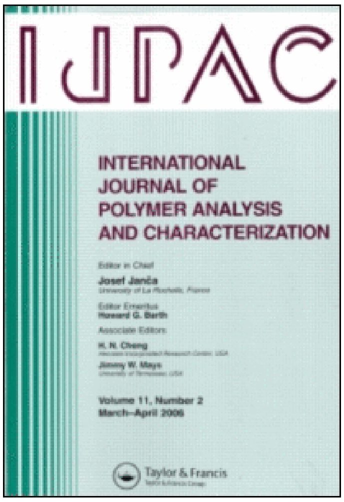

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MECHANICAL, MORPHOLOGICAL, AND THERMAL CHARACTERIZATION OF COMPRESSION-MOLDED POLYMER BIOCOMPOSITES

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In the present communication, synthesis and characterization of short* Saccaharum cilliare *fiber reinforced resorcinol–formaldehyde (RF) polymer matrix-based composites through compression molding technique are reported. Experimental results reveal that when* Saccaharum cilliare *fibers are incorporated into the resorcinol–formaldehyde polymer matrix, mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance of the matrix increase up to 30% fiber loading and then decrease for higher fiber loading. Morphological and thermal studies of the matrix,* Saccaharum cilliare *fiber, and short fiber-reinforced polymer composites have also been carried out. The results obtained emphasize utilization of these fibers as potential reinforcing materials in bio-based polymer composites.

***Keywords*:** Mechanical characterization; Morphological and thermal analysis; Polymer matrix

INTRODUCTION

Polymers have replaced a number of conventional materials in various applications during the past number of years.[1–3] The awareness of using natural fibers as complementary materials in polymeric materials is growing to a larger extent because of their renewable and eco-friendly nature. The most important advantages of using polymers in place of other traditional materials are the ease of processing, cost reduction, and productivity.[4,5] Recently, biofibers have attracted the attention of material scientists because of the advantages these fibers offer over conventional reinforcement materials.[6,7] Biofiber-reinforced polymers offer a number of advantages over other conventional materials when specific properties are compared. These biofibers are inexpensive, with low density, easy availability, nonabrasiveness, biodegradability, noncorrosiveness, friendly to health, and have highly specific properties.[8–10] In most of the applications, the properties of polymers

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are modified using fillers and fibers to fit high strength/high modulus requirements. Fiber-reinforced polymer composites constitute a significant proportion of the engineered materials market ranging from daily used goods to sophisticated function applications. These materials are able to meet miscellaneous design requirements with significant advantages.

The use of biofiber in the development of polymeric materials for useful applications in a number of fields is increasing very rapidly because it plays a significant role in reducing the dependence on nonrenewable resources.[11,12] It has been observed that farming harvest and by-products found in an abundant amount are the main resources of biomass. Currently, environmental policies of nearly all countries stress the incorporation of biofibers in various products. Natural fibers are particularly used in the automotive industry, where a number of products can be produced by using natural fibers as reinforcement.[13–15] With regard to the environmental advantages, these biofibers are suitable alternatives for synthetic fibers as reinforcements in polymers.[16,17] Synthetic fibers can cause health problems and are on the whole difficult to recycle. Composites made from either bioplastics or biofiber are called biocomposites.[18,19] Currently biofiber-reinforced polymer composites are being used because of their good mechanical properties, simplicity in fabrication, economy, and other features.[20,21] Thermosetting resins have the features of good processability, water resistance, and chemical inertness. The mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance are greatly improved by reinforcement.[22,23]

Saccaharum cilliare fiber is abundantly found in Himachal Pradesh, India. Traditionally this fibrous material found in the Himalayan region has been used by the local people for making low-cost articles like ropes, bags, boots, socks, and mats. The literature survey has shown scanty information on utilization of this fiber as reinforcing material in polymer composites.[8–15] Keeping in view the easy availability and many other eco-friendly advantages, the aim of this work is to study the mechanical properties of *Saccaharum cilliare* fiber-reinforced resorcinol formaldehyde (RF) resin based polymer biocomposites.

EXPERIMENTAL PROCEDURE

Materials

Resorcinol (Qualigens Chemicals Ltd.) and formaldehyde solution (Qualigens Chemicals Ltd.) were used as received.

Resorcinol-formaldehyde (RF) was used as matrix polymer.

The lignocellulosic material used as the reinforcing material in the biocomposite was short *Saccaharum cilliare* fiber 3 mm in length.

Synthesis of Resorcinol-Formaldehyde Resin

Resorcinol-formaldehyde (RF) resin was synthesized by the standard method developed in our material science research laboratory.[10,11] Resorcinol and formaldehyde were taken in different molar ratios (1.0:1.0, 1.0:1.5, 1.0:2.0, 1.0:1.5, and 1.0:3.0) by weight in a reaction kettle and were mixed with the help of mechanical stirrer. Since the reaction is exothermic, proper care was taken to maintain the temperature between 40° and 45°C for the initial hour. Then the temperature was increased to 50°C, and the mixture was heated at this temperature until complete resinification. Then the heating was stopped and the resin was cooled. The resin synthesized was then transferred to a specially made mold. Resin sheets of size 150 mm × 150 mm × 5.0 mm were prepared by a closed mold method as described elsewhere.[9–16] 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 55°C for 5 h.

Synthesis of *Saccaharum cilliare* Fibe-Reinforced Polymer Composites

Saccaharum cilliare fibers were first thoroughly washed with detergent powder. Then the fibers were soaked in hot distilled water for 7 h, dried for 72 h in air at room temperature, followed by drying at 100°C for 24 h to adjust them to a moisture content of 1–2%, and then stored in a vacuum desiccator. Dried *Saccaharum cilliare* fibers were chopped into dimensions of 3 mm. This was followed by thorough mixing of *Saccaharum cilliare* fibers with resorcinol–formaldehyde resin using a mechanical stirrer with different loadings (10, 20, 30, and 40%) in terms of weight. The surfaces of molds to be used were lubricated on the inner side with oleic acid to allow easy removal of the composites. The above mixture was poured into specially made molds. The mixture was then spread equally on the surface of the molds. Composite sheets of size 150 mm × 150 mm × 5.0 mm were prepared by compression molding technique on a compression molding machine. Compression molding was performed in a hot press using a mold preheated to 50°C. Material first placed in the hot open mold was left for about 7 min, and then the mold was closed. Composite sheets were prepared by hot pressing the mold at 50°C for 30 min. The pressure applied ranged from 3 to 4 MPa depending on the loading of reinforcing material. All the specimens were then post-cured at 50°C for 12 h.

Analysis of Mechanical Properties of Samples

Tensile Strength Test. The tensile strength test was conducted on a computerized universal testing machine (Hounsfield H25KS). Specimens of dimensions 100 mm × 10 mm × 5 mm were used for the analysis. The tensile test was conducted in accordance with ASTM D 3039 method and at the constant strain rate of 10 mm/min.

Compressive Strength Test. The compression test was conducted in accordance with ASTM D 3410 method. The composite sample was held between the two platforms and the strain rate was fixed at 10 mm/min and the total compression range was 7.5 mm.

Flexural Strength Test. The flexural strength of samples was also tested on a computerized universal testing machine. The three-point bend flexural test was conducted in accordance with ASTM D 790 method.

Wear Test. Wear test of the sample was conducted on a wear and friction monitor (Ducom TR-20L). Wear resistance of composites was carried out as per ASTM D 3702 method.

Thermal Studies

Thermal analysis of polymeric materials gives us a good account of their thermal stability. Thermal analysis comprises various methods such as thermogravimetric analysis (TGA)/differential thermal analysis (DTA), and derivative thermogravimetry (DTG). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) studies of samples were carried out in nitrogen atmosphere on a thermal analyzer at a heating rate of 10°C/min.

Morphological Studies

Morphological analysis of different samples was carried out by studying scanning electron micrography (SEM) micrographs. The excitation energy used was 5 keV. To achieve good electrical conductivity, all samples were first carbon sputtered followed by sputtering a gold palladium mixture before examination. SEM micrographs of the samples show the morphology of the green polymer composites prepared. These SEM micrographs of the samples give us information about the morphology of the resin and its respective biocomposite. These micrographs clearly show the difference between loaded and unloaded matrix

RESULTS AND DISCUSSIONS

Analysis of mechanical properties of polymer composite materials is one of the most important tools in the study of the behavior of polymer composite materials. It has been proved to be an efficient method to study the behavior of the materials under various mechanical conditions. Mechanical properties of fiber-reinforced composites generally depend on the (i) nature of the matrix material, (ii) distribution and orientation of the reinforcing fibers, and (iii) the nature of the fiber-matrix interfaces and the interphase region.

Mechanism of Synthesis of Resorcinol-Formaldehyde Resin

Resorcinol is a very reactive compound and readily combines with formaldehyde to form methylene derivative.[10,11] In this reaction, methylol group occupies either the position ortho to both hydroxyl groups or ortho to one and para to other, as shown in Figure 1(A). The reaction is carried out in neutral medium as resorcinol is very reactive towards formaldehyde. Reaction between formaldehyde and resorcinol proceeds vigorously towards the thermosetting state when they are heated together. Hence, proper care must be taken while carrying out the reaction. Methylolated resorcinol condenses with formaldehyde molecules and other resorcinol molecules to form a polymeric structure, as shown in Figure 1(B). In this reaction, resorcinol nuclei are joined together through methylene bridges to give complex molecule. Complete methylene bridging is shown in Figure 1(C).

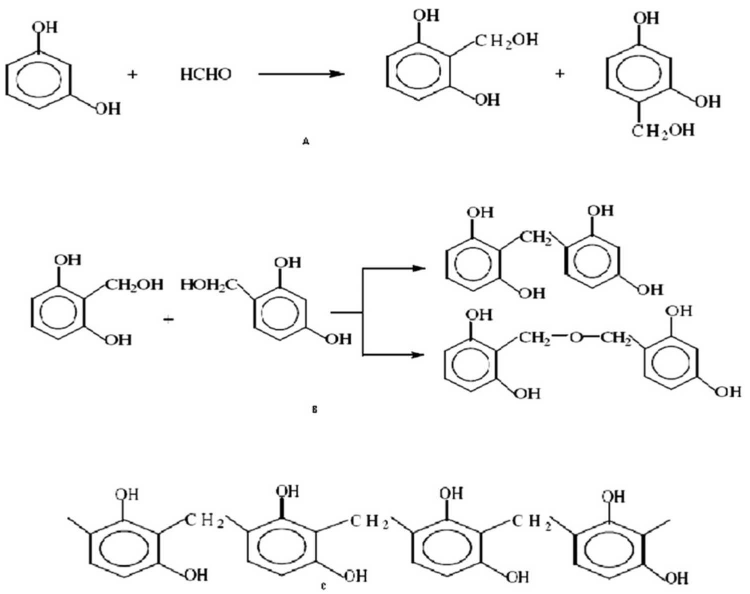


Figure 1. (A) Formation of methylol derivative, (B) condensation reaction between methylated resorcinol to form polymeric structure, (C) methylene bridging in polymerized resorcinol molecules.

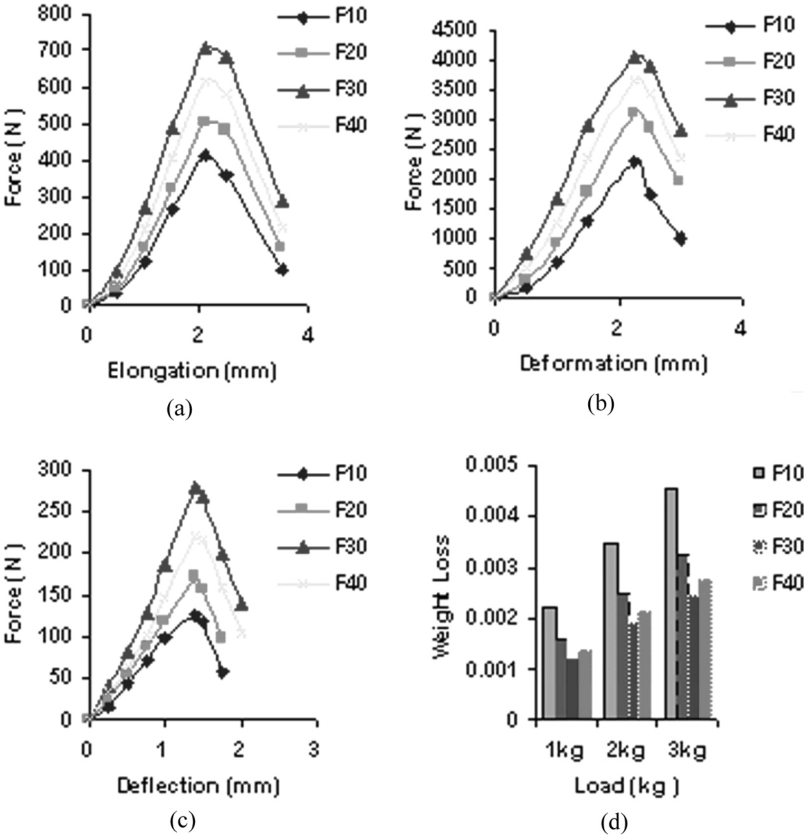
Optimization of Resorcinol-Formaldehyde Resin

Optimization of resorcinol–formaldehyde resin was done by studying the mechanical properties such as tensile strength, compressive strength, flexural strength, and wear resistance. It has been observed that RF samples with the ratio 1.0:1.5 exhibit higher mechanical properties than samples with other ratios.[10,11] The ratio (1.0:1.5) of resorcinol and formaldehyde showing optimum mechanical properties was taken for further preparation *Saccaharum cilliare* fiber-reinforced resorcinol–formaldehyde polymer composites.

Effect of Fiber Reinforcement on the Mechanical Properties of RF Matrix–Based Polymer Composites

Tensile Strength. It has been observed that tensile strength of polymer composites increases on reinforcement with *Saccaharum cilliare* fiber. Composites with 30 wt.% loading bear maximum load (707.37 N) followed by 40%, 20%, and 10% loadings (615.00 N, 502.00 N, and 411.00 respectively) (Figure 2(A)).

Compressive Strength. Compressive strength of *Saccaharum cilliare* fiber-reinforced RF matrix has been found to increase with the increase in fiber content in the composite. It has been found that on fiber reinforcement compressive strength increases to a much greater extent. The compressive properties of the composites as a function of load and deformation are presented in Figure 2(B). From the graph it is evident that initially compressive force increases with the increase in fiber content but beyond 30% fiber content a significant decrease in compressive strength



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

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

is observed. It is clear from the figure that composites with 10, 20, 30, and 40% loadings bear loads of 2286.50 N, 3093.5 N, 4057.00 N, and 3650.00 N respectively.

Flexural Strength. Similar trends as obtained in tensile strength and compressive strength tests have been observed for flexural strength results. The flexural properties of samples as a function of force (in terms of load) and deflection are shown in Figure 2(C). It is clear from the figure that composites with 10, 20, 30, and 40% loadings bear loads of 127.47 N, 170.00 N, 278.37 N, and 221.00 N, respectively.

Wear Test. As evident from Figure 2(D), the wear rate of RF matrix decreases appreciably when reinforced with fiber. Maximum wear resistance behavior is shown by composite with 30% loading followed by 40, 20, and 10% loading.

Stress–Strain Analysis.

Tensile Stress–Strain Behavior. Tensile stress–strain behavior is explained on the basis of the load elongation measurements. Since both stress and strain

Table I. Values of various parameters obtained from tensile stress–strain curve at different loadings

Fiber loading (wt.%)	Ultimate tensile stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Tensile modulus N/mm^2
10	8.22	7.01	8.46	1.32	227.66
20	10.04	8.37	9.52	1.53	275.17
30	14.14	11.39	12.97	1.25	397.22
40	12.30	10.39	11.68	1.10	341.14

are obtained by dividing the load and elongation by constant factors, the stress–strain curve have the same shape as the load-elongation curve. Different parameters derived from the tensile stress–strain analysis are shown in Table I.

Compressive Stress–Strain Behavior. The compressive stress–strain behavior is also explained on the basis of the load-deformation measurement. When the load exceeds a value corresponding to the yield strength, the specimen undergoes gross plastic deformation. It is permanently deformed if the load is released to zero. Different parameters from the tensile stress–strain curve are shown in Table II.

Flexural Stress–Strain Curve. Flexural stress–strain behavior has also been explained on the basis of the load deflection measurements. The flexural stress–strain curve has also the same shape as the load-deflection curve. Different parameters derived from the tensile stress–strain curve are shown in Table III.

In order to achieve effective fiber reinforcement, interfacial strength between the *Saccaharum cilliare* fiber and polymer matrix is the most essential factor. The interfacial area plays a major role in determining the strength of composite material because each fiber forms an individual interface with the matrix.[10–15] Interfacial bonding is a result of good wetting of the fibers by the RF matrix as well as the formation of a chemical bond between the fiber surface and the RF matrix. Hence the interface plays a key role in controlling the mechanical properties of a composite. It can be concluded that different degrees of reinforcement effects are achieved by the addition of *Saccaharum cilliare* fibers to RF matrix-based

Table II. Values of various parameters obtained from compressive stress–strain curve at different loadings

Fiber loading (wt.%)	Ultimate compressive stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Compressive modulus N/mm^2
10	45.72	37.57	42.63	1.16	1224.75
20	61.82	51.36	57.39	1.42	1443.04
30	81.14	68.00	74.59	1.04	2167.56
40	73.00	61.48	68.39	1.37	1949.53

Table III. Values of various parameters from flexural stress–strain curve for different percentage loadings

Fiber loading (wt.%)	Ultimate flexural stress N/mm^2	Yield strength N/mm^2	Fracture stress N/mm^2	Standard deviation	Flexural modulus N/mm^2
10	38.24	31.27	36.21	0.95	2287.67
20	52.50	43.79	48.01	1.23	3143.71
30	84.41	74.21	81.09	1.26	5107.42
40	71.40	63.62	69.10	1.06	4284.78

polymer. The adhesion is usually the strongest in polar polymers capable of forming hydrogen-bonds with hydroxyl groups available on the fiber surface. It has been observed that mechanical properties increase up to 30% fiber loading and then decrease. The mechanical strength of RF composites levels off at high fiber loading. This behavior can be explained by the fact that at higher fiber loading the fiber-fiber contact dominates the resin matrix-fiber contact, which decreases the mechanical properties beyond 30% loading.

Additionally, when fiber-reinforced RF composites were subjected to a load, *Saccaharum cilliare* fibers acted as carriers of load and the stress was transferred from the matrix to the reinforcing material, resulting in enhanced mechanical properties of the polymer composites. At low percentage of fiber loading, the orientation of fibers was poor as the fibers were not capable of transferring load to one another, and stress accumulated at certain points of the composite, which led to lower mechanical properties. At 30% levels of loading the population of the *Saccaharum cilliare* fibers is just right for maximum orientation, and the fibers actively participate in stress transfer, which accounts for maximum results obtained in the case of this loading. As discussed, modulus showed a clear continuous increase up to 30% fiber loading in the case of random orientation. At higher levels of *Saccaharum cilliare* fiber loading, the increased population of fibers led to agglomeration, and stress transfer was partially blocked, resulting in lowering of mechanical properties beyond 30% loading.

Morphological Study of Polymer Composites

Morphological results (Figures 3(A)–(F)) clearly show that when resin matrix is reinforced with different loadings of fiber, morphological changes take place depending upon the interfacial interaction between the varying loadings of fiber and the resin matrix.

Thermal Analysis of RF Resin and Its Polymer Composites

Thermal analysis of raw *Saccaharum cilliare* fiber, polymeric resorcinol–formaldehyde resin, and polymer composites studied was investigated as a function of percentage weight loss with the increase in temperature. In the case of raw fiber, in the beginning depolymerization, dehydration, and glucosan formation took place

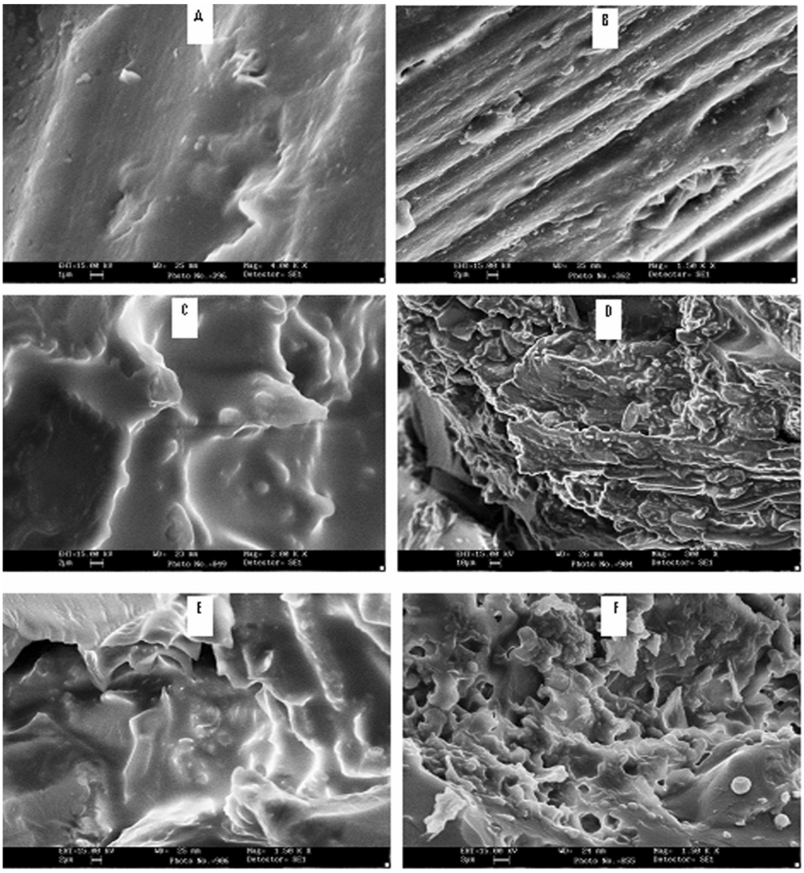


Figure 3. SEM images of (A) RF resin and (B) *Saccaharum cilliare* fiber (C, D, E, & F) composites with 10, 20, 30, and 40% loadings.

between the temperature ranges of 26.0° and 195.0°C followed by the cleavage of C–H, C–C, and C–O bonds. The initial decomposition temperature (IDT) has been found to be 212°C and the final decomposition temperature (FDT) to be 471°C. On the other hand, in the case of RF resin, it is single-stage decomposition, the observed initial decomposition temperature is 299.0°C, and the final decomposition of the resin took place at 990.0°C. It has been observed that for polymer composites (10%) initial decomposition temperature is 241.0°C, and the final decomposition

Table IV. Thermogravimetric analysis of RF, SC, and SF-Rnf-RF composites

Sr. no.	Sample code	IDT (°C)	wt.% loss	FDT (°C)	wt.% loss	Final residue (%)
1.	SC	212	12.45	471	67.44	32.66
2.	RF Resin	299	22.64	990	51.78	48.22
3.	SF-Rnf-RF	241	23.67	935	69.37	31.67

Table V. Differential thermal analysis of SC, RF, and SF-Rnf-RF composites

Sr. no.	Sample code	Exothermic/endothermic peaks °C(μV)
1.	SC	326.0 (81); 430.0 (203)
2.	RF resin	65 (−1.0); 244 (8.0); 280 (6.0)
3.	SF-Rnf-RF	74 (−7.5); 81 (−10.3)

of the composite took place at 935.0°C. These values are between the degradation temperatures observed for matrix and the fiber. This indicates that the presence of cellulose fibers affects the degradation process of the polymer composites. The initial decomposition (IDT) temperature and final decomposition temperature (FDT) of fiber, resin, and biocomposite are presented in Table IV. These studies are further supported by differential thermal analysis (DTA), summarized in Table V. These results are consistent with the results reported earlier.[10–14]

CONCLUSIONS

Mechanical properties of randomly oriented intimately mixed *Saccaharum cilliare* fiber-reinforced resorcinol–formaldehyde composites were investigated with special reference to fiber loading. Various test methods were used for complete mechanical characterization of natural fiber-reinforced composites. The mechanical behavior has been strongly supported by the SEM and thermal analysis. Finally, it can be concluded that by utilizing *Saccaharum cilliare* fiber, we can prepare user-friendly and cost-effective composite materials possessing suitable mechanical properties.

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