

# CHAPTER 2

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## Materials and Experimental Techniques

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## 2.1 MATERIALS

### 2.1.1 Oil Palm Fibres

Oil palm empty fruit bunches were collected from Oil Palm India Ltd., Kottayam, Kerala, India and fibres were processed by retting technique. The oil palm empty fruit bunch (OPEFB) fibres were separated, cleaned off pithy materials and dried. The average length of a fibre is approximately 15cms. Oil palm mesocarp fibres were collected from palm oil mill after the extraction of oil from fruits. These fibres were cleaned off from oily matter and pithy materials. The physical and chemical characteristics of oil palm fibres are discussed in chapter 3 and are already reported elsewhere.<sup>1</sup>

### 2.1.2 Glass Fibre Mat

M/s Ceat Ltd, Hyderabad, India, supplied multidirectional short E-glass strand mat. The fibre length was 50mm. They are high silicate materials having high strength to weight ratio. The important physical and mechanical properties of glass fibre are given Table 2.1.<sup>2</sup>

**Table 2.1** Physical and Mechanical Properties of Glass

Diameter ( $\mu\text{m}$ )	5 - 25
Density (g/cc)	2.54
Tensile strength (GPa)	1.7 - 3.5
Young's modulus (GPa)	66 - 72
Elongation at break (%)	3

### 2.1.3 Phenol Formaldehyde Resin

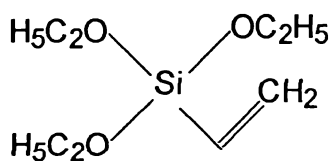
Phenol formaldehyde (PF) resole type resin is used and is procured from M/s West Coast Polymers Pvt. Ltd., Kannur, Kerala, India. The physical, chemical and mechanical characteristics of the PF resin are given in Table 2.2.

**Table 2.2** Typical Properties of Phenol Formaldehyde Resole Resin

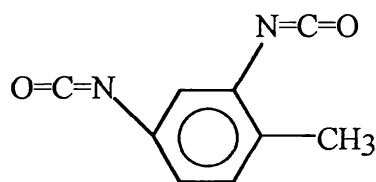
Liquid resin	
Appearance	Deep brown colour
Viscosity (cps)	18 – 22 s. on Ford cup B4
Water tolerance	1 : 8
Solid content (%)	50 ± 1
Cured resin	
Density (g/cc)	1.3
Tensile strength (MPa)	10
Young's modulus (MPa)	375
Elongation at break (%)	2
Flexural strength (MPa)	10
Flexural modulus (MPa)	1875
Izod impact strength (kJ/m <sup>2</sup> )	20

#### 2.1.4 Chemicals

Acrylic acid, acrylonitrile monomer, NaOH, KMnO<sub>4</sub>, acetic anhydride and benzoyl peroxide were used for fibre surface modifications. These chemicals were of reagent grades. The structures of the coupling agents, triethoxy vinyl silane and toluene 2,4-diisocyanate used are given below.



Tri ethoxy vinyl silane (A 151)



Toluene 2,4-diisocyanate

These chemicals were procured from M/s Union Carbide Co., Montreal, Canada and Poly Sciences, USA respectively.

## 2.2 CHEMICAL COMPOSITION OF OIL PALM FIBRES

Chemical composition of fibres was estimated according to ASTM procedures. Lignin-ASTM D1106; Holocellulose-ASTM D1104; Ash content-ASTM D1102; Alcohol-benzene solubility-ASTM D1107; Ether solubility-ASTM D1108; One per cent caustic soda solubility-ASTM D1109; Water solubility-ASTM D1110

## 2.3 RESIN MODIFICATION

The PF resin was treated with benzoyl peroxide. Different quantities ( 0.1, 0.5 and 1% of the resin) of the peroxide were added into the resin and stirred for one hour for intimate mixing. The peroxide can act as a free radical initiator and can take part in the crosslinking reactions.

## 2.4 FIBRE SURFACE MODIFICATIONS

***Mercerisation:*** Fibres were immersed in 5% solution of sodium hydroxide for different time intervals such as 72, 48 and 24 hrs. at room temp. Fibres were then washed many times in distilled water and finally washed with water containing a little acetic acid and dried.

***Acetylation:*** Fibres were pre-treated with 2% sodium hydroxide for about half an hour in order to activate the hydroxyl groups on the cellulose and lignin. Fibres were subjected to acetylation with acetic anhydride in acetic acid medium. Conc.  $H_2SO_4$  acts as a catalyst in this reaction. Fibres were washed in distilled water and then dried.

***Peroxide treatment:*** Fibres were coated with benzoyl peroxide in acetone solution after alkali pre-treatment. Saturated solution of the peroxide in acetone was used. Finally, the treated fibres were then dried

***Permanganate treatment:*** Fibres were pre-treated with sodium hydroxide and then dipped in permanganate solution in acetone for about 2-3 minutes. The permanganate solutions of concentrations 0.01, 0.05 and 0.1% were used. Fibres were washed in distilled water and finally dried.

***<sup>60</sup>Co $\gamma$ -ray irradiation:*** Oil palm fibres were exposed to  $\gamma$ -ray irradiation from a <sup>60</sup>Co source at a dose rate of 0.1Mrad per hour for about 30hrs.

***Isocyanate treatment:*** The alkali treated fibres were taken in a round-bottomed flask and soaked in chloroform containing dibutyl tin dilaurate catalyst. Toluene diisocyanate was added dropwise into the flask using a pressure equalising funnel. The reaction was allowed to take place for two hours with continuous stirring. Fibres were purified by refluxing with acetone and then washed with distilled water and dried in oven.

***Silane treatment:*** The pre-treated fibres were dipped in alcohol water mixture (60:40) containing tri ethoxy vinyl silane coupling agent. The pH of the solution was maintained between 3.5 and 4. Fibres were washed in distilled water and dried.

***Acrylation:*** Fibres were mixed with 10% NaOH for about 30minutes at room temperature. The solution was decanted and the wet product treated with solution containing different concentrations of acrylic acid. The reaction was allowed to be carried out for about one hour at 50°C. Fibres were washed with water/alcohol mixture and dried.

***Acrylonitrile grafting:*** Fibres were bleached with 2% alkali for 30 minutes and then oxidised with 0.02mL<sup>-1</sup> KMnO<sub>4</sub> (liquor ratio, 1:150) for 10 minutes. The fibres were further washed with water and then soaked in 1% H<sub>2</sub>SO<sub>4</sub> containing acrylonitrile in the ratio 30:1. The sample was then placed in a thermostatic water bath, and the temperature was kept at 50°C for 2 hours without any disturbance. The sample was then washed with water thoroughly and dried. The grafted fibre was isolated from any homopolymer formed (PAN) by soxhlet extraction using dimethyl formamide.

***Latex modification:*** Fibres were given a latex coating by dipping in natural rubber latex having 10% dry rubber content after pre-treatment with NaOH.

## 2.5 COMPOSITE PREPARATION

Oil palm empty fruit bunch fibre having higher cellulose content and mechanical properties than mesocarp fibre was selected for reinforcing PF resin. Prepreg route was followed for the preparation of composites. Hand lay up method followed by compression moulding was adopted for composite fabrication. Fibres were chopped into desired lengths (10, 20, 30 and 40mm) and dried in oven at 60-70°C for about 2 hrs. These chopped fibres were uniformly spread in a mould cavity. Mould was then closed and pressure applied to form a single mat. The mat was then impregnated in the resin and the prepreg was kept at room temperature up to a semicured stage. It was then pressed at 100°C to get a three dimensionally crosslinked network. Composites with different fibre loading (20, 30, 40 and 50wt.%) were prepared and properties evaluated. It has already been reported that composite containing oil palm fibre with 40mm length and a loading of 40 wt.% resulted in better reinforcement and provided optimum properties.<sup>3</sup>

The glass fibre mats were sized. Glass mat reinforced PF resin composites with various fibre loading (10, 23, 27, 40 and 45 wt.%) were prepared as described above. Effect of fibre loading on the mechanical properties was analysed. Hybrid composite was prepared by arranging randomly oriented short glass and oil palm fibre mats as alternate layers. It was then soaked in PF resin and cured under hot pressing. By keeping the total fibre loading of the hybrid composite constant ie.40wt.%, the relative volume fractions of the individual fibres were changed. Composites having different volume ratio of glass/oil palm fibre such as 1:0, 0.7:0.3, 0.5:0.5, 0.3:0.7, 0.1:0.9, 0.08:0.92, 0.04:0.96 & 0:1 were prepared.

## 2.6 SCANNING ELECTRON MICROSCOPY AND OPTICAL MICROSCOPY

The SEM photographs of fibre surfaces and cross sections of untreated and treated fibres were taken using scanning electron microscope Philips model PSEM-500. The tensile and impact fractograph of the composites were taken to study the

fracture mechanisms and interface adhesion of the composites. The crack propagation and fibre dispersion in composites were analysed by using an optical microscope of Leitz Metallux 3, Germany.

## **2.7 IR SPECTROSCOPY**

The modified fibre surfaces were characterised by IR spectroscopy. KBr disk method is followed in taking IR spectra. The instrument used was Shimadzu infrared spectrophotometer IR-470.

## **2.8 THERMOGRAVIMETRIC ANALYSIS**

Thermogram of untreated and treated fibres and composites were taken in an inert atmosphere at a heating rate of 10°C/min. Shimadzu thermal analyser DT-40 was used for the study.

## **2.9 MECHANICAL TESTS**

Strength of the oil palm fibres was determined using FIE electronic tensile testing machine TNE-500. The fibres were mounted in a fixture made of paperboard with a central window and pulled at a strain rate of 20 mm/min. The gauge length was 50 mm and 20 mm in the case of OPEFB fibre and oil palm mesocarp fibre, respectively. Strength, Young's modulus and elongation at break were evaluated.

Test specimens were cut from the composite sheets. Tensile testing was carried using FIE electronic tensile testing machine TNE-500 according to ASTM D 638-76 at a strain rate of 50mm/min. Three point flexure properties were also tested using the same machine according to ASTM D 790. Impact tester of Ceast Torino, Italy was used to test the unnotched izod impact strength of the composites. It was tested according to ASTM D 256. Hardness of the composites was checked on a shore D Hardness Durometer on ASTM D 2240. Density of the samples was determined by displacement method according to ASTM D 792.

## 2.10 STRESS RELAXATION

The stress relaxation experiments in oil palm fibre and the composite samples were carried out at ambient temperature on a Zwick Universal testing machine, model 1474 in uniaxial tension according to ASTM D638. The gauge lengths were fixed at 30 and 50mm for the fibre and composite samples respectively and tested at a speed of 5mm/min. The strain was held constant after the required level was reached and the decay in stress was recorded as a function of time for about 3hrs. The samples were tested at three different strain levels, 3, 10 & 17% for fibre and 1, 2 & 3% for composites to study the effect of strain level on the relaxation mechanism.

## 2.11 DYNAMIC MECHANICAL ANALYSIS

A dynamic mechanical thermal analyser of Polymer laboratories (Model PL-Mk II) was employed for dynamic mechanical property evaluation of the composites. Samples of dimension  $5 \times 1 \times 0.25 \text{cm}^3$  were used for testing. The testing temperature ranged from 25 to  $150^\circ\text{C}$  and the experiment was carried out at frequencies 0.1, 1, 10, 50 and 100Hz. The experiment was performed under tensile mode at a strain amplitude of 0.1%.

## 2.12 WATER SORPTION STUDIES

**Oil palm fibres:** About 0.5 gms of dried oil palm empty fruit bunch fibre having an appropriate length of 5cm and oil palm mesocarp fibres were taken for the water sorption study. The diameter of the fibres was noted. The samples were immersed in distilled water, mineral water and water containing salt at different temperature 30, 50, 70 and  $90^\circ\text{C}$  in a thermostatically controlled air oven. Increase in weight of the samples was noted at specific time intervals. This process was continued till equilibrium was reached.

**Composites:** For water sorption experiments rectangular samples of 10x10mm size were cut from the composite sheets. Corners of the samples were curved to avoid non-uniform water diffusion. The thickness of the samples was



measured. Samples were immersed in distilled water and the experiment was carried out as described above. The values obtained were found to be perfectly reproducible. The mole percent uptake  $Q_t$  for water by 100g. of the polymer was plotted against the square root of time. The  $Q_t$  value can be expressed as

$$Q_t = \frac{Me(w) / Mr(w)}{Mi(s)} \times 100 \quad (2.1)$$

where  $Me(w)$  is the mass of water at equilibrium,  $Mr(w)$  is the relative molecular mass of water i.e. 18 and  $Mi(s)$  is the initial mass of the sample. At equilibrium,  $Q_t$  was taken as the mole percent uptake at infinite time. i.e.  $Q_\infty$ . The water sorption of polymers was calculated as number of moles of water absorbed by 100g of the polymer.

### 2.13 AGEING STUDIES

**Thermal ageing:** Composite samples were cut into specified dimension according to ASTM standards for mechanical testing. It was then placed in an air oven at 100°C for about three days. Samples were then allowed to cool to room temperature.

**Water ageing:** Composite samples were kept in distilled water at room temperature for two weeks to attain a saturation level. Samples were taken out and air dried.

**Boiling water ageing:** Samples were kept in boiling water for 2hrs. and then air dried.

**Radiation ageing:** Composite samples were irradiated from a  $^{60}\text{Co}$   $\gamma$  ray source. The samples were given 0.1, 1, 10, 50, and 100 Mrad dose.

**Biodegradation:** The composite samples were inoculated with two fungi *Trichoderma* and *Aspergillus*. Inoculation was done at the cut portions of the composites and the samples were kept in a moist environment. Samples were kept for several months under the same condition.

## 2.14 ELECTRICAL PROPERTY MEASUREMENTS

Rectangular pieces of the composites having an approximate dimension, 1x1x0.25 cm<sup>3</sup> were used for the measurement. The samples were coated with conductive silver paint on both sides. Copper wires were fixed as electrodes on either side. The measurement was carried out at room temperature using a 4192 LF Impedance Analyser (Hewlett-Packard Co., Palo Alto, CA, USA) at a frequency range of 10KHz – 10MHz. The resistance, capacitance and dissipation factors (tan δ) were measured directly. The volume resistivity (ρ<sub>v</sub>), dielectric constant (ε') and dielectric loss (ε'') were calculated from the following relationships.

Volume resistivity of the composites is given by the following eqn.

$$\rho_v = \frac{R \cdot A}{t} \quad \Omega \text{ cm} \quad (2.2)$$

where R is the volume resistance, A is the area and t is the thickness of the sample.

The dielectric constant of the composites is given by,

$$\epsilon' = \frac{C \cdot t}{\epsilon_0 \cdot A} \quad (2.3)$$

where C is the capacitance, ε<sub>0</sub> is the permittivity of air (8.85x10<sup>-12</sup> Fm<sup>-1</sup>).

The dielectric loss factor is given by,

$$\epsilon'' = \epsilon' \cdot \tan \delta \quad (2.4)$$

## REFERENCES

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- 3 M. S. Sreekala, S. Thomas, N. R. Neelakantan, *J. Polym. Eng.*, **16**, 265 (1997)