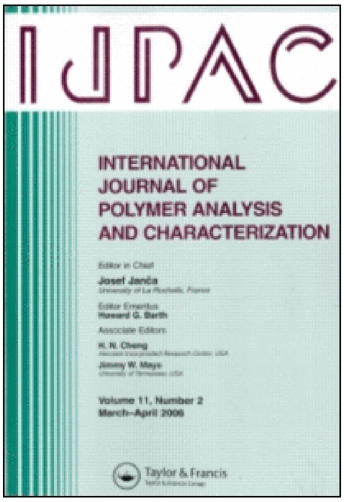

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Morphological, Thermal, and Physicochemical Characterization of Surface Modified *Pinus* Fibers

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Abstract: In recent years, interest in using natural fibers in a number of applications especially in biocomposites has grown because they are eco-friendly, lightweight, combustible, nontoxic, low cost and easy to recycle. On the other hand, the lack of good interfacial adhesion and poor resistance to moisture absorption and chemicals make the use of natural fibers less attractive. Chemical treatment of the lignocellulosic fiber can stop the moisture absorption process, clean the fiber surface, chemically modify the surface or increase the surface roughness. Silane treatment of natural fibers is a promising process for improving physical and chemical properties of fibers. The work presented in this article gives insight into the effect of silane treatment on physical and chemical properties of *Pinus* fibers. Further polymer composites were prepared using urea-formaldehyde as a novel polymer matrix resin. The silane-treated and untreated fibers along with polymer composites have been characterized by various techniques such as scanning electron microscopy (SEM), Fourier transform-infrared spectrophotometry (FT-IR) and thermo-gravimetric/differential thermal analysis along with DTG studies. Composites prepared were also subjected to the evaluation of different mechanical, physical, and chemical properties.

Keywords: Morphological behavior; Natural fibers; Physicochemical properties; Polymer composites; Silane treatment; Thermal behavior

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INTRODUCTION

With increasing environmental awareness throughout the world, recently there has been growing interest in finding new applications for natural fibers that are traditionally used for making such products as carpets, ropes and mats in combination with other materials.[1–3] Biomass-based lignocellulosic natural fibers have become special materials of the present age because of the enormous advantages these natural fibers offer over synthetic fibers.[4–6] In the past two decades, synthetic fibers such as nylon, glass, and carbon have been widely used for a number of applications. In order to provide particular properties and to reduce the final cost of products, these toxic fibers have been incorporated into polymer matrices. But these synthetic fibers have a number of disadvantages, especially regarding the environment.[7–9] Therefore, recently the synthesis of polymeric materials made from renewable resources has been the object of significant research effort due to increasing environmental concerns.

Natural fibers obtained from renewable resources have a number of advantages over traditional synthetic fibers. Properties such as renewability, biodegradability, high filling effect, light weight, easy availability, nonabrasiveness, acceptable specific strength properties, ease of separation, enhanced energy recovery, noncorrosive nature, high toughness, low cost, good thermal properties, reduced tool wear, and reduced dermal and respiratory irritation provide attractive eco-friendliness to the resulting natural fibrous materials.[10–12] Efforts have been made by various researchers to substitute synthetic fiber with biodegradable natural fiber to effectively use these natural fibers in a number of applications, especially in polymer composite materials.[13–15] In fact, several studies reporting natural fiber-reinforced polymer composites have shown that the incorporation of lignocellulosic natural fibers improves the mechanical properties of the polymer matrices.[16–18] It has been observed that the behavior of natural fibers usually depends on different factors such as source of fiber, weather variability, harvest period, quality of the soil, climate at the specific geographic location, and the preconditioning. Depending on their origin, natural fibers can be classified as seed, bast, leaf, or fruit fibers. The components of natural fibers include cellulose, hemicelluloses, lignin, pectin, waxes and water-soluble substances.

In spite of a number of advantages, natural fibers also have few disadvantages. One of the serious problems related to the use of lignocellulosic natural fibers is their higher water absorption, lower chemical resistance and lower thermal stability.[19,20] In order to improve the existing properties of natural fibers, various chemical modifications such as change of functionality, inter- and intramolecular gelation, silanes treatment, acetylation and graft copolymerization have been tried. Chemical modifications are considered to optimize the interfaces of fibers. Chemicals may activate hydroxyl groups or introduce new moieties that can effectively interlock with the cellulose and induce required properties in the polymer. Further, the potential use of lignocellulosic natural fibers as a reinforcement for polymer matrices is greatly harmed by their hydrophilic character, high capacity for moisture and poor adhesion between them and the matrix. As a result, considerable efforts are currently being directed toward improving the quality of the interfacial bonding between the polymer and fibers by surface modification of the lignocellulosic fibers.

The literature survey has revealed that not many studies have been made on the incorporation of new functionalities onto the lignocellulosic *Pinus* fiber.[21,22] It has been observed that these materials lose their strength when exposed to moisture and humid environment. This study is part of a series assessing the physical and chemical properties of lignocellulosic natural fibers for their applications in a number of fields, especially in fiber-reinforced composites. This article discusses the study of surface modifications of lignocellulosic *Pinus* fibers through silanes treatment and is aimed at evaluating the physical, chemical, morphological and thermal properties of treated and untreated fibers. Further, polymer composites were prepared using different dimensions of *Pinus* fibers as reinforcing material and urea-formaldehyde resin as a novel polymer matrix.

EXPERIMENTAL SECTION

Materials and Methods

Pinus fibers were collected from local resources in the Himalayan region. Reagent grade chemicals, namely sodium hydroxide (NaOH), ethanol, acetone and aminopropyl triethoxy silanes were used for surface modifications of the fibers. Urea formaldehyde solution (Qualigens Chemicals Ltd. Co.) was used as received. In the present research work, we used amino resin such as urea-formaldehyde (UF) as polymer matrix. Lignocellulosic *Pinus* fibers were initially thoroughly washed with detergent powder and then soaked in distilled water for 3 h. Then these fibers were dried for 48 h in air at room temperature, followed by drying at 100°C for 24 h to adjust the moisture content to 1–2%, and then stored in a vacuum dessicator. These dried fibers were designated untreated fibers. The untreated fibers were subsequently subjected to extraction with acetone for 72 h in Soxhlet apparatus, followed by washing with double-distilled water and air drying to remove waxes and water-soluble ingredients prior to chemical treatments.

Mercerization of *Pinus* Fibers

Generally, the first step in chemical treatment of natural fibers is the mercerization process (pretreatment process). Lignocellulosic *Pinus* fibers were immersed in 2% NaOH solution for different time intervals (45–315 min) at room temperature for the optimization of time. The fiber were then taken out and thoroughly washed with double-distilled water for removal of any NaOH content. However, the final washing of these natural fibres was done with 2% acetic acid in order to neutralize the last traces of NaOH used. Finally, the fibers were washed again with fresh distilled water and dried in an oven at 70°C to a constant weight. These fibers were then kept in an air dryer for 24 h. After the optimization of time, the mercerization of these fibers was also carried out in different concentrations of NaOH solutions (2–14%) at the optimized time period to study the effect of concentration of NaOH on mercerization of the fibers.

Silane Treatment

Silane treatment of *Pinus* fibers was carried out with aminopropyl triethoxy silane; 2% of the silanes solution was prepared by mixing aminopropyl triethoxy silane with an ethanol/water mixture in the ratio 60:40. This solution was allowed to stand for 1 h. The pH of the solution was maintained between 3.5 and 4, using METREPAK pHydrion buffers and pH indicator strips. Mercerized *Pinus* fibers (2–12% NaOH) were dipped in this solution and were allowed to stand for 1.5 h. The ethanol/water mixture was drained out and the fibers were dried in air and then in an oven at 70°C to a constant weight.

Evaluation of Physical and Chemical Properties

It has been observed that the modification of the surface of natural fibers affects the crystalline regions of cellulosic materials, so it affects many physical and chemical properties of the fibers such as swelling, moisture absorbance, thermal behavior, water uptake, and chemical resistance. Silane treated/untreated *Pinus* fibers thus prepared were investigated for the evolution of physical and chemical properties such as swelling, moisture absorbance, water uptake and chemical resistance.

Swelling Behavior in Different Solvents

The swelling of the surface-modified and raw samples of *Pinus* fibers was determined by treatment with different solvents such as methanol, isobutanol, carbon tetrachloride and water. Known initial weights W_i of the silane-treated samples and raw sample were immersed in 100 mL of solvent at room temperature for 72 h. The samples were filtered, the excess solvent was removed with the help of filter paper, and then the final weight W_f was noted on a Libror AEG-220 Shimadzu electronic balance.

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 Study at Different Relative Humidities

Moisture absorbance studies of different natural fibers were carried out at various humidity levels (20–100). The silane-treated and raw samples of *Pinus* fibers were dried at 50°C in an oven until a constant weight was obtained. Moisture absorbance percentage was found by placing the known weight W_i of dry silane-treated and raw samples in a humidity chamber (Swastika), which was set at a particular humidity level for about 2 h, and then the final weights W_f of the samples exposed at a particular relative humidity (RH) were taken. The same procedure was repeated at different humidities ranging from 20 to 100%. The percent moisture absorbance was calculated from the increase in initial weight in the following manner:

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

Water Uptake Behavior

Small wicks of the silane-treated and raw *Pinus optiva*, diameter 7 mm, were prepared, a mark was drawn on the wick, and then it was dipped into a beaker containing water. The rise of water through capillary action in each fiber wick was noted at different time intervals (12–72 h).

Chemical Resistance in 1 N NaOH and 1 N HCl

Samples of 100 mg of silane-treated and raw *Pinus* fibers were put in 100 mL of 1 N NaOH and 1 N HCl, losses in weights were studied at different time intervals (12–72 h), and the percent chemical resistance (P_{cr}) was calculated by the method reported earlier:

$$\text{Percent chemical resistance } (P_{cr}) = \frac{T_w - W_{\text{aci}}}{T_w} \times 100$$

where T_w = total weight and W_{aci} = weight after a certain interval.

Synthesis of Urea-Formaldehyde Resin

Urea-formaldehyde resin was synthesized by the standard method developed in our laboratory.[15,20,21] 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 with the help of mechanical stirrer. The reaction was carried out in an alkaline medium. Suitable conditions of temperature and pH were maintained while carrying out the reaction, as reported earlier.[15] After the completion of resinification, the resin was cooled and ammonium chloride was added in a pinch to increase the bonding between the molecules. The synthesized resin was then transferred to a specially made mold. Resin sheets of 150 mm × 150 mm × 5.0 mm in size were prepared by a closed mold method as described elsewhere.[15–20] 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. The cured samples were then subjected to various mechanical, thermal, and morphological characterizations.

Fabrication of Polymer Composites

The *Pinus* fibers of different dimensions were mixed thoroughly with urea-formaldehyde resin using a mechanical stirrer with suitable loadings (1.0:0.3) in terms of weight.[8] These fibers were used in three different forms:

1. Particle reinforcement: *Pinus* fibers were ground to a powder and filtered through a sieve of pore size 200 microns.
2. Short-fiber reinforcement: *Pinus* fibers chopped into 3 mm size were used as short fibers for the fabrication of polymer composites.
3. Long-fiber reinforcement: *Pinus* fibers chopped into 6 mm size were used as long fibers for the fabrication of urea-formaldehyde matrix-based polymer composites.

The above mixture was poured into specially made molds. The surfaces of the 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 surfaces of the mold. Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by the compression molding technique in a hot press using a mold that was preheated to 110°C. Composite sheets were then prepared by hot pressing the mold at 130°C for 30 min under a pressure of 3–4 MPa. All the specimens were then post-cured at 120°C for 12 h.

Mechanical Properties

Tensile Strength

The tensile strength test was conducted on a computerized universal testing machine. Specimens of dimension 100 mm × 10 mm × 5 mm were used for the analysis. The tensile test was conducted in accordance with ASTM D 3039 method. The test was conducted at constant strain rate of 10 mm/min. The force was applied until the failure of the sample and load-elongation curve was obtained.

Compression Test

The compression test was conducted in accordance with ASTM D 3410 method. The test was conducted at the constant strain rate of 10 mm/min, and the total compression range was 7.5 mm.

Flexural Test

The three-point bend flexural test was conducted in accordance with ASTM D 790 method. The test was conducted at the constant strain rate of 2.54 mm/min.

Wear Test

The wear test of the sample was conducted on a wear and friction monitor. Wear resistance of composites was carried out as per ASTM D 3702 method.

Physicochemical Properties of Fiber-Reinforced Polymer Composites

Swelling Behavior

Swelling of the composite samples was studied in different solvents such as methanol, isobutanol, carbon tetrachloride, and water for 15 days as discussed earlier for fibers.

Moisture Absorbance

Moisture absorbance studies of different polymer composite samples were carried out at various humidity levels (varying from 20 to 100%); each sample was set at a particular humidity level for about 12 h, as discussed earlier for fibers.

Chemical Resistance

For the chemical resistance test, the dried specimens were immersed in 100 mL of 1 N NaOH and 1 N HCl for different intervals of time (24–144 h). After this, the samples were filtered, dried, and weighed. The percent chemical resistance (Pcr) was calculated in terms of weight loss, as per the method reported earlier for fibers.

Characterization of Raw/Surface-Modified *Pinus* Fibers and Respective Polymer Composites

Infrared Spectroscopy (IR)

IR spectra of the raw and surface-modified *Pinus* fibers were taken with KBr pellets on a Perkin Elmer RXI Spectrophotometer.

Scanning Electron Microscopy (SEM)

Scanning electron microscopic (SEM) studies of raw/surface-modified *Pinus* fibers along with polymer resin matrix and composites were carried out on a scanning electron microscope (LEO 435 VP). Scanning was synchronized with the microscopic beam in order to maintain a small size over a large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three-dimensional appearance with high resolution was obtained.

Thermal Analysis

Thermal analysis of natural and synthetic polymers gives us a good account of their thermal stability. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies of the samples were carried out in nitrogen atmosphere on a thermal analyzer (Perkin Elmer) at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Reaction Parameters for Surface Modifications of *Pinus* Fibers

The availability of the number of active sites on the polymer backbone of natural fibers affects the extent of the surface modifications such as grafting, mercerization and silanes treatment. The most important variables that affect the mercerization and silanes treatments are the

Table I. Effect of reaction time on mercerization of *Pinus* fibers

Sample no.	Time (min)	% Wt. loss
1	0	0
2	45	10.90
3	90	14.07
4	135	17.26
5	180	21.12
6	225	23.20
7	270	24.84
8	315	26.02
9	360	25.19
10	405	25.35

reaction parameters like reaction time and concentration of NaOH. Extensive studies were made to optimize these parameters for further carrying out the silanes treatment of *Pinus* fibers for application in various fields.

It has been observed that reaction time very much affects the mercerization process. Reaction time has been optimized by determining the maximum weight loss for *Pinus* fiber. Percentage weight loss of *Pinus* fibers as a function of time is presented in Table I.

In the case of mercerization of *Pinus* fibres, maximum mercerization has been observed at time of 315 minutes as shown in Table I. The decrease in weight loss beyond optimum reaction time is due to the excessive deposition of sodium ions over surface modification and other side reactions, which may not favor further weight loss.

Evaluation of Physical and Chemical Properties of Silane-Treated *Pinus* Fiber

Silane-treated and raw *Pinus* fibers were studied with regard to the evaluation of physical and chemical properties such as swelling, moisture absorbance, water uptake, and chemical resistance.

Swelling Behavior Study on *Pinus* Fibers

It has been observed that after silane treatment, the swelling of raw fibers decreases. In the case of *Pinus* fibers, raw fibers showed maximum swelling in water (139.28%) followed by swelling in methanol (121.36%), isobutanol (111.85%), and carbon tetrachloride (93.48%). However,

Table II. Effect of silane treatment on % swelling behavior of *Pinus* fibers in different solvents

Sample no.	% Mercerization	Water	Methanol	Isobutanol	Carbon tetrachloride
1	0	139.28	121.36	111.85	93.48
2	2	131.57	112.43	103.83	89
3	4	122.42	103.47	91.78	71.45
4	6	117.28	96.58	83.58	67.28
5	8	100.28	85.95	72.25	60.21
6	10	74.57	66.75	52.57	37.29
7	12	93.85	70.48	63.51	45.18
8	14	99.71	74.83	68.82	54.38

silane-treated fibers showed less swelling, as seen in Table II. Further, it has been observed that 10% mercerized silane-treated *Pinus* fibers showed less swelling, followed by 12, 14, 8, 6, 4, and 2%. From the above discussion it can be concluded that raw *Pinus* fibers show greater swelling in water than other solvents. Swelling ability reflects the relation between void structure in backbone polymer and size of solvent molecules both for protic and aprotic solvents. This is due to greater affinity of water for hydroxyl groups of cellulose present in natural fibers, resulting in more penetration of water into matrix than other solvents. In the case of silane-treated fibers, it has been observed that swelling varies as a function of percentage mercerization (Pm) and nature of the solvent. In silane-treated fibers, the water and alcohols do not interact to the same extent as with raw fibers due to the blockade of active sites on natural fibers' backbone by silane treatment, which causes the change in sorption. In particular, for the raw or treated fibers, the percentage of swelling decreases from H_2O to methanol and then to isobutanol and carbon tetrachloride, in order. This may be due to the fact that the nonpolar hydrocarbon part, i.e., alkyl group, resists the formation of hydrogen bond and such resistance increases with the size of the alkyl group.

Moisture Absorbance Study on *Pinus* Fibers

Raw *Pinus* fibers showed 1.69, 2.17, 2.98, 3.54, and 3.97% moisture absorbance at 20, 40, 60, 80, and 100% humidity levels, respectively. However, silane-treated fibers showed less moisture absorption, as seen in Table III. Further, it has been observed that 10% mercerized silane-treated *Pinus* fibers showed less moisture absorbance followed by 12, 14, 8, 6, 4, and 2%.

Table III. Effect of silane treatment on % moisture absorption behavior of *Pinus* fibers at different relative humidity levels

		Hum				
Sample no.	% Mercerization	20	40	60	80	100
1	0	1.69	2.17	2.98	3.54	3.97
2	2	1.62	1.94	2.9	3.39	3.82
3	4	1.57	1.86	2.37	3.29	3.71
4	6	1.49	1.73	2.24	3.18	3.63
5	8	1.41	1.69	2.11	3.08	3.52
6	10	1.31	1.57	1.97	2.91	3.38
7	12	1.35	1.62	2.02	2.98	3.42
8	14	1.38	1.65	2.07	3.04	3.48

On the basis of the above results, it has been concluded that surface modifications of the raw *Pinus* fibers have a great impact on the moisture absorbance. There has been a decrease in percent moisture absorbance (% Mabs) with increase in silane treatment (percent mercerization), which is due to the fact that with increase in Pm, the sites for maximum moisture absorbance are blocked after the incorporation of silane chains by surface modification, which exhibits less affinity for moisture than the original fibers.

Water Uptake of *Pinus* Fibers

Raw *Pinus* fibers showed water uptake of 9.07, 11.68, 13.05, 15.84, 17.12, and 18.41 cm at 12, 24, 36, 48, 60, and 72 h respectively. However, silane-treated fibers showed less water uptake, as seen in Table IV. It has been observed that 10% mercerized silane treated fibres showed lowest water uptake followed by 12, 14, 8, 6, 4, and 2%, respectively.

Chemical Resistance of *Pinus* Fibers

Raw *Pinus* fibers showed 28.32, 34.73, 39.42, 43.73, 47.93, and 52.76% weight loss in 1 N HCl and 39.83, 46.78, 50.52, 55.35, 59.85, and 63.72% weight loss in 1 N NaOH at 12, 24, 36, 48, 60, and 72 h respectively. However, silane-treated fibers showed less weight loss, as seen in Table V. It has also been observed that 6% mercerized silane-treated fibers showed the lowest weight loss followed by 8, 10, 4, and 2%.

Table IV. Effect of silane treatment on water uptake behavior of *Pinus* fibers at different time intervals

Sample no.	% Mercerization	12 h	24 h	36 h	48 h	60 h	72 h
1	0	9.07	11.68	13.05	15.84	17.12	18.41
2	2	8.92	11.49	12.98	15.69	17.03	18.32
3	4	8.78	11.31	12.87	15.42	16.82	18.27
4	6	8.65	11.22	12.69	15.27	16.72	18.15
5	8	8.49	11.12	12.41	15.14	16.62	18.01
6	10	8.27	10.87	12.17	14.84	16.27	17.37
7	12	8.38	10.96	12.29	14.98	16.41	17.67
8	14	8.45	11.08	12.35	15.03	16.51	17.83

Characterization of Raw and Surface-Modified Natural Fibers

Infrared Spectroscopy (IR)

The IR spectra of raw *Pinus* fibers showed a broad peak at 3396.4 cm^{-1}, which is due to the bonded OH groups and at 2923.1, 1456.9, and

Table V. Effect of silane treatment on chemical resistance (in % wt. loss) of *Pinus* fibers at different time intervals against (a) 1 N HCl and (b) 1 N NaOH

Sample no.	% Mercerization	12 h	24 h	36 h	48 h	60 h	72 h
		(a) 1 N HCl					
1	0	28.32	34.73	39.42	43.73	47.93	52.76
2	2	26.71	32.74	37.93	42.82	46.25	51.83
3	4	25.81	31.98	36.47	41.93	45.62	50.62
4	6	24.98	30.52	35.74	39.93	44.762	49.72
5	8	24.25	29.43	34.83	38.78	43.94	48.99
6	10	22.32	26.72	30.21	35.81	39.75	44.05
7	12	22.97	27.84	31.95	36.72	40.96	45.82
8	14	23.37	28.94	32.79	37.94	42.83	47.82
		(b) 1 N NaOH					
1	0	39.83	46.78	50.52	55.35	59.85	63.72
2	2	38.87	45.12	49.14	54.24	58.36	62.52
3	4	37.14	44.25	48.19	53.82	57.12	61.03
4	6	36.79	43.83	47.93	52.83	56.74	60.62
5	8	36.34	42.95	47.37	51.95	54.53	59.71
6	10	33.25	39.23	42.78	47.74	50.85	54.78
7	12	34.86	40.63	44.92	49.52	52.21	56.72
8	14	35.91	41.15	45.78	50.32	53.32	58.36

1036.0 cm^{-1} due to –CH$_2$, C–C, and C–O stretching, respectively. In the case of grafted silane fibers, the additional broad intense bands around 1235.0 and 1106.2 cm^{-1} were obtained due to the stretching of Si–O–cellulose and –Si–O–Si bonds, respectively.

Morphological Study

Silane treatment gave surface coating to the fibers. Since these fibers exhibited micropores on their surface, the coupling agent penetrated into the pores and formed a mechanically interlocked coating. The scanning electron micrographs easily verify the difference between the raw cellulosic *Pinus* fibers and surface-modified fiber (Figure 1).

Thermal Analysis

For *Pinus* fiber initial decomposition temperature (IDT) has been found to be 223°C (% wt. loss 23.45) and the final decomposition temperature (FDT) to be 507°C (% wt. loss 64.44), while after silane treatment IDT has been found to be 215°C (% wt. loss 18.74) and FDT to be 500°C (% wt. loss 74.37).

From the above discussion it is clear that silane treatment affects the properties of *Pinus* fibers. By mercerizing lignocellulosic fibers with different concentrations of NaOH for different intervals prior to carrying out surface modification through silane treatment activation of lignocellulosic *Pinus* fibers was done so as to open the active sites of the cellulose backbone. The important modification done by alkaline treatment is the disruption of hydrogen bonding in the network structure, which causes increase in surface roughness. This treatment removes a certain amount of lignin, wax, and oils covering the external surface of the fiber cell wall, depolymerizes cellulose, and exposes the short-length crystallites. Addition of aqueous sodium hydroxide (NaOH) to natural fiber promotes the ionization of the hydroxyl group to the alkoxide.

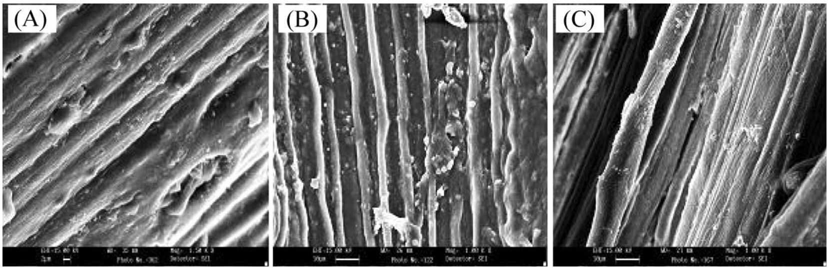


Figure 1. SEM of raw (A), mercerized (B), and silane-treated (C) *Pinus* fibers.

Natural fibers, being lignocellulosic, are highly hydrogen bonded polymers, and silane molecules are not in a position to penetrate beyond the surface of the cellulose substrate, hence without activation through sodium hydroxide only a small amount of surface modification occurred. A coupling agent such as aminopropyl triethoxy silane was used in fiber treatment in order to improve the interface properties. Since natural fibers exhibited micropores on theirs surface, the coupling agent penetrated into the pores and formed a mechanically interlocked coating on their surface. Therefore, the hydrocarbon chains provided by the application of silane restrain the swelling of the fiber by creating a cross-linked network due to covalent bonding. The chemical treatment of lignocellulosic fibers results in formation of complexes with the hydroxyl group of the cellulose and thus reduces the moisture absorption of the fiber.

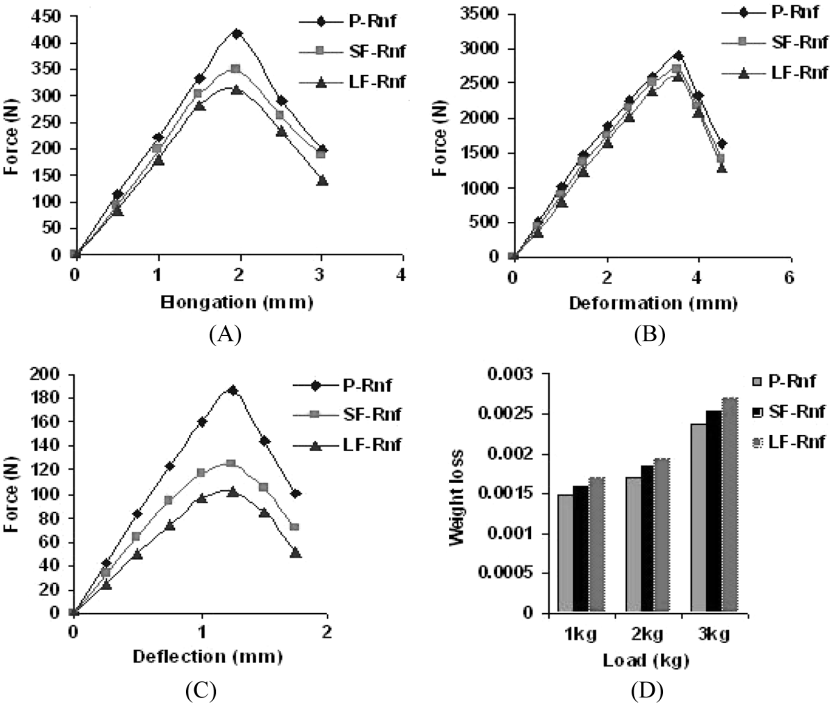
Optimization of Urea-Formaldehyde Resin for Fabrication of Polymer Composites

It has been observed that urea-formaldehyde resin in the ratio 1.0:2.5 exhibits optimum mechanical properties.[15,20,21] This ratio (1.0:2.5) could bear a load of 128.12 N with an extension of 1.84 mm. In compressive test the samples of ratio 1.0:2.5 could bear a load of 991 N at a compression of 3.51 mm, while in flexural tests the samples of ratio 1.0:2.5 could bear a maximum load of 59 N at a deflection of 0.776 mm. Further, the sample of ratio 1.0:2.5 exhibits maximum wear resistance, hence it was taken for further preparation of polymer composites.

Mechanical Properties of Urea-Formaldehyde Matrix-Based Composites

In the tensile strength test, it has been observed that *Pinus* fiber-reinforced polymer composites with particle reinforcement showed more tensile strength, which was followed by short-fiber and long-fiber reinforced composites (Figure 2(A)). It is clear from Figure 2(A) that the samples of (i) particle-reinforced composite could bear a load of 417.0 N at an extension of 1.91 mm, (ii) short fiber-reinforced composite could bear a load of 347 N at an extension of 1.95 mm, and (iii) long fiber-reinforced composite could bear a load of 312 N at an extension of 1.97 mm.

In the compressive strength test (i) particle-reinforced composite could bear a load of 2897.0 N with compression of 3.51 mm, (ii) short fiber-reinforced composite could bear a load of 2703.00 N with



(A) (B)

(C) (D)

Figure 2. Load elongation (A), deformation (B), and deflection (C) curves and wear resistance (D) of fiber-reinforced composites.

compression of 3.53 mm, and (iii) long fiber-reinforced composite could bear a load of 2603.00 N with compression of 3.56 mm (Figure 2(B)). Flexural strength of polymer resin matrix has been found to follow the same trend as is observed for tensile and compressive strength. It has been found that with particle reinforcement, flexural strength increases to a much greater extent than short and long fiber-reinforcement (Figure 2(C)). It is clear that the samples of (i) particle-reinforced composite could bear a load of 187.00 N with deflection of 1.23 mm, (ii) short fiber-reinforced composite could bear a load of 125.00 N with compression of 1.24 mm, and (iii) long fiber-reinforced composite could bear a load of 102.00 N with compression of 1.25 mm. As evident from Figure 2(D) wear rate of UF matrix decreases appreciably when it is reinforced with *Pinus* fibers. It was observed that particle reinforcement decreases the wear rate to a much greater extent than short- and long-fiber reinforcement.

Table VI. Swelling behavior (in %) of polymer composites in different solvents

Sample	Water	Methanol	Isobutanol	Carbon tetrachloride
UF resin	0.17	0.15	0.12	0.07
P-Reinforced	5.15	4.96	4.85	4.75
SF-Reinforced	5.27	5.08	5.05	4.87
LF-Reinforced	5.49	5.28	5.18	5.05

Swelling, Moisture Absorbance, and Chemical Resistance Behavior of Polymer Composites

Pinus fiber-reinforced polymer composites with different dimensions show different swelling in different solvents (Table VI). It has been observed that the swelling of *Pinus* fiber-reinforced urea-formaldehyde composites in different solvents follows the trend: $H_2O > CH_3OH > C_4H_9OH > CCl_4$. The swelling of polymer composites increases with increase in fiber dimension due to greater affinity of water for OH groups present in the fiber-reinforced polymer composites.

The moisture absorbance at different humidity levels as a function of fiber length is given in Table VII. It has been found that moisture absorbance (Mabs) increases with increase in humidity level ranging from 20 to 100% with increase in fiber dimension (Particle < Short < Long fiber).

It has been observed that resistance towards chemicals decreases with the increase in percent loading (Table VIII). This may be due to an increase in fiber content in the composite, which is vulnerable to the chemical attack, resulting in a decreased resistance towards the chemicals.

Table VII. Moisture absorption behavior (in %) of polymer composites at different relative humidity levels

	Hum				
Sample	20	40	60	80	100
UF resin	0.00015	0.00027	0.00039	0.00056	0.00073
P-Reinforced	0.00058	0.00076	0.00092	0.00099	0.00106
SF-Reinforced	0.00067	0.00092	0.00099	0.00114	0.00118
LF-Reinforced	0.00068	0.00097	0.00106	0.00114	0.00124

Table VIII. Chemical resistance (in % wt. loss) of polymer composites at different time intervals against (a) 1 N HCl (b) 1 N NaOH

Sample	24 h	48 h	72 h	96 h	120 h	144 h
			(a) 1 N HCl			
UF resin	1.07	2.12	3.07	4.21	4.67	5.03
P-Reinforced	6.07	6.92	7.96	8.79	9.58	11.58
SF-Reinforced	6.12	6.97	8.09	8.83	9.71	11.68
LF-Reinforced	6.26	7.08	8.19	8.89	9.79	11.73
			(b) 1 N NaOH			
UF resin	1.47	2.57	3.07	4.57	4.73	5.41
P-Reinforced	6.18	7.08	8.16	8.91	9.69	11.72
SF-Reinforced	6.25	7.12	8.28	8.97	9.75	11.79
LF-Reinforced	6.32	7.32	8.45	9.1	9.97	11.99

Morphological Analysis of Polymer Biocomposites

Morphological investigations (Figure 3) clearly indicate that proper mixing of *Pinus* fiber with the urea-formaldehyde resin takes place in

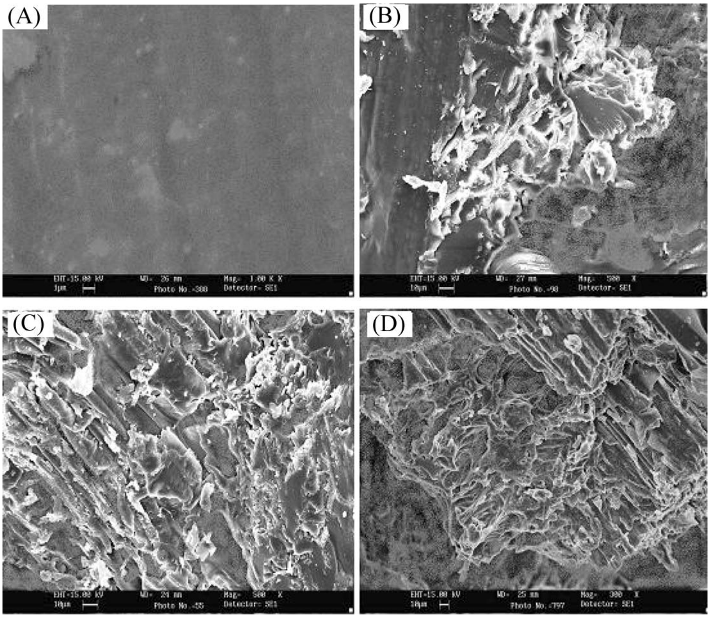


Figure 3. SEM images of urea-formaldehyde resin composite (A) and with particle (B), short (C), and long (D) fiber reinforcements.

the biocomposites thus synthesized. The micrographs also show the distinction in the morphology of the polymer composites of different fiber dimensions and their parent polymer matrix (urea-formaldehyde).

CONCLUSION

It has been observed that silane treatment of *Pinus* fiber helps in improving its physical and chemical properties. It has also been observed that mechanical properties of polymer composites increase with the incorporation of fiber into the polymer matrix due to the transfer of stress from the matrix to the fiber. However, mechanical properties of polymer composites showed a slight decrease with the increase in the dimension of lignocellulosic fiber, and excellent results are obtained when the *Pinus* fibers used had particle form.

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