type hand injection moulding machine into a mould. Oriented composites were prepared by closely aligning the extrudates in a mould and then compression moulding at a temperature of 120°C.

For the melt mixing studies, mixing was carried out in a Brabender Plasticorder (Model PLE 331). In order to optimise the mixing parameters, composites were prepared by varying the mixing time, rotor speed and chamber temperature.
2.5 Characterisation of composite properties

2.5.1 Mechanical properties

Tensile properties were measured using an Instron Universal Testing Machine model 1121 at a crosshead speed of 50 mm/min and a gauge length of 50 mm. Size of the specimens was 120 mm x 12.5 mm x 3 mm. Mechanical property evaluation was carried out at temperatures below and above ambient using Instron model 3010 temperature cabinet and controller. Low temperatures (below RT) were obtained using liquid nitrogen supplied by a pressurefed system attached to the temperature controller. Temperatures above ambient were obtained by electrical heating. The temperatures studied were -30, 0, 28, 40, 60 and 80°C. The parameters drawn from the results reported here are the average of at least five determinations.

Samples were conditioned at the test temperature for a period of 10 min. prior to testing. The conditioning was necessary for obtaining reproducible results. In order to study the time dependent behaviour of the composites, testing was done at different crosshead speeds, viz. 5, 50 and 500 mm/min.

The flexural properties were evaluated using specimens measuring 25 x 12.5 x 2.5 mm. A three-point bend fixture attached to INSTRON testing machine was used.

2.5.2 Rheological measurements

The melt rheological measurements were carried out using an Instron Capillary Rheometer model 3211 at different plunger speeds of 0.06 to 20 mm/min. The capillary used was made of tungsten carbide with a length to diameter (l/d) ratio of 33.4 and an angle of entry of 90°. The sample was placed inside the barrel of the extrusion assembly and forced down into the capillary with a plunger. After
a residence time of 5 min, the melt was extruded through the capillary at predetermined plunger speeds. The initial position of the plunger was kept constant in all experiments and shear viscosities at different shear rates were obtained from a single charge of material. The measurements were carried out at three different temperatures, i.e., 125, 135 and 145°C.

The shear stress at each plunger speed is obtained from the equation,

\[ \tau = \frac{F}{4A_p (l_c / d_c)} \]  \hspace{1cm} (2.1)

where \( F \) is the force on the plunger, \( A_p \) is the cross-sectional area of the plunger, and \( l_c \) and \( d_c \) are the length and diameter of capillary, respectively.

The shear rate at the wall was determined using the equation,

\[ \dot{\gamma} = \frac{(3n' + 1)}{4n'} \frac{32Q}{\pi d_c^3} \]  \hspace{1cm} (2.2)

where \( Q \) is the volumetric flow rate which is given by

\[ Q = \frac{V_{xh}}{60} \frac{\pi d_b^2}{4} \]  \hspace{1cm} (2.3)

where \( V_{xh} \) is the plunger speed (mm min\(^{-1}\)) and \( d_b \) is the diameter of the barrel.

The factor \( (3n' + 1)/4n' \) is the Rabinowitch correction applied to calculate the true shear rate at the wall. The flow behaviour index \((n')\) given by

\[ n' = \frac{d(\log \tau)}{d(\log \dot{\gamma})} \]  \hspace{1cm} (2.4)

is obtained by the regression analysis of the plot of \( \log \tau \) versus \( \log \dot{\gamma} \).

Bagley's correction\(^2\) for the pressure drops at the capillary entrance was not applied because this correction factor becomes negligible for capillaries with high \( l/d \) ratios. The viscosity \((\eta)\) is calculated using the equation:

\[ \eta = \frac{\tau}{\dot{\gamma}} \]  \hspace{1cm} (2.5)
The melt flow index (MFI) was determined using a Davenport Melt Flow Indexer with 21.6 kg load. The measurements were made at a temperature of 145°C.

2.5.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were carried out in a DuPont thermogravimetric analyser. Samples were scanned from 30-650°C at a heating rate of 20°C/min.

2.5.4 Dynamic mechanical analysis

Rectangular specimens having a size of 70 x 10 x 2.5 mm$^3$ were used for the dynamic mechanical experiments. The dynamic moduli and mechanical damping (tan δ) were measured by a direct reading dynamic viscoelastometer, Rheovibron DDV-III. The temperature range over which properties were determined was 27 to 130°C at a heating rate of 1°C/min. For LDPE and 10% fibre loaded composite, low temperature measurements were made up to -120°C. The samples were tested at various frequencies such as 3.5, 11 and 35 Hz. The amplitude of oscillation was 0.1%.

2.5.5 Stress relaxation

Zwick Universal Testing machine (model 1465) was employed for stress relaxation measurements in uniaxial tension at 28°C. Specimens measuring 120 x 12.5 x 2.5 mm$^3$ were used. The test specimens were pulled to the required strain level at a crosshead speed of 2 mm/min. After the appropriate strain ($\varepsilon_0$) was reached, the relaxation in stress keeping the sample at this strain was recorded as a function of time for a time span covering about 10,000 s. The rate of relaxation has been calculated as
relaxation rate (\%) = \left( \frac{a_1 - a_2}{a_1} \right) \times 100 \quad (2.6)

where \(a_1\) and \(a_2\) are stress decay values at time \(t_1\) and \(t_2\), respectively. The stress decay was calculated as \(\sigma_t/\sigma_0\), where \(\sigma_0\) is the initial stress, i.e., the stress at zero time \((t = 0)\) and \(\sigma_t\) is the stress at subsequent times. Relaxation modulus, \(E_r(t)\) is given by

\[ E_r(t) = \frac{\sigma_t}{\varepsilon_0} \quad (2.7) \]

**2.5.6 Electrical properties**

The capacitance, resistance and dissipation factor were measured directly using a 4192 LF Impedance Analyser (Hewlett-Packard, USA) by varying the frequencies \((10 \text{ Hz}-10 \text{ MHz})\) at room temperature. Disc samples of 2 mm thickness and 10 mm diameter were used. The test samples were coated with conductive silver paint on either sides and copper wires were fixed on both sides of the samples as electrodes.

Dielectric constant \(E'\) was calculated from the capacitance using the equation

\[ E' = \frac{Ct}{E_0A} \quad (2.8) \]

where \(E_0\) is the permittivity of air \((8.85 \times 10^{-12} \text{ F m}^{-1})\), \(C\) the capacitance, \(A\) the area of cross section of the sample and \(t\) the thickness of the sample.

Volume resistivity \(\rho\) can be calculated from resistance using the equation,

\[ \rho = \frac{RA}{t} \quad (2.9) \]

where \(R\) is the resistance. The electrical conductivity \(\sigma\) is calculated according to the following equation

\[ \sigma = 1/\rho \quad (2.10) \]
The dissipation factor \(\tan \delta\) was calculated using the equation,

\[
\tan \delta = \frac{E''}{E'}
\]

(2.11)

where \(E''\) is the dielectric loss.

### 2.5.7 Environmental effects

Water sorption experiments and UV radiation ageing has been carried out to follow the environmental effects. Disc specimens having 20 mm diameter and 2.5 mm thickness were used for studying the kinetics of water absorption. The specimens were immersed in distilled water and the per cent weight change was determined until equilibrium value is reached. After immersion in distilled water, samples were removed at different times, wiped with filter paper to remove surface water and weighed using an analytical balance with 0.1 mg resolution. Water induced dimensional changes were measured with a micrometer having an accuracy of 0.01 mm.

The molar sorption \(Q_t\) of water by the composite at time \(t\) was calculated using

\[
Q_t \text{ (mol\%)} = \frac{W_2 - W_1}{18xW_1} \times 100
\]

(2.12)

where \(W_1\) = Weight of dry specimen

\(W_2\) = Weight of wet specimen

The molar sorption at equilibrium (infinite time) is represented by \(Q_\infty\).

In order to study the effect of UV radiation on the mechanical properties the specimen were exposed to UV radiation in a weatherometer as per ASTM G53.

### 2.6 References
