# Chapter 3

# Materials and Methods

In this chapter, materials used in the fabrication of lime sludge filled HDPE composites, experimental procedures involved and the instrumentation used in the characterization of the composites are described.

## 3.1   Materials

HDPE grade 5108L is supplied by Haldia Petrochemicals Ltd. with a melt flow index of 1.9 g/min (@190 °C, 2.16kg) and density of 0.95 g/cm$^3$. Maleic anhydride grafted HDPE (MAPE), grade OPTIM-E156, is obtained from Pluss Polymers Pvt. Ltd., Gurgaon (India) with a melt flow index of 7 g/min (@190 °C, 2.16kg) and density of 0.953 g/cm$^3$. It is HDPE with 1.2% maleic anhydride grafted on it. PP (grade AM120N) is supplied by Reliance Polymers with a melt flow index of 1.2 g/min (@230 °C, 2.16 kg). Epoxy (Lapox-12) and hardener are obtained from Perfect Trading Company, Kolkata (India). Raw lime sludge (Fig. 3.1) is collected from the dump yard of the Hindustan Paper Corporation Limited (HPCL) paper mill at Jagiroad, Assam (India). The raw lime sludge is ground manually with mortar and pestle for 10 min and then passed through a number 170 sieve corresponding to a sieve opening size of 90$\mu$m. However, it is revealed through morphological studies that the particle size of lime sludge range from 1 to 4 $\mu$m. The lime sludge is heated at 110 °C for 2 hours to remove any residual moisture content in a hot air oven (model: 114/14, make: Reico) before blending. Stearic acid is supplied by HiMedia Laboratories Pvt. Ltd., Mumbai, India. Ethanol is provided by Merck Specialities Pvt. Ltd., Mumbai, India.

Coir fibre (Fig. 3.1(b)) is obtained locally and surface treated with 5% NaOH solution to remove any lignin from its surface. Fibres are washed three times with

tap water to remove debris, dusts and contaminants and dried at room temperature
for 48 h. The mercerization process consisted of immersing coir fibre (200g) in an
aqueous solution (2L) of 5% (w/v) NaOH for 1 h at room temperature, followed by
washing ten times with distilled water in order to allow the absorbed alkali leach
from the fibres. Subsequently, these washed fibres are naturally dried for 48 h and
then dried at 50 °C in an oven for 8 h. The dried fibres are sealed in a container
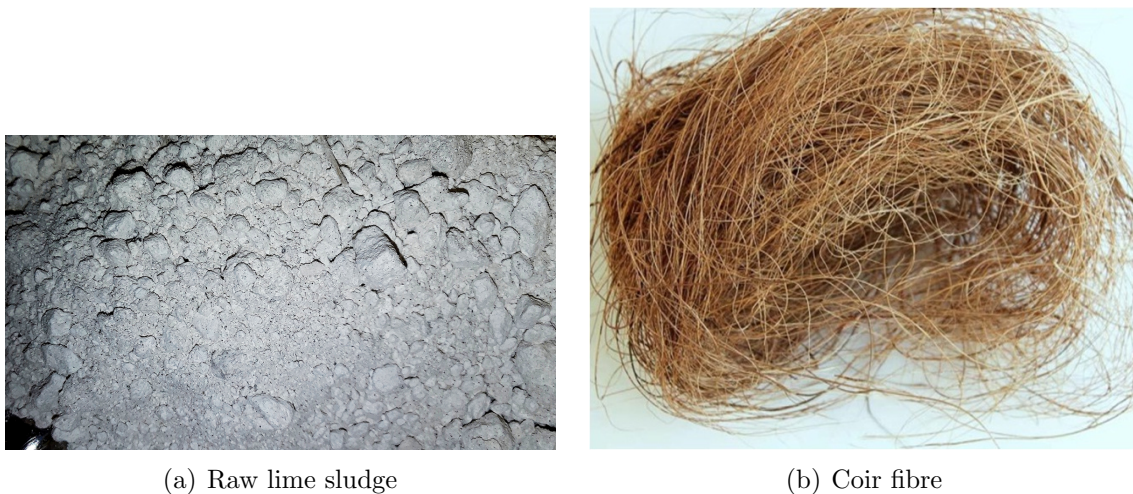prior to composite fabrication to avoid atmospheric contamination [161, 170].



(a) Raw lime sludge                           (b) Coir fibre

**Figure 3.1:** Raw lime sludge and coir fibre used in the fabrication of composites.

## 3.2   Sample preparation

Raw and modified lime sludge is used as a filler in various types of polymeric matrices
*viz.* HDPE, HDPE-PP blends, HDPE-MAPE and epoxy. Additionally lime sludge is
also used as filler in coir based HDPE and epoxy composites. The sample preparation
procedures for the different composites are given in the following sub-sections.

### 3.2.1   Raw lime sludge filled HDPE composites

HDPE in form of granules and lime sludge with various weight percents (5, 10, 15,
20, 25 and 30 wt%) is blended together in a co-rotating twin screw extruder (model:
EX100, make: Voltam) as shown in Fig. 3.2; thereby fabricating lime sludge – HDPE
composites of 5, 10, 15, 20, 25 and 30 wt% lime sludge dispersed in a polymeric
matrix. The extruder screws are rotated at 20 rpm in order to ensure a better
dispersion of lime sludge within the polymeric matrix. The temperature profiles in
the barrel heating zones are maintained at 180 °C while that at the outlet nozzle is

maintained at 175 °C. The blended polymeric composites in the form of wires are cooled and cut into pellets. Finally, the tensile, flexure and impact test specimens are molded from the blended pellets, by using an injection molding machine (model: IM100, make: Voltam) shown in Fig. 3.2(b). The injection pressure is fixed at 25 kg/cm²g and barrel temperature at 200 °C during molding. The test specimens prepared with varying weight fractions of lime sludge is shown is Fig. 3.3.
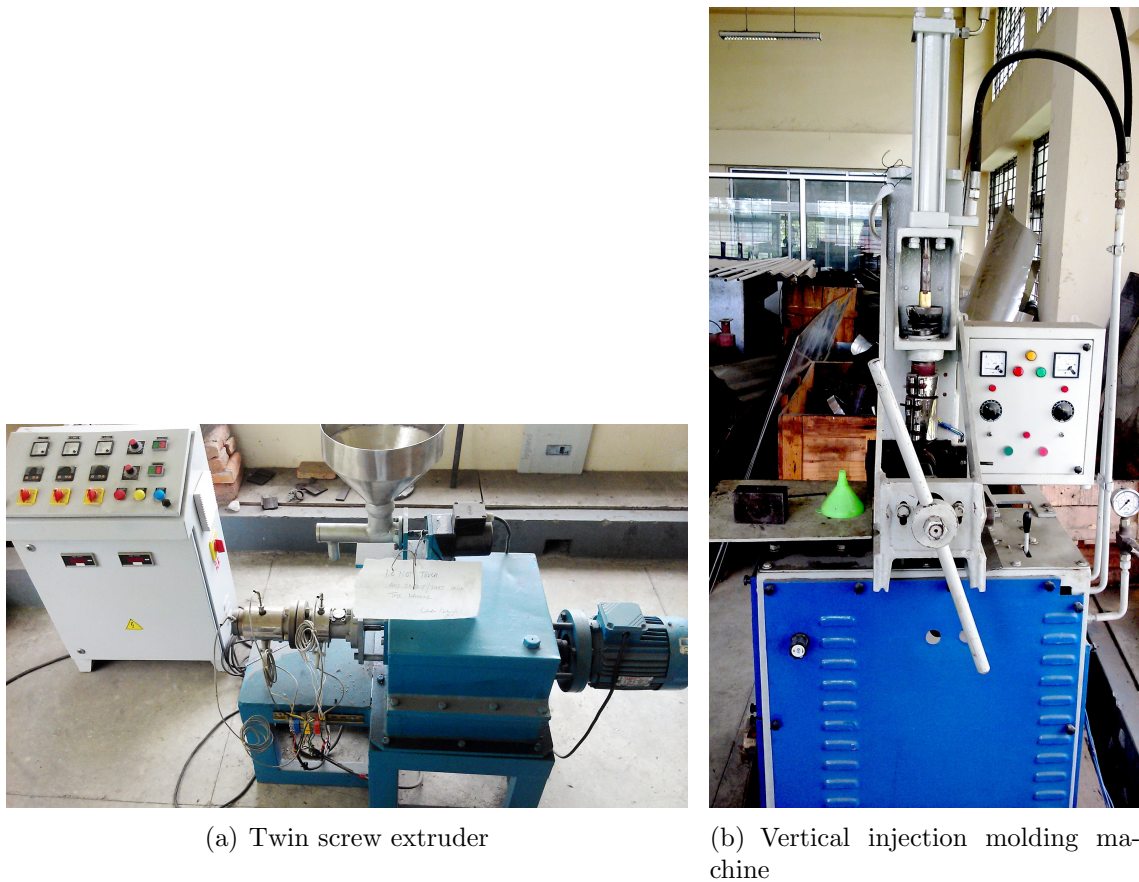


(a) Twin screw extruder

(b) Vertical injection molding machine

**Figure 3.2:** Twin screw extruder and injection molding machine used in sample preparation.

### 3.2.2 Stearic acid coated lime sludge filled HDPE composites

Raw lime sludge is stearic acid (SA) coated using the process suggested by Lin et al. [148]. Hundred grams of $CaCO_3$ was mixed with a 400 mL solution mixture of water and methanol in volume ratio of 3:1. The suspension is stirred for 2 h to completely wet the particles. Then, it is heated to and maintained at 80 °C. A 6 wt% SA dissolved in ethanol solvent was gradually added to the suspension drop by drop in order to create a monolayer of SA on the lime sludge particles [148]. After 2 h

of reaction time, surface-treated calcium carbonate particles, which settled at the bottom of the beaker, were dried in an oven at 105 °C overnight. Varying weight percents SA-coated lime sludge (5, 10, 15, 20, 25, and 30 wt%) are blended and molded in similar fashion as mentioned above to fabricate test specimens of SA coated lime sludge filled HDPE composites.
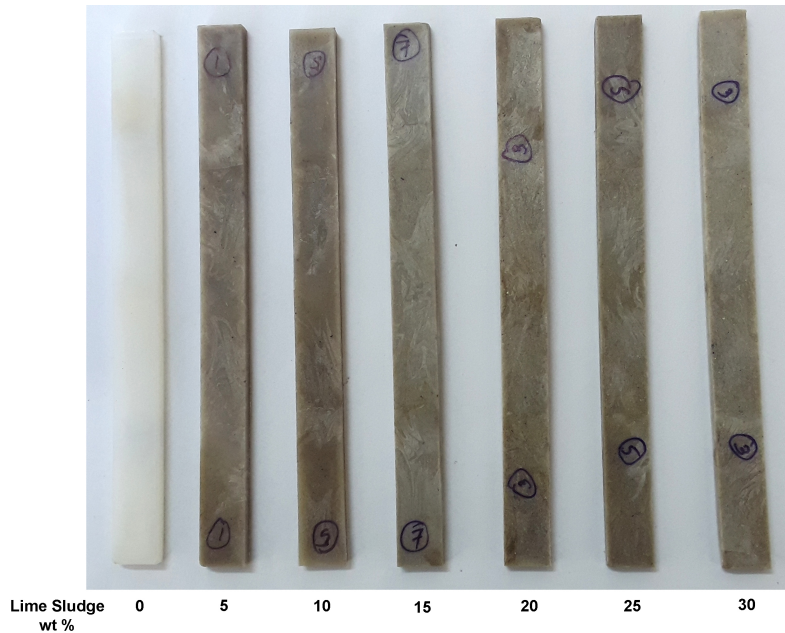


**Figure 3.3:** Injection molded specimens of lime sludge filled HDPE composites with varying lime sludge wt %. .

The designation of composites fabricated in sections 3.2.1 and 3.2.2 and the weight fractions of their corresponding constituents are shown in Table 3.1.

**Table 3.1:** Raw and stearic acid coated lime sludge filled HDPE composites along with their weight fractions.

| Designation | Lime sludge (wt%) | HDPE (wt%) | Surface modified |
|---|---|---|---|
| Pure HDPE | 0 | 100 | No |
| 5 LS HDPE | 5 | 95 | No |
| 10 LS HDPE | 10 | 90 | No |
| 15 LS HDPE | 15 | 85 | No |
| 20 LS HDPE | 20 | 80 | No |
| 25 LS HDPE | 25 | 75 | No |
| 30 LS HDPE | 30 | 70 | No |
| 5 LSSC | 5 | 95 | stearic acid |
| 10 LSSC | 10 | 90 | stearic acid |
| 15 LSSC | 15 | 85 | stearic acid |
| 20 LSSC | 20 | 80 | stearic acid |
| 25 LSSC | 25 | 75 | stearic acid |
| 30 LSSC | 30 | 70 | stearic acid |

### 3.2.3   Lime sludge filled maleic anhydride grafted HDPE (MAPE) composites

Maleic anhydride acts a compatibilizer in polymeric composites which enhances the interfacial adhesion at the filler-matrix boundary; thereby increasing the mechanical properties of the composites. Hence, maleic anhydride grafted HDPE (MAPE) is used in this case in order to study the effect of a compatibilizer on the lime sludge filled HDPE composites. Hence, varying weight fractions of lime sludge filled in MAPE composites are blended and injection molded in a similar manner as mentioned in section 3.2.1.

### 3.2.4   Lime sludge filled HDPE-MAPE blends

Additionally, lime sludge filled HDPE-MAPE blends are also fabricated in similar fashion as mentioned in section 3.2.1 with varying weight fractions of lime sludge, HDPE and MAPE in the composites.

The test specimens prepared with varying weight fractions of lime sludge, HDPE and MAPE are shown in Table 3.2.

**Table 3.2:** Lime sludge filled MAPE and HDPE-MAPE blends along with their weight fractions.

| Designation | Lime sludge (wt%) | HDPE (wt%) | MAPE (wt%) |
|---|---|---|---|
| HDPE/LS/MAPE (89/10/1) | 10 | 89 | 1 |
| HDPE/LS/MAPE (79/20/1) | 20 | 79 | 1 |
| HDPE/LS/MAPE (69/30/1) | 30 | 69 | 1 |
| HDPE/LS/MAPE (87/10/3) | 10 | 87 | 3 |
| HDPE/LS/MAPE (77/20/3) | 20 | 77 | 3 |
| HDPE/LS/MAPE (67/30/3) | 30 | 67 | 3 |
| HDPE/LS/MAPE (85/10/5) | 10 | 85 | 5 |
| HDPE/LS/MAPE (75/20/5) | 20 | 75 | 5 |
| HDPE/LS/MAPE (65/30/5) | 30 | 65 | 5 |

### 3.2.5   Lime sludge filled HDPE-PP blends

Granular HDPE and PP are blended along with lime sludge filler in different weight fractions using a twin screw extruder as shown in Table 3.3 and subsequently, injection molded into composites in a manner similar to the composites mentioned above.

**Table 3.3:** Lime sludge filled HDPE-PP blends and their weight fractions.

| Designation | Lime sludge (wt%) | HDPE (wt%) | PP (wt%) |
|---|---|---|---|
| 5L -85H-10P | 5 | 85 | 10 |
| 10L-80H-10P | 10 | 80 | 10 |
| 15L-15H-70P | 15 | 15 | 70 |
| 20L-10H-70P | 20 | 10 | 70 |

### 3.2.6 Lime sludge filled coir-epoxy composites

Lime sludge filled short coir fibre reinforced epoxy composites are fabricated by randomly dispersing 30 wt % of 8 mm long coir fibres in an epoxy matrix. Earlier studies suggest that the recommended length for short fibre composites is less than 10 mm, preferably 8 mm which was considered by Rana et al. [205] and Geethamma et al. [84]. Coir fibre lengths of 8 mm are considered as it can be easily chopped from long fibres without coiling of the short fibres. The idea behind choosing 8 mm long coir fibres is to differentiate the composites between short and long fibre reinforced composites i.e. 8 mm fibre reinforced composites are classified as short fibre composites while continuous fibre composites are classified as long fibre reinforced composites.

The fibre composites are fabricated by using a compression molding machine (make: SANTEC) at a pressure of 10 kg/cm$^2$ for 24 hours (curing time) (refer Fig. 3.4). The epoxy and hardener is used in the ratio of 10:1. For fabrication of composite, a handmade mold of dimension 120 x 80 x 5 mm$^3$ as shown in Fig. 3.5 is fabricated with mild steel. The mold is applied with a silicon based mold releasing spray, for speedy removal of the composite. Epoxy resin with its corresponding hardener is thoroughly mixed to harden the matrix upon curing. Initially, lime sludge filled epoxy composites are prepared in order to study the effect of lime sludge on the epoxy matrix. Subsequently, lime sludge filled short and long coir fibre reinforced epoxy composites are prepared in order to study the effect of lime sludge as a supplementary agent in coir fibre-epoxy composites. In case of short coir fibre composites, chopped coir fibres are mixed with the resin and gently poured inside the mold. The closed mold is then compressed using compression molding for curing time of 24 hours at lab temperature. Lime sludge in these epoxy and coir-epoxy composites is incorporated in weight fractions of 3, 6, 9 and 12 wt % respectively. Lime sludge filled long coir fibre (120 mm, 30 wt %, axially aligned) reinforced epoxy composites are also fabricated in similar fashion with varying contents of lime sludge *viz.* 3, 6, 9 and 12 wt % respectively. In case of long coir fibre composites, the fibres are uniaxially aligned in the direction of loading, while in case of short coir fibre composites, fibres are randomly dispersed in the matrix. The lime sludge filled coir

epoxy composites and their weight fractions are tabulated in Table 3.4.



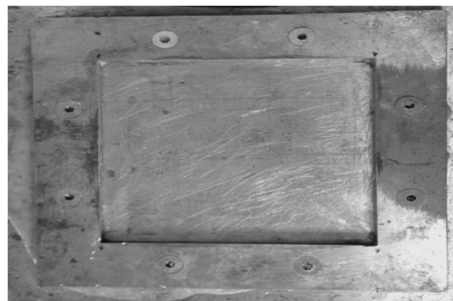**Figure 3.4:** Compression molding machine.



**Figure 3.5:** Mild steel mold used during compression molding.

### 3.2.7 Lime sludge filled coir-HDPE composites

Moreover, randomly dispersed short coir fibre (8 mm long) reinforced HDPE and HDPE-MAPE composites are fabricated using the method described in section 3.2.1 in order to study the effect of 5 wt % MAPE addition to varying weight fractions of coir and HDPE in the composites. Subsequently, test specimens were fabricated by incorporating varying weight fractions of lime sludge in 20 wt % coir fibre reinforced HDPE-MAPE composites. It is found that 20 wt % of coir fibre addition provided the highest tensile strength in coir-HDPE-MAPE composites. Hence, lime sludge content is varied subsequently, keeping the coir fibre content fixed at 20 wt % in order to study the effect of lime sludge on coir-HDPE-MAPE composites. The variation of constituting components in these composites are provided in the Table 3.5.

**Table 3.4:** Lime sludge filled HDPE-PP blends and their weight fractions.

| Designation | Lime sludge (wt%) | Epoxy (wt%) | Coir (wt%) |
|---|---|---|---|
| Pure Epoxy | - | 100 | - |
| 3LS-97 Epoxy | 3 | 97 | - |
| 6LS-94 Epoxy | 6 | 94 | - |
| 9LS-91 Epoxy | 9 | 91 | - |
| 12LS-88 Epoxy | 12 | 88 | - |
| 30 Coir - Epoxy (8mm) | - | 70 | 30 |
| 3LS -30 Coir - Epoxy (8mm) | 3 | 67 | 30 |
| 6LS - 30 Coir - Epoxy (8mm) | 6 | 64 | 30 |
| 9LS - 30 Coir - Epoxy (8mm) | 9 | 61 | 30 |
| 12LS -30 Coir - Epoxy (8mm) | 12 | 58 | 30 |
| 30 Coir - Epoxy (long) | - | 70 | 30 |
| 3LS -30 Coir - Epoxy (long) | 3 | 67 | 30 |
| 6LS - 30 Coir - Epoxy (long) | 6 | 64 | 30 |
| 9LS - 30 Coir - Epoxy (long) | 9 | 61 | 30 |
| 12LS -30 Coir - Epoxy (long) | 12 | 58 | 30 |

**Table 3.5:** Lime sludge filled coir reinforced HDPE and HDPE-MAPE blends along with their weight fractions.

| Designation | Lime sludge (wt%) | Coir (wt%) | HDPE (wt%) | MAPE (wt%) |
|---|---|---|---|---|
| HDPE/CF (90/10) | - | 10 | 90 | - |
| HDPE/CF (80/20) | - | 20 | 80 | - |
| HDPE/CF (70/30) | - | 30 | 70 | - |
| HDPE/CF/MAPE (85/10/5) | - | 10 | 85 | 5 |
| HDPE/CF/MAPE (75/20/5) | - | 20 | 75 | 5 |
| HDPE/CF/MAPE (65/30/5) | - | 30 | 65 | 5 |
| HDPE/LS/CF/MAPE (65/10/20/5) | 10 | 20 | 65 | 5 |
| HDPE/LS/CF/MAPE (60/15/20/5) | 15 | 20 | 60 | 5 |
| HDPE/LS/CF/MAPE (55/20/20/5) | 20 | 20 | 55 | 5 |

## 3.3   Mechanical property testing

The tensile and flexural properties of injection molded composites are measured using a universal testing machine (model: H100K-S, make: Hounsfield) of capacity 100KN. Both tensile and flexural testing is conducted at a crosshead speed of 1 mm/min using a 250N load cell. Flexural load is applied up to a vertical displacement of 25 mm and the stress corresponding to load at 25 mm flexural displacement is computed as the flexural stress. Five specimens corresponding to each composition of polymeric composites are tested and their mean result is reported for each composite. Detailed experimental values of each test specimen, the values of their means and standard deviation are tabulated in Appendix I for each type of composites tested. The notched Izod impact test, for all composite systems is conducted using

a digital pendulum impact testing machine (model: P/N0963.000, make: CEAST Spa Italy). Tensile, flexure and impact testing of the composites are conducted according to ASTM D638 (specimen V), ASTM D7264 and ASTM D256 standards respectively. Test specimen dimensions fabricated for the three mechanical tests are provided in Table 3.6. Test specimens are shown in Fig. 3.6.

**Table 3.6:** Summary of test specimen dimensions for injection molded samples.

| Test type | length | breadth | thickness | Remarks |
|---|---|---|---|---|
| Tensile | 63.5 | 3.2 | 3.2 | gauge length = 7.62 mm |
|  |  |  |  | length of narrow section = 9.53 mm |
| Flexure | 150 | 13 | 4 | span between supports = 120 mm |
| Impact | 63.5 | 12.7 | 3.2 | notch width = 0.54 mm |

**TENSILE TEST SPECIMEN (ASTM D638 Specimen V)**

**FLEXURE TEST SPECIMEN (ASTM D7264)**

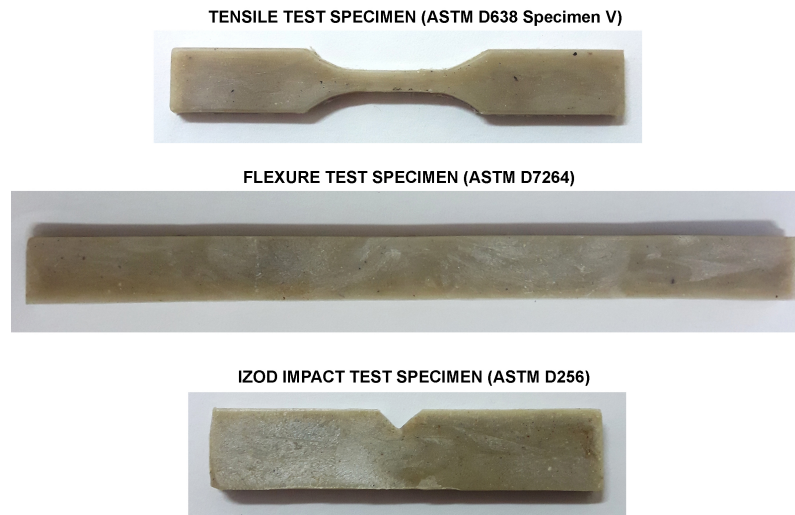**IZOD IMPACT TEST SPECIMEN (ASTM D256)**

**Figure 3.6:** Injection molded test specimens fabricated as per ASTM standards (in this case, pictures of lime sludge filled HDPE composites).

Moreover, tensile and flexural properties of compression molded lime sludge-coir-epoxy composites are measured using a Universal Testing Machine (Make: Zwick, Model - Z010) as per ISO 527-2 and ISO 178 respectively as a crosshead speed of 2 mm/min respectively. The compression molded samples fabricated (lime sludge filled short and long coir fibre reinforced epoxy composites) are shown in Fig. 3.7. Compression molded tensile and flexure test specimens before and after their testing as per ISO standards are shown in Fig. 3.8. Test specimen dimensions fabricated for these two mechanical tests are provided in Table 3.7. Additionally, Shore D hardness of the composites are measured using a Digital Shore D Durometer (model: 0114882, make: Yuzuki), taking care that the surface of the samples remain flat. Tensile and flexural testing of composites conducted on the universal testing machine is shown in Fig. 3.9.

**Table 3.7:** Summary of test specimen dimensions for compression molded samples.

| Test type | length | breadth | thickness | Remarks |
|---|---|---|---|---|
| Tensile | 150 | 10 | 4 | gauge length = 115 mm |
| Flexure | 80 | 10 | 4 | span between supports = 64 mm |
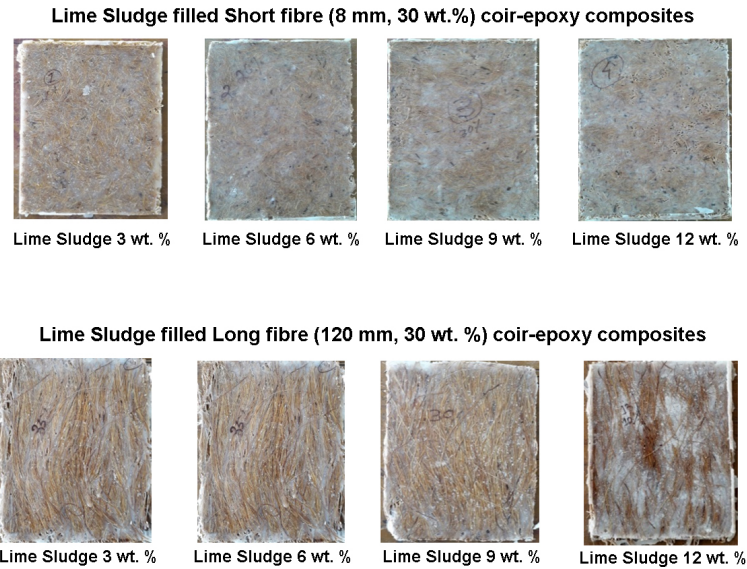


**Figure 3.7:** Compression molded lime sludge-coir-epoxy plates.
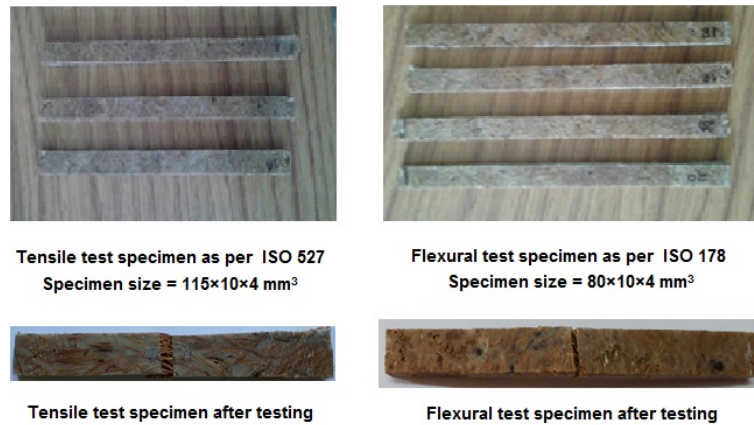


**Figure 3.8:** Compression molded tensile and flexure test specimens (lime sludge filled coir-epoxy composite) before and after testing as per ISO standards.

The tensile parameters are calculated from the stress vs. strain curves derived from the load vs. displacement curves obtained upon testing. The stress ($\sigma$) and strain ($\epsilon$) are calculated using the Eqs. (3.1) and (3.2) respectively. The elastic or tensile modulus (E) is obtained from the slope of stress vs. strain curves in the elastic region using the the Eqs. (3.3).

$$\sigma = \frac{\text{F}}{\text{A}} \qquad\qquad (3.1)$$

$$\epsilon = \frac{\delta L}{L} \tag{3.2}$$

$$E = \frac{\sigma}{\epsilon} \tag{3.3}$$

where F, A, $\delta L$ and L are the load applied, cross sectional area of the specimen, increment in the length (displacement) and gauge length of the specimen respectively. Additionally, for a rectangular sample under a load in a three-point bending setup, the flexural strength ($\sigma_f$) and modulus ($E_f$) are calculated from flexural stress vs. flexural strain curves obtained experimentally using the Eqs. (3.4) and (3.5).

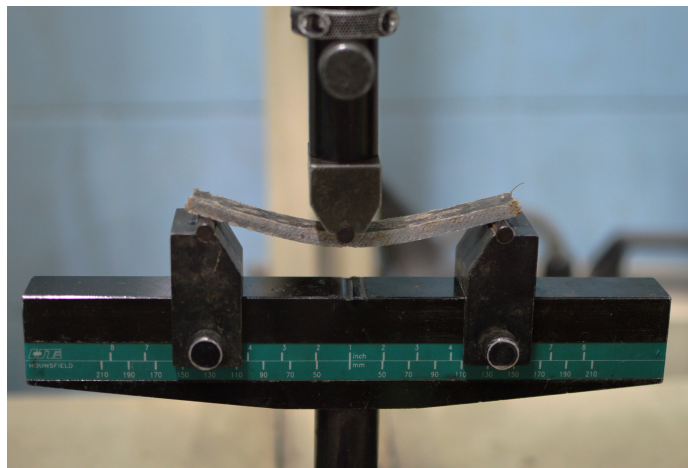$$\sigma_f = \frac{3Fl}{2wh^2} \tag{3.4}$$

$$E_f = \frac{Fl^3}{4wh^3d} \tag{3.5}$$

where F, l, w, h and d are the load applied, length of the support (outer) span, width of the specimen, thickness of the specimen and deflection due to the load F applied at the middle of the beam respectively.
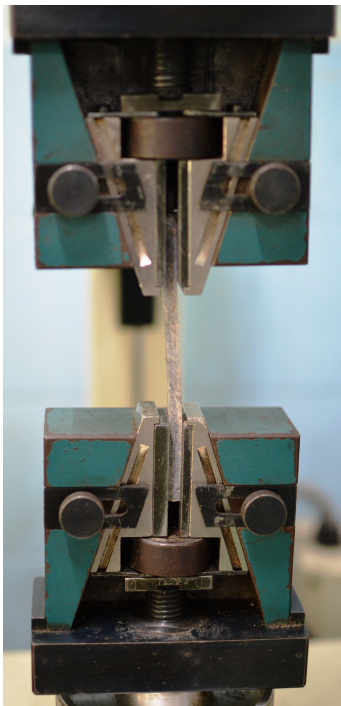


(a) Tensile testing.                              (b) Flexural testing.

**Figure 3.9:** Tensile and flexural testing of composites conducted in the universal testing machine.

# 3.4   Thermal property testing

Effect of lime sludge addition on the thermal properties of lime sludge filled composites are studied using differential scanning calorimetry (DSC) and thermo-gravimetric (TG) analyses. Important thermal parameters such as melting temperature, onset melting temperature, heat of fusion, heat of crystallization, degree of crystallinity, onset crystallization temperature, crystallization temperature and thermal stability at higher temperatures are studied for these composites.

## 3.4.1   DSC analysis

A differential scanning calorimeter  (model: Q20, make: TA instruments, USA) as shown in Fig. 3.10(a) having a standard aluminium pan is used in obtaining the DSC thermograms. The heating rate and cooling rate is maintained at $10\,°C/min$ and nitrogen is used as a sweeping gas. Approximately 10 mg of sample is loaded without further treatment, heated from -70 °C to 200 °C, held isothermally at 200 °C for 1 minute and subsequently cooled to 30 °C. DSC thermograms are plotted for varying weight fractions of lime sludge filled HDPE composites (10LS HDPE,20 LS HDPE and 30 LS HDPE) and HDPE-PP blends (20L-10H-70P and 15L-15H-70P) respectively. Please refer Table 3.1 and Table 3.3 for sample designations and their corresponding component weight fractions.

## 3.4.2   TG analysis

The thermo-gravimetric analysis (TGA) is done by a Shimadzu, Japan thermogravimetric analyzer, TG50 as shown in Fig. 3.10(a). Subsequently, DTA thermograms are calculated from the DSC thermograms. Samples weighing about 6 mg each are heated from 25 °C to 600 °C in nitrogen at a flow rate of 30 ml/min with a heating rate of 10 °C/min. TGA and DTA thermograms are plotted for pure HDPE, pure PP, lime sludge-HDPE composites (10LS HDPE, 20 LS HDPE, 30 LS HDPE), stearic acid coated lime sludge-HDPE composites (10 LSSC, 20 LSSC and 30 LSSC) and lime sludge-HDPE/PP blends (10L-80H-10P and 15L-15H-70P) respectively. Please refer Table 3.1 and Table 3.3 for sample designations and their corresponding component weight fractions.

# 3.5 Characterization techniques

Lime sludge filled polymeric composites are characterized by techniques such as Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction (XRD), inductively coupled plasma optical emission spectrometry (ICP-OES) and scanning electron microscopy (SEM). The equipment and methodologies used for characterization of the composites using these techniques are provided in the following sections.

## 3.5.1 FTIR spectroscopy

The infrared spectra of the samples are recorded by Fourier transform infrared (FTIR) spectrophotometer (model: Impact 410, make: Nicolet, Madison, USA) using KBr pellets in the wave number range from 400 to 4000cm$^{-1}$. Spectrographs were obtained for lime sludge (LS), pure HDPE, stearic acid coated lime sludge-HDPE composites (10 LSSC, 20 LSSC and 30 LSSC) respectively.Please refer Table 3.1 for sample designations and their corresponding component weight fractions.

## 3.5.2 XRD analysis

X-ray diffraction study of lime sludge powder sample is conducted at room temperature (27 °C) using a Miniflex 200 (Miniflex, UK) Rigaku X-ray diffractometer with CuK$\alpha$ radiation ($\lambda = 1.5418$Å) as shown in Fig. 3.10(b). The scanning rate used is 5°min$^{-1}$ over a range of $2\theta = 10°$ to $70°$ for the above study. Peak positions observed on the XRD pattern are indexed according to JCPDS 5-586 of the International Center for Diffraction Data to search for the presence of CaCO$_3$ in lime sludge through its crystalline structure.

## 3.5.3 ICP-OES analysis

The elemental contents in lime sludge are estimated using an inductively coupled plasma optical emission spectrometry (ICP-OES) (model: 2100 DV, make: Optima Bridgeport, USA) following the methods of Naozuka et al. [171]. Elemental concentrations are determined by using an aqueous solution of acid digested lime sludge. 1 g of powdered lime sludge sample is added to 30 mL concentrated nitric acid and 5 mL of concentrated hydrochloric acid. The vessel is immediately closed after acid addition and then the solution is digested inside a hot air oven at 100 °C. Upon digestion of the lime sludge sample, it is cooled and diluted up to 100 mL with distilled water. Subsequently, elemental compositions are determined using ICP-OES

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(a) DSC and TGA analyzer        (b) XRD machine

**Figure 3.10:** DSC-TGA analyzer and powder XRD machine.

</div>

technique as shown in Fig. 3.11(a).

### 3.5.4   SEM analysis

Morphological studies on the fractured surfaces of tensile specimens of various lime sludge filled composites are conducted using a scanning electron microscope (SEM) (model: JSM6390LV, make: JEOL)as shown in Fig. 3.11 under the secondary electron mode. The samples are sputter coated with platinum to prevent electrical charging before being examined under the SEM.



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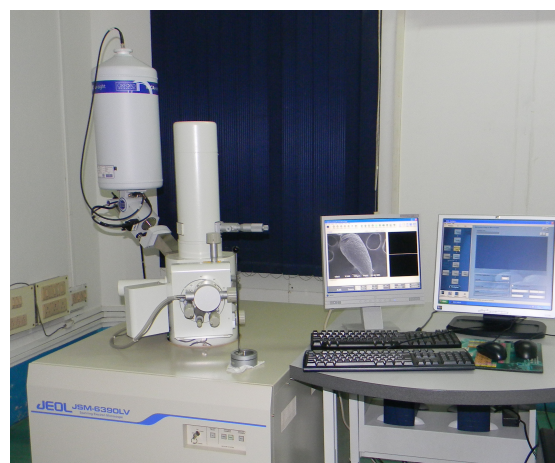
(a) ICP-OES analyzer        (b) SEM

**Figure 3.11:** ICP-OES analyzer and SEM.

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### 3.5.5 Water absorption measurement

Water absorption (WA) properties are measured according to ASTM D57098. The specimens are dried overnight at 70 °C in an oven before undergoing the test. WA is calculated by weighing the specimens before and after immersion in distilled water at room temperature (25 °C). The weighing process is repeated every 24 h until the weights of all the specimens reached a constant saturation point. The WA % is calculated using Eq. (3.6).

$$\mathrm{WA}(\%) = \frac{W_a - W_b}{W_b} \qquad (3.6)$$

where $W_a$ and $W_b$ are the weights of the specimen before and after immersion, respectively.