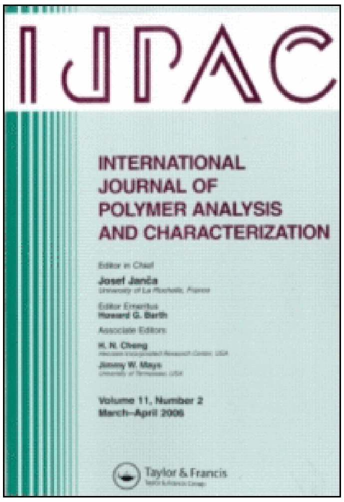


**International Journal of Polymer Analysis and Characterization**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

# Silane Functionalization of *Saccaharum cilliare* Fibers: Thermal, Morphological, and Physicochemical Study

Vijay Kumar Thakur[ab]; Amar Singh Singha[c]; Inderjeet Kaur[d]; Ramkumar Pudukotai Nagarajarao[e]; Yang Liping[ab]
[a] Temasek Laboratories, Nanyang Technological University, Singapore [b] School of Materials Science and Engineering, Nanyang Technological University, Singapore [c] Department of Chemistry, National Institute of Technology, Hamirpur, India [d] Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla, India [e] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

**To cite this Article** Thakur, Vijay Kumar , Singha, Amar Singh , Kaur, Inderjeet , Nagarajarao, Ramkumar Pudukotai and Liping, Yang(2010) 'Silane Functionalization of *Saccaharum cilliare* Fibers: Thermal, Morphological, and Physicochemical Study', International Journal of Polymer Analysis and Characterization, 15: 7, 397 — 414

**To link to this Article: DOI:** 10.1080/1023666X.2010.510106

**URL:** http://dx.doi.org/10.1080/1023666X.2010.510106

*International Journal of Polymer Anal. Charact*, 15: 397–414, 2010

ISSN: 1023-666X print
DOI: 10.1080/1023666X.2010.510106

# SILANE FUNCTIONALIZATION OF *Saccaharum cilliare* FIBERS: THERMAL, MORPHOLOGICAL, AND PHYSICOCHEMICAL STUDY

**Vijay Kumar Thakur,[1,2] Amar Singh Singha,[3] Inderjeet Kaur,[4] Ramkumar Pudukotai Nagarajarao,[5] and Yang Liping[1,2]**
[1]*Temasek Laboratories, Nanyang Technological University, Singapore*
[2]*School of Materials Science and Engineering, Nanyang Technological University, Singapore*
[3]*Department of Chemistry, National Institute of Technology, Hamirpur, India*
[4]*Department of Chemistry, Himachal Pradesh University, Summer Hill, Shimla, India*
[5]*School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore*

***Lignocellulosic natural fibers are promising materials for use as reinforcement in composites for a wide variety of polymers. Silane treatment through aminopropyl triethoxy silane as a simple and convenient method for surface modification of*** **Saccaharum cilliare** ***fibers is introduced in this article. The surfaces of lignocellulosic fibers have been treated with silane coupling agent for evaluating the physicochemical properties. Scanning electron microscopy (SEM), Fourier transform-infrared spectrophotometry (FT-IR), thermogravimetric/differential thermal/derivative thermogravimetry (TGA/DTA/DTG), absorption in different solvents, moisture absorbance, water uptake, and chemical resistance measurements were used as characterization techniques for evaluating the nature of these surface-modified lignocellulosic natural fibers. Additionally, polymer composites were prepared using*** **Saccaharum cilliare** ***fibers as reinforcement and phenol-formaldehyde as novel polymer matrix resin. Effect of fiber dimension on mechanical properties of polymer matrix resin such as tensile strength, compressive strength, flexural strength, and wear resistance properties was evaluated. Polymer composites prepared were also subjected to evaluation of morphological and physicochemical properties.***

***Keywords***: Mechanical, morphological, and physicochemical characterizations; Silane treatment

## INTRODUCTION

The development of polymeric materials from lignocellulosic renewable raw fibrous resources has increased significantly during the past few years.[1,2] Natural fiber–based lignocellulosic materials are considered the materials of the present age because of the advantages these natural fibers offer over synthetic fibers.[3–5]

Submitted 18 January 2010; accepted 11 June 2010.

Correspondence: Amar Singh Singha, Department of Chemistry, National Institute of Technology, Hamirpur – 177005 HP, India. E-mail: assingha@gmail.com

In an attempt to reduce the final cost of products and to incorporate particular properties, toxic synthetic fibers have been largely used as reinforcing materials in polymer matrices. But these synthetic fibers have a number of disadvantages, especially regarding to the environment.[6,7] Further, synthetic fibers can cause health problems and are on the whole difficult to utilize since polymer materials with high synthetic fiber content have low energy values and high ash content.

Lignocellulosic natural fibers obtained from renewable resources offer a number of advantages over traditional synthetic fibers.[8,9] It has been observed that properties such as renewability, nonabrasiveness, acceptable specific strength properties, ease of separation, enhanced energy recovery, biodegradability, high filling effect, light weight, easy availability, noncorrosive nature, high toughness, low cost, good thermal properties, reduced tool wear, and reduced dermal and respiratory irritation provide an attractive ecofriendly quality to the resulting materials composed of natural fibers.[10–12] Keeping in view the ecofriendly advantages of green polymeric materials, a large number of industries throughout the world are initiating the design and engineering of these products.[13–15]

Efforts have been made by various researchers to substitute synthetic fibers with biodegradable natural fibers to effectively use these natural fibers in a number of applications, especially in polymer composite materials.[16,17] Natural fiber–reinforced polymers offer significant advantages over other conventional materials when specific properties are compared.[18–23] These polymer composites have different applications in diverse fields, ranging from appliances to spacecrafts. Natural fibers such as *Saccaharum cilliare*, *Hibiscus sabdariffa*, flax, jute, pinus, and oil palm fibers have proven to be good reinforcements in polymer matrices.[24–26] Natural fibers are greatly affected by environmental conditions. These natural fibers are susceptible to moisture present in the environment, which affects the properties of materials composed of these fibers, and have lower mechanical properties than synthetic fibers. To improve the existing properties of natural fibers, various surface chemical modifications such as silanes treatment, mercerization, etherification, acetylation, and graft copolymerization have been used most frequently.[27,28] Among various types of biofibrous materials, *Saccaharum cilliare* fibers are abundantly found in Himachal Pradesh and have high potential as a renewable fabric in various applications, especially in polymer composites. Even though a large number of research papers have been published on various natural fibers and their composites, an effort has been made in the present work to introduce a new natural fiber, *Saccaharum cilliare*, as one of the grass fibers and its use as reinforcement in the development of new eco-friendly materials.

## EXPERIMENTAL SECTION

### Materials and Methods

Reagent grade chemicals namely sodium hydroxide (NaOH), ethanol, acetone, aminopropyl triethoxy silane, phenol, and formaldehyde solution supplied by Qualigens Chemicals Ltd. Co. were used as received. *Saccaharum cilliare* fibers were collected from local resources of the Himalayan region. For the preparation of polymer composites in the present research work, phenolic resin such as phenol-formaldehyde (PF) has been used as novel polymer matrix resin.

## Instruments Used

Weights of the samples were taken on a Shimadzu electronic balance (Libror AEG-220), thermal studies were carried out on thermal analyzer (PerkinElmer), and SEM micrographs were taken on a LEO 435VP scanning electron microscope. IR spectra of raw and surface-modified *Saccaharum cilliare* fibers were taken with KBr pellets on a PerkinElmer RXI Fourier transform-infrared spectrophotometer. Moisture absorbance study was carried out on Swastika humidity chamber. Curing of polymer resin and composite samples was done on a Santech India Ltd compression molding machine. Tensile, compressive, and flexural strength tests were performed on a Hounsfield H25KS computerized universal testing machine. Wear test was performed on a Ducom TR 20 L Wear and Friction Monitor.

## Pretreatment of Lignocellulosic *Saccaharum cilliare* Fibers

Lignocellulosic *Saccaharum cilliare* fibers were purified through Soxhlet extraction in acetone for 72 h by standard method described elsewhere.[14,15]

## Mercerization of *Saccaharum cilliare* Fibers

Lignocellulosic *Saccaharum cilliare* 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 thoroughly washed and dried in an oven at 70°C to a constant weight as per standard method.[11,14] 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 *Saccaharum cilliare* fibers was carried out with aminopropyl triethoxy silane. First, 2% of the silane solution was prepared by mixing aminopropyl triethoxy silanes 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 *Saccaharum cilliare* 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 affects many physical and chemical properties of fibers such as absorption, thermal behavior, moisture absorbance, water uptake, and chemical resistance.[11,14,15] Silane-treated/untreated *Saccaharum cilliare* fibers thus prepared were subjected to evaluation of physical and chemical properties such as absorption behavior, moisture absorbance behavior, water uptake, and chemical resistance.

**Absorption behavior in different solvents.** Absorption behavior of the surface-modified and raw samples of *Saccaharum cilliare* fibers was determined by treatment with water, isobutanol, carbon tetrachloride, and methanol as per standard method.[14,15] The percent absorption was calculated from the increase in initial weight in the following manner:

$$\text{Percent absorption } (Pabs) = \frac{W_f - W_i}{W_i} \times 100$$

**Moisture absorbance study at different relative humidities.** Moisture absorbance studies onto different natural fibers were carried out at various humidity levels (20–90) as per standard method.[14,15] The percent moisture absorbance was calculated from the increase in initial weight in the following manner:

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

**Chemical resistance in 1 N NaOH and 1 N HCl.** The percent chemical resistance ($P_{cr}$) behavior was calculated as per the method reported earlier [14,15]:

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

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

**Water uptake behavior.** The water uptake behavior was studied at different time intervals (12–72 h) as per standard method.[14,15]

## Fabrication of Polymer Composites

For the fabrication of polymer composites, phenol-formaldehyde polymer resin matrix was synthesized by the modified standard method developed in our laboratory by taking phenol and formaldehyde 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) in the reaction kettle.[24] *Saccaharum cilliare* fibers of different dimensions were mixed thoroughly with phenol-formaldehyde resin using a mechanical stirrer with suitable loading (1.0:0.1) in terms of weight.[8,9,11,27] These fibers were used in three different forms (particle, short, and long fiber reinforcement) for the fabrication of phenol-formaldehyde matrix–based polymer composites.[11] Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by the compression molding technique.

## Mechanical Characterizations

The tensile, compressive, flexural, and wear tests were conducted at ambient laboratory conditions in accordance with ASTM D 3039, ASTM D 3410, ASTM D 790, and ASTM D 3702 methods respectively.[8,9]

### Physicochemical Properties of Fiber-Reinforced Polymer Composites

A literature survey shows that natural fiber–reinforced polymer composites are sensitive to moisture absorption and water absorption. Particularly, in studying the development of natural fiber–reinforced polymer resin matrix–based composite, interest lies in its behavior against weathering conditions. Therefore, a comprehensive study on phenol-formaldehyde polymer resin matrix–based composites has been carried out by analyzing their absorption behavior in different solvents, moisture absorbance behavior at different humidity levels, and chemical resistance behavior against HCl and NaOH solutions of one normal (1 N) concentration as per standard method.[14,15]

### Characterization of Raw/Surface-Modified *Saccaharum cilliare* Fibers and Respective Polymer Composites

**Infrared spectroscopy (IR).** IR spectra of the raw and surface-modified *Saccaharum cilliare* fibers were taken with KBr pellets on PerkinElmer RXI Spectrophotometer.

**Scanning electron microscopy (SEM).** Scanning electron microscopic (SEM) studies of raw/surface-modified *Saccaharum cilliare* fibers along with polymer resin matrix and composites were carried out on a LEO 435 VP electron microscopy machine.

**Thermal analysis.** Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and derivative thermogravimetric (DTG) studies of various samples were carried out in nitrogen atmosphere on a thermal analyzer (PerkinElmer) at a heating rate of 10°C/min.

## RESULTS AND DISCUSSION

### Reaction Parameters for Surface Modifications of *Saccaharum cilliare* Fibers

The availability of the number of active sites on the polymer backbone of natural fibers affects the extent of surface modifications such as grafting, mercerization, and silane treatment. The most important variables that affect mercerization and silane treatments are reaction parameters like reaction time and concentration of NaOH. Extensive studies were made to optimize these parameters for further carrying out the silane treatment of *Saccaharum cilliare* fibers for application in various fields.

### Effect of Reaction Time

Reaction time has been optimized by determining the maximum weight loss for *Saccaharum cilliare* fiber. Percentage weight loss of *Saccaharum cilliare* fibers as a function of time is presented in Table I. In the case of mercerization of *Saccaharum cilliare* fibers, maximum mercerization was observed at time 270 min, as shown in Table I. The decrease in weight loss beyond optimum reaction time is due to the excessive deposition of sodium ions over the surface and other side reactions, which may not favor further weight loss.

**Table I.** Effect of reaction time on mercerization of *Saccaharum cilliare* fibers

| Sr. no. | Time (min.) | % Wt. loss |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 45 | 10.51 |
| 3 | 90 | 15.34 |
| 4 | 135 | 17.12 |
| 5 | 180 | 20.20 |
| 6 | 225 | 21.37 |
| 7 | 270 | 24.46 |
| 8 | 315 | 22.63 |
| 9 | 360 | 22.89 |

## Evaluation of Physical and Chemical Properties of Surface-Modified Fibers

**Absorption behavior study on *Saccaharum cilliare* fibers.** The ability to absorb any solvent depends on the relationship between the void structure in backbone polymer and the size of solvent molecules both for protic and aprotic solvents. It has been observed that after silane treatment, the absorption capacity of raw fibers decreases. In the case of *Saccaharum cilliare* fibers, it has been observed that raw fibers showed maximum absorption in water (154.00%), followed by absorption in methanol (125.84%), isobutanol (114.72%), and carbon tetrachloride (97.29%). However, silane-treated fibers showed lower absorption, as seen in Table II. Further, it has been observed that 8% mercerized silane-treated *Saccaharum cilliare* showed lower absorption, followed by 10%, 12%, 6%, 4%, and 2%, as shown in Table II. The increase in percent absorption for 10% and 12% mercerized silane fibers beyond the optimum reaction time may be due to the excessive deposition of sodium ions over the fiber surface and other side reactions, which may not favor further weight loss, and hence there could not be effective grafting of silane molecules on the cellulosic fibers. However, the exact mechanism behind this behavior is still under investigation.

From the above discussion, it has been observed that raw *Saccaharum cilliare* fibers show maximum absorption in water compared to other solvents. This is due to greater affinity of water for hydroxyl groups present in natural fiber cellulose, resulting in more penetration of water into the matrix than the other solvents. In the case

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

| Sr. no. | % Mercerization | Water | Methanol | Isobutanol | Carbon tetrachloride |
|---|---|---|---|---|---|
| 1 | 0 | 154.00 | 125.84 | 114.72 | 97.29 |
| 2 | 2 | 120.14 | 97.38 | 89.39 | 74.2 |
| 3 | 4 | 112.42 | 90.75 | 79.48 | 63.38 |
| 4 | 6 | 95.85 | 77.28 | 67.28 | 49.28 |
| 5 | 8 | 70.14 | 52.47 | 40.14 | 29.15 |
| 6 | 10 | 78.85 | 62.94 | 50.12 | 35.28 |
| 7 | 12 | 83.85 | 69.37 | 61.28 | 42.41 |

of silane-treated fibers, it has been observed that absorption behavior varies as a function of percentage mercerization (Pm) and nature of the solvent. In silane-treated fibers, water and alcohol 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 raw or treated fibers, the percentage of absorption 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 the alkyl group.

**Moisture absorbance study on *Saccaharum cilliare* fibers.** Raw *Saccaharum cilliare* showed 1.89%, 2.23%, 3.05%, 3.61%, and 4.04% moisture absorbance at 20%, 40%, 60%, 80%, and 90% humidity levels respectively. However, silane-treated fibers showed lower moisture absorption, as seen in Table III. Further, it has been observed that 8% mercerized silane-treated fibers showed lower moisture absorbance followed by 10%, 12%, 6%, 4%, and 2%. These results can also be explained on the same basis as discussed above.

From the above data, it has been observed that silane treatment onto raw *Saccaharum cilliare* fibers have a great impact on the moisture absorbance behavior. There was a decrease in percent moisture absorbance (% Mabs.) with 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 as than the original fibers.

**Water uptake behavior of *Saccaharum cilliare* fibers.** Raw *Saccaharum cilliare* fibers showed water uptake of 9.21, 11.79, 13.12, 15.89, 17.19, and 18.57 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 has been observed that 8% mercerized silane-treated fibers showed lower moisture absorbance, followed by 10%, 12%, 8%, 6%, 4%, and 2%.

**Chemical resistance behavior of *Saccaharum cilliare* fibers.** Raw *Saccaharum cilliare* fibers showed 32.86%, 37.85%, 45.76%, 49.85%, 54.14%, and 57.62% weight loss in 1 N HCl and 42.89%, 49.63%, 55.32%, 59.89%, 62.35%, and 66.78% weight loss in 1 N NaOH at 12, 24, 36, 48, 60, and 72 respectively. However,

**Table III.** Effect of silane treatment on percent moisture absorption behavior of *Saccaharum cilliare* at different relative humidity levels

| Sr. no. | % Mercerization | Hum = 20 | Hum = 40 | Hum = 60 | Hum = 80 | Hum = 90 |
|---|---|---|---|---|---|---|
| 1 | 0 | 1.89 | 2.23 | 3.05 | 3.61 | 3.94 |
| 2 | 2 | 1.57 | 1.91 | 2.87 | 3.32 | 3.71 |
| 3 | 4 | 1.51 | 1.74 | 2.31 | 3.22 | 3.59 |
| 4 | 6 | 1.42 | 1.69 | 2.18 | 3.09 | 3.51 |
| 5 | 8 | 1.27 | 1.56 | 2.05 | 2.87 | 3.38 |
| 6 | 10 | 1.31 | 1.61 | 2.09 | 2.93 | 3.41 |
| 7 | 12 | 1.35 | 1.64 | 2.11 | 2.99 | 3.46 |

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

| Sr. no. | % Mercerization | 12 h | 24 h | 36 h | 48 h | 60 h | 72 h |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 9.21 | 11.79 | 13.12 | 15.89 | 17.19 | 18.57 |
| 2 | 2 | 8.83 | 11.41 | 12.83 | 15.45 | 16.95 | 18.21 |
| 3 | 4 | 8.71 | 11.23 | 12.74 | 15.31 | 16.67 | 18.13 |
| 4 | 6 | 8.58 | 11.15 | 12.69 | 15.19 | 16.53 | 17.87 |
| 5 | 8 | 8.15 | 10.75 | 12.05 | 15.02 | 16.15 | 17.25 |
| 6 | 10 | 8.39 | 10.89 | 12.12 | 14.72 | 16.27 | 17.32 |
| 7 | 12 | 8.47 | 11.03 | 12.25 | 14.85 | 16.38 | 17.59 |

silane-treated fibers showed lower weight loss, as seen in Table V. Further, it has been observed that 8% mercerized silane-treated fibers showed lowest weight loss followed by 12%, 10%, 8%, 6%, 4%, and 2%.

## Characterization of Raw and Surface-Modified Natural Fibers

**Infrared spectroscopy (IR).** The IR spectra of raw *Saccaharum cilliare* fiber showed a broad peak at 3361.3 cm$^{-1}$ due to bonded OH groups and at 2921.9, 1428.7, and 1056.6 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 1230.7 and 1120.2 cm$^{-1}$ were obtained due to the stretching of Si-O-cellulose and –Si-O-Si bonds, respectively.

**Morphological study.** It has been observed that silane treatment gave surface coating to the fibers and surface features of fibers that are not clearly visible. Since these fibers exhibited micro pores 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 *Saccaharum cilliare* fibers and surface-modified fibers (Figure 1).

**Thermal analysis.** In thermal analysis of raw *Saccaharum cilliare* fibers (Figure 2), the initial decomposition temperature (IDT) has been found to be 214°C (wt.% loss 13.45) and the final decomposition temperature (FDT) to be 473°C (wt.% loss 66.34). In the case of silane-treated fibers (Figure 3), the initial decomposition temperature (IDT) has been found to be 217°C (wt.% loss 17.58)

**Table V(a).** Effect of silane treatment on chemical resistance (in terms of % wt. loss) of *Saccaharum cilliare* fibers at different time intervals against 1 N HCl

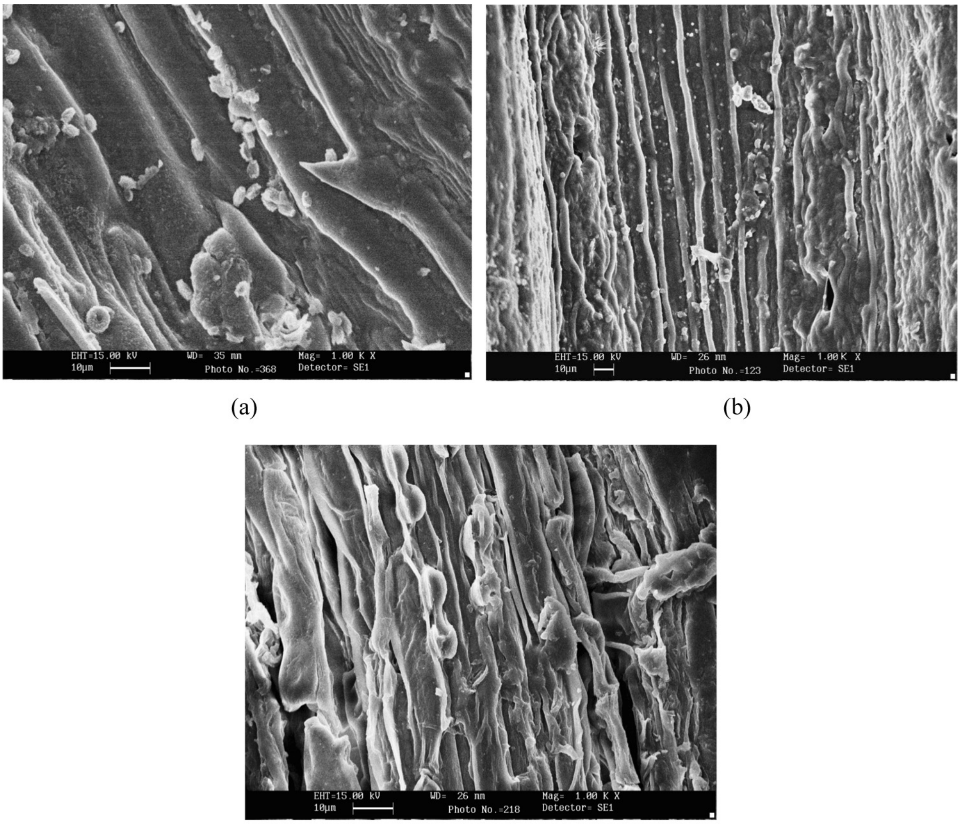
| Sr. no. | % Mercerization | 12 h | 24 h | 36 h | 48 h | 60 h | 72 h |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 32.86 | 37.85 | 45.76 | 49.85 | 54.14 | 57.62 |
| 2 | 2 | 31.53 | 36.87 | 44.24 | 48.32 | 53.05 | 56.25 |
| 3 | 4 | 30.73 | 35.74 | 43.56 | 47.36 | 52.12 | 55.34 |
| 4 | 6 | 29.76 | 34.22 | 41.63 | 45.49 | 51.34 | 55.84 |
| 5 | 8 | 26.84 | 31.67 | 38.85 | 42.52 | 48.43 | 52.72 |
| 6 | 10 | 28.13 | 32.94 | 39.46 | 43.14 | 49.63 | 53.25 |
| 7 | 12 | 29.23 | 33.73 | 40.42 | 44.95 | 50.35 | 54.42 |

**Table V(b).** Effect of silane treatment on chemical resistance (in terms of % wt. loss) of *Saccaharum cilliare* fibers at different time intervals against 1 N NaOH

| Sr. no. | % Mercerization | 12 h | 24 h | 36 h | 48 h | 60 h | 72 h |
|---|---|---|---|---|---|---|---|
| 1 | 0 | 42.89 | 49.63 | 55.32 | 59.89 | 62.35 | 66.78 |
| 2 | 2 | 41.53 | 48.85 | 54.73 | 58.85 | 61.78 | 65.59 |
| 3 | 4 | 40.34 | 47.45 | 54.11 | 57.45 | 60.53 | 64.37 |
| 4 | 6 | 39.62 | 46.93 | 53.63 | 56.15 | 59.83 | 63.47 |
| 5 | 8 | 36.34 | 44.35 | 50.34 | 53.64 | 57.13 | 60.96 |
| 6 | 10 | 37.85 | 45.48 | 51.15 | 54.89 | 58.35 | 61.93 |
| 7 | 12 | 38.95 | 46.41 | 52.73 | 55.78 | 59.01 | 62.95 |

and the final decomposition temperature (FDT) to be 497°C (wt.% loss 60.46). These results are further supported by DTA and DTG analysis.

From the above discussion it is clear that silane treatment affects the physical and chemical properties of *Saccaharum cilliare* fibers. Activation of lignocellulosic



(a) (b)

(c)

**Figure 1.** (a) SEM of raw *Saccaharum cilliare* fiber; (b) SEM of mercerized *Saccaharum cilliare* fiber; and (c) SEM of silane-treated *Saccaharum cilliare* fiber.

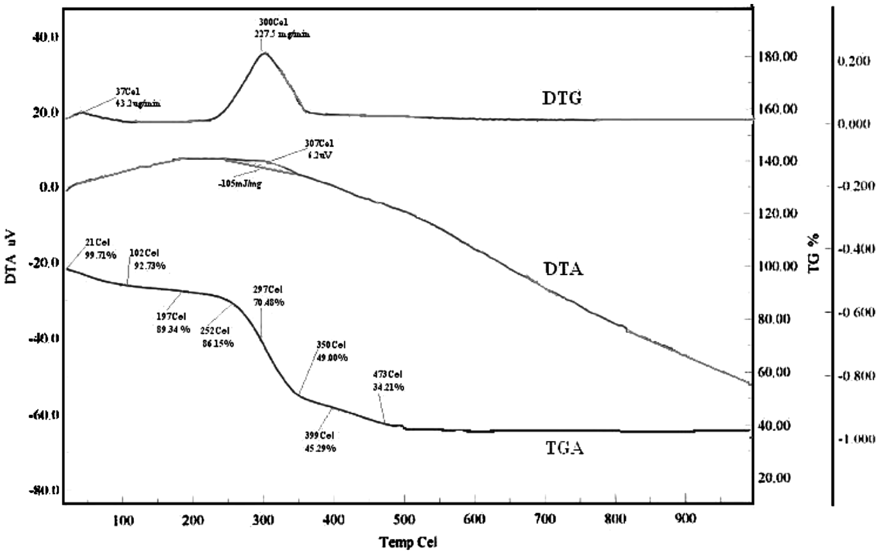


Figure 2. TGA/DTA/DTG analysis of raw *Saccaharum cilliare* fiber.

*Saccaharum cilliare* fibers has been carried out by mercerizing these lignocellulosic fibers with different concentrations of NaOH for different intervals prior to 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

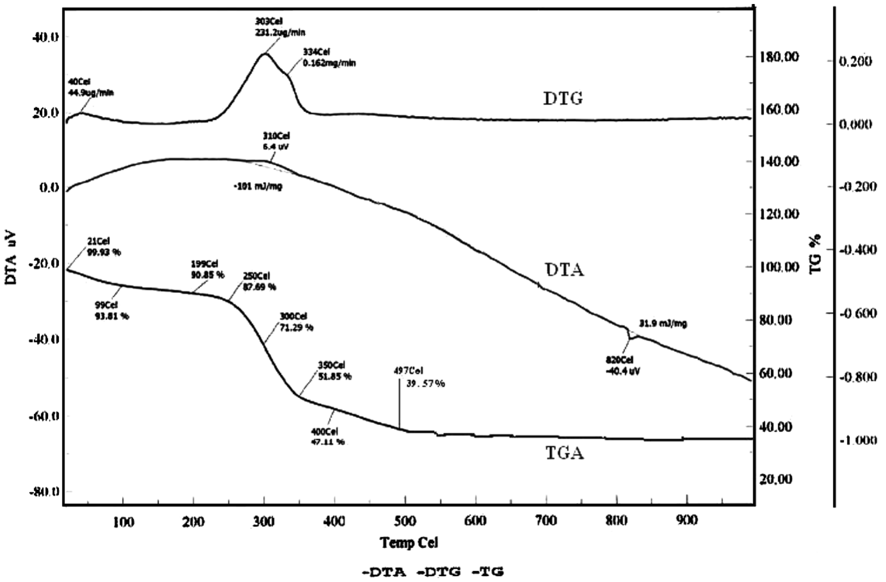


Figure 3. TGA/DTA/DTG analysis of silane-treated *Saccaharum cilliare* fiber.

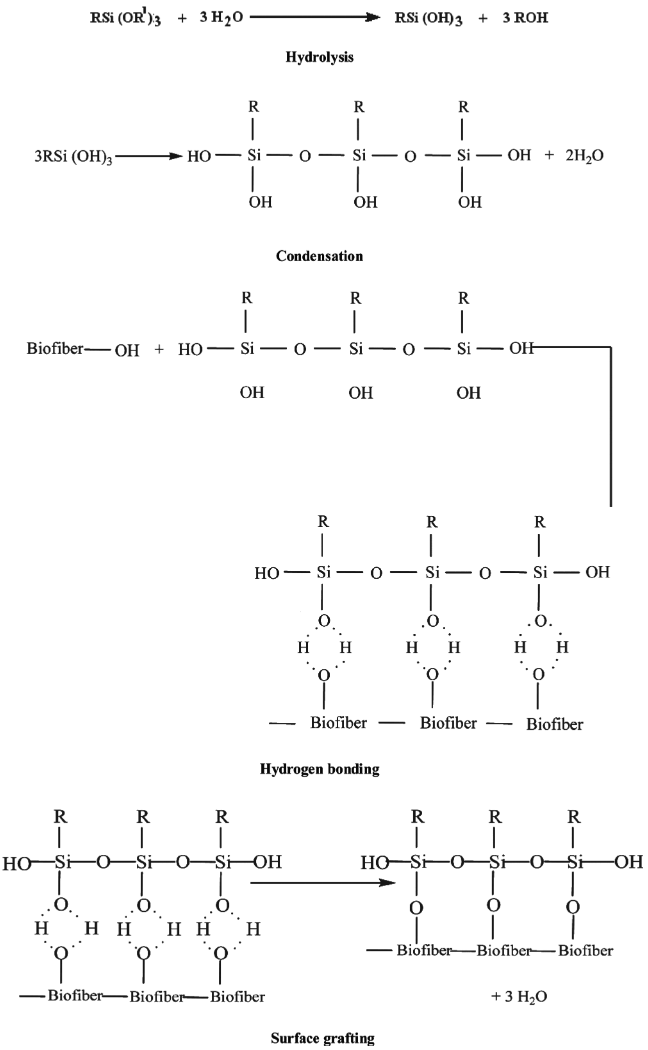
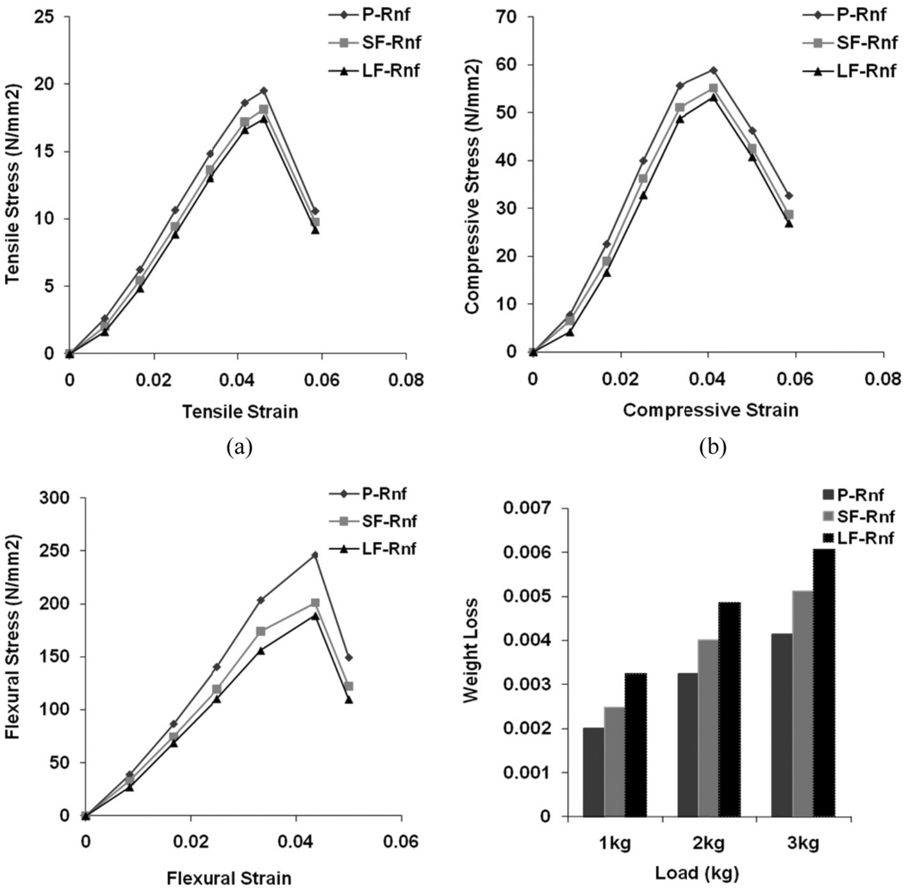


Figure 4. Various steps for silane treatment of *Saccaharum cilliare* fiber.

an 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. An 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 would occur, due to the fact that 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.

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



(a) (b) (c) (d)

**Figure 5.** Tensile (a), compressive (b), flexural stress-strain (c), and wear resistance (d) results of *Saccaharum cilliare* fiber-reinforced composites with particle, short, and long fiber reinforcement.

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 exhibit micro pores on their surface, the coupling agent penetrated into the pores and formed a mechanically interlocked

**Table VI.** Parameters from tensile stress-strain curves

| Polymer | Ultimate tensile stress, N/mm$^2$ | Yield strength N/mm$^2$ | Fracture stress, N/mm$^2$ | Standard deviation | Tensile modulus N/mm$^2$ |
|---|---|---|---|---|---|
| PF | 9.40 | 8.10 | 8.70 | 0.72 | 207.70 |
| P – Rnf | 19.52 | 16.57 | 18.33 | 0.77 | 427.87 |
| SF – Rnf | 18.14 | 14.21 | 17.15 | 0.82 | 381.72 |
| LF – Rnf | 17.42 | 13.64 | 16.57 | 0.68 | 361.57 |

**Table VII.** Parameters from compressive stress-strain curve

| Polymer | Ultimate compressive stress, N/mm$^2$ | Yield strength, N/mm$^2$ | Fracture stress, N/mm$^2$ | Standard deviation | Compressive modulus, N/mm$^2$ |
|---|---|---|---|---|---|
| PF | 31.94 | 26.07 | 29.14 | 0.87 | 771.00 |
| P – Rnf | 58.91 | 51.66 | 54.67 | 1.41 | 1431.51 |
| SF – Rnf | 55.41 | 48.32 | 52.89 | 1.37 | 1292.34 |
| LF – Rnf | 53.24 | 46.73 | 51.24 | 1.17 | 1233.35 |

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. Silanes undergo hydrolysis, condensation, and bond formation stage. Silanols can form polysiloxane structures by reaction with hydroxyl group of the fibers. The reaction schemes for silane treatment of natural *Saccaharum cilliare* fibers are given in Figure 4.

## Mechanical Properties of Phenol-Formaldehyde Matrix-Based Composites

It has been observed that *Saccaharum cilliare* fiber-reinforced polymer composites with particle reinforcement exhibit higher mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance, followed by short fiber and long fiber–reinforced composites (Figure 5). This may be due to larger surface area of reinforcement in particle form as compared to short and long fibers, resulting in better interfacial bonding strength. Different parameters obtained from the stress-strain curves of fiber-reinforced composites are shown in Tables VI–VIII.

From these results it is clear that interfacial bonding strength between the *Saccaharum cilliare* fibers and polymer matrix is the most essential factor to achieve good fiber reinforcement. The interfacial bonding strength depends on the surface topology of the fibers. The interface acts as a "binder" and transfers load between the matrix and the reinforcing fibers. Interfacial bonding is a result of good wetting of the fibers by the PF matrix as well as the formation of a chemical bond between the fiber surface and the PF matrix. It can be concluded that different degrees of reinforcement effects are achieved by the addition of different dimensions of natural fibers to PF polymer matrix. This may be due to the different adhesion strength

**Table VIII.** Parameters from flexural stress-strain curve

| Polymer | Ultimate flexural stress, N/mm$^2$ | Yield strength N/mm$^2$ | Fracture stress, N/mm$^2$ | Standard deviation | Flexural modulus N/mm$^2$ |
|---|---|---|---|---|---|
| PF | 119.34 | 107.37 | 114.98 | 0.75 | 3582.94 |
| P – Rnf | 246.00 | 231.57 | 239.58 | 1.12 | 8179.23 |
| SF – Rnf | 201.26 | 191.61 | 196.37 | 1.14 | 6492.31 |
| LF – Rnf | 189.59 | 178.37 | 184.75 | 1.15 | 6011.38 |

**Table IX.** Absorption 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 | 3.23 | 3.12 | 3.03 | 2.94 |
| SF – Rnf | 3.45 | 3.27 | 3.16 | 3.09 |
| LF – Rnf | 3.49 | 3.37 | 3.25 | 3.19 |

between matrices and fibers. The adhesion is usually the strongest in polar polymers capable of forming hydrogen bonds with hydroxyl groups available on the fiber surface. The chemical bonding accounts for the adhesion between PF resin and cellulose of fiber. Still higher bond strength obtained for PF resin matrix is due to the possible reaction between the methylol groups of the resin and the hydroxyl group of cellulose.

## Physicochemical Behavior of Polymer Composites and Chemical Resistance

**Absorption behavior.** *Saccaharum cilliare* fiber-reinforced polymer composites with different dimensions show different absorption behavior in different solvents (Table IX). It has been observed that the absorption behavior of *Saccaharum cilliare* fiber-reinforced phenol-formaldehyde composites in different solvents follows the trend: $H_2O > CH_3OH > C_4H_9OH > CCl_4$. The absorption 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 has been depicted in Table X.

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

| Sample | Hum = 20 | Hum = 40 | Hum = 60 | Hum = 80 | Hum = 90 |
|---|---|---|---|---|---|
| PF Resin | 0.00009 | 0.00018 | 0.00027 | 0.00043 | 0.00052 |
| P – Rnf | 0.00022 | 0.00034 | 0.00055 | 0.00061 | 0.00071 |
| SF – Rnf | 0.00028 | 0.00039 | 0.00058 | 0.00071 | 0.00078 |
| LF – Rnf | 0.00035 | 0.00048 | 0.00062 | 0.00078 | 0.00084 |

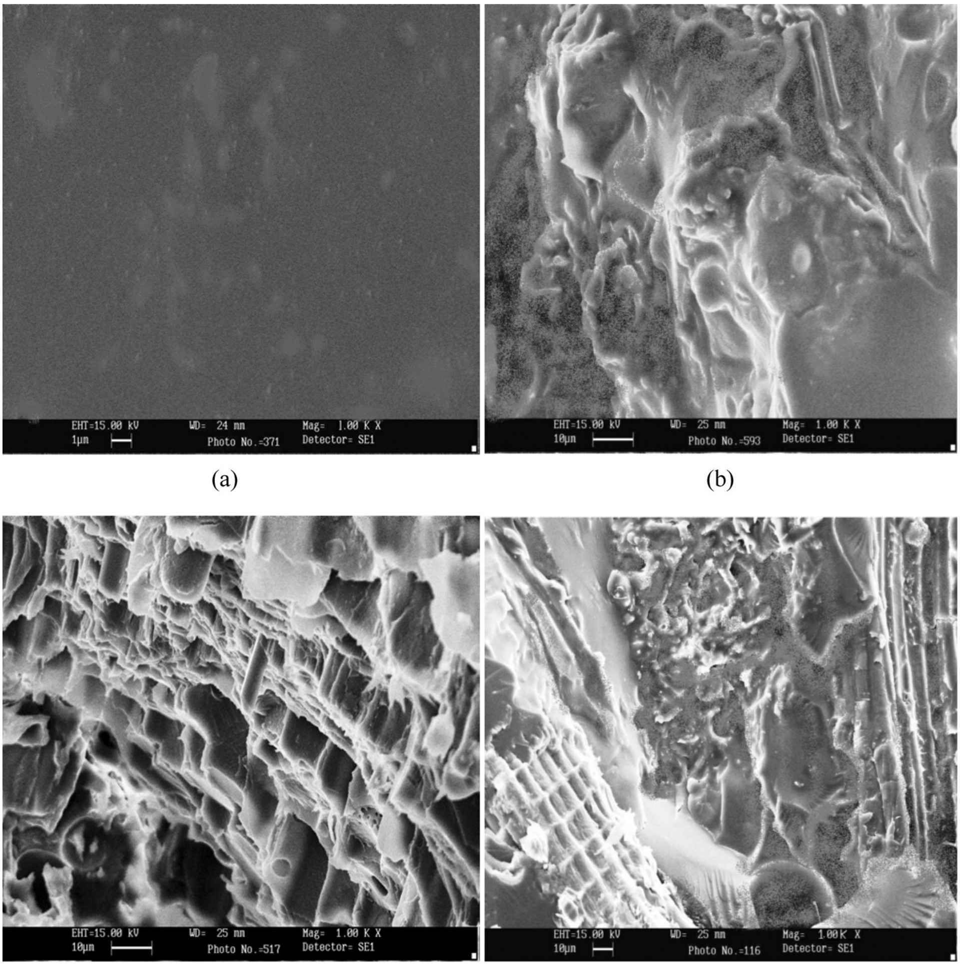
**Table XI(a).** Chemical resistances (in terms of % wt. loss) of polymer composites at different time intervals against 1 N HCl

| Sample | 24 h | 48 h | 72 h | 96 h | 120 h | 144 h |
|---|---|---|---|---|---|---|
| PF resin | 1.09 | 2.13 | 3.09 | 4.23 | 4.68 | 5.04 |
| P – Rnf | 3.38 | 4.61 | 5.41 | 6.35 | 7.5 | 9.15 |
| SF – Rnf | 3.41 | 4.67 | 5.53 | 6.48 | 7.61 | 9.24 |
| LF – Rnf | 3.58 | 4.73 | 5.61 | 6.53 | 7.68 | 9.33 |

**Table XI(b).** Chemical resistances (in terms of % wt. loss) of polymer composites at different time intervals against 1 N NaOH

| Sample | 24 h | 48 h | 72 h | 96 h | 120 h | 144 h |
|---|---|---|---|---|---|---|
| PF resin | 1.52 | 2.59 | 3.12 | 4.62 | 4.72 | 5.45 |
| P – Rnf | 3.72 | 4.86 | 5.59 | 6.82 | 7.81 | 9.32 |
| SF – Rnf | 3.77 | 4.94 | 5.7 | 6.89 | 7.88 | 9.41 |
| LF – Rnf | 3.84 | 5.08 | 5.78 | 7.02 | 8.04 | 9.5 |

It has been found that moisture absorbance (Mabs) increases with increase in humidity level ranging from 20% to 90% with increase in fiber dimension (particle < short < long fiber).



(a) (b)

(c) (d)

**Figure 6.** SEM images of (a) PF resin, (b, c, and d) *Saccaharum cilliare* fiber-reinforced composites with particle, short, and long fiber reinforcement.

**Chemical resistance behavior.** It has been observed that resistance towards chemicals decreases with the increase in fiber dimension (Table XI). This may be due to weaker bond strength in short and long fiber–reinforced composites, which is vulnerable to chemical attack, resulting in decreased resistance towards the chemicals.

### Morphological Analysis of Polymer Biocomposites

Morphological investigations (Figure 6) clearly indicate that proper mixing of *Saccaharum cilliare* fibers 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 (Figure 6).

## CONCLUSION

It has been observed that surface modification of *Saccaharum cilliare* fibers through silane treatment helps in improving the physicochemical properties of natural fibers. The properties like moisture absorbance, chemical resistance, absorption behavior, and water uptake vary directly with the silane treatment. In the case of polymer composites it has been observed that mechanical properties increase with the incorporation of fibers into the polymer matrix. This is possible because of 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 *Saccaharum cilliare* fibers, and excellent results were obtained when the *Saccaharum cilliare* fibers were used in the particle form. The results of investigation of absorption, moisture, and chemical resistance behavior of composites show that the composites are sensitive to moisture absorption along with reduced chemical resistance due to the hydrophilic behavior of the *Saccaharum cilliare* fibers. In spite of these limitations, *Saccaharum cilliare* fibers can be a suitable substitute for synthetic fibers as a green reinforcing material for the preparation of various industrially important polymer matrix–based composites.

## REFERENCES

1. 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.
2. 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.
3. 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.
4. 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.

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. and Charact.* 5 (3): 247–256.
6. 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. Character.* 13 (2): 95–107.
7. 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. Character.* 10 (5): 373–386.
8. 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.
9. Singha, A. S., and V. K. Thakur. 2008. Mechanical properties of natural fiber reinforced polymer composites. *Bull. Mater. Sci.* 31 (5): 91–99.
10. Singha, A. S., and V. K. Thakur. 2009. Synthesis and characterization of short *Grewia optiva* fiber based polymer composites. *Polymer Composite* 31 (3): 459–470.
11. Singha, A. S., and V. K. Thakur. 2009. Synthesis and characterization of silane treated *Grewia* optiva fibers. *Int. J. Polym. Anal. Character.* 14 (4): 301–321.
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. Character.* 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. Character.* 10(3): 179–194.
14. Singha, A. S., V. K. Thakur, I. K. Mehta, Shama Anjali, A. J. Khanna, R. K. Rana, and A. K. Rana. 2009. Surface modified *Hibiscus sabdariffa* fibers: Physico-chemical, thermal and morphological properties evaluation. *Int. J. Polym. Anal. Character.* 14 (8): 695–711.
15. Singha, A. S., Shama Anjali, and V. K. Thakur. 2008. X-ray diffraction, morphological and thermal studies on methylmethacrylate graft copolymerized *Saccharum cilliari* fiber. *Int. J. Polym. Anal. Character.* 13: 447–462.
16. Singha, A. S., and V. K. Thakur. 2009. Fabrication and characterization of S. cilliare fiber reinforced polymer composites. *Bull. Mater. Sci.* 32 (1): 49–58.
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): 1–9.
19. 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.
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. 2009. Chemical resistance, mechanical and physical properties of biofiber based polymer composites. *Polym.-Plast. Technol. Eng.* 48 (7): 736–744.
22. Hasipoglu, H. N., E. Yilmaz, O. Yilmaz, and H. Caner. 2005. Preparation and characterization of maleic acid grafted chitosan. *Int. J. Polym. Anal. Character.* 10 (5): 313–327.
23. Singha, A. S., and V. K. Thakur. 2008. Mechanical, thermal and morphological properties of G. optiva fiber/polymer matrix composites. *Polym.-Plast. Technol. Eng.* 48 (2): 201–208.
24. Singha, A. S., and V. K. Thakur. 2008. Fabrication and study of lignocellulosic Hibiscus sabdariffa fiber reinforced polymer composites. *Bioresource* 3 (4): 1173–1186.

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., Shama Anjali, 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): 07–13.
27. Singha, A. S., and V. K. Thakur. 2009. Morphological, thermal and physico-chemical characterizations of surface modified pinus fibers. *Int. J. Polym. Anal. Character.* 14 (3): 271–289.
28. 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. Character.* 10 (3): 153–167.