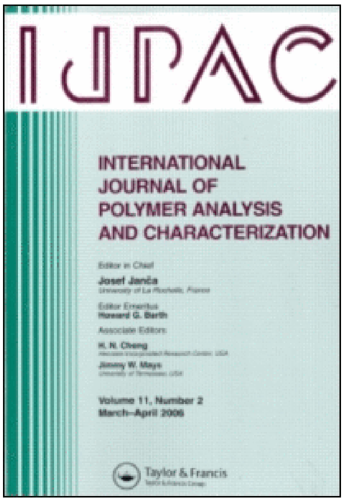

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Singha, Amar Singh and Thakur, Vijay Kumar(2009) 'Synthesis and Characterizations of Silane Treated *Grewia optiva* Fibers', International Journal of Polymer Analysis and Characterization, 14: 4, 301 — 321
To link to this Article: DOI: 10.1080/10236660902871470
URL: http://dx.doi.org/10.1080/10236660902871470

International Journal of Polymer Anal. Charact., 14: 301–321, 2009
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ISSN 1023-666X print
DOI: 10.1080/10236660902871470

Synthesis and Characterizations of Silane Treated *Grewia optiva* Fibers

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Abstract: In recent years, interest has grown in natural fibers as promising materials for a number of applications, particularly in polymer composite materials because they offer a number of advantages such as nontoxicity, eco-friendliness, combustibility, light weight, and low cost. Surface modification of *Grewia optiva* fibers through silane treatment as a simple and convenient method using aminopropyl triethoxy silane is introduced in the article. Natural fibers have been treated with silane coupling agent for evaluating their physicochemical properties (swelling in different solvents, moisture absorbance, water uptake, and chemical resistance). Thermogravimetric analysis/differential thermal analysis/derivative thermogravimetry (TGA/DTA/DTG), SEM microscopy, and Fourier transform-infrared spectrophotometry (FT-IR) measurements were used as characterization techniques for evaluating the nature of these untreated/treated natural fibers. Also, polymer composites were fabricated using these fibers as reinforcing materials and phenol-formaldehyde (PF) as polymer matrix. The effect of fiber dimension on the mechanical properties of the polymer matrix resin such as tensile strength, compressive strength, flexural strength, and wear resistance was evaluated. Polymer composites prepared were also evaluated for morphological, thermal, and physicochemical properties.

Keywords: Natural fibers; Physicochemical properties; Polymer composites; Silane treatment

Submitted 17 December 2008; accepted 18 January 2009.

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INTRODUCTION

Recently, there has been growing interest in finding new applications for available polymers along with their derivatives.[1–6] Natural polymers, especially biofibers, have been exploited for centuries, and potential new applications for these ever-present renewable resources are still being sought, mainly in response to environmental concerns.[7,8] Various examples can be found in domestic life all around the world of effective utilization of various natural fibers. Decrease in fossil resources and their high prices has led to the increasing interest in the development of biodegradable materials based on renewable resources such as biofibers. In fact, biomass-based lignocellulosic natural fibers have become sought after materials of the present age because of the enormous advantages these fibers offer over synthetic fibers.[9,10] Synthetic fibers such as carbon, nylon, glass, and aramids have been widely used for a number of applications for more than two decades. But these synthetic fibers have a number of disadvantages, especially regarding the environment and their handling.[11,12]

Natural fibers have been used in the past as a raw material for different applications. In recent years, greater attention has been paid to their use in a number of applications, including these fibers as reinforcement for polymer materials.[13,14] Currently, biofiber-reinforced polymer composites materials are replacing materials such as ceramics, metal, and glass in various fields. Effective utilization of biofibers, derived from a number of renewable resources, as reinforcing material in polymer matrix-based composite materials provides positive environmental benefits. These polymer materials offer several advantages over conventional materials including lightness, resistance to corrosion, and ease of processing.[15–17] The most important advantages of lignocellulosic biofibers over traditional synthetic fiber reinforcements such as glass fibers are: noncorrosiveness, low density, low cost, reduced wear, high toughness, good specific properties, and biodegradability.[18,19] The most important constituents of lignocellulosic natural fibers are cellulose, hemicelluloses, lignin, and wax. Natural fibers like pinus, *Grewia optiva*, sisal, flax, *Hibiscus sabdariffa*, jute, and oil palm have all been proved to be good reinforcements in polymer matrices.[20,21] The properties of natural fibers depend mainly on the source, age, and separating techniques of the fiber. In spite of a number of advantages, these natural fibers also have a few disadvantages. Natural fibers are sensitive to moisture present in the environment, which can impair the properties of materials fabricated by utilizing these biofibers.[22,23] In fact, the potential use of natural fibers as reinforcing materials in polymer matrices is greatly affected by their hydrophilic character, high capacity for moisture absorption, and poor adhesion between them and the matrix.[24,25]

In order to improve the existing properties of natural fibers, various surface chemical modifications such as change of functionality, inter- and intramolecular gelation, silanes treatment, mercerization, etherification, acetylation, and graft copolymerization have been used most frequently.[26,27] Chemical modifications may activate hydroxyl groups or introduce new moieties that can effectively interlock with the cellulose and induce required properties in the polymer. As a result, considerable effort is currently being directed toward improving the quality of the interfacial bonding between the polymer and fibers by surface modification of lignocellulosic fibers.

Among various types of natural fibrous materials, *Grewia optiva* fibers have high potential as a reinforcing material in polymer composites.[15–27] Though the Himalayan region is full of natural biomass, this precious wealth of nature has not been exploited for improved end products. The literature survey has revealed that not many studies have been made on incorporation of new functionalities onto the lignocellulosic *Grewia optiva* fiber. Traditionally, this fibrous material belonging to the Himalayan region is used by the local people for making low-cost articles like socks, boots, mats, ropes, and bags. It has been observed that these materials loose their strength when exposed to moisture or humidity. The work reported in the present communication is part of comprehensive research work initiated in our laboratory to effectively use eco-friendly biofibers in a number of applications. This study is concerned with the evaluation of the physicochemical, morphological, and thermal properties of silane-treated and untreated *Grewia optiva* fibers. Further polymer composites were fabricated using different dimensions of *Grewia optiva* fibers as reinforcing material and phenol-formaldehyde resin as novel polymer matrix.

EXPERIMENTAL SECTION

Materials and Methods

Reagent grade chemicals, namely sodium hydroxide (NaOH), ethanol, acetone, aminopropyl triethoxy silane, and phenol formaldehyde solution supplied by Qualigens Chemicals Ltd. Co., were used as received. *Grewia optiva* fibers were collected from local resources of the Himalayan region. In the present research work we have used the phenolic resin phenol-formaldehyde (PF) as novel polymer matrix resin.

Pretreatment of Lignocellulosic *Grewia optiva* Fibers

Lignocellulosic *Grewia optiva* 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. The dried fibers were designated as untreated fibers. These untreated fibers were subsequently subjected to extraction with acetone for 72 h in a 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 *Grewia optiva* Fibers

Generally, the first step in chemical treatment of natural fibers is the mercerization process (pretreatment process). Lignocellulosic *Grewia optiva* fibers were immersed in 2% NaOH solution for different time intervals (45–315 min) at room temperature for the optimization of time. The fibers were then taken out and thoroughly washed with doubled-distilled water for removal of any NaOH content. However, the final washing of these natural fibers was given 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 drier 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 *Grewia optiva* fibers was carried out with aminopropyl triethoxy silane. First, 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 *Grewia optiva* 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

Since surface modification of natural fibers affects the crystalline regions of cellulosic materials, it has an impact on many physical and chemical properties of fibers such as swelling, thermal behavior, moisture absorbance, water uptake, and chemical resistance. Silane-treated/untreated *Grewia optiva* fibers thus prepared were studied for the evolution of physical and chemical properties such as swelling behavior, moisture absorbance, water uptake, and chemical resistance.

Swelling Behavior in Different Solvents

Swelling behavior of the surface-modified and raw samples of *Grewia optiva* fibers was determined by treating with water, isobutanol, methanol, and carbon tetrachloride. Known initial weights W_i of the silanes-treated samples and raw sample were immersed in 100 mL of solvents at room temperature for 72 h. The samples were filtered and the excess solvent was removed with the help of filter paper, then the final weight W_f was determined 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 onto different natural fibers were carried out at various humidity levels (20–100). The silanes-treated and raw samples of *Grewia optiva* fibers were dried at 50°C in the oven until a constant weight was obtained. Moisture absorbance percentage was found by placing the known weight W_i of dry silanes-treated and raw samples in a humidity chamber (Swastika make), which was set at a particular humidity level for about 2 h, and then the final weights W_f of the samples exposed to 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.

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

Water Uptake Behavior

Small wicks of the silanes-treated and raw *Grewia optiva*, 7 mm in diameter, were prepared and a mark was drawn on each wick, which was then 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

To study chemical resistance, 100 mg of silanes-treated and raw *Grewia optiva* fibers were put in 100 mL of 1 N NaOH and 1 N HCl; losses in weight were studied at different time intervals (12–72 h), and the percent chemical resistance (P_{cr}) was calculated as per the method reported earlier:

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

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

Synthesis of Phenol-Formaldehyde Resin

Phenol-formaldehyde resin was synthesized by the standard method developed in our laboratory.[16,22,23] Suitable conditions of temperature, acidity of the medium, and pH were maintained while carrying out the reaction as reported earlier.[22,23] The resin synthesized was then transferred to a specially made mold. Resin sheets of size 150 × 150 × 5.0 mm were prepared by a closed-mold method described elsewhere.[19–23] The cured samples were then subjected to various mechanical, thermal, and morphological characterizations.

Preparation of Lignocellulosic Natural Fiber-Reinforced Polymer Composites

Grewia optiva fibers of different dimensions were mixed thoroughly with phenol-formaldehyde resin using a mechanical stirrer with suitable loadings (1.0:0.1) in terms of weight.[9] These fibers were used in three different forms:

1. Particle reinforcement: *Grewia optiva* fibers were ground to a powder and filtered through a sieve of pore size 200 microns.
2. Short-fiber reinforcement: *Grewia optiva* fibers chopped into 3 mm size were used as short fibers for the fabrication of polymer composites.

3. Long-fiber reinforcement: *Grewia optiva* fibers chopped into 6 mm size were used as long fibers for the fabrication of phenol-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 evenly on the surface of the mold. Composite sheets of the size 150 × 150 × 5.0 mm were prepared by the compression molding technique in a hot press using a mold preheated to 150°C. The material was first placed in a hot oven and left there for about 7 min, and then the mold was closed. Composite sheets were prepared by hot pressing the mold at 150°C for 30 min. The pressure applied ranged from 3 to 4 MPa depending on the reinforcing material.[22,23] All the specimens were then post-cured at 150°C for 12 h.

Mechanical Characterizations of Fiber-Reinforced Polymer Composites

Tensile Strength

The tensile strength test was conducted on Computerized Universal Testing Machine. Specimens of dimension 100 × 10 × 5 mm were used for the analysis. The tensile test was conducted in accordance with ASTM D 3039 method. The test was carried out at the constant strain rate of 10 mm/min. Force was applied until the failure of the sample and load-elongation curve was obtained.

Compressive Test

The compression test was conducted in accordance with ASTM D 3410 method. The test was carried out 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 carried out 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

Polymer composites are very sensitive to the environmental conditions because their physical, chemical, and mechanical properties are influenced by moisture content. The full potential of polymer resin composites can be realized in practical applications by studying their physical and chemical properties. Therefore, a study on swelling behavior in different solvents, moisture absorbance at different humidity levels, and chemical resistance behavior against 1 N HCl and 1 N NaOH of phenol-formaldehyde polymer resin matrix–based composites has been carried out.

Swelling Behavior

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

Moisture Absorbance

Moisture absorbance studies into different polymer composites samples were carried out at various humidity levels (varying from 20 to 100%), with each humidity level held 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 *Grewia optiva* Fibers and Respective Polymer Composites

Infrared Spectroscopy (IR)

IR spectra of the raw and surface-modified *Grewia optiva* 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 *Grewia optiva* fibers along with polymer resin matrix and composites were carried out on an Electron Microscopy Machine (LEO 435 VP). Since these materials are nonconducting, they were gold plated. Scanning was synchronized with a microscopic beam in order to maintain the 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 a good account of their thermal stability. Thermogravimetric 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°C/min.

RESULTS AND DISCUSSION

Optimization of Reaction Parameters for Surface Modifications of *Grewia optiva* Fibers

In carrying out the surface modifications of lignocellulosic natural fiber, various parameters play a key role. Among the most important variables, which affect the mercerization and silanes treatments, are the reaction parameters such as time interval for which the reaction is carried out, reaction time, and concentration of NaOH used for carrying out the mercerization. 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. In order to carry out the surface modification of *Grewia optiva* fibers through silanes treatment, extensive studies were performed to optimize these parameters.

Effect of Reaction Time

Reaction time very much affects the mercerization; it has been optimized by determining the maximum weight loss for *Grewia optiva* fiber. Percentage weight loss of *Grewia optiva* fibers as a function of time is presented in Table I.

Table I. Effect of reaction time on mercerization of *Grewia optiva* fibers

Sample no.	Time (min)	% Wt. loss
1	0	0
2	45	4.25
3	90	6.46
4	135	8.52
5	180	10.01
6	225	12.34
7	270	10.40
8	315	10.68
9	360	10.92

In the case of mercerization of *Grewia optiva* fibers, maximum mercerization was observed at the time of 225 min, as shown in Table I. The decrease in weight loss beyond optimum reaction time is due to the excessive deposition of sodium ions during surface modification and other side reactions, which may not favor further weight loss.

Evaluation of Physical and Chemical Properties of Silane-Treated *Grewia optiva* Fiber

Silane-treated and raw *Grewia optiva* fibers were tested for the evolution of physical and chemical properties such as swelling behavior, moisture absorbance behavior, water uptake, and chemical resistance.

Swelling Behavior Study on *Grewia optiva* Fibers

Swelling ability reflects the relationship between void structure in backbone polymer and size of solvent molecules both for protic and aprotic solvents.[21,26,27] It has been observed that after silane treatment, the swelling of raw fibers decreases. In the case of *Grewia optiva* fibers, it was observed that raw *Grewia optiva* fibers showed maximum swelling in water (84.28%), followed by swelling in methanol (61.00%), isobutanol (54.28%), and carbon tetrachloride (39.28%). However, silane-treated fibers showed lower swelling, as shown in Table II.

Further, it was observed that 6% mercerized silane-treated *Grewia optiva* fibers showed lower swelling followed by 8, 10, 4, and 2%. From the above discussion, it was observed that raw *Grewia optiva* fibers show maximum swelling in water compared to other solvents. This is due to greater affinity of water for hydroxyl groups present in natural fiber

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

Sample no.	% Mercerization	Water	Methanol	Isobutanol	Carbon tetrachloride
1	0	84.28	61.00	54.28	39.28
2	2	76.71	45.71	39.71	35.42
3	4	57.14	38.14	28.57	25.42
4	6	39.42	24.28	20.00	15.71
5	8	48.42	28.57	24.28	21.00
6	10	57.42	33.57	26.71	23.85

cellulose, resulting in more penetration of water into the matrix than other solvents. In the case of silane-treated fibers, it has been observed that swelling behavior varies as a function of percentage mercerization (Pm) and nature of solvent. In silane-treated fibers, water and alcohols do not interact to the same extent as with raw fibers due to blockade of active sites on natural fiber backbone by silane treatment, which causes change in the sorption behavior. In particular, for raw or treated fibers, the percentage of swelling has been found decreased from H_2O to methanol and then to isobutanol and carbon tetrachloride. 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 alkyl group.

Moisture Absorbance Study on *Grewia optiva* Fibers

Raw *Grewia optiva* fibers showed 1.40, 1.78, 2.73, 3.15, and 3.67% moisture absorbance at 20%, 40%, 60%, 80%, and 100% humidity levels, respectively. However, silane-treated fibers showed lower moisture absorption, as shown in Table III. Further, it was observed that 6% mercerized silane-treated *Grewia optiva* fibers showed lower moisture absorbance followed by 8, 10, 4, and 2%.

From the above data, it was observed that silane treatment onto raw *Grewia optiva* fibers has a great impact on the moisture absorbance behavior. There was a decrease in percent moisture absorbance (% M_{abs}) with an increase in silane treatment (% Mercerization), which is due to the fact that with increase in Pm, the sites for maximum moisture absorbance are blocked after incorporation of silane chains through surface modification by showing less affinity for moisture than the original fibers.

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

Sample no.	%Mercerization	Hum 20	40	60	80	100
1	0	1.40	1.78	2.73	3.15	3.67
2	2	1.17	1.67	2.56	3.02	3.46
3	4	0.96	1.59	2.43	2.78	3.25
4	6	0.73	1.27	2.17	2.37	2.77
5	8	0.79	1.38	2.29	2.49	2.98
6	10	0.87	1.45	2.35	2.67	3.15

Water Uptake Behavior of *Grewia optiva* Fibers

Raw *Grewia optiva* fibers showed water uptake of 5.75, 8.38, 15.25, 11.26, 13.52, and 16.25 cm at 12, 24, 36, 48, 60, and 72 h respectively. However, silane-treated fibers showed lower water uptake, as seen in Table IV. Further, it was observed that 6% mercerized silane-treated fibers showed lowest water uptake followed by 8, 10, 4, and 2%.

Chemical Resistance Behavior of *Grewia optiva* Fibers

Raw *Grewia optiva* fibers showed 15.00, 20.29, 27.37, 32.62, 38.73, and 43.52% weight loss in 1 N HCl and 21.00, 24.67, 32.72, 38.63, 47.94, and 51.72% weight loss in 1 N NaOH at 12, 24, 36, 48, 60, and 72 h respectively. However, silane-treated fibers showed lower weight loss, as seen in Table V,. Further, it was observed that 6% mercerized silane-treated fibers showed lowest weight loss followed by 8, 10, 4, and 2%.

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

Sample no.	% Mercerization	12 h	24 h	36 h	48 h	60 h	72 h
1	0	5.75	8.38	11.26	13.52	15.25	16.25
2	2	5.36	7.47	10.94	13.35	15.12	16.15
3	4	5.01	7.29	10.82	12.98	15.01	16.03
4	6	4.73	7.05	9.97	12.27	14.38	15.44
5	8	4.84	7.17	10.43	12.58	14.73	15.81
6	10	4.93	7.23	10.68	12.83	14.87	15.95

Table V. Effect of silane treatment on chemical resistance (in terms of % wt. loss) of *Grewia optiva* 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	15	20.29	27.37	32.62	38.73	43.52
2	2	13.78	19.81	25.48	31.93	37.62	42.17
3	4	13.35	19.69	24.05	31.36	37.02	41.42
4	6	11.57	17.53	22.51	29.57	35.61	39.62
5	8	11.95	18.21	23.07	30.05	35.99	40.52
6	10	12.64	18.86	23.47	30.48	36.58	40.95
(b) 1 N NaOH							
1	0	21	24.67	32.72	38.63	47.94	51.72
2	2	16.73	23.62	30.93	37.26	45.87	49.84
3	4	15.17	22.41	29.45	36.53	44.29	48.37
4	6	13.86	19.15	27.31	34.41	40.71	45.77
5	8	14.37	20.17	28.27	32.35	42.37	47.32
6	10	14.84	21.49	29.12	33.57	43.38	48.12

Analysis and Characterization of Raw and Surface-Modified Lignocellulosic Natural Fibers

Infrared Spectroscopy (IR)

IR spectra of raw *Grewia optiva* fiber showed a broad peak at 3420.8 cm^{-1} due to bonded OH groups and at 2923.7, 1460.3, and 1033.8 cm^{-1}due to $–CH_2$, C–C, and C–O stretching, respectively. In the case of grafted silane fibers, additional broad intense bands around 1227.0 and 1119.0 cm^{-1} were obtained due to the stretching of Si-O-cellulose and –Si–O–Si bonds, respectively.

Morphological Study

It was observed that silane treatment gave a surface coating to the fibers, and surface features of fibers are not clearly visible. Since these fibers exhibited micropores on their surface, the coupling agent penetrated into the pores and formed a mechanically interlocked coating on their surface. The scanning electron micrographs could easily verify the difference between raw cellulosic *Grewia optiva* fibers and surface-modified fibers (Figure 1).

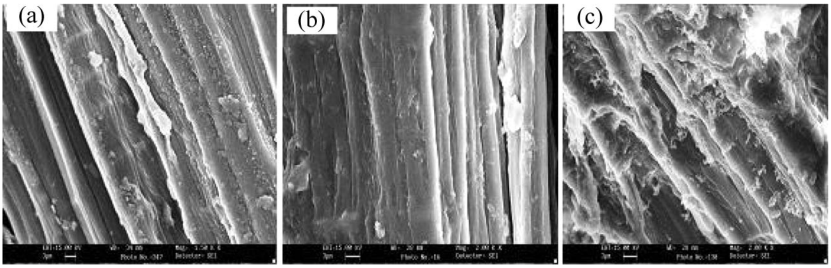


Figure 1. SEM of raw, mercerized, and silane-treated (a, b, and c) *Grewia optiva* fibers.

Thermal Analysis

In thermal analysis of *Grewia optiva* fibers, the initial decomposition temperature (IDT) was found to be 200°C (% wt. loss 7.25) and the final decomposition temperature (FDT) to be 501°C (% wt. loss 87.44). In the case of silane-treated fiber, the initial decomposition temperature (IDT) was found to be 199°C (% wt. loss 9.10) and the final decomposition temperature (FDT) to be 510°C (% wt. loss 60.57).

From the above discussion it is clear that silane treatment affects the properties of *Grewia optiva* fibers. Activation of lignocellulosic *Grewia optiva* fibers was carried by mercerizing these lignocellulosic fibres with different concentrations of NaOH for different intervals prior to carrying out surface modification through silane treatment so as to open the active sites of the cellulose backbone for surface treatment. 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.

Otherwise, without such activation only a small amount of surface modification occurred, which is due to the fact that natural fibers, being lignocellulosic, are highly hydrogen bonded polymer, and silane molecules are not in a position to penetrate beyond the surface of the cellulose substrate. In the present study, modification of the lignocellulosic fibers has been attempted by chemical modification through silane treatment for the fabrication of natural fiber-reinforced polymer composites. Coupling agents usually improve the degree of cross-linking in the interface region and offer a perfect bonding result. Alkoxy silanes are able to form bonds with hydroxyl groups. Coupling agents such as aminopropyl triethoxy silane were used in fiber treatment in order to improve the interface properties. Since natural fibers exhibited micropores on their 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 Phenol-Formaldehyde Resin for Fabrication of Polymer Composites

Optimization of phenol-formaldehyde resin was done by taking into account the mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance.[16,22,23] It has been observed that phenol-formaldehyde resin in the ratio 1:1.5 exhibits optimum mechanical properties, so this ratio was taken for further fabrication of polymer composites.

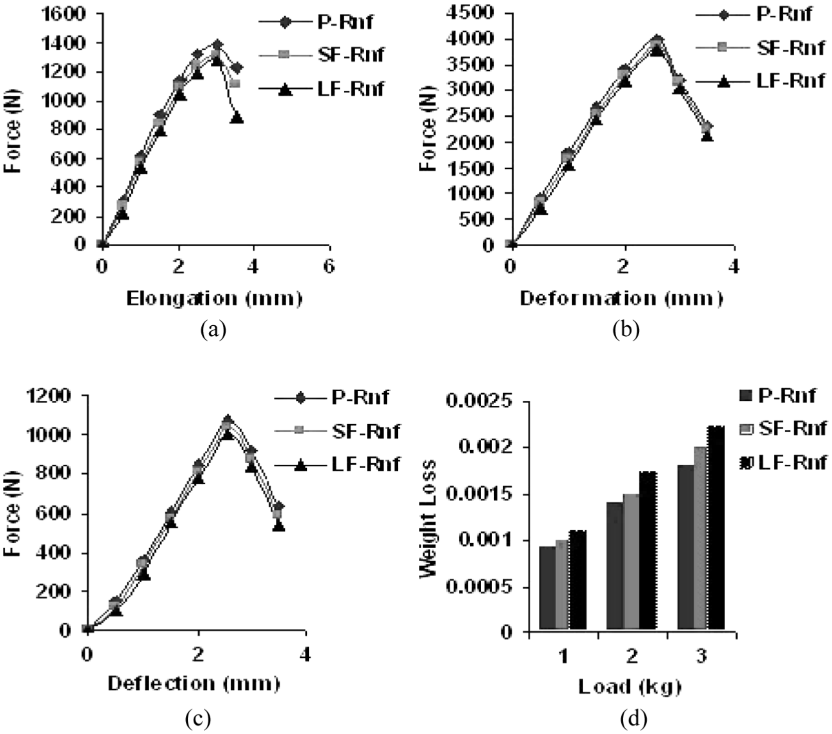
Mechanical Characterizations of Phenol-Formaldehyde Matrix-Based Composites

Tensile Strength Test

The tensile strength of polymer matrix was found to increase on reinforcement with lignocellulosic *Grewia optiva* fibers when used in particle, short-, and long-fiber reinforcements. In the tensile strength test, it was observed that *Grewia optiva* fiber-reinforced polymer composites with particle reinforcement showed the greatest tensile strength, followed by short-fiber and long-fiber-reinforced composites (Figure 2A). It is clear from Figure 2A that the samples of (i) particle-reinforced composite could bear a load of 1387.00 N at an extension of 2.8 mm, (ii) short-fiber-reinforced composite could bear a load of 1315.00 N at an extension of 2.91 mm, and (iii) long-fiber-reinforced composite could bear a load of 1275.00 N at an extension of 2.94 mm.

Compressive Strength Test

The effect of fiber dimension on compressive strength of phenol-formaldehyde resin matrix with raw *Grewia optiva* fibers was also studied and showed an increase of the mechanical performance for polymer



(a) (b)

(c) (d)

Figure 2. Load elongation/deformation/deflection and wear resistance curve of fiber-reinforced composites (a, b, c, and d).

composites containing reinforcing fibers in the particle, short-, and long-fiber reinforcements when compared with virgin matrix. The compressive properties of the *Grewia optiva* fibers reinforced *RF* composites as a function of load and deformation are presented in Figure 2B. In the compressive strength test: (i) particle-reinforced composite could bear a load of 3997.5 N with compression of 2.60 mm, (ii) short-fiber-reinforced composite could bear a load of 3867.50 N with compression of 2.64 mm, and (iii) long-fiber-reinforced composite could bear a load of 3775.50 N with compression of 2.67 mm (Figure 2B).

Flexural Strength Test

Analogous trends as obtained in tensile and compressive strength tests were also observed for flexural strength results. It was found that with particle reinforcement, flexural strength increases to a much greater extent than with short- and long-fiber reinforcement (Figure 2C). It is clear that the samples of (i) particle-reinforced composite could bear a load of 1071.47 N with deflection of 2.57 mm, (ii) short-fiber-reinforced composite could bear a load of 1039.00 N with deflection of 2.66 mm, and (iii) long-fiber reinforced composite could bear a load of 1000 N with deflection of 2.69 mm.

Wear Resistance Test

It is evident from Figure 2D that wear rate of PF matrix decreases appreciably when it is reinforced with *Grewia optiva* fibers. It was observed that particle reinforcement decreases with wear rate to a much greater extent than short- and long-fiber reinforcement.

Physicochemical Behavior of Polymer Composites and Chemical Resistance

Swelling Behavior

Grewia optiva fiber-reinforced polymer composites with different dimensions show different swelling behavior in different solvents (Table VI). It was observed that the swelling behavior of *Grewia optiva* fiber-reinforced phenol-formaldehyde composites in different solvents follows the trend: $H_2O > CH_3OH > C_4H_9OH > CCl_4$. The swelling behavior 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.

Moisture Absorbance Behavior

The moisture absorbance behavior at different humidity levels as a function of fiber length is depicted in Table VII. It was found that moisture absorbance (M_{abs}) increases with increase in humidity level ranging from 20 to 100% and with increase in fiber dimension (particle < short < long fiber).

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

Sample	Water	Methanol	Isobutanol	Carbon tetrachloride
PF resin	0.12	0.09	0.07	0.03
P-Rnf	3.17	3.05	2.93	2.85
SF-Rnf	3.32	3.12	3.07	3.01
LF-Rnf	3.45	3.26	3.21	3.11

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

	Hum				
% Loading	20	40	60	80	100
PF resin	0.00009	0.00018	0.00027	0.00043	0.00058
P-Rnf	0.00012	0.00025	0.00037	0.00054	0.00062
SF-Rnf	0.00018	0.00035	0.00043	0.00061	0.00068
LF-Rnf	0.00024	0.00042	0.00049	0.00067	0.00075

Chemical Resistance Behavior

In the case of chemical resistance behavior, it was observed that resistance towards chemicals decreases with the increase in percentage loading (Table VIII). This may be due to the increase in fiber content in the composite, which is vulnerable to the chemical attack, resulting in decreased resistance towards the chemicals.

Morphological Analysis of Polymer Biocomposites

Morphological investigations (Figure 3) clearly indicate that proper mixing of *Grewia optiva* fiber with the phenol-formaldehyde resin takes place in the biocomposites thus synthesized. These micrographs also show the distinction in the morphology of the polymer composites of different fiber dimensions and their parent polymer matrix (phenol-formaldehyde) (Figure 3).

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

% Loading	24 h	48 h	72 h	96 h	120 h	144 h
(a) 1 N HCl						
PF resin	1.09	2.13	3.09	4.23	4.68	5.04
P-Rnf	3.27	4.44	5.25	6.2	7.34	8.97
SF-Rnf	3.31	4.49	5.34	6.29	7.37	9.01
LF-Rnf	3.37	4.64	5.41	6.34	7.48	9.16
(b) 1 N NaOH						
PF resin	1.52	2.59	3.12	4.62	4.72	5.45
P-Rnf	3.58	4.69	5.41	6.59	7.62	9.2
SF-Rnf	3.61	4.74	5.49	6.68	7.67	9.21
LF-Rnf	3.89	5.09	5.78	7.05	8.04	9.54

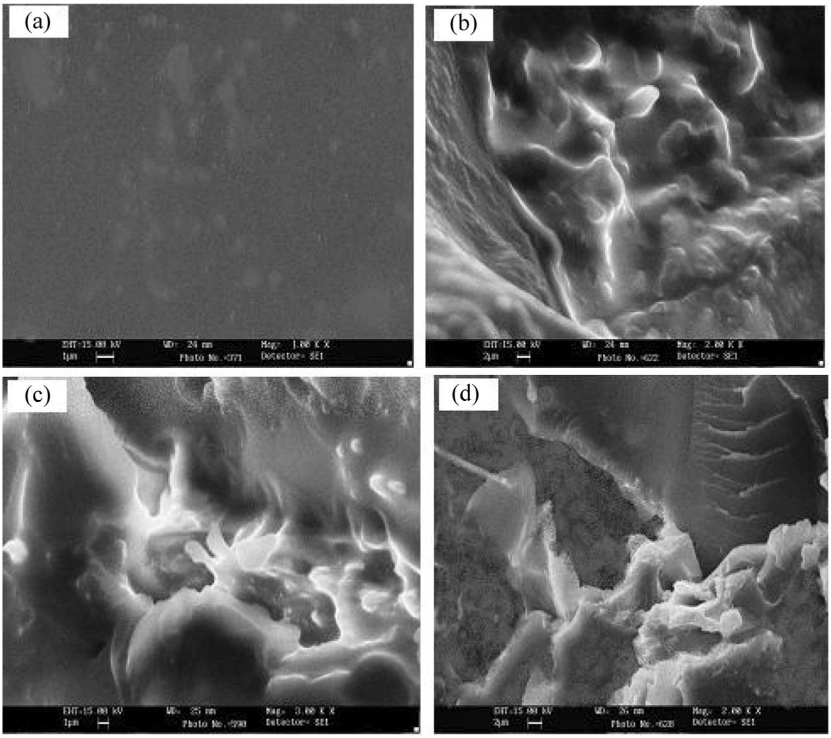


Figure 3. SEM images of (a) phenol-formaldehyde resin composite with particle, short-, and long-fiber reinforcements (b, c, and d).

CONCLUSION

It was found that surface modification of *Grewia optiva* fibers through silane treatment helps in improving the properties of the natural fiber. The properties like moisture absorbance, chemical resistance, swelling behavior, and water uptake vary directly with the silane treatment. Morphological and thermal studies have revealed that the texture of fiber changes with the coating of silane on *Grewia optiva* fibers. Further 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; excellent results are obtained when the *Grewia optiva* fibers used were in the particle form. The results of swelling, moisture, and chemical resistance behavior of composites show that the composites are sensitive to swelling, moisture absorption, and with reduced chemical resistance due to the hydrophilic behavior of the lignocellulosic fiber. In spite of these limitations, *Grewia optiva* fibers can be a suitable alternative to toxic synthetic fibers. In a further communication, the effect of silane treatment on mechanical properties will be reported.

REFERENCES

[1] Hasipoglu, H. N., E. Yilmaz, O. Yilmaz, and H. Caner. (2005). Preparation and characterization of maleic acid grafted chitosan. *Int. J. Polym. Anal. Charact.* **10**(5), 313–327.

[2] Lee, K. E., B. T. Poh, N. Morad, and T. T. Teng. (2008). Synthesis and characterization of hydrophobically modified cationic acrylamide copolymer. *Int. J. Polym. Anal. Charact.* **13**(2), 95–107.

[3] Fan, P., W. Xu, C. Lu, H. Zou, and B. Wang. (2006). Improving the compatibility of polycarbonate/UHMWPE blends through gamma-ray irradiation. *Int. J. Polym. Anal. Charact.* **11**(6), 429–440.

[4] Kaushik, A., and P. Singh. (2005). Synthesis and characterization of castor oil/trimethylol propane polyol as raw materials for polyurethanes using time-of-flight mass spectroscopy. *Int. J. Polym. Anal. Charact.* **10**(5), 373–386.

[5] Anbarasan, R., G. P. Kalaignan, T. Vasudevan, and A. Gopalan. (1999). Characterization of chemical grafting of polyaniline onto wool fiber. *Int. J. Polym. Anal. Charact.* **5**(3), 247–256.

[6] Geng, Z. C., J. X. Sun, S. F. Liang, F. Y. Zhang, Y. Y. Zhang, F. Xu, and R. C. Sun. (2006). Characterization of water- and alkali-soluble hemicellulosic polymers from sugarcane bagasse. *Int. J. Polym. Anal. Charact.* **11**(3), 209–226.

[7] Sun, X.-F., R. C. Sun, P. Fowler, and M. S. Baird. (2004). Physicochemical characterization of lignin isolated with high yield and purity from wheat straw. *Int. J. Polym. Anal. Charact.* **9**(5), 317–337.

[8] Singha, A. S., A. Shama, and V. K. Thakur. (2008). X-ray diffraction, morphological and thermal studies on methylmethacrylate graft copolymerized *Saccharum cilliari* fiber. *Int. J. Polym. Anal. Charact.* **13**, 447–462.

[9] Singha, A. S., and V. K. Thakur. (2008). Mechanical properties of natural fiber reinforced polymer composites. *Bull. Mater. Sci.* **31**(5), 791–799.

[10] Chauhan, G. S., I. Kaur, B. N. Misra, A. S. Singha, and B. S. Kaith. (2000). Evaluation of optimum grafting parameters and the effect of ceric ion initiated grafting of methyl methacrylate onto jute fiber on the kinetics of thermal degradation and swelling behaviour. *Polym. Degradation Stab.* **69**, 261–265.

[11] Nacher, L. S., J. E. C. Amoros, M. D. S. Moya, and J. L. Martinez. (2007). Mechanical properties of polyester resins in saline water environments. *Int. J. Polym. Anal. Charact.* **12**(5), 373–390.

[12] Yarysheva, L. M., O. V. Arzhakova, A. A. Dolgova, A. L. Volynskii, E. G. Rukhlya, and N. F. Bakeev. (2007). Structure of polymer blends based on solvent-crazed polymers. *Int. J. Polym. Anal. Charact.* **12**(1), 65–75.

[13] Hassan, M. M., M. R. Islam, and M. A. Khan. (2005). Influence of additives on the performance of photografted jute yarn with 3-(trimethoxysilyl) propylmethacrylate. *Int. J. Polym. Anal. Charact.* **10**(3), 179–194.

[14] Kaith, B. S., and S. Kalia. (2007). Synthesis and characterization of graft co-polymers of flax fiber with binary vinyl monomers. *Int. J. Polym. Anal. Charact.* **12**(5), 401–412.

[15] Singha, A. S., and V. K. Thakur. (2008). Synthesis and characterization of S. cilliare fiber reinforced green composites. *Int. J. Plast. Technol.* **11**, 835–851.

[16] Singha, A. S., and V. K. Thakur. (In press). Synthesis, characterization and study of pine needles reinforced polymer matrix based composites. *J. Reinf. Plast. Compos.*

[17] Singha, A. S., and V. K. Thakur. (2008). Evaluation of mechanical properties of natural fiber reinforced polymer composites. *Int. J. Plast. Technol.* **12**, 913–923.

[18] Singha, A. S., and V. K. Thakur. (2009). Mechanical, morphological and thermal properties of pine needles reinforced polymer composites. *Int. J. Polym. Mater.* **58**(1), 21–31.

[19] Singha, A. S., and V. K. Thakur. (2009). Mechanical, thermal and morphological properties of G. optiva fiber/polymer matrix composites. *Polym. Plast. Technol. Eng.* **48**(2), 201–208.

[20] Singha, A. S., and V. K. Thakur. (2008). Saccaharum cilliare fiber reinforced polymer composites. *E-Journal Chem.* **5**(4), 1055–1062.

[21] Singha, A. S., and V. K. Thakur. (In press). Synthesis and characterization of short Grewia optiva fiber based polymer composites. *Polym. Compos.*

[22] Singha, A. S., and V. K. Thakur. (2008). Fabrication and study of lignocellulosic Hibiscus sabdariffa fiber reinfirced polymer composites. *Bioresource* **3**(4), 1173–1186.

[23] Singha, A. S., and V. K. Thakur. (2008). Synthesis and characterization of Grewia optiva fiber reinforced PF matrix based polymer composites. *Int. J. Polym. Mater.* **57**(12), 1059–1074.

[24] Sahoo, P. K., R. Mohapatra, A. Sahoo, N. DebSarkar, and S. K. Swain. (2005). Characterization, biodegradation, and water absorbency of chemically modified tossa variety jute fiber via pulping and grafting with acrylamide. *Int. J. Polym. Anal. Charact.* **10**(3), 153–167.

[25] Singha, A. S. and V. K. Thakur. (2008). Fabrication of Hibiscus sabdariffa fiber reinforced polymer composites. *Iran. Polym. J.* **17**(7), 782–791.

[26] Singha, A. S., A. Shama, and V. K. Thakur. (2008). Pressure induced graft co-polymerization of acrylonitrile onto Saccharum cilliare fiber and evaluation of some properties of grafted fibers. *Bull. Mater. Sci.* **31**(1), 7–13.

[27] Singha, A. S., and V. K. Thakur. (2009). Morphological, thermal and physico-chemical characterizations of surface modified pinus fibers. *Int. J. Polym. Anal. Charact.* **14**(3), 271–289.