CHAPTER 3

EXPERIMENTAL METHODS

This Chapter describes the determination of composition and the processing methods involved in the compounding of renewable reinforcing filler with the polypropylene matrix. Four different reinforcing fillers were used and given below are the pictures of reinforcing fillers used for the present study.

➤ Corn Husk (CH)

➤ Sea weed (SW)

a. Red sea weed
b. Brown sea weed

➤ Banana fiber (BF)

a. Banana fruit stem
b. Banana fruit stem fiber
Spent Coffee Grounds (CG)

a. Spent coffee grounds  b. Dried coffee cakes

It also deals with the experimental procedures adopted for the studies of FT-IR, tensile strength, tensile modulus, impact strength, hardness, TGA, DTA, DSC, water absorption, SEM and biodegradation studies of the reinforcing filler and composite materials.

3.1 MATERIALS, CHEMICALS AND REAGENTS

3.1.1 Preparation of biocomposites

The commercially available and industrially important polypropylene was used in the present study as a matrix material. Three different grades of polypropylene were used as the matrix material for the present research work. Co-polymer grade polypropylene (Repol C080)–P1, Co-polymer grade polypropylene (Repol B650)–P1 and Homo-polymer grade (Repol HIIO)–P2 supplied by Reliance Industries.

Renewable reinforcing filler materials like corn husk and banana fruit stem were collected from the local vegetable market. Two types of non-edible seaweeds (Brown and red) were collected from the eastern coastal region near Killakari, Tamil Nadu, coffee grounds were collected from local coffee day shops.

Two different grades of compatibilizers used were maleic anhydride grafted polypropylene-MAPP (Amplify GR 216) with density of 0.875 g/cm³ was obtained from Dow Chemicals (Bhimrajka Implex Ltd) and (Exxelor PO1020) with density of 0.9 g/cm³ was supplied by Exxon Mobile India Private Limited.
Sulphuric acid, sodium hydroxide, anhydrous sodium sulphate, copper sulphate and toluene of analytical grade were supplied by Sigma Aldrich, ethyl alcohol and petroleum ether were supplied by R.R.scientific chemicals, Chennai.

### 3.1.2 Biodegradation Testing (ASTMD5338)

#### Composting Apparatus

A series of atleast twelve composting vessels (one test substance, one blank, one positive and one negative control, all in three replicates) of 2L of volume were used.

- **Water Bath**, used to maintain the temperature of the composting vessels at 58°C.
- **Pressurized-Air System**, to provide CO\(_2\)-free, water saturated air to each of the composting vessels.
- Carbon dioxide-trapping apparatus for each composting vessel
- Three 5000-ml bottles fitted with gas sparging and containing KOH as carbon-dioxide scrubbing solution.
- **Flexible Tubing**, non-permeable to carbon dioxide.
- **Stoppers**, equipped with gas-sampling parts.
- **Analytical balance**, to weigh test specimen.
- 100-ml burette, HCl (0.05 N), pH meter, analytical equipment for measuring dry solids (at 105°C), volatile solids (at 550°C), volatile fatty acids by aqueous-injection chromatography, total Kjeldahl nitrogen and carbon concentrations.
Reagents used

- **Potassium hydroxide** solution was prepared by dissolving KOH in distilled water. Filtered and standardised solutions are stored by sealing as a clear solution to prevent absorption of CO₂ from the air.

- **Analytical-grade cellulose**, with a particle size of less than 20μm as positive control.

3.2 PREPARATION OF REINFORCING FILLER

**Corn husk and sea weed** were used as such without any modification to compare the properties of the composite with respect to the type and weight percentage of the filler content with the virgin matrix material. Originally, the renewable filler were washed thoroughly with water to remove the impurities, dried in sunlight for 2 days and oven dried at 80°C for 24h, ground into powder using a food processor to get filler powder. The powdered filler are passed into the sieve shaker to get uniform particle size of ≤75μm.

![Figure 3.1: Corn husk powder and sea weed powder](image)

a) Waste banana fruit stems were collected from local vegetable and fruit market. The skins of the stem were scraped and juice of the stem is removed by roll milling machine. The fiber obtained was washed thoroughly with water to remove the impurities, dried in sunlight for 2 days, then oven dried at 80°C for 24h, ground into powder using a food processor and then sieved to size of ≤75μm.
10g of banana fiber powder was treated with alkaline solution under mild condition by soaking them in 17.5 wt% sodium hydroxide solution for 2h in a glass beaker at room temperature. The effect of alkali on cellulose fiber is a swelling reaction, during which the natural crystalline structure of the cellulose relaxes. The resulting mixture was filtered off and the residue obtained was washed with dilute hydrochloric acid and then with distilled water to separate the fibers.

b) Spent coffee grounds obtained from the local coffee shops were washed thoroughly with water to remove the impurities, dried in sunlight for 2 days and then oven dried at 80°C for 24h. The coffee cakes were ground into powder using a food processor and then sieved to size of ≤75μm.
Figure 3.4: Converting spent coffee grounds into coffee cakes and to coffee grounds

The moisture content in the reinforcing fillers were controlled to be less than 5% and stored in sealed polyethylene bags before compounding. Three levels of fillers (10 wt%, 20 wt% and 30 wt%) loading were designed for sample preparation.

Table 3.1: Chemical constituents of filler chosen for the present work

<table>
<thead>
<tr>
<th>Natural filler</th>
<th>Cellulose (%)</th>
<th>Hemi Cellulose (%)</th>
<th>Lignin (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn Husk</td>
<td>40</td>
<td>45</td>
<td>7</td>
</tr>
<tr>
<td>Sea weeds</td>
<td>12-13</td>
<td>5-6</td>
<td>2</td>
</tr>
<tr>
<td>Banana fiber</td>
<td>43</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Coffee Grounds (Caffeines-0.02 - 0.08)</td>
<td>13.2-18.4</td>
<td>-</td>
<td>4.5-6.3</td>
</tr>
</tbody>
</table>

3.3 DETERMINATION OF COMPOSITION OF FILLERS

The fillers were estimated for moisture, fat, ash, crude fiber, protein and carbohydrate content using the procedure given below.

3.3.1 Moisture

5g of filler was weighed and taken in a porcelain dish and dried by keeping it in electric oven at 105°C for 5h. The fillers were than cooled in the desiccators and
weighed. From the loss in weight, moisture content of the fillers can be determined according to the equation 3.1

\[
\text{Moisture % by weight} = \frac{100(W_1 - W_2)}{(W_1 - W)} \tag{3.1}
\]

\(W_1\) = weight in gram of the dish with the material before drying.

\(W_2\) = weight in gram of the dish with the material after drying.

\(W\) = weight in gram of the empty dish.

### 3.3.2 Total Ash

Weighed quantity of filler was taken in a porcelain dish, kept in the muffle furnace at 550ºC - 600ºC for 1h, then cooled and weighed. The weight of the residue obtained after heating was calculated using the equation 3.2.

\[
\text{Total ash % by weight} = \frac{100(W_2 - W)}{(W_1 - W)} \tag{3.2}
\]

\(W_1\) - Weight in gram of the dish with dried material.

\(W_2\) - Weight in gram of the dish with the ash.

\(W\) - Weight in gram of the empty dish.

### 3.3.3 Fat

A known quantity of dried filler material was taken in a flask and refluxed with petroleum ether for about 10h-12h in a soxhlet extraction apparatus. The solvent was evaporated from extraction flask completely on a steam bath. After evaporation of solvent, residual fat content was calculated.

### 3.3.4 Crude Fiber

Weighed quantity of fat free, moisture free, bio filler was taken in a flask, and refluxed with dilute sulphuric acid (1.25%) for 30 minutes, and it is washed with water number of times to free from acid and to remove the residue. The filler material is further
refluxed with NaOH solution (1.25%) for 30 minutes then washed with water and ethyl alcohol and dried in an air oven. It is kept in the muffle furnace at 600°C till all the organic matter is burnt. Weight loss gives the crude fiber content.

\[
\text{Crude fiber} = \frac{10,000(W_1 - W_2)}{W(100 - M)}
\]

Where:
- \(W\) - Weight of the filler
- \(W_2\) - Loss in the muffle furnace
- \(W_1\) - Weight of the crucible residue with material
- \(M\) - Moisture, percent by weight, in the material.

### 3.3.5 Protein

In a round bottomed flask, 0.25gm of material, 10gm of anhydrous sodium sulphate, 0.2gm-0.3gm copper sulphate and 20ml of concentrated sulphuric acid are added and heated for 30min. Protein present in it will be converted into ammonia with the acid present. The excess acid was then titrated against standard sodium hydroxide with few drops of methyl red indicator.

\[
\text{Total protein \% by weight} = \frac{875(B-A)N}{W(100-N)}
\]

Where:
- \(B\) - Volume in ml of the standard NaOH solution used to neutralize the acid in the blank determination
- \(A\) - Volume in ml of the standard NaOH solution used to neutralize excess of acid in the test with the material.
- \(N\) - Normality of the standard NaOH solution
- \(W\) - Weight in gram of the material taken for the test.
3.3.6 Carbohydrate

Carbohydrate content is estimated by separating the sum of the total moisture, ash, crude fat, crude fiber and crude protein values from the total 100% by weight of the sample.

\[
\text{Carbohydrate} = [100-(\text{moisture + ash + fat + fiber + protein})] \quad (3.5)
\]

3.4 PREPARATION OF BIO FILLER REINFORCED POLYPROPYLENE COMPOSITES

Polypropylene granules, bio fillers and compatibilizer were pre-dried in an air oven at 80°C for 4h and mixed well before blending. The compounding materials were meltblended by directly adding into the feeding zone of twin screw extruder (Figure 3.5) (HAAKE Rheomex OS, PTW16 Thermo Scientific, Germany). Blending was carried out at a temperature range of 210°C, 200°C, 190°C, 180°C and 150°C at a screw speed of 75rpm. The process of mixing with fillers after transfer of polymer materials into mould was completed within 80 seconds to avoid heat loss and to ensure thorough mixing. Compression force of 100kN was applied to the molten polymer mix for about 20 minutes. Mould was cooled by circulating cold water through the columns around the mould.

Figure 3.5: Twin screw extruder and extruded strands
Composite samples which were extruded form the mould were in the form of strands, which were further chopped into smaller pellets further characterization and for making test samples according to ASTM standard. Composites of following composition were prepared as given in Table 3.2

Table 3.2: Types of PP used for preparation of natural fillers reinforced polypropylene composites

<table>
<thead>
<tr>
<th>Polymer Matrix</th>
<th>Corn Husk</th>
<th>Sea Weed (Red/Brown)</th>
<th>Banana Fiber</th>
<th>Coffee Grounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Polymer (P1)</td>
<td>P1CC/P1-Repol C080</td>
<td>P1SW/P1-Repol C080</td>
<td>P1BF (Untreated) P1TBF (Treated) P1-Repol B650</td>
<td>P1CG/P1-Repol B650</td>
</tr>
<tr>
<td>Homo-Polymer (P2)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>P2CG/P2-Repol HII0</td>
</tr>
</tbody>
</table>

3.4.1 Corn husk Composites

Mixing of polypropylene matrix material and the corn husk filler was done by taking 300 g of polypropylene with varying percentage of powdered and sieved filler, corn husk (10 wt%, 20 wt%, 30wt%) and toluene (processing aid) in the twin screw extruder. The details of ingredients taken for PP - corn husk composite for compounding are shown in Table 3.3.
Table 3.3: Composition polypropylene- corn husk composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (%)</th>
<th>Corn husk (%)</th>
<th>Toluene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1CH10</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P1CH20</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>P1CH30</td>
<td>50</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

3.4.2 Sea weed Composites

3.4.2.1 Brown sea weed composites

Mixing of compounding materials was done as per the above method similar to corn husk with polypropylene. The details of ingredients taken for compounding PP – brown sea weed composite are as shown in Table 3.4.

Table 3.4: Composition of polypropylene/ brown seaweed composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (%)</th>
<th>Brown Sea weed (%)</th>
<th>Toluene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1BSW 10</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P1BSW 20</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>P1BSW 30</td>
<td>50</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

3.4.2.2 Red sea weed composites

The details of ingredients taken for PP/red sea weed composite for compounding are shown in Tables 3.5.
### Table 3.5: Composition of polypropylene/ Red sea weed composites

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (%)</th>
<th>Red Sea weed (%)</th>
<th>Toluene (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1RSW 10</td>
<td>85</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>P1RSW 20</td>
<td>70</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>P1RSW 30</td>
<td>50</td>
<td>30</td>
<td>20</td>
</tr>
</tbody>
</table>

#### 3.4.3 Banana Fiber Composites

The chopped banana fruit stem fibers were washed thoroughly with water to remove the adhered contaminants and dried in an air oven at 100°C for 24h. The dried banana fibers were then ground using food processor then sieved to obtain uniform size of ≤75μm. 10g of banana husk was treated with alkaline solution under mild condition i.e., soaked in a concentrated 17.5wt% sodium hydroxide solution for 2h in a glass beaker at room temperature. This was done to remove hemicelluloses and pectin from the banana fruit stem fibers. The important modification occurring here is the removal of hydrogen bonding in the network structure.

The following reaction takes place as a result of alkali treatment.

\[
\text{Fiber-OH} + \text{NaOH} \rightarrow \text{Fiber-O}^- \text{Na}^+ + \text{H}_2\text{O} \quad (3.6)
\]

The effect of alkali on cellulose fiber is a swelling reaction, during which the natural crystalline structure of the cellulose relaxes. The resulting mixture was filtered off and the residue obtained was washed with distilled water to separate the fibers. The alkali treated fibers were then neutralized by 1M of hydrochloric acid at 80°C for 2h. It was done to incorporate excess of -OH group to the fibers, then it was further washed with distilled water repeatedly.

\[
\text{Fiber-O}^- \text{Na}^+ + \text{H}^+\text{Cl}^- \rightarrow \text{Fiber-OH} + \text{NaOH} \quad (3.7)
\]
2kg of polypropylene was taken as matrix material and are blended with varying percentage of both treated and untreated filler and silicone oil (50ml) as the processing aid as shown in the following Tables 3.6 and 3.7.

**Table 3.6: Composition of Polypropylene- Untreated Banana fiber Composites**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (%)</th>
<th>Banana Fiber (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1UBF 10</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>P1UBF 20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>P1UBF 30</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

**Table 3.7: Composition of Polypropylene- Treated Banana fiber Composites**

<table>
<thead>
<tr>
<th>Sample</th>
<th>PP (%)</th>
<th>Banana Fiber (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1TBH 10</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>P1TBH 20</td>
<td>80</td>
<td>20</td>
</tr>
<tr>
<td>P1TBH 30</td>
<td>70</td>
<td>30</td>
</tr>
</tbody>
</table>

**3.4.4 Spent Coffee Ground Composites**

Compounding of spent coffee ground filler with polypropylene was done by two different methods.

**3.4.4.1 Spent coffee ground composites with varying percentage of MAPP**

2kg of matrix material was blended with constant (20%) filler content and varying percentage (1%, 3% and 5%) of compatibilizer (MAPP) as shown in Table 3.8 and Table 3.9. Two different polypropylene used for compounding are

- Co-Polymer grade Polypropylene – P1
- Homo-Polymer grade Polypropylene – P2
The following reaction takes place as a result of MAPP treatment.

Scheme 1: Coupling mechanism of natural fiber/ maleated PP composites
Based on the previous report of John.Z.Lu et al [17], coupling mechanism of MAPP in PP composites is prepared (Scheme:1.1). Through the dehydration, double acid on MAPP are transferred into maleic anhydride groups with a closing ring, but this reaction is reversible with an initiator, some PP and MAPP molecules become free radicals (Scheme:1.2 &Scheme 1.3). Non radicals may switch with free radicals to form new radicals (Scheme:1.4 &Scheme 1.5). Two PP radicals may combine together and form new PP molecule with a large molecular weight(Scheme:1.6). One PP radical may react with one MAPP radical to form a maleic anhydride grafted PP molecule (Scheme: 1.7).

Two MAPP radicals may react with each other to form saturated and unsaturated MAPP molecule (Scheme 1.8) and even produce two unsaturated MAPP molecules. A MAPP radical may also react with a double C-C bond at the end (or) on the branch of PP molecular chain (Scheme 1.9). This coupling reaction is preferred for copolymer PP also. MAPP radicals react with hydroxyl group of the spent coffee ground to form a grafted copolymerization structure (Scheme 1.10), one is the copolymer with diester bonds, where as another has the half ester structure. Secondary bonding is also involved in spent coffee ground/PP composites. As shown in Scheme 1.11 a hydrogen atom of hydroxyl group on the cellulose may form hydrogen bonds with the oxygen atom of a maleic anhydride group. Also a hydrogen atom on the maleic anhydride group of a MAPP molecule may form the H-bond with an oxygen atom on the Maleic anhydride group of another MAPP molecule (Scheme 1.12).
### Table 3.8: Composition of P1CG composites with varying percentage of MAPP(A)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polypropylene (Co polymer %)</th>
<th>Spent coffee grounds (%)</th>
<th>MAPP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1CG 20(A0)</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>P1CG 20(A1)</td>
<td>79</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>P1CG 20(A3)</td>
<td>77</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>P1CG 20(A5)</td>
<td>75</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

### Table 3.9: Composition of P2CG composites with varying percentage MAPP(A)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polypropylene (Homo polymer %)</th>
<th>Spent coffee grounds (%)</th>
<th>MAPP (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2CG 20(A0)</td>
<td>80</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>P2CG 20(A1)</td>
<td>79</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 20(A3)</td>
<td>77</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>P2CG 20(A5)</td>
<td>75</td>
<td>20</td>
<td>5</td>
</tr>
</tbody>
</table>

#### 3.4.4.2 Spent coffee grounds composite with varying percentage of reinforcing filler

2kg of polypropylene (Homo polymer- Repol HIIO) was taken as a matrix material and are blended with varying percentage of powdered and sieved filler (spent coffee grounds) at constant (1%) compatibilizer (MAPP). Here different grades of compatibilizers [Amplify GR 216 (A), Excelor PO 1020 (E)] were used for compounding as shown in Table 3.10 and Table 3.11.
Table 3.10: Composition of P2CG (A) composites with varying percentage of filler

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polypropylene (Homo-polymer %)</th>
<th>Spent coffee grounds (%)</th>
<th>MAPP(A)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2CG0(A1)</td>
<td>99</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 10(A1)</td>
<td>89</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 20(A1)</td>
<td>79</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 30(A1)</td>
<td>69</td>
<td>30</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.11: Composition of P2CG (E) composites with varying percentage of filler

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polypropylene (Homo-polymer %)</th>
<th>Spent coffee grounds (%)</th>
<th>MAPP(E)(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P2GG 0(E1)</td>
<td>99</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 10(E1)</td>
<td>89</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 20(E1)</td>
<td>79</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>P2CG 30(E1)</td>
<td>69</td>
<td>30</td>
<td>1</td>
</tr>
</tbody>
</table>

3.5 CHARACTERISATION TECHNIQUES

Mechanical Testing were carried out as per American Standard Testing Methods (ASTM). Four tests were performed on the bio composites namely tensile strength, impact strength, hardness and water absorption test. Scanning electron microscopy (SEM) was used to study the morphology of the composites.

3.5.1 Sample Preparation

All the composite samples used for testing mechanical properties were machined into shape by grinding machine according to the ASTM standards and the cut edges were made smooth using sand paper to have a control on the specimen dimension.
3.5.2 Conditioning

The test specimens were conditioned at 23±2°C and 50±5% relative humidity for 40h prior to the testing.

3.5.3 Mechanical Properties

3.5.3.1 Tensile Properties

Tensile strength is a measurement of the ability of a material to withstand forces that tend to pull it apart and to what extent the material stretches before breaking. Tensile modulus, an indication of the relative stiffness of a material, can be determined from a stress-strain diagram. Tensile properties were studied as per ASTM-D 3039 using Instron testing machine (Model 6025 UK), at 10 mm/minute cross-head speed, using specimen with a width of 25 mm, length of 200mm and thickness of 3mm. A distance of 115mm is kept in between the grips. Five specimens were tested for each sample.

TENSILE STRENGTH

Tensile strength or tenacity is the stress at the breaking point of the test specimen. Tensile strength is obtained from the experimental data using equation (3.8)

\[
\text{Tensile strength} = \frac{\text{Load at break}}{\text{Original cross-sectional area}}
\]

\[
= \frac{L}{b \times D} \quad (3.8)
\]

Where \( L \) = the load applied in N,
\( b = \) the width in mm and
\( D = \) the thickness in mm.
TENSILE MODULUS

Tensile modulus is given by equation (3.9)

\[ \text{Tensile Modulus} = \frac{\text{Tensile stress}}{\text{Tensile strain}} \]

\[ = \frac{\text{Difference in load (N)}}{\text{Difference in extension (mm)}} \]

\[ = \frac{\Delta P}{\Delta \delta} \quad (3.9) \]

3.5.3.2 Impact Strength

The unnotched Izod impact strength of each sample was tested as per ASTM D256-88. All the samples were tested as unnotched so that they would be more sensitive to the transition between ductility and brittleness. Specimens, having thickness 3.2 mm with 10mm cross-section and 64 mm long were clamped in the base of the pendulum testing machine so that they were cantilevered upward. The pendulum was released and the force consumed in breaking the sample was calculated.

3.5.3.3 Hardness

Hardness of the composite material was measured using durometer-type D as per ASTM D2240 specimen with 3mm thickness. The surface of the specimen was flat over sufficient area to permit pressure foot to contact the specimen over an area having 6mm radius for the indenter point. The specimen was placed on a hard horizontal surface. The durometer was held in a position in the point of indenter atleast 12 mm from any edge of the specimen. The durometer had a pointed indenter projecting below the base of the pressure foot. The indenter was pressed into the plastic specimen, so that the base rests on the plastic materials surface and the amount of indentation was registered directly on the dial indicator. Hardness was determined at five different positions on the specimen at least 6mm apart and arithmetic mean was taken.
3.5.3.4 Water absorption Properties

Water absorption property was determined by swelling the samples in distilled water for 48h at 30°C. The sample dimension was 10×10×3 mm. The percentage of water absorbed by the specimen is calculated using equation (3.7).

\[ \% \text{ of water absorption} = \frac{(W_2 - W_1)}{W_1} \times 100 \quad (3.7) \]

Where, \( W_1 \) is the initial weight of the sample and \( W_2 \) is the weight of the sample after immersion in water for different time intervals (2h, 24h, 168h, and 480h) at 30°C.

3.5.4 Thermal Properties

3.5.4.1 Thermo Gravimetric Analysis (TGA)

Analyses were performed on a Netzsch STA 409 thermogravimetric analyzer. The instrument was calibrated with calcium oxalate and aluminium supplied by Netzsch. The samples (about 50mg) were heated from ambient temperature to 800 °C under a continuous flow of nitrogen or air (60 ml/min), at 10°C/min. The thermal degradation temperature was taken as the midpoint temperature at which 50% weight loss occurred.

3.5.4.2 DIFFERENTIAL SCANNING CALORIMERY (DSC)

The DSC was performed on a Netzsch DSC-200 differential scanning calorimeter. The instrument was calibrated with indium supplied by Netzsch. Measurements were performed under a continuous flow of nitrogen (60 ml/min). All samples (about 10mg in weight) were heated from ambient to 400°C and the thermograms were recorded at a heating rate of 10°C/min. The glass transition temperature was taken as the midpoint of the heat capacity change.
3.5.5 MORPHOLOGICAL PROPERTIES

3.5.5.1 SCANNING ELECTRON MICROSCOPY (SEM)

A JEOL JSM-6360 field emission scanning electron microscope was used and the samples were prepared by coating gold on the surface of the sample for SEM measurement.

![Figure 3.6: Scanning electron microscopy](image)

3.5.6 Determination of aerobic biodegradation of plastic materials in soil (ASTM D5338)

This method was used for determining aerobic biodegradation of the composites. This test method determines the degree and rate of aerobic biodegradation of bio-composites on exposure to a controlled composting environment under environmental conditions. The rate of biodegradation is monitored by determining the percentage yield of carbon dioxide from carbon present in the test specimen.
3.5.6.2 Sample Preparation

An inoculum was collected from the municipal solid waste with organic fractions, which was stabilized in the laboratory in order to obtain low CO$_2$ production. The inoculum was further screened to discard large items present in it like glass, stones, wood etc. Volatile solids, dry solids and carbon content of all the test substances were determined according to Test Method D 4129. The soil was sieved to <10mm and stored at 4°C for seven days. $P^H$ of the soil was measured using $P^H$ meter (microprocessor $P^H$ 211) by dispersing 10gram of soil sample in 50ml of distilled water.

Roughly 600 g of dry solids of inoculum is weighed and mixed with about 100 g of dry solids of the sample, the dry solids content of the mixture in the vessel is adjusted approximately 50% with distilled water. Vessel with all of the contents was immediately weighed before initiation of the composting process. Total weight of dry solids was determined by weight loss method after drying the sample to 105°C for one day. The blank was also prepared with inoculum alone. Reference cellulose was used as a positive control. Only $\frac{3}{4}$th of the volume of test vessel was filled with test mixture giving sufficient headspace, which is required to provide enough space for manual shaking of the test mixture and also for aeration of the composting vessels. Oxygen levels was closely controlled during the first week and measured at least twice daily.
3.5.6.3 Operating Procedure

The composting vessels are incubated in the dark or in diffuse light for a period of 90 days in an enclosure that is free from toxic vapour which may inhibit the growth of microorganisms. The temperature was maintained at 58°C. The composting vessels were shaken weekly to prevent extensive channelling, providing uniform attack on the test specimen and an even distribution of moisture. During the whole course of the test, adjustments were made to ensure proper composting conditions and the air flow is adjusted to maintain the concentration of carbon di oxide at least 2% volume, to determine the level of carbon di oxide in the exhaust air.

3.5.6.4 End Testing

At the end of the test, vessels with the contents were weighed to determine the dry solids concentration remaining in the composted material. Volatile solids contents were determined from the weight loss. The total carbon content ($C_i$) of the test material was determined by elemental analysis from which theoretical quantity of carbon dioxide evolution of the test sample was calculated. The amount of $CO_2$ produced in the test sample and in the blank was determined by titration with 0.05N HCl using phenolphthalein as indicator. This was performed for three replicates and the mean was determined. This was done frequently for 3 to 4 days for first three weeks and once in a week till maximum period of 90 days.
**Calculation**

1. The total carbon content (Ci) in the test material was determined by elemental analysis.

2. Cumulative CO₂ produced in grams (Cg test) from the test sample, was calculated.

3. Cumulative CO₂ produced in grams (Cg blank) from the blank (compost) sample, was calculated.

4. Percentage of biodegradation was determined by dividing the net average gaseous carbon produced in the test compound by the original average amount of carbon in the test compound and multiplying it by 100.

\[
\% \text{ of Biodegradation} = \frac{\text{mean } C_g (\text{test}) - \text{mean } C_g (\text{blank})}{C_i} \times 100
\]

Where \( C_g \) - Amount of gaseous carbon produced in gram and \( C_i \). Amount of carbon in test compound added in gram

The percentage of biodegradation is calculated by dividing the average net gaseous-carbon production of the test compound by the original average amount of carbon in the test compound and multiplying by 100. Percentage of aerobic biodegradation relative to positive reference (cellulose) over time is reported graphically as shown in Figure 3.9.

*Figure 3.9: Graph showing percentage of biodegradation of the composites*