STUDY OF MECHANICAL PROPERTIES OF UREA-FORMALDEHYDE THERMOSETS REINFORCED BY PINE NEEDLE POWDER

Amar S. Singha,* and Vijay Kumar Thakur

Lignocellulosic fibers have received much more attention than ever before from the research community all over the world during the past few years because of their enormous advantages. A study on the preparation of new series of polymer composites using Pine Needles as a reinforcing material in Urea - Formaldehyde resin has been made. Mechanical properties of intimately mixed particle reinforced (Pine Needles) composites have been studied. Effects of different loading of reinforcement in terms of weight % on static mechanical properties such as tensile, compressive, flexural and wear properties have also been evaluated. The Urea-Formaldehyde resin prepared was subjected to evaluation of its optimum mechanical properties. The reinforcing of the resin with Pine Needles was accomplished in particle size of 200 micron by employing optimized resin. The present work reveals that mechanical properties of the Urea-Formaldehyde resin increases to a considerable extent when reinforced with Pine Needle Particles. Thermal (TGA/DTA/DTG) and morphological studies (SEM) of the resin and polymer composites thus synthesized have also been studied. The results obtained suggest that Pine Needles can be a premium candidate for the reinforcement of high-performance polymer composites.

Keywords: Lignocellusic fibers; Biocomposites; Reinforcement; Mechanical properties

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INTRODUCTION

Polymeric materials, especially those obtained from renewable resources such as natural fibers, have attracted an increasing attention during the last few years due to environmental concerns. These lignocellulosic fibers are considered as the most suitable alternative to synthetic fibers for use in various fields (Bledzki et al. 1996, 1998, 1999; Chauhan et al. 2000; Singha and Thakur 2007, 2008a-d). The use of lignocellulosic fibers as reinforcing materials in polymer matrix composites provides positive environmental benefits with respect to ultimate disposability and best utilization of raw materials (Singha et al. 2008e-h). At present various studies are ongoing to find ways to use eco-friendly lignocellulosic bio-fibers in place of toxic synthetic fibers in various applications (Singha and Thakur 2007; Panthapulakkal et al. 2006; Chauhan et al. 1999, 2000; Saheb et al. 1999; Bhatnagar et al. 2005).

The advantages of natural fibers over usual reinforcing fibers such as glass and carbon fibers are: low cost, low density, high toughness, acceptable specific strength, enhanced energy recovery, recyclability, biodegradability, etc. (Chauhan et al. 1999,
2000; Debapriya 2004; Jacob et al. 2006; Singha et al. 2008i,j). It has been observed that lignocellulosic fibers reinforced composites have properties similar to traditional synthetic fiber reinforced composites. The properties of lignocellulosic fibers mainly depend upon their chemical composition. Chemical composition of fibers depends on various factors. It varies with the geographic location, climate, type of fiber, plant part, and soil conditions, etc. Lignocellulosic fibers consist of carbohydrates, lignin, and extraneous components. The carbohydrate portion of fiber is comprised of cellulose and hemicelluloses, etc. Lignocellulosic fibers, along with wood fiber and other plant fibers, are composed of a large percentage of cellulose, which makes them the most abundant natural polymer. Cellulose is principally responsible for the strength of natural fibers because of its specific properties such as high degree of polymerization and linear orientation, etc.

Lignocellulosic fiber reinforced composites have been studied and reviewed by many workers (Bledzki et al. 1996, 1998, 1999; Nabi et al. 1999; Nakagaito et al. 2004; Bhatnagar et al. 2005; Gatenholm et al. 1993). Moreover during the past decade numbers of significant industries such as the automotive, construction, or packaging industries have shown massive interest in the development of new biocomposites materials. One of the most appropriate examples of this is the substitution of inorganic fibers such as glass or aramid fibers by natural fibers as filler (Bledzki et al. 1999; Chauhan et al. 1999; Hagstram et al. 2001).

Though the Himalayan region is full of natural biomass, yet this precious wealth of nature is not being exploited for better end products. Among various types of natural bio-material, Pine Needles have high potential as a reinforcing material in polymer composites. Pine Needles are a major cause of fire during the summer season when plants shed these needles. The burning of this biomass causes not only environmental pollution but also destroys the flora and fauna. Literature review has shown very little information on the use of Pine Needles as reinforcing material in polymer composites Therefore in the present communication we have reported the preparation of Pine Needle Particles reinforced Urea-Formaldehyde (U-F) matrix based polymer composites. The composites thus prepared have been subjected for the evaluation of mechanical, morphological and thermal properties.

EXPERIMENTAL

Materials

Urea (extra pure), formaldehyde solution (37-41%), and sodium hydroxide (pure) supplied by Qualigens Chemicals Ltd. were used as received. Pine Needles of particle dimensions 200 microns were used as reinforcement.

Synthesis of Urea- Formaldehyde Resin

Urea – Formaldehyde resin was synthesized by the standard method developed in our Applied Chemistry research laboratory (Singha and Thakur 2007, 2008a-c). Urea 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 the reaction kettle and were mixed by stirring with the help of a
mechanical stirrer as reported in our earlier our. The reaction was carried out in an alkaline medium. Since the reaction is exothermic, proper care was taken to maintain the temperature between 50-60°C, for initial 2 hours. Then the temperature was increased to 80-85 °C at pH 5.5-6 and the reaction mixture was heated at this temperature until the resinification started. After the completion of resinification the resin was cooled, and then a pinch of ammonium chloride was added to increase the bonding between the molecules. The resin synthesized was then transferred into a specially made mold. Resin sheets of size 150 mm x 150 mm x 5.0 mm were prepared by a compression molding (Singha and Thakur 2008 a-c) on compression molding machine (SANTECH INDIA Ltd). The mold 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 120°C for 7 hr. The cured samples were then subjected to evaluation of various mechanical and thermal studies.

Pretreatment of Pine Needles

Pine needles collected from local resources were initially washed thoroughly with detergent powder. After this these needles were soaked in hot distilled water for 3 h, dried for 48 h in air at room temperature followed by drying at 100 °C for 24 h to adjust the moisture content to 1 to 2%, and then stored in a vacuum dessicator. Then these fibers were ground into a powder particle of 200 microns size. The presence of moisture in the fiber may affect the chemical reaction between the lignocellulosic material and polymer matrix and results in poor adhesion. Physico-chemical characteristics of the pine needles are presented in the Table 1.

Table 1. Physical and Chemical Composition of Pine Needles

<table>
<thead>
<tr>
<th>Physical Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Length of Pine Needles</td>
<td>170-250mm</td>
</tr>
<tr>
<td>2. Diameter</td>
<td>0.7-1.31mm</td>
</tr>
<tr>
<td>3. Colour (when dry)</td>
<td>Brown</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lignin</td>
<td>33.37 %</td>
</tr>
<tr>
<td>2. Holocellulose</td>
<td>67.29%</td>
</tr>
<tr>
<td>3. Ash</td>
<td>2.71%</td>
</tr>
<tr>
<td>4. Extractives</td>
<td>15% (In hot water)</td>
</tr>
<tr>
<td>5. Pentosan</td>
<td>11.57%</td>
</tr>
</tbody>
</table>

Synthesis of Polymer Biocomposites

In order to fabricate Pine Needle reinforced polymer composites, Pine Needles particles were mixed thoroughly with Urea-Formaldehyde resin using a mechanical stirrer with different loadings (10, 20, 30, and 40 %) in terms of weight. The above mixture was poured into a specially designed mold. The inside surface of the mold was
coated 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 mold. Composite sheets of size 150 mm x 150 mm x 5.0 mm were prepared on a compression molding machine (SANTECH INDIA Ltd). Compression molding was performed in a hot press using a preheated mold (110°C). The material was kept for about 5 min in a hot open mold then closed. Composite sheets were prepared by hot pressing the mold at 130°C for 30 min. The pressure applied ranged from 2 to 4 MPa, depending on the loading of reinforcing material. All the specimens were then post-cured at 120°C for 12 hr.

**Analysis of Mechanical Properties of Polymer Matrix and Composites**

Tensile, compressive, flexural, and wear tests were performed on specimens cut from the above fabricated polymer matrix and composite materials. For tensile, compressive, and flexural strengths the measurements were made on a Computerized Universal Testing Machine (HOUNSFIELD H25KS). The wear testing was done on a Wear & Friction Monitor (DUCOM- TR-20L). The specimens of dimension 100 mm × 10 mm × 5 mm were used for analysis. The tensile and compression tests were conducted in accordance with ASTM D 3039 and ASTM D 3410 methods, respectively. The three-point bending flexural test was conducted in accordance with ASTM D 790 method. Wear resistance tests of composites were carried-out as per ASTM D 3702 method. Seven specimens of each sample were used for the measurement of the above mechanical properties at ambient laboratory environment, and results obtained for the best sample (nearer to average results) have been plotted in Fig. 2. Further average results have been reported for various parameters derived from tensile, compressive, and flexural test analysis.

**Morphological Analysis of Polymer Samples**

For morphological studies, a Scanning Electron Microscope (SEM) was used to reveal the fibre orientation in reinforced thermoset composites together with information concerning the nature of the bond between the fibres and matrix. The specimens were placed on a stub, coated with platinum, and inserted into the scanning barrel. The scanning barrel was under vacuum to prevent interference of scanning picture due to the presence of air. Magnification, focus, contrast, and brightness of the result were adjusted to produce the best micrographs.

**Thermal Analysis of Polymer Composites**

Thermal analysis includes a group of analytical methods in which the properties of a polymeric material are measured as a function of temperature. Thus, dynamic thermogravimetric analysis involves a physical measurement in which the weight loss is recorded as a function of the temperature while the substance is subjected to a controlled temperature programme. TGA is used to characterize the decomposition and thermal stability of materials under a variety of conditions, and to examine the kinetics of the physico-chemical processes occurring in the given polymer material. The mass change characteristics of a material are strongly dependent on the experimental conditions such as the shape and nature of the sample holder, sample mass, physical form, the nature and pressure of the atmosphere in the sample chamber, and the scanning rate. At the same
time, DTA is used to compare the specific temperature discrepancy between a sample and an inert reference material, when both are heated together. In DTG the mass change with respect to temperature (dm/dT) is plotted against temperature. It has been observed that a DTG curve contains no more information than the original TG curve. These curves are frequently preferred when comparing results with DTA curves because of the visual similarity.

RESULTS AND DISCUSSION

Mechanical properties of resin matrix were found to increase when reinforced with natural fibrous material. The evaluation of mechanical properties included study of tensile strength, compression strength, wear resistance and stress-strain etc. Further, these mechanical properties were used as a parameter to reflect the advantages of composites as compared to those of the resin matrix by itself. Generally, mechanical properties of fiber reinforced composites depend on the nature of the matrix, distribution, and orientation of the reinforcing material, the nature of the fiber–matrix interface, and the interphase region.

Mechanism of Synthesis of Urea – Formaldehyde Resin:

The mechanism of polymerization reaction between urea and formaldehyde follows two steps (Singha and Thakur 2008a-c). The first step involves the reaction between urea and formaldehyde to form methylol urea. Since urea is tetra-functional, the initial reaction may lead to the formation of tetra-methylol derivative of urea (as shown in Fig. 1a) due to sufficient ratio of formaldehyde. The rate at which reaction between methylol urea (I) and (II) takes place depends upon temperature, pH, and the ratio of formaldehyde to urea (F/U). To control the reaction and to favor the formation of dimethylol urea, the reaction conditions must be slightly alkaline (pH of 7-8). The next step during polymerization reaction involves condensation between the nucleophilic nitrogen of monomeric methylol urea and the electrophilic carbonyl carbon of formaldehyde to form polymer molecules (Singha and Thakur 2007). The reaction is carried out at 80-90 °C, and reaction speed is controlled by the acidity of the medium (pH 5.5-6). As the reaction proceeds, larger molecules with cross linked structures are formed. At the required level, reaction is arrested by neutralization (pH 7.5-8). Further condensation reaction must be closely watched and controlled, otherwise excessive linkage will lead to the gelatization of the resin. Under acidic conditions methylol urea condenses by elimination of water by any of the paths shown in Fig 1b.

Optimization of Urea – Formaldehyde Resin

Optimization of urea-formaldehyde resin was done by taking into account the mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance.
Fig. 1. Formation of methylol derivatives of urea (Singha and Thakur 2008a-c) shown in (a) while the condensation of methylol urea by elimination is shown in (b).
It has been observed that in case of tensile test U-F samples of ratio 1.0: 2.5 bore more load as compared to samples of other ratios (Singha and Thakur 2008a-c). This ratio (1.0:2.5) bore a maximum load of 128.0 N with an extension of 1.84 mm. Tensile stress for this ratio has been found to be 2.56 x10^6 Pa at a strain of 0.0306 (Singha and Thakur 2007). In compression test the samples of ratio 1.0: 2.5 bore a maximum load of 991.0 N at a compression of 3.51 mm. Compressive stress for this ratio has been found to be 19.82 x10^6 Pa at a strain of 0.058. In flexural test the samples of ratio 1.0: 2.5 bore a maximum load of 59.0 N at a deflection of 0.776 mm. Flexural stress for this ratio has been found to be 1.18 x10^6 Pa at strain 0.012.

Further it has been observed that wear rate of samples of ratio 1.0:2.5 was less as compared to other samples. Loss of material was due to abrasion and friction of samples with the disc. The wear resistance results also support the tensile, compressive, and flexural results, as brittle materials have higher wear rate and low tensile, compressive and flexural strength (Singha and Thakur 2008a-c).

Hence the ratio (1.0:2.5) of urea and formaldehyde showing optimum mechanical properties was taken for further preparation of biomass reinforced Urea-Formaldehyde polymer composites.

**Effect of Reinforcement on the Mechanical Properties of U-F Resin Based Biocomposites**

**Tensile strength**

It was observed that tensile strength of composites increases on reinforcement with *Pine Needle Particles*. Composites with 30% loading bore maximum load (417.8 N), followed by 40%, 20%, and 10% loadings (355.0, 301.5, and 244.8 N) respectively. A tensile stress-strain curve was constructed from the load elongation measurements. Tensile stress was obtained on dividing the load by the original area of the cross section of the specimen. The strain used for the stress-strain curve was the average linear strain, which was obtained on dividing the elongation of the gage length of the specimen by its original length. Since both the stress and strain were obtained by dividing the load and elongation by constant factors, the stress-strain curve has the same shape as the load-elongation curve. In a stress-strain curve a point where the stress causes sudden deformation without any increase in the force is called the yield strength. In a tensile test, fracture stress is defined as the load at fracture divided by the cross-sectional area of the specimen. The plot of stress vs. strain for *Pine Needle Particles* reinforced polymer composites is shown in Fig. 2A. From the figure it is clear that in the elastic region stress is linearly proportional to strain. When the load exceeds a value corresponding to the yield strength, the specimen undergoes plastic deformation. It is permanently deformed if the load is released to zero.

The stress at which plastic deformation takes place depends upon the sensitivity of the strain measurements. Further during plastic deformation there is a gradual transition from elastic to plastic behavior, and the point at which plastic deformation begins is difficult to define with precision. Different parameters (yield stress, fracture stress, tensile modulus) derived from the tensile stress-strain curve are shown in Table 2.
Compressive strength

Like tensile strength, compressive strength of U-F matrix was found to increase with increase in Pine Needle Particles loading in the polymer matrix. Composite with 30; 40, 20, and 10 percent loading bore a load of 2897.8, 2570.8, 2323.1, and 1895.8N, respectively. A compressive stress-strain curve was also constructed from the load deformation measurements. The plot of compressive stress vs. strain for Pine Needle Particles reinforced polymer composites is shown in Fig. 2B. From figure it is clear that in the elastic region stress is linearly proportional to strain. Different parameters derived from the compressive stress-strain curve are given in Table 3.

Flexural strength

Similar trends as obtained in tensile strength and compressive strength tests were also observed for flexural strength results. Polymer composite with 30; 40, 20, and 10 percent loading bore a load of 187.0, 155.0, 127.0, and 107.1 N, respectively. A flexural stress-strain curve was constructed from the load deflection measurements. The flexural stress-strain curve also had the same shape as the load-deflection curve. The plot of flexural stress vs. strain for Pine Needle Particles reinforced polymer composites is shown in Fig. 2C. Different parameters derived from the flexural stress-strain curve are given in Table 4.

Wear test

It was observed that particle reinforcement decreased the wear rate to a higher extent as compared to that of polymer resin matrix (Fig. 2D). Maximum wear resistance behaviour was observed for polymer composite with 30% loading, followed by 40, 20, and 10% loading.

<p>| Table 2. Values of Various Parameters obtained from Tensile Stress-Strain Curve at Different Loadings |</p>
<table>
<thead>
<tr>
<th>Loading (Wt. %)</th>
<th>Ultimate Tensile Stress (UTS) Pa</th>
<th>Yield Strength (YS) Pa</th>
<th>Fracture Stress (FS) Pa</th>
<th>Standard Deviation</th>
<th>Tensile Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Resin</td>
<td>2.56x10^8</td>
<td>1.95x10^8</td>
<td>2.27 x10^8</td>
<td>0.98</td>
<td>87.47x10^6</td>
</tr>
<tr>
<td>10%</td>
<td>4.89x10^6</td>
<td>3.99x10^6</td>
<td>4.15x10^6</td>
<td>1.47</td>
<td>152.62x10^6</td>
</tr>
<tr>
<td>20%</td>
<td>6.02x10^6</td>
<td>5.17x10^6</td>
<td>5.31x10^6</td>
<td>1.50</td>
<td>183.29x10^6</td>
</tr>
<tr>
<td>30%</td>
<td>8.34x10^6</td>
<td>7.32x10^6</td>
<td>7.57 x10^6</td>
<td>1.34</td>
<td>257.42x10^6</td>
</tr>
<tr>
<td>40%</td>
<td>7.10 x10^6</td>
<td>5.91x10^6</td>
<td>6.23 x10^6</td>
<td>1.55</td>
<td>217.89x10^6</td>
</tr>
</tbody>
</table>
The performance of natural fiber-reinforced polymer composites is controlled by the properties of the fiber-matrix adhesion (or bonding). A prime requirement for successful use of reinforcement properties of lignocellulosic material is good interfacial bonding, to ensure load transfer from matrix to reinforcement. A basic understanding of interfacial properties and a quantitative characterization of interfacial adhesion/bonding strength can help in evaluating the mechanical behavior and capabilities of composite materials. Mechanical properties of lignocellulosic fiber reinforced polymer composites depend upon (i) the extent of fiber-matrix bonding and ii) the load transfer from matrix to reinforcement (Singha and Thakur 2008c-j; Jayaraman 2003; Li et al. 2000). The higher the magnitude of bonding, the better will be the mechanical properties (Jayaraman 2003; Li et al. 2000; Bledzki et al. 1998; Bledzki and Gassan 1999). Further, the properties depend upon the surface area of the reinforcing material. The larger the surface area of the reinforcing material, the better will be interaction between the polymer matrix and the reinforcement, resulting in better properties.
Table 3. Values of Various Parameters obtained from Compressive Stress-Strain Curve at Different Loading.

<table>
<thead>
<tr>
<th>Loading (Wt. %)</th>
<th>Ultimate Compressive Stress (UCS) Pa</th>
<th>Yield Strength (YS) Pa</th>
<th>Fracture Stress (FS) Pa</th>
<th>Standard Deviation (FS)</th>
<th>Compression Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Resin</td>
<td>19.82 x10^6</td>
<td>18.07 x10^6</td>
<td>19.07 x10^6</td>
<td>1.12</td>
<td>340.0 x10^6</td>
</tr>
<tr>
<td>10%</td>
<td>37.90 x10^6</td>
<td>33.30 x10^6</td>
<td>35.70 x10^6</td>
<td>1.35</td>
<td>693.4 x10^6</td>
</tr>
<tr>
<td>20%</td>
<td>46.47 x10^6</td>
<td>41.40 x10^6</td>
<td>43.90 x10^6</td>
<td>1.45</td>
<td>831.0 x10^6</td>
</tr>
<tr>
<td>30%</td>
<td>57.94 x10^6</td>
<td>54.40 x10^6</td>
<td>56.10 x10^6</td>
<td>1.53</td>
<td>983.0 x10^6</td>
</tr>
<tr>
<td>40%</td>
<td>51.40 x10^6</td>
<td>47.37 x10^6</td>
<td>49.93 x10^6</td>
<td>1.58</td>
<td>926.0 x10^6</td>
</tr>
</tbody>
</table>

Table 4. Values of Various Parameters from Flexural Stress-Strain Curve at Different Loading

<table>
<thead>
<tr>
<th>Loading (Wt. %)</th>
<th>Ultimate Flexural Stress(UFS) Pa</th>
<th>Yield Strength (YS) Pa</th>
<th>Fracture Stress (FS) Pa</th>
<th>Standard Deviation</th>
<th>Flexural Modulus</th>
</tr>
</thead>
<tbody>
<tr>
<td>UF Resin</td>
<td>17.70 x10^6</td>
<td>11.35 x10^6</td>
<td>15.17 x10^6</td>
<td>1.15</td>
<td>1900.77 x10^6</td>
</tr>
<tr>
<td>10%</td>
<td>35.00 x10^6</td>
<td>25.17 x10^6</td>
<td>31.19 x10^6</td>
<td>1.23</td>
<td>2378.04 x10^6</td>
</tr>
<tr>
<td>20%</td>
<td>41.10 x10^6</td>
<td>29.02 x10^6</td>
<td>36.17 x10^6</td>
<td>1.12</td>
<td>2784.55 x10^6</td>
</tr>
<tr>
<td>30%</td>
<td>56.17 x10^6</td>
<td>43.21 x10^6</td>
<td>51.51 x10^6</td>
<td>1.05</td>
<td>3800.81 x10^6</td>
</tr>
<tr>
<td>40%</td>
<td>47.25 x10^6</td>
<td>37.75 x10^6</td>
<td>43.92 x10^6</td>
<td>1.14</td>
<td>3191.05 x10^6</td>
</tr>
</tbody>
</table>

In case of Pine Needle Particles reinforced UF matrix based polymer composites extensive bonding takes place most probably between the hydroxyl / methylol groups of the matrix and hydroxyl groups of cellulosic reinforcement, resulting in strong structure, which ultimately accounts for better mechanical properties when compared with mechanical properties of the polymer matrix. The bonding strength between polymer matrix and lignocellulosic Pine Needle Particles also depends on the surface topology of the particles. The adhesion / bonding between the polymer matrix and the reinforcement...
is a result of good wetting of the Pine Needle Particles by the UF matrix as well as the formation of a chemical bond between the Pine Needle Particles surface and the UF matrix (Singha and Thakur 2008j).

From the above results it is clear that different loadings of reinforcement have a bearing on the mechanical properties of the polymer composite. This may be due to the different adhesion strength between matrices and reinforcements. It has been observed that loading of Pine Needle Particles beyond 30% results in decreased mechanical properties of the UF matrix based polymer composites. This probably happens due to the agglomeration of Pine Needle Particles at higher loadings, which decreases the reinforcement-matrix contact and hence lowers the magnitude of mechanical properties. Further, during the preparation of polymer matrix composites, Pine Needle Particles acted as carrier of load and transferred stress from the matrix along the reinforcement, which resulted in composites with good mechanical properties.

### Thermal Analysis of Samples

Thermal (TGA/DTA/DTG) studies of samples were carried-out in a nitrogen atmosphere on a thermal analyzer (Perkin Elmer) at a heating rate of 10 °C/min. The objective of thermal analysis is to study the effect of heating on the materials so that stability of the materials at elevated temperature could be known for its applications in various fields. In this method a change in thermal stability is examined in terms of percentage weight loss as a function of temperature. At the same time DTA involves comparing the precise temperature difference between a sample and an inert reference material.

Thermo-gravimetric analysis (TGA) of raw fiber, polymeric resin, and biocomposite with 10% loading was studied as a function of % weight loss with the increase in temperature. In case of raw fiber, in the beginning depolymerization, dehydration, and glucosan formation took place between the temperature ranges of 26.0°C to 190.0°C, followed by the cleavage of C-H, C-C and C-O bonds. The initial decomposition (IDT) temperature was 223°C, and the final decomposition temperature was 507°C (Singha and Thakur 2008i,j). On the other hand, in case of polymeric resin (urea formaldehyde) the initial decomposition temperature was 238.0°C, and the final decomposition of the resin took place at 995.0 °C. The degradation temperatures (IDT &FDT) for natural fiber reinforced composites fell between the degradation temperatures for the matrix and the fibers (Figs. 3-5). It was observed that for polymer composites initial decomposition temperature was 231.0°C, and the final decomposition of the composite took place at 815.0°C, which indicates that the presence of cellulose fibers had a significant effect on the thermal stability of the polymer matrix. This could be probably due to the disturbance in the original crystal lattice of the polymer matrix by the Pine Needle Particles. These results indicate that the composite is thermally less stable as compared to resin matrix by itself. Similar behaviour was also observed with other loadings. These results are further supported by DTA/DTG studies and are consistent with the results reported earlier (Singha et al. 2007; Singha and Thakur 2008c-j)
SEM Analysis of Samples

In order to evaluate the changes in surface morphology of the reinforcing material and polymer matrix on reinforcement, these were subjected to scanning electron microscopic (SEM) studies. The excitation energy used was 5 keV. To achieve good electric 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 polymer composites prepared. On comparison, these micrographs clearly show the difference in the morphology of the composites when compared with the morphology of the reinforcing material and the polymer matrix separately (Figs. 6A-F). Morphological results clearly show that when polymer resin matrix was reinforced with the different loadings of Pine Needle Particles, surface modifications took place, depending upon the bonding between the varying loading of reinforcement and the polymer resin matrix. In case of lower loading (10 or 20 percent) there was weak bonding between the matrix and the reinforcement (Figs. 6C-D) and hence lower mechanical properties as compared to 30% loading. In case of 30% loading there was intimate mixing of the reinforcement with the resin matrix (Fig. 6E), which resulted in a polymer composite with higher mechanical properties. However at higher Pine Needle Particles content (beyond 30%), agglomeration of particles took place, which resulted in decreased mechanical properties (Fig. 6F).
Fig. 6. SEM images of (A) UF resin (B) pine needles (C, D, E, & F) composite with 10, 20, 30, & 40% loading, respectively (magnification of 1K X).
CONCLUSIONS

1. Various test methods were adopted for complete mechanical characterization of polymeric Urea-Formaldehyde resin and lignocellulosic fiber reinforced polymer composites.

2. Mechanical properties of Pine Needle reinforced polymer composites were investigated as a function of the chemical nature of matrix polymer and the content of the reinforcing material.

3. The mechanical properties of Pine Needle reinforced UF resin based composites were found to be higher than those of UF resin by itself. Polymer composite with 30% fiber loading exhibited maximum mechanical strength. Fiber loading beyond 30% was found to decrease mechanical properties due to agglomeration of fibers.

ACKNOWLEDGEMENT

The authors wish to thank Director, National Institute of Technology Hamirpur (H.P.) INDIA for providing the basic laboratory facilities. The authors would also like to thank Prof. Lucian A. Lucia and unknown potential reviewers for their healthy comments in improving the quality of present research paper. Financial assistance from University Grant Commission (New Delhi) provided through grant no. F.NO.-30-80/2004 (SR) and Ministry of Human Resource Development (MHRD- New Delhi) is also highly acknowledged.

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Article submitted: April 29, 2008; Peer review completed: June 5, 2008; Revised version accepted: Jan. 6, 2009; Published: Jan. 11, 2009.