Physico-chemical and Mechanical Characterization of Natural Fibre Reinforced Polymer Composites

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Polymer biocomposites based on resorcinol-formaldehyde resin matrix, reinforced with pine needles were fabricated by compression moulding technique and further developed in our laboratory. Mechanical properties such as flexural strength, tensile strength, compressive strength and wear resistance of pine needles-reinforced phenolic resin matrix based composites were evaluated to assess the prospect of using the lignocellulosic fibres as a new environmental friendly material in engineering applications. The addition of pine needles into the polymeric matrix promotes a significant improvement in the composite properties. Effect of fibre dimension on mechanical properties was evaluated. It has been observed that polymer composites obtained by particle reinforcement exhibit better mechanical properties as compared to short and long fibre reinforcement. Morphological and thermal properties of the polymer matrix and fibre reinforced green composites have also been studied. In case of morphological features, the results clearly show that when polymer resin matrix is reinforced with fibres of different dimensions, morphological changes take place depending on the fibres’ dimension. In case of thermal behaviour, the results obtained clearly indicate that the presence of lignocellulosic pine needles affects the thermal stability of polymer matrix. The values of initial decomposition temperature and final decomposition temperature for polymer composite have been found to be in between those of matrix and the fibre which indicate that the composite is slightly less stable thermally as compared to resin matrix. These composites were further subjected to identical characterization tests such as swelling under different solvents, moisture absorption and chemical resistance analysis, etc. It has been observed that particle reinforced composites exhibit higher resistance to swelling, moisture absorption and chemical resistance behaviour.

INTRODUCTION

The study and utilization of natural polymers such as natural fibres in various fields go back to ancient times as man's early scientific activities [1-2]. Various examples can be found in domestic life all around the world regarding effective utilization of various natural fibres [3-5]. However, the availability of a large number of synthetic materials and their biochemical properties has changed market for natural polymers. It is only during last few years that the significance of eco-friendly materials has been realized all over the world to a greater extent [6-8]. Principally these traditional ancient
Materials have rapidly evolved over the last decade, due to their environmentally friendly advantages. Natural fibres have been used in the past as a raw material for different applications. In recent years, greater attention has been paid to their use in a number of applications including these fibres as reinforcing materials for polymer matrices [9-11]. At present, natural fibre reinforced polymer composites materials are gradually replacing materials such as metal, ceramics, glass, etc. in the various industrial fields. The use of natural fibres, derived from a number of renewable resources as reinforcing fibres in both thermoplastic and thermoset matrix composites provide positive environmental benefits and offer numerous advantages over conventional materials including lightness, resistance to corrosion, ease of processing, etc. [12-14]. The advantages of natural fibres over conventional fibre reinforcements such as glass fibres include low cost, non-corrosive, low density, reduced wear in processing equipment, good specific properties, high toughness, biodegradability and most important is their ecological friendliness because these natural fibres can be produced from renewable resources [15-17]. The inherent biodegradability of natural fibres also means that it is important to control the environment, in which the polymers are used to prevent premature degradation. Natural fibres are widely used in polymeric materials to improve mechanical properties [18-20]. Natural fibres (e.g. cotton, flax, hemp, jute) can generally be classified as bast, leaf or seed-hair fibres. Most important constituents of natural fibres are cellulose, hemicelluloses, lignin, wax, etc. Natural fibres like pine, sisal, flax, hibiscus sabdariffa, jute, etc. have all been proved to be good reinforcements in thermoset and thermoplastic matrices.

The properties of natural fibres depend mainly on the source, age and separating techniques of the fibre. Himachal Pradesh being a hilly state is blessed with vast natural fibrous materials. Because of inaccessibility to these hilly areas, such precious wealth of nature is not still exploited commercially for better end use [5-8,13-15]. Among various types of natural fibres, pine needles have high potential as a reinforcing material in polymer matrices based composites. Since not much information is available in the literature therefore a comprehensive research programme has been started in our laboratory to synthesize pine needles-reinforced polymer composites using different polymer matrices. In the present work we report some of our investigations on the synthesis and study of various properties of pine needles-reinforced resorcinol-formaldehyde (RF) resin matrix based polymer biocomposites. The main objectives of this research work were:

- Efficient employment of pine needles as reinforcement in the production of green polymer composites.
- To study the effect of fibre dimension on the mechanical properties of the polymer matrix and the polymer composites.
- To study the physico-chemical properties of fibre reinforced polymer composites so as to assess the possibility of using these materials in a number of applications.

**EXPERIMENTAL**

**Materials and Methods**

Natural fibrous material used as a reinforcement in the polymer composite was pine needles collected from local resources. Pine needles generally contain various constituents such as cellulose, hemicellulose, lignin, pectin, etc. [19]. Different physico-chemical properties of pine needles are shown below:

**Physical Characteristics**
- Length of pine needles: 170 - 250 mm
- Diameter: 0.7 - 1.31 mm
- Colour (when dry): brown

**Chemical Characteristics**
- Lignin: 33.37%
- Holocellulose: 67.29%
- Ash: 2.71%
- Extractives: 15% (in hot water)
- Pentosan: 11.57%

The fibres prior to use were washed thoroughly with detergent powder because fibre products are generally dirty and contain some impurities which may affect the bonding between the fibres and the...
polymer matrix. Then, these fibres were washed with distilled water and dried in an air oven at 70°C for 12 h and in a vacuum oven at 67°C for 3 h before preparation of the composites. These fibres were used in three forms as shown below:

- Particle reinforcement (200 μ)
- Short fibre reinforcement (3 mm)
- Long fibre reinforcement (6 mm)

Phenolic resin resorcinol-formaldehyde (RF) synthesized in the laboratory was used as thermosetting polymer matrix. For this, resorcinol-formaldehyde solution and sodium hydroxide were kindly supplied by Qualigens Chemicals Ltd. and were used as received.

**Testing Instruments**

Curing of samples was performed by compression moulding machine (Santech India Ltd.). Thermal studies were carried out on a Perkin Elmer thermal analyzer and SEM micrographs were taken by a LEO 435VP scanning electron microscope. Tensile, compressive and flexural strength tests were performed on a Hounsfield H25KS computerized universal testing machine. Wear test was performed on a DUCOM-TR-20L Wear & Friction Monitor.

**Synthesis of Resorcinol-formaldehyde Resin**

Resorcinol-formaldehyde resin was synthesized by the standard method which was further modified in our laboratory [6,18]. While carrying out the reaction, suitable conditions of temperature, acidity of the medium and pH were maintained [18]. Resorcinol and formaldehyde were taken in different molar ratios (1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:2.5 and 1.0:3.0) by weight, in a reaction kettle and were mixed with the help of mechanical stirrer. Since the reaction was exothermic, proper care was taken to maintain the temperature between 40-45°C, for initial 1 h. Then temperature was increased to 50°C and the mixture was heated at this temperature till the completion of resinification reaction. Finally, the heating was stopped and the resin was cooled. Polymeric resin formed as a result of polymerization has been found to be deep brown in colour, having a viscosity of 625.8 cP at room temperature (25°C) with a solid content of 57.5%. The resin synthesized was then transferred to specially made moulds. In order to avoid adhesion of the polymer resin with the walls of the moulds and to allow its easy removal, the surfaces of moulds were coated on the inside with oleic acid. Resin sheets of size 150 mm × 150 mm × 5.0 mm were prepared by a closed mould method described somewhere else [11-18]. The mould was then closed and kept under pressure (4.0 MPa) until the resin was set into a hard mass. All the specimens were post-cured at 55°C for 5 h. The cured samples were then subjected to various mechanical, thermal and morphological characterizations.

**Fabrication of Polymer Composites**

**Particle Reinforced Composites**

Composite sheets were prepared by hot pressing the mould at 50°C. Pine needles were grinded to a powder and filtered through a sieve of pore size 200 microns. A specific amount of resorcinol-formaldehyde (RF) resin and pine needles were taken and mixed thoroughly by suitable loading (1.0:0.1) [5]. The above mixture was poured into specially made moulds. The surfaces of moulds were coated on the inside with oleic acid to avoid adhesion of the mixture and to allow easy removal of the composites. The mixture was then spread equally on the surface of the moulds. Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by compression moulding technique on compression moulding machine. Compression moulding was performed in a hot press using a mould preheated to 50°C for 30 min. The pressure applied ranged from 3 to 4 MPa depending on the loading of reinforcing material. All the specimens were then post-cured at 50°C for 12 h.

**Short Fibre Reinforced Composites**

Pine needles were chopped into 3 mm size and mixed with a weighed amount of resorcinol-formaldehyde (RF) polymer resin. Composite sheets were prepared as per method discussed above.

**Long Fibre Reinforced Composites**

Pine needles were cut into 6 mm length and mixed with a weighed amount of the polymer resin. Curing of samples was carried out as per the method discussed earlier.
Characterization of Resin and Polymer Composite Samples

Tensile Strength Test
The tensile strength test was conducted on a computerized universal testing machine. The tensile test was conducted in accordance with ASTM D 3039 method. The sample of 10 cm length was clamped into the two jaws of the machine. Each end of the jaws covered 2 cm length of the sample. Tensile strength was studied over the rest of 6 cm gauze length. Reading of the tensile strength test instrument for Newton force and extension were initially set at zero. The test was conducted at the constant strain rate of the order of 10 mm/min. Tensile stress was applied until the failure of the sample and load-extension curve was obtained. Seven specimens of each sample have been used for the measurement of the above mechanical properties at ambient laboratory environment and average results are reported.

Compressive Strength Test
Compression strength of samples was also tested on a Hounsfield H25KS computerized universal testing machine. Composite sample was held between the two platforms and the strain rate was fixed at 10 mm/min whereas the total compression range was 7.5 mm. The compression stress was applied until the sample failed. Total compression per unit force was noted.

Flexural Strength Test
Flexural strength of samples was also tested on the computerized universal testing machine. The three-point bend flexural test was conducted in accordance with ASTM D 790 method.

Wear Test
The wear test of the testing sample was conducted on a DUCOM-TR-20L Wear & Friction Monitor. The disc was cleaned with Emery paper and it was fixed at 500 rpm. The inner diameter of steel disc was 80 mm. Initial weight of the sample was noted and the sample pin was fixed in the jaws of wear testing machine. Then machine was set to display zero wear and friction. The samples were tested with different loads varying between 1.0 to 3.0 kg. For each load the machine was allowed to run for 15 min and the readings were recorded. After 15 min the sample was taken out from the machine and weighed again. Then loss in weight due to abrasion was calculated and this weight loss was used as the measure of wear.

SEM Study
In order to evaluate changes in the surface morphology of polymer composite, resorcinol-formaldehyde resin matrix polymer and composites fabricated with different dimensions of pine needles were analyzed by scanning electron microscopy (SEM). The excitation energy used was 5 keV. To achieve good electrical conductivity all samples were first carbon sputtered followed by sputtering a gold palladium mixture before examination. SEM micrographs of the samples show the morphology of the biocomposites prepared. These micrographs clearly show the difference between unloaded and loaded resorcinol-formaldehyde resin matrix.

Thermal Analysis
Thermal analysis of polymeric materials provides some basic information regarding thermal stability of materials. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies of samples were carried out in nitrogen atmosphere on a Perkin Elmer thermal analyzer at a heating rate of 10ºC/min. TGA is used to characterize the decomposition and thermal stability of materials under a variety of conditions. Principally in TGA analysis a change in thermal stability is examined in terms of percentage weight loss as a function of temperature while simultaneously DTA involves comparing the precise temperature difference between a sample and an inert reference material, while heating both. DTG is a type of thermal analysis in which the rate of material weight changes upon heating versus temperature is plotted and it is used to simplify the recorded weight versus temperature.

Physico-chemical Behaviour of Polymer Composites
During the fabrication of natural fibre reinforced polymer resin matrix based composite particular interest lies in its behaviour against weathering conditions [3,15,20]. The effect of environmental conditions on the polymer biocomposites has been studied by a number of researchers and has been the
subject of much debate recently. The commercial viability of the newly fabricated natural fibre reinforced resin matrix based composites lies in their physical and chemical properties. Keeping in mind the commercial viability a comprehensive study on swelling behaviour in different solvents, moisture absorbance at different humidity levels and chemical resistance behaviour against 1 N HCl and 1 N NaOH of resorcinol-formaldehyde polymer resin matrix based composites has been carried out to assess the potential application of these lignocellulosic fibres as reinforcing material in a number of engineering parts.

Swelling Behaviour
Swelling behaviour of the pine needles reinforced resorcinol-formaldehyde resin matrix based polymer composites was evaluated by studying the swelling in different solvents such as carbon tetrachloride, methanol, isobutanol and water. The above study was carried out to observe the effect of polar and non-polar nature of various solvents on the swelling properties of polymer composites so as to assess the properties in various possible applications. For the swelling test, the specimens were dried in an oven for a specified time at a particular temperature and then cooled in a desiccator. A known weight \( W_i \) of the initial samples was immersed in 100 mL volume of different solvents at room temperature for 15 days. The samples were filtered and the excess solvent was removed with the help of filter paper, patted dry with a lint free cloth and then the final weight \( W_f \) was noted. The percent swelling was calculated from the increase in initial weight in the following manner:

\[
\text{Percent swelling} \ (P_s) = \frac{W_f - W_i}{W_i} \times 100
\]

Moisture Absorbance
Moisture absorbance studies onto different samples were carried out at various humidity levels (varying from 20 to 100\%). Moisture absorbance was found out by placing a known weight \( W_i \) of dry samples in a humidity Swastika heating chamber which was set at a particular humidity level for about 12 h and then the final weight \( W_f \) of the samples exposed at a particular relative humidity (RH) was taken. The percent moisture absorbance was then calculated in the following manner:

\[
\text{Moisture absorbance} \ (\% M_{abs}) = \frac{W_f - W_i}{W_i} \times 100
\]

Chemical Resistance
For the chemical resistance test, the dried specimens were immersed in each 100 mL volume of 1 N NaOH and 1 N HCl at different intervals of time (24-144 h). After this the samples were filtered out, dried and weighed. The percent chemical resistance \( (P_{cr}) \) was calculated in terms of weight loss in the following manner:

\[
\text{Percent chemical resistance} \ (P_{cr}) = \frac{T_i - W_{aci}}{T_i} \times 100
\]

where \( T_i \) is initial weight and \( W_{aci} \) is weight after certain interval.

RESULTS AND DISCUSSION
Physico-chemical, mechanical, morphological and thermal characterizations have been found to be most trusted tools in determining the overall behaviour of polymer composites. It has been observed that particularly mechanical analysis is the most significant tool in studying the behaviour of polymer composites under various conditions of tension, compression, composition of fibre composites, etc. In this context we have studied the mechanical properties such as tensile strength, compressive strength, flexural strength, wear resistance and physico-chemical properties of pine needles-reinforced polymer composite.

Mechanism of Synthesis of Resorcinol-formaldehyde Resin
Polymers based on resorcinol-formaldehyde resin are generally synthesized by the condensation of resorcinol with formaldehyde. The nature of the product formed as a result of polymerization reaction between resorcinol and formaldehyde primarily depends upon the molar ratio of the reactants and temperature used [6-15]. In the present work
Resorcinol-formaldehyde resin has been synthesized by the reaction of resorcinol with formaldehyde in the molar ratio of 1:1.5 in a neutral medium. Resorcinol is a reactive compound and combines rapidly with formaldehyde to form methylene derivative. In this reaction methylol group occupies either the position ortho to both hydroxyl groups or ortho to one and para to the other. While carrying out the reaction proper care must be taken in order to avoid any undesirable incident. In the polymerization reaction, methylolated resorcinol condenses with formaldehyde molecules and other resorcinol molecules to form polymeric structure. In these reactions resorcinol nuclei are joined together through methylene bridges to give complex molecule.

**Optimization of Resorcinol-formaldehyde Resin**

It has been observed that resorcinol-formaldehyde resin in the ratio 1:1.5 exhibits optimum mechanical properties [1,18]. This ratio (1.0:1.5) could bear a load of 250.8 N with an extension of 2 mm (Figure 1a). In compressive test the samples of ratio 1.0:1.5 could bear a load of 1370 N at a compression of 2.17 mm while in flexural test the samples of ratio 1.0:1.5 could bear a maximum load of 117.8 N at a deflection of 1.0 mm (Figures 1b and 1c). Further, the sample of

![Graphs showing load-elongation, load-deformation, load-deflection, and wear resistance tests.](image)

**Figure 1.** Load elongation/deformation/deflection and wear resistance curve of resorcinol-formaldehyde (RF) resin.
ratio 1.0:1.5 exhibits maximum wear resistance (Figure 1d) hence it was taken for further preparation of polymer composites.

**Mechanical Properties of Resorcinol-formaldehyde Matrix Based Polymer Composites**

It has been observed that the performance of natural fibre reinforced polymer composites is controlled by the properties of the fibre-matrix adhesion/bonding [1-5]. A primary requirement for effective use of reinforcement properties of natural fibres is good interfacial bonding (or adhesion) between the resorcinol-formaldehyde polymer matrix and lignocellulosic pine needles. The interfacial adhesion/bonding characteristics have a significant effect on the strength of fibre reinforced polymer composites [9-11]. The deviations from linearity in case of load-elongation/deflection/deformation curves are an indication of the beginning of initial matrix cracking. Under tensile, compression and flexural tests, the initial key change in slopes of the curves is an indication of a main crack in the polymer matrix or the commencement of fibre breakdown. From the above mentioned results, it is clear that in order to achieve good fibre reinforcement; interfacial bonding between the lignocellulosic natural fibres and polymer matrix is considered as the most essential factor. Hence an essential understanding of interfacial properties and a quantitative characterization of interfacial adhesion/bonding strength can help in evaluating the mechanical behaviour and capabilities of polymer composite materials [11-20]. The mechanical properties of polymer composites have been found to depend solely upon (i) extent of fibre-matrix bonding and (ii) the load transfer from matrix to reinforcement. In case of fibre reinforced RF matrix based composites, extensive bonding takes place between the hydroxyl/methylol groups of polymer matrix and hydroxyl groups of lignocellulosic fibres resulting in strong structure which ultimately accounts for better mechanical properties when compared with mechanical properties of the polymer matrix. The bond strength also depends upon surface topology of the fibre. The adhesion/bonding between the polymer matrix and the reinforcement is a result of good wetting of the fibres by the RF matrix as well as the formation of a chemical bond between the lignocellulosic fibre surface and the polymer matrix. In addition, there are also secondary forces of interactions between the growing resorcinol-formaldehyde polymers and the non-crystalline hemicellulosic and lignocellulosic molecules of the pine needles.

**Tensile Strength**

It has been observed that tensile strength of polymer composites increases upon reinforcement with pine needles when used in (1.0:0.1 %) fibres loading. Polymer composites with particle reinforcement bore maximum load followed by short and long fibre reinforcement (Figure 2a). It has been observed that polymer composite with particle, short and long fibre reinforcement bears loads of 531.47, 471.8 and 426.0 N at elongation of 2.01, 2.05 and 2.12 mm, respectively.

**Compressive Strength**

Compressive strength of resorcinol-formaldehyde resin matrix has been found to increase on reinforcement with pine needles. It has been found that on particle reinforcement compressive strength increases to a much greater extent as compared to short and long fibre reinforcement. The compressive properties of the composites as the function of load and deformation are presented in Figure 2b. It is clear from the figure that polymer composite with particle, short and long fibre reinforcement bears loads of 2776.5, 2676.8 and 2602.7 N at deformation of 2.25, 2.29 and 2.34 mm, respectively.

**Flexural Strength**

Similar trends as obtained in tensile strength and compressive strength tests have been observed for flexural strength results. The flexural properties of samples as a function of force (in terms of load) and deflection are shown in Figure 2c. It is clear from the figure that polymer composite with particle, short and long fibre reinforcement bears loads of 191.48, 131.53 and 107.25 N at deflection of 1.30, 1.33 and 1.37 mm, respectively.

**Wear Test**

It is clearly evident from Figure 2d that wear rate of resorcinol-formaldehyde (resorcinol-formaldehyde)
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Figure 2. Load elongation/deformation/deflection and wear resistance curve of fibre-reinforced composites. (P: particle; SF: short fibre; LF: long fibre).

resin matrix decreases appreciably as reinforcement with pine needles. It is observed that particle reinforcement decreases the wear rate by particle reinforcement to a much greater extent as compared to short and long fibre reinforcement.

Physico-chemical Behaviour of Polymer Composites
Pine needles-reinforced polymer composites with different dimensions show different swelling behaviours in different solvents (Table 1). It has been observed that the swelling behaviour of pine needles-reinforced resorcinol-formaldehyde composites in different solvents follows the trend: \( \text{H}_2\text{O} > \text{CH}_3\text{OH} > \text{C}_4\text{H}_9\text{OH} > \text{CCl}_4 \). The swelling behaviour of polymer composites increases with increase in fibre dimension due to greater affinity of water for OH groups present in the fibre reinforced polymer composites.

The moisture absorbance behaviour at different humidity levels as a function of fibre length has been depicted in Table 2. It has been found that moisture absorbance \( (M_{\text{abs}}) \) increases with increase in humidity level ranging from 20 to 100% with increase in fibre dimension (particle < short < long fibre).

In the case of chemical resistance behaviour, it has been observed that resistance towards chemicals
decreases with the increase in fibre dimension (Tables 3a and 3b). This may be due to decrease in fibre matrix bonding due to the composites, whether short or long fibre forms is being vulnerable to the chemical attack resulting in decreased resistance towards the chemicals [12].

It has been observed that polymer composites are sensitive to environmental conditions. The physical and chemical properties are influenced by the fibre dimension. In water absorption behaviour, it has been observed that the extent of water absorption of pine needles-reinforced polymer composites depends upon relative humidity of the environment, different fibre dimensions and type of polymer used. It has also been observed that particle reinforced composites show better physical properties as compared to short and

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water</th>
<th>Methanol</th>
<th>Isobutanol</th>
<th>Carbon tetrachloride</th>
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<tbody>
<tr>
<td>RF Resin</td>
<td>0.14</td>
<td>0.12</td>
<td>0.09</td>
<td>0.05</td>
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<tr>
<td>P-Rnf</td>
<td>3.28</td>
<td>3.21</td>
<td>3.11</td>
<td>3.02</td>
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<tr>
<td>SF-Rnf</td>
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<td>3.36</td>
<td>3.27</td>
<td>3.21</td>
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<tr>
<td>LF-Rnf</td>
<td>3.61</td>
<td>3.48</td>
<td>3.38</td>
<td>3.31</td>
</tr>
</tbody>
</table>

P: particle; SF: short fibre; LF: long fibre; RF: resorcinol-formaldehyde.

<table>
<thead>
<tr>
<th>Loading (%)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Resin</td>
<td>0.00012</td>
<td>0.00025</td>
<td>0.00034</td>
<td>0.00052</td>
<td>0.00069</td>
</tr>
<tr>
<td>P-Rnf</td>
<td>0.00031</td>
<td>0.00041</td>
<td>0.00062</td>
<td>0.00077</td>
<td>0.00088</td>
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<tr>
<td>SF-Rnf</td>
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<td>0.00051</td>
<td>0.00068</td>
<td>0.00081</td>
<td>0.00098</td>
</tr>
<tr>
<td>LF-Rnf</td>
<td>0.00041</td>
<td>0.00062</td>
<td>0.00071</td>
<td>0.00082</td>
<td>0.00101</td>
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</tbody>
</table>

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<table>
<thead>
<tr>
<th>Loading (%)</th>
<th>24 h</th>
<th>48 h</th>
<th>72 h</th>
<th>96 h</th>
<th>120 h</th>
<th>144 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Resin</td>
<td>1.10</td>
<td>2.17</td>
<td>3.12</td>
<td>4.25</td>
<td>4.71</td>
<td>5.07</td>
</tr>
<tr>
<td>P-Rnf</td>
<td>3.45</td>
<td>4.68</td>
<td>5.45</td>
<td>6.39</td>
<td>7.55</td>
<td>9.21</td>
</tr>
<tr>
<td>SF-Rnf</td>
<td>3.54</td>
<td>4.72</td>
<td>5.58</td>
<td>6.53</td>
<td>7.68</td>
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<td>LF-Rnf</td>
<td>3.64</td>
<td>4.79</td>
<td>5.67</td>
<td>6.59</td>
<td>7.76</td>
<td>9.38</td>
</tr>
</tbody>
</table>

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</tr>
</thead>
<tbody>
<tr>
<td>RF Resin</td>
<td>1.52</td>
<td>2.59</td>
<td>3.12</td>
<td>4.62</td>
<td>4.77</td>
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<tr>
<td>P-Rnf</td>
<td>3.83</td>
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<td>6.86</td>
<td>7.85</td>
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<tr>
<td>SF-Rnf</td>
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<td>5.73</td>
<td>6.89</td>
<td>7.92</td>
<td>9.46</td>
</tr>
<tr>
<td>LF-Rnf</td>
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<td>5.12</td>
<td>5.83</td>
<td>7.09</td>
<td>8.12</td>
<td>9.58</td>
</tr>
</tbody>
</table>

P: particle; SF: short fibre; LF: long fibre; RF: resorcinol-formaldehyde.
long fibre reinforced composites. This may be due to weaker bonding in short and long fibre reinforced composites which might have promoted micro-crack formation at the interface as well as non-uniform stress transfer due to fibre agglomeration in the matrix [12]. The increase in moisture absorbance shown by short fibre reinforced composites is explained on the basis that moisture diffuses into polymer matrices during aging under humid environment and properties of fibre reinforced polymer composite are degraded as a result of attack by absorbed moisture on the fibre content in the fibre/matrix interface/interphase region and the matrix itself.

Morphological Study of Polymer Biocomposites
Morphological results (Figure 3) show that there is a proper intimate mixing of pine needles with the resorcinol-formaldehyde resin matrix in the polymer composites thus synthesized. Morphological results evidently demonstrate that when polymer resin matrix is reinforced with the different fibre dimensions, morphological changes take place depending upon the interfacial interaction between the varying dimension of fibre and the resin matrix.

Thermal Behaviour of Resorcinol-formaldehyde Resin and its Composites
Thermogravimetric analysis (TGA) of raw pine needles, polymeric resorcinol-formaldehyde resin and biocomposites was studied as a function of percentage weight loss with the increase in temperature. In case of pine needles, at first depolymerization, dehydration and glucosan formation took place between the temperature ranges of 230ºC to 191ºC followed by the

![Figure 3. SEM images of (a) resorcinol-formaldehyde resin, (b), (c), and (d) composites with particle, short and long fibre reinforcement, respectively.](image-url)
cleavage of C-H, C-C and C-O bonds [13-15]. Initial decomposition temperature (IDT) and final decomposition temperature (FDT) for pine needles have been found to be 200ºC and 600ºC, respectively (Figure 5). On the other hand, for resorcinol-formaldehyde resin, the observed initial decomposi-

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**Figure 4.** TGA/DTA/DTG analysis of resorcinol-formaldehyde resin.

**Figure 5.** TGA/DTA/DTG analyses of cellulosic pine needles.
tion temperature is 299.0ºC and the final decomposition temperature of the resin took place at 990.0ºC (Figure 4) [12]. It has been observed that for biocomposites with long fibre reinforcement, the initial and final decomposition temperatures were 240.0ºC and 940.0ºC, respectively (Figure 6). In differential thermal analysis differential thermogravimetric analysis of fibre reinforced composites, it has been observed that in addition to exothermic peaks there are also endothermic peaks at different temperatures as compared to parent polymer matrix. By comparison of the magnitude and location of peaks found in the DTA/DTG curves it is evident that there is a change in the thermal behaviour of polymer matrix when reinforced with cellulosic fibres. These results indicate that the presence of cellulose fibres affects the degradation process of the biocomposites. Further, these results show that polymer composites are thermally little bit less stable as compared to polymeric resorcinol-formaldehyde resin matrix. Similar behaviour is expected with particle and short fibre reinforcement [2,12]. These results are consistent with results reported earlier [2,11-13].

From the above results, it is clear that particle reinforcement is more effective than short and long fibre reinforcement. This may be due to larger surface area and more fibre/matrix interaction in case of particle reinforced composites as compared to short and long fibre reinforced polymer composites [5]. Basically for a composite to be an effective load bearing system, the fibres and matrix must cooperate. This cooperation between the natural fibres and the polymer matrix depends upon the presence of the interface. The interfacial strength depends on the surface topology of the natural fibres. The interface acts as a 'binder' and it transfers the load between the matrix and reinforcing fibres. The interfacial area plays a major role in determining the strength of polymer composite material because each fibre forms an individual interface with the matrix. Cellulose is the major component in natural fibres and contains strong hydroxyl groups in its structure which tend to form hydrogen bonds within the macromolecule itself, along with hydroxyl groups of phenolic resin. It can be concluded that different degrees of reinforcement effects are achieved by the addition of pine needles to resorcinol-formaldehyde resin matrix based polymer composites. Indeed during the fabrication of polymer composites, it is essential to study the interfacial properties of the natural fibres and their interaction with the polymer matrix.
composites with pine needles, these lignocellulosic fibres acted as carrier of load and transferred stress from the matrix along the reinforcement which resulted in composites with good mechanical properties.

CONCLUSION

Statistical test methods were adopted for mechanical characterization of lignocellulosic pine needles-reinforced polymer composites. Mechanical properties of polymer composites increase with the incorporation of fibre into the polymer matrix due to the transfer of stress from the matrix to the fibre. In case of mechanical behaviour, resorcinol-formaldehyde resin matrix based polymer composites showed a slight decrease with the increase in the dimension of lignocellulosic fibre and excellent results are obtained when the pine needles are used in "particle form". The results of swelling, moisture and chemical resistance behaviour of composites were reported and these could be used as determining parameters for the end applications of these composites. Physico-chemical studies of polymer composites carried out show that these composites are sensitive to swelling, moisture and chemical resistance conditions due to the hydrophilic nature of the lignocellulosic fibre. In spite of these limitations the pine needles can be an appropriate alternative to synthetic fibres as a reinforcing material for the preparation of various polymer matrix based green composites.

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