Influence of Chemical Modification on the Mechanical, Morphological and Thermal Properties of Pine Needles Reinforced Thermosetting Composites

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Abstract: Natural fibers are widely used as reinforcement in composites. Pine needles are one of the major biowaste generated by *Pinus roxburgii* plant. This species found abundantly in the forests of Himachal Pradesh. In this work composites of urea-resorcinol-formaldehyde (URF) reinforced with pine needles fibers were prepared. Pine needles fibers were chemically modify to improve their compatibility with matrix. Pine needles were mercerized with NaOH solution and acetylated in order to increase their hydrophobic character. The chemically modified fibers were characterized with FTIR, ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopy and SEM. The composites were prepared with treated and untreated fibers containing 30% fibers by weight using compression molding technique. The morphology of the materials thus obtained was evaluated by SEM. The chemical modifications of fibers improve fiber- matrix adhesion and also have markedly effect on mechanical properties of composites. Moreover the thermal resistance of these composites was improved on chemical modification. These results indicate that chemically modified fibers exhibit better compatibility with the polymer matrix than that of untreated fiber.

Keywords: Polymer composites, Surface treatment, Pine needles, Thermosetting matrix

Introduction

Emerging community concerns and a growing environmental awareness throughout the world has forced the researchers to synthesize new green materials and processes that enhance the environmental quality of products[1-4]. At present large number of industries throughout the world are initiating the design and engineering of new products with eco-friendly advantages. Sustainable development and eco-efficiency are of prime importance to the majority of international companies. In this perspective biodegradability, eco-friendliness, easy availability and light weight *etc*. have become important considerations in the fabrications of new products. At present various workers are focusing their attention on use of lignocelluloses fibers in place of synthetic fibers in various fields especially as reinforcing fillers[5-10].

Natural fiber reinforced polymer composites have recently been preferred over composites prepared with ceramic and metal matrix because of their better properties.

The use of natural fibers, derived from a number of renewable resources, as reinforcing fibers in both thermoplastic and thermoset matrix composites provides positive environmental benefits and offer numerous advantages over conventional materials including lightness, resistance to corrosion, abrasion and ease of processing *etc.*[16-19]. The commercial importance of polymers has derived intense applications in the form of composites in various fields *viz.* in aerospace, automotive, marine, infrastructure, military *etc.* Natural fibers like flax, *Hibiscus sabdariffa*, pinus, jute, pineapple leaf fiber, oil palm fiber have all been proved to be good reinforcements in thermoset and thermoplastic matrices[20-24]. Pine needles are abundantly found in the Himalayan region. The exceptional mechanical characteristics of this fiber has triggered its use in composites and found applications in automotive and civil construction. Keeping in view the easy availability and many other eco-friendly advantages we have used this fiber as reinforcing material for the preparation of urea-resorcinol-formaldehyde (URF) resin based composites. The composites so prepared were subjected to evaluation of their mechanical, morphological and thermal properties.

Experimental

Pine needles were thoroughly washed with detergent powder. After this these fibers were soaked in hot distilled water for 3 h, dried for 48 h in air at room temperature followed by drying in a hot air oven at 105-110 °C for 12 hours. Fibers was cut to the size of 0.5 cm. Mercerization was carried out by keeping fibers in 10 wt% NaOH solution at room temperature for 3 hours. After mercerization fibers were washed with water to remove the excess soda until pH≈7 was reached and then these fibers were dried in hot air oven at 100 ºC for 3 hours. Pine needles were acetylated as follows: the fibers were immersed in pure acetic acid at room temperature for 1 h, then removed and immersed in acetic anhydride acidified with 0.1 wt% sulphuric acid for 5 minutes at room temperature. Finally, the samples were rinsed with water until pH ≈ 7 was reached and dried at 100 ºC for 5 hours. The acetylated fibers were labeled as PNac, the mercerized ones were labeled as PNm and unmodified fibers were labeled as PN.

Synthesis of urea-resorcinol- formaldehyde resin

Urea-formaldehyde resin (UF) was synthesized by the standard method developed in our Applied Chemistry research laboratory[15]. Urea-formaldehyde in the ratio (1.0:2.5) were taken by weight, in the reaction kettle and was mixed with varying ratio of resorcinol (0.5, 1.0,1.5, 2.0 and 2.5) by weight with the help of mechanical stirrer. 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 ^{0}C, for initial 2 hours. Then temperature was increased to 80-85 ^{0}C at pH 5.5-6 and the mixture was heated at this temperature, till the resinification started. After the completion of resinification the resin was cooled and ammonium chloride was added in pinch to increase the bonding between the molecules. The resin synthesized was then transferred to a specially made mould. Resin sheets of size 150 mm x 150 mm x 5.0 mm were prepared by a closed mold method as described elsewhere[4]. 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 h.

Synthesis of polymer composites

The composite samples were prepared in compression molding machine (Santech India Ltd). The Pine needles (modified and unmodified) were mixed thoroughly with Urea-resorcinol-formaldehyde resin using mechanical stirrer with 30% loadings in terms of weight.

The above mixture was poured into a specially made mold. The surfaces of molds 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 mold. Composite sheets of size 150 mm x 150 mm x 5.0 mm were prepared by compression molding technique on compression Molding Machine. Compression molding was performed in a hot press using a mold preheated to 110 °C. The material first placed in a hot open mold was left for about 5 min and then the mold was closed. Composite sheets were prepared by hot pressing the mold at 130 °C for 30 min. The pressure applied ranges from 3-4 MPa depending on the loading of reinforcing material. All the specimens were then post cured at 120 °C for 12 h. the composites thus prepared were labeled using the representations as URF/PN, URF/PNm,URF/PNac for unmodified, mercerized and acetylated fibers based composites respectively.

Characterization techniques

Infrared spectroscopy

IR spectra of unmodified and modified fibers were recorded in a FTIR- pike miracle ATR, Digilab scimitar series using horizontal attenuated totally reflectance technique (FTIR-HATR) using a FTIR-BOMEM-100 Spectrometer. The FTIR-HATR technique works by passing a radiation beam through a crystal made of a high refractive index infrared-transmitting material, which is then totally internally reflected at the surface. The sample is bought in contact with the totally reflecting surface of the ATR crystal; the evanescent wave is attenuated in regions of the infrared spectrum where the sample absorbs energy. Each spectrum represents 128 co-added scans rationed against a reference spectrum obtained by recording 128 co-added scans of empty HATR cell.

^{13}C magic angle nuclear magnetic resonance (^{13}C MAS NMR)

^{13}C MAS NMR spectra of cannabis fibers were recorded in a Varian mercury Plus BB 300 MHz spectrometer operating at 75.34 MHz for ^{13}C with contact time of 1 ms and recycle time of 20 s and 128 scans for single accumulation.

Scanning electron microscopy (SEM)

The cannabis fibers and its composites were observed using a scanning electron microscope (LEO VP 435). The samples were gold coated by sputtering technique and observed under different magnifications. Composite fracture surface analyses were performed after immersing the materials in liquid nitrogen for 10 min.

Tensile strength test

The tensile strength test was conducted on computerized universal testing machine (Hounsfield H25KS). The specimens of dimension 100 mm x 10 mm x 5 mm   were used for analysis. The tensile test was conducted in accordance with ASTM D 3039 method. The test was conducted at the constant strain rate of 10 mm/min. Force was applied till the failure of the sample and load - elongation curve was obtained. Each sample was tested for seven times.

Compressive strength test

Compression strength of samples was tested on computerized universal testing machine. The compression test was conducted in accordance with ASTM D 3410 method. 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 till the failure of sample. Total compression per unit force was noted.

Flexural strength test

Flexural strength of samples was also tested on 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 sample was conducted on wear & friction monitor (DUCOM- TR-20 L). Wear resistance of composites was carried-out as per ASTM D 3702 method. 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 from 1.0 to 3.0 kg. For each load the machine was allowed to run for 15 minutes and the readings were recorded. After 15 minutes 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.

Stress -strain analysis

Stress-strain diagram expresses a relationship between a load applied to a material and the deformation of the material, caused by the load. Stress-strain diagram was obtained from tensile, compressive and flexural tests. Stress was calculated as usual by dividing the applied load with the initial annular cross-sectional area, while strain is defined as the ratio of the displacement and the initial length.

Thermal analysis of samples

Thermal analysis of natural and synthetic polymers gives us good account of thermal stability of materials. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) studies of samples were carried-out in nitrogen atmosphere on a thermal analyzer (Perkin Elmer) at a heating rate of 10 $^{\circ}$C /min.

Results and Discussion

Chemical composition of Pine needles has been shown in Table 1.

Table 1. Various components of *Pinus roxburgii* fiber

Sample Code	Cellulose	Hemi-cellulose	Lignin	Others
Pinus roxburgii	60%	20%	15%	5%

FTIR-HATR spectra

The FTIR-HATR spectra of PN (A), PNm (B) and PNac (C) are shown in Figure 1. Compared with the curve of unmodified fiber, the spectra of mercerized and acetylated fiber have many differences. After the mercerization process, the bands at 1730 and 1245 cm^{-1}, attributed to the stretching vibrations of C=O and C-O groups respectively, disappeared. These kinds of groups are present in lignin and hemicelluloses structures. After acetylating reaction, new acetyl groups were added to the cellulose, as indicated in curve (C) with the vibrations at 1740 (-C=O) and 1240 cm^{-1} (C-O). The spectrum of unmodified fiber shows an absorption peak at 1375 cm^{-1} attributed to the C-H bending vibration. After esterification, the added contribution of the acetyl (-C-CH$_3$) stretching vibration intensifies this absorption peak.
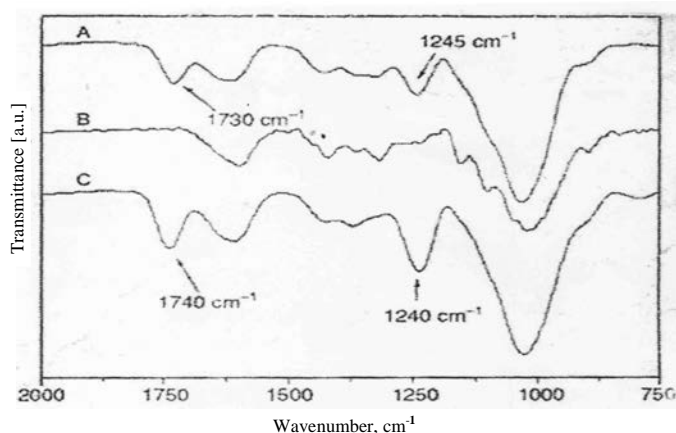
Figure 1. Pine needle fibers FTIR-HATR spectra: unmodified (A), mercerized (B) and acetylated (C)

^{13}C MAS NMR spectroscopy

The mercerization and acetylation reactions of pine cellulose were also studied by solid-state ^{13}C MAS NMR spectroscopy. The NMR spectra of PN (A), PNm (B) and PNac (C) samples are shown in Figure 2. In spectrum A, all noticeable signals of carbohydrate moiety carbon atoms occur between 50 and 110 ppm. The signal at 21 ppm is assigned to the CH3 carbon of the hemicellulose acetyl groups. The signals at 105 ppm (C-1), 89 ppm (C-4 of crystalline cellulose), 84 ppm (C-4 of amorphous cellulose), 75 ppm (C-5), 73 ppm (C-2 and C-3) and 64 ppm (C-6) have been observed. The intensity of C-4 signal at 89 ppm of crystalline cellulose decreased comparatively to the signal at 84 ppm, as shown by the comparision of spectrum A to spectra B and C. the C-6 signal in A shifted from 64 to 62 ppm in B and C. These changes may indicate that the crystalline structure of cellulose was partially disrupted by the break of α- cellulose hydrogen bonds by mercerization and acetylation reactions. The degree of substitution (DS) obtained by acetylation in PNac was 0.90 (substitution of 30% in the 3 OH groups of each cellulose monomer). This value was obtained by area deconvolution of the peak at 21 ppm in spectrum C attributed to the –CH$_3$ of the acetyl group generated by the acetylation reaction and related to the deconvoluted area of the peak at 105 ppm (C-1).
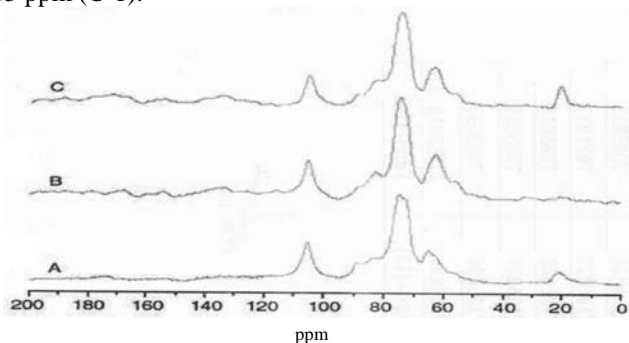

Figure 2. Pine needle fibers ^{13}C MAS solid-state NMR spectra: unmodified (A), mercerized (B) and acetylated (C)

Scanning electron microscopy

The fiber is actually a bundle of hollow sub-fibers. The fibril-like structures of fibers can be observed in the fracture image SEM (Figure 3(a)). Over these structures it was observed the presence of impurities, composed by parenchymatous cells and others constituents of the fiber as lignin, hemicelluloses and waxes. After alkaline treatment of sisal fibers was observed the extraction of these surface constituents (Figure 3(b)). Therefore, the exposition of hydroxyl groups (Equation (1)) of cellulose microfibers occurred and this treatment should improve the acetylation process (Figure 3(c)) of all hydroxyl groups present in the cellulose structure (carbons 2, 3 and 6 in Equation 2) in the acetylating reaction.

$$\text{cellulose-OH} + \text{NaOH} \longrightarrow \text{cellulose-ONa} + \text{H}_2\text{O} + \text{impurities} \qquad (1)$$
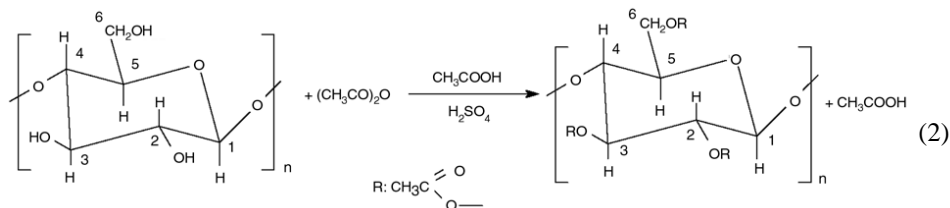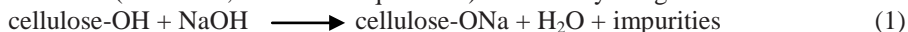
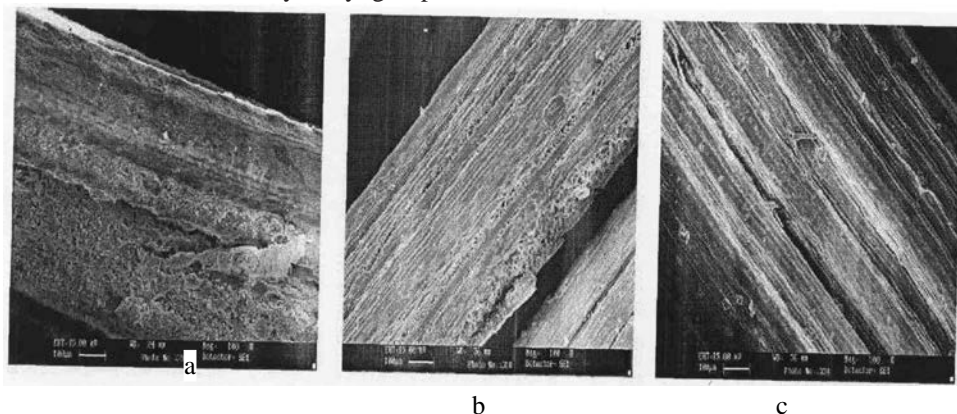Hydroxyl groups in the cellulose structure (2)

Figure 3(a-c). SEM micrographs of PN, PNac and PNm

*Mechanism of synthesis of urea - resorcinol-formaldehyde resin*

The chemical reaction is supposed to take place in two steps[16]. First step involves the reaction between urea and formaldehyde to form methylol urea. Since urea is tetra functional, initial reaction may leads to the formation of tetra methylol derivative of urea (as shown in Scheme 2).


urea   methylol urea   dimethylol urea

I   **II**
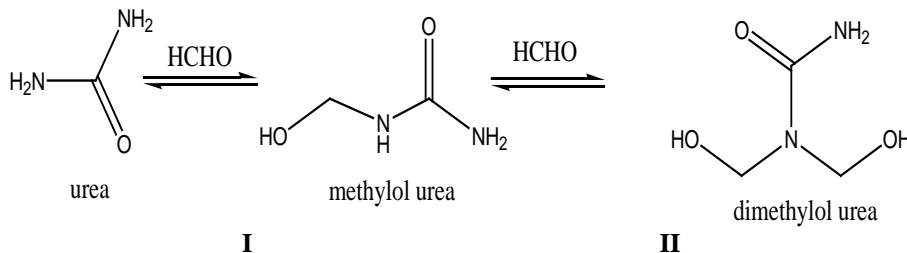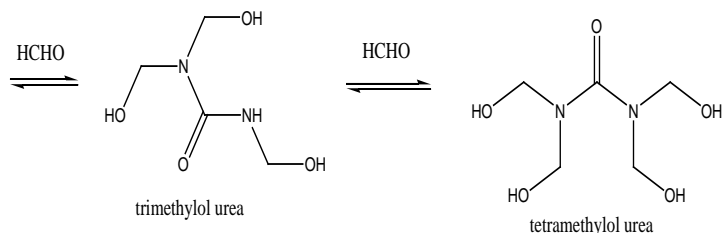
Scheme 2. Formation of methylol derivatives of urea

However slightly alkaline medium (pH of 7-8) control the reaction and favor the formation of dimethylol urea. Since these methylol ureas are non adhesive in nature so condensation does not take place. However the condensation takes place in acidic medium. Therefore the reaction is carried out at 80-90 ^{0}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, the reaction is arrested by neutralization (pH 7.5-8). The condensation is closely watched and controlled at the stages of production because if the reaction is allowed to continue, cross linking leads to the gelatization of the resin. Under acidic conditions methylol urea condenses by elimination of water between either of four steps (as shown in Scheme 3). Under acidic conditions methylol urea condenses by elimination of water between either of four steps (as shown in Scheme 3).
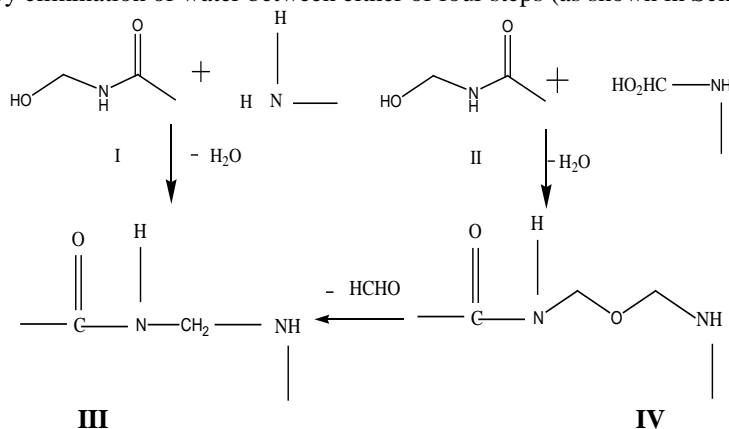

Scheme 3. Condensation of methylol urea by elimination

Resorcinol have great affinity towards formaldehyde solution and react readily to form methylene derivative[14]. In this reaction methylol group either occupies *ortho* or *para* position to hydroxyl groups as shown below in Scheme 4.
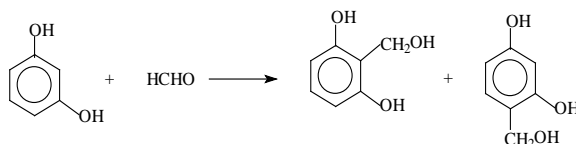

Scheme 4. Formation of methylol derivative

Methylolated derivatives then condense with other formaldehyde molecules to form polymeric structure as shown in Scheme 5. In this reaction resorcinol joined together either by methylene or ethereal linkages to give complex molecules.
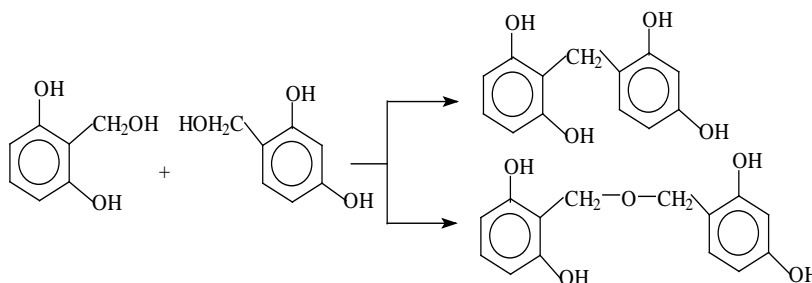
Scheme 5. Condensation reaction between methylated derivatives to form polymeric structure

Then these complex molecules further condense to give more complex structures and in this way result into three dimensional network as present in Scheme 6.
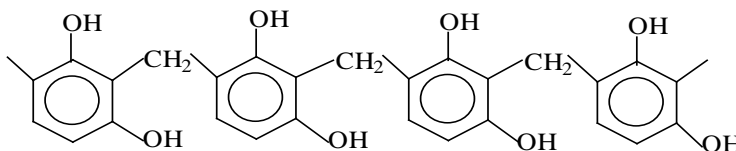
Scheme 6. Network of RF polymer

Mechanical strength

The tensile strength results of URF and its composites with unmodified and modified fibers are depicted in Figure 4(a). A gradual increase in the tensile strength was observed in URF composites reinforced with unmodified and modified fibers to that of the pure matrix. The composites with PNm presented the highest tensile strength values followed by PNac and PN. The effect of surface treatment of fiber on the tensile properties of the composite is more apparent. A good dispersion of the fibers in the polymer matrix produces a uniform medium for transferring the stress and as a result the tensile strength is increased. In addition, reinforcement of the interfacial phases due to chemical treatment is the main reason for the enhancement of the modulus of the system in comparison with URF and those samples with unmodified fibers. The increase in the tensile strength could be explained on the basis that after chemical treatment of fiber hemicelluloses, waxes and other impurities are removed from the fiber and there is good fiber- matrix adhesion which leads to better tensile strength. Similar results have been obtained for compressive and flexural strengths of these composites. It has been observed that the tensile strength of URF is 55.5 MPa and URF/PN composites are 63.8 MPa, URF/PNm is 98.7 MPa and URF/PNac is 102.3MPa. The compressive strength has been found to be 116.2 MPa for URF and 238.8, 413 and 497.6 MPa for URF/PN, URF/PNm and URF/PNac respectively (Figure 4(b)). Similarly the flexural strength of these composites has the values 20.1, 30.5, 42.6 and 45.4 MPa for URF URF/PN, URF/PNm and URF/PNac respectively (Figure 4(c)). Different stresses have been calculated from tensile, compressive and flexural curves and are presented in Tables 2-4. Wear resistance of these composites has also been improved. It has been observed from Figure 4(d) that the wear rate of URF matrix was and URF, URF/PN, URF/PNm and URF/PNac respectively.
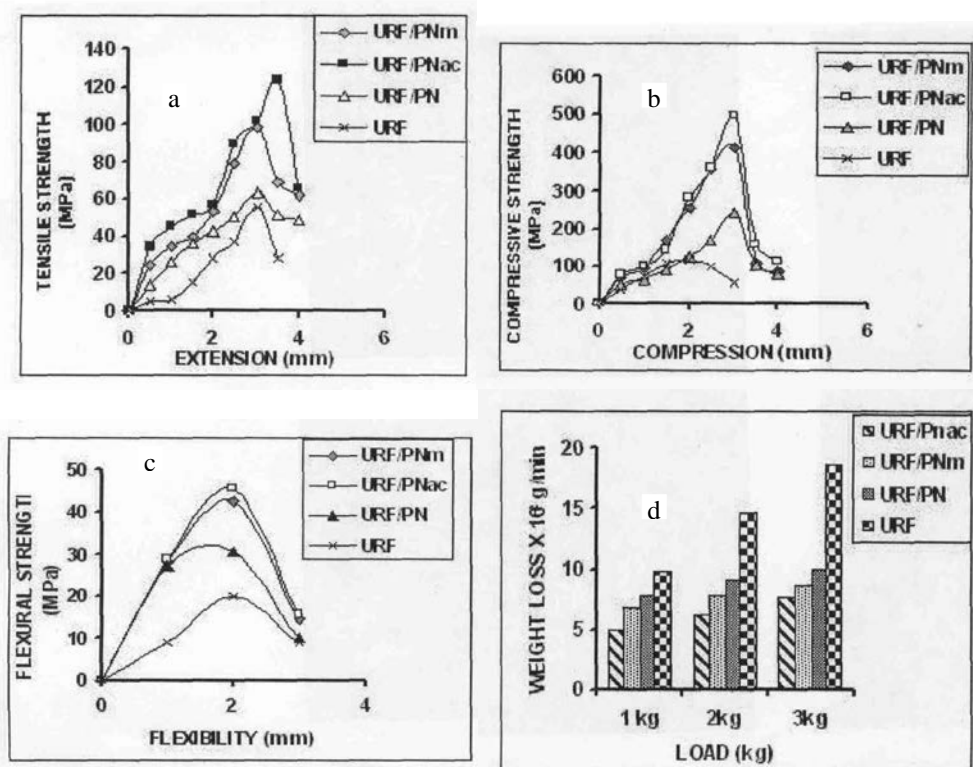
Figure 4(a-d). Load-extension, compression, flexibility and wear resistance curves of URF, URF/PN, URF/PNac and URF/PNm composites

Table 2. Various stresses calculated from tensile load/extension curves of URF and URF based composites

Sample Code	Ultimate Stress MPa	Working Stress MPa	Yielding Stress MPa	Fracture Point MPa	Modulus MPa	S.D.±
URF	21.3	12.5	15.8	17.50	756.9	1.23
URF/PN	31.8	20.3	20.5	21.96	876.4	1.49
URF/PNac	44.3	21.0	27.5	28.82	1234.9	1.99
URF/PNm	38.7	19.5	22.9	24.22	1000.8	2.01

Table 3. Various stresses calculated from Compressive load/compression curves of URF and URF based composites

Sample Code	Ultimate Stress MPa	Working Stress MPa	Yielding Stress MPa	Fracture Point MPa	Modulus MPa	S.D.±
URF	46.48	29.8	34.5	38.9	1198	1.56
URF/PN	85.92	56.9	64.5	78.9	2272	1.67
URF/PNac	156	123.4	146.8	137.9	3617	1.89
URF/PNm	129	89.45	103.4	113.5	3240	2.34

Table 4. Various stresses calculated from Flexural load/flexibility curves of URF and URF based composites

Sample Code	Ultimate Stress MPa	Working Stress MPa	Yielding Stress MPa	Fracture Point MPa	Modulus MPa	S.D.±
URF	6.06	3.20	4.90	4.10	234.6	1.93
URF/PN	9.36	6.78	7.45	8.09	335.7	2.11
URF/PNac	17.60	11.76	13.54	14.98	427.0	1.63
URF/PNm	12.04	8.98	10.23	10.99	378.9	1.5

Thermal analysis

Thermo-gravimetric analysis (TGA) of materials such as raw fiber, polymeric resin and composites was studied as a function of % weight loss *vs.* increase in temperature. For raw fiber Initial decomposition (IDT) temperature is 214 ^{0}C and final decomposition temperature is 473.0 ^{0}C (Table 5). In raw fiber, in the beginning various reactions such as depolymerization, dehydration and glucosan formation took place between the temperature ranges of 26.0 ^{0}C to 200.0 ^{0}C. In case of urea-resorcinol- formaldehyde it is single stage decomposition and the initial decomposition temperature (IDT) is 239.0 ^{0}C and the final decomposition of the resin took place at 990.0 ^{0}C (Table 5). It has been observed that for raw Pine needles reinforced composites initial decomposition temperature is 228.0 ^{0}C and the final decomposition of the composite took place at 781.0 ^{0}C whereas for URF/PNac and URF/PNm the initial decomposition started at 238 and 231 ^{0}C and ended at 834 and 809 ^{0}C respectively. (Table 5). These values are between the degradation temperatures observed for matrix and the fiber. This indicates that the presence of cellulose fibers affects the degradation process of the composites. Also it has been found that acetylated Pine needles reinforced composites are thermally more stable as compared to mercerized and raw fiber reinforced composites. These studies are further supported by differential thermal analysis (DTA) Table 6). This was consistent with results reported earlier[16].

Table 5. Thermogravimetric analysis of URF and URF based composites

Sample Code	IDT ^{0}C	% wt. loss	FDT ^{0}C	% wt. loss	Final residue, %
PN	214	13.45	473	76.34	13.56
URF	239	21.48	990	85. 31	14.49
URF/PN	228	27.51	781	80.63	19.67
URF/PNac	238	18.90	834	79.80	20.20
URF/PNm	231	20.82	809	81.23	17.77

Table 6. DTA and DTG analysis of URF and URF based composites

Sample Code	Exothermic/ Endothermic Peaks ^{o}C µV	Exothermic Peaks, Temperature ^{o}C, mg/min
PN	328.0 (87); 432.0 (213)	78[34]; 209[78]; 389[156]
URF	204[7.8]; 259[8.2]	196[318.7];213[0.25]; 257[251.1]; 323[0.137]
URF/PN	100(2.9); 246(34)	123[89.6]; 198[112]; 254[114.8]
URF/PNac	289(2.1); 478(-12)	98[56]; 156[178]; 456[145.3]
URF/PNm	321(1.2); 501(-8.9)	89[45]; 317[221]; 523[234]

SEM

Figure 5(a-d) shows the photomicrographs of the URF-Pine needles composites. The samples were fractured in liquid nitrogen prior to observation with scanning electron microscopy (SEM). In these micrographs existence of phase adherence between fiber and matrix can be observed. An increase in adhesion between the phases occurs in the composites prepared with modified fibers. The interphase adhesion allows stress transfer from matrix to the fiber and accounts for the superior mechanical strength. Adherence predominates due to increased hydrophobic character of fibers after chemical treatment. As it may be seen, the sample without chemical treatment of its fibres is pulled out easily and some holes are noticed around the fibres which imply that there are weak interactions between the filler and polymer. The breaking mode of fibres has been changed with chemical treatment and breakage of both fibres and matrix occur simultaneously.
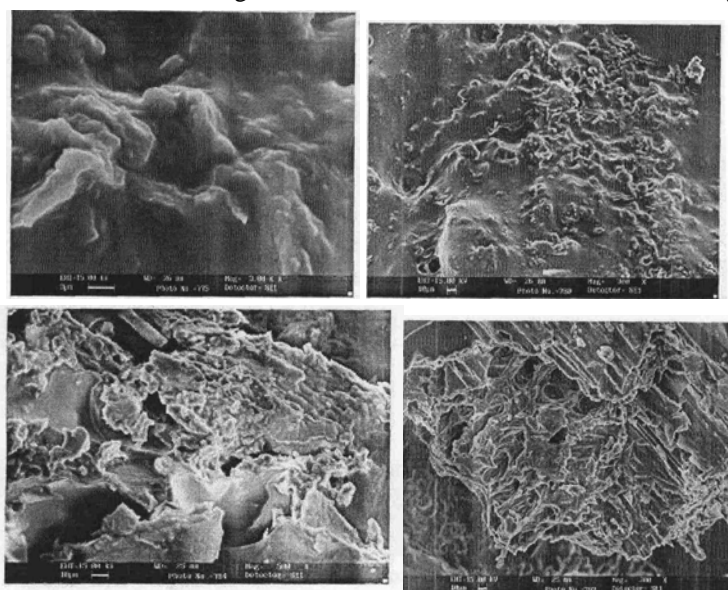

Figure 5(a-d). SEM micrographs of URF, URF/PN, URF/PNac and URF/PNm

Conclusion

This research work presents an analysis of the interfacial behavior of lignocellulosic fiber reinforced composites based on URF and Pine needles fibers. Two chemical modification methods (acetylation and mercerization) were applied on fibres under study. The composite samples were prepared by compression molding method with 30% fiber by weight. The interfacial adhesion, morphology and the mechanical properties of the samples were studied and the concluding results are as follows.

- FTIR spectra of treated fibers after the mercerization process shows the bands at 1730 and 1245 cm^{-1}, attributed to the stretching vibrations of C=O and C-O groups respectively, disappeared. After acetylating reaction, new acetyl groups were added to the cellulose, as indicated in curve (C) with the vibrations at 1740 (-C=O) and 1240 cm^{-1} (C-O).
- The solid -state ^{13}C MAS NMR was changed by acetylation with a degree of substitution (DS) of 0.90.
- SEM Micrographs showed that the best encapsulation of fibers by polymer matrix is observed in samples of treated fibers.

- Chemical treatment of lignocellulosic fillers results in better dispersion of the filler into the polymer matrix and leads to higher impact resistance in comparison with samples containing filler with no chemical treatment.
- The chemical treatment of fibers improves interaction of fibers with the URF matrix, which owes to superior mechanical strength of these composites.

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