INVESTIGATION ON TENSILE STRENGTH OF CELLULOSE MICROFIBRIL REINFORCED POLYMER COMPOSITES

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Received October 10, 2019

This research work aims to find the tensile stress and the tensile modulus of cellulose microfibril (CMF) reinforced epoxy polymer composites. CMFs were extracted from banana fibers using the acid-alkali treatment. Scanning electron microscopy (SEM) images revealed the isolation of α-cellulose of 1-2 µm after the acid-alkali treatment. Thermogravimetric analysis showed an increase in the thermal resistance of CMFs up to 380°C, compared to 260 °C for untreated natural fiber. The influence of three parameters, namely NaOH% (w/w), fiber diameter (µm) and fiber volume% (w/w), on the tensile behavior of composites was investigated. Response surface methodology (RSM), a DOE tool, was used for determining the composition of different specimens. A three-factor, three-level Box-Behnken Design (BBD) model of RSM was selected for investigating the effect of input variables on the tensile behaviors and to obtain the optimization conditions. By solving the regression equations and analyzing the 3D response surface plots obtained from BBD, the optimized desirability ramp values were obtained. The optimized tensile stress and tensile modulus values were 41.78 MPa and 10380 MPa, respectively, using optimized values of NaOH% (w/w), fiber diameter (µm) and fiber volume% (w/w) of 18.32, 250 and 4.05 respectively.

Keywords: Box-Behnken Design, response surface methodology, optimization approach, microfibrils, epoxy composites, tensile strength

INTRODUCTION

Natural fiber-reinforced composites are in the research focus with a view of replacing synthetic composites for many reasons. Natural fiber-reinforced composites can possibly diminish the carbon print and environmental pollution, while improving the biodegradability of composites. Nowadays, natural fiber-reinforced composites find many applications and can replace synthetic composites in most structural and non-structural applications. Natural fibers are used in different ways for fabricating composites: as woven mats, or non-woven, short, micro- and nano-sized fibers.[1] Cellulose is the primary element in natural fiber that provides it with adequate strength to withstand huge loads. Cellulose microfibrils and cellulose nanofibrils have gained much attention in structural composites applications.[2] Chemical treatments are applied to natural fibers for achieving better interaction with the polymer matrix and to improve the mechanical properties of natural fiber-reinforced composites.[3] Edeerozey *et al.* chemically treated kenaf fiber with a NaOH solution for attaining better interaction with the matrix. Also, chemical treatment cleans the surface of the fiber, limits moisture absorption, and increases the surface roughness of the fiber. It was observed that the chemical treatment enhances the mechanical properties, compared to those of untreated fibers.[4]

Feng *et al.* studied the effect of using a compatibilizer with kenaf fiber and the structural changes induced when treated kenaf fiber was added as reinforcement of polypropylene. Maleated polypropylene (MAPP) was used to improve the adhesion between kenaf fiber and the polypropylene matrix. This coupling agent improved the bonding strength and enhanced the crystallization temperature of polymer composites.[5] Kalia *et al.* reviewed different chemical treatments applied to natural fibers, their application in real-world conditions when they are used as reinforcement in polymer composites. Chemical treatments modify the surface of natural fibers and provide better adhesive interaction with

the polymer achieving higher load-carrying abilities, as compared with those of untreated natural fiber composites.[6] Rokbi *et al.* investigated the effect of chemical treatment of natural fiber-reinforced composites on their flexural strength. Alfa fiber, extracted from *Stipa tenacissima*, was alkali treated with different alkali doses, and the flexural properties of natural fiber-reinforced composites were studied. The results showed that alkali treatment altered the hydrophilic characteristic of natural fiber and improved the adhesion between the matrix and the fiber. This increased the mechanical and thermal properties of chemically treated natural fiber-reinforced composites.[7] Kabir *et al.* compared the effect of different surface treatments on natural fibers for advanced composite applications. Some surface treatments, such as alkali, permanganate, isocyanide, peroxide and saline, improved mechanical strength and dimensional stability, compared with those of pristine samples.[8]

Joseph *et al.* investigated the thermal properties of sisal short fiber reinforced polypropylene (PP) matrix composites. Sisal fibers were chopped, treated with a $KMnO_4$ solution and then used to reinforce PP to make composites. TGA results of the treated fiber composites showed improved thermal properties, as compared to those of untreated fiber composites.[9] Zhou *et al.* studied the interface and bonding mechanism of chemically treated and untreated fibers with a polymer matrix. The mechanical properties of natural fiber-reinforced composites were improved by optimizing the interaction of plant fiber with the polymer matrix. The authors suggested some guidelines to improve the interaction of natural fiber with the polymer matrix.[10] Sepe *et al.* investigated the mechanical properties of chemically treated hemp fiber-reinforced composites. (3-Glycidyloxypropyl) trimethoxysilane acts as a coupling agent and, along with alkaline treatment, improves the mechanical properties of hemp fiber-reinforced composites.[11] Rashed *et al.* studied the tensile strength of jute fiber-reinforced composites. The effects of parameters, such as alkali treatment (compared to no treatment), fiber size (1, 2 and 4 mm) and fiber loading (5, 10, 15 wt%) were considered. They analyzed the tensile behavior and performed fractographic observations.[12-13]

Ochi examined the mechanical properties of kenaf fiber-reinforced composites. The author investigated the effect of thermal treatment on the tensile properties of kenaf fiber. The bio-degradability of kenaf/PLA composites was also analyzed.[14] Additionally, kenaf fibers were treated with an alkaline solution before being used as reinforcement in epoxy composites. A thermal degradation test was carried out and the results showed improved thermal stability of the treated kenaf fiber composites, compared to untreated kenaf fiber ones.[15] Malkapuram *et al.* reviewed some recent developments in polypropylene based composites reinforced with various natural fibers. In general, abundantly available natural fibers, such as jute, coir, banana hemp and flax fibers, are used as reinforcement. Banana fibers, treated with 10% NaOH solution, have been demonstrated to improve the thermo-physical properties of composites, compared with untreated fibers.[16-17]

Harish *et al.* evaluated the mechanical properties of coir fiber-reinforced composites. Coir fiber was cut into short pieces and then used to reinforce an epoxy matrix. The tensile testing results showed coir fiber as a suitable reinforcement for low load-bearing applications.[18] Haque *et al.* investigated the physical-mechanical properties of polypropylene composites reinforced with chemically treated palm and coir fibers. The fibers were added at five loading levels, from 15 to 35 wt%, relative to the matrix, and mechanical tests, such as tensile, flexural and impact analyses, were carried out. The results proved that the 30 wt% fiber loaded sample showed better mechanical properties.[19] Lee *et al.* fabricated polypropylene composites reinforced with long and discontinuous natural fibers and investigated their mechanical properties.[20] Ornaghi *et al.* explored the hybridization effect of curaua and glass fibers on the mechanical and dynamic properties of composites. They found that an increase in the weight percentage of curaua had a minimum effect, compared to that of glass fiber.[21] Akil *et al.* reviewed kenaf fiber-reinforced composites. Kenaf fibers are readily available and are used as reinforcement in various ways. NaOH treated kenaf fiber increases the tensile and flexural properties of epoxy composites, but the thermal resistance decreased, compared to that of untreated kenaf fiber-reinforced composites.[22] Prasad *et al.* investigated jowar, sisal and bamboo reinforced composites under mechanical testing. The fibers were reinforced at 40% vol. ratio and tested them in terms of tensile and flexural strengths.[23] Sathishkumar *et al.* investigated the tensile and

flexural behaviors of snake grass fiber-reinforced composites. Untreated chopped snake grass fibers were added to isophthalic polyester resin and it turned out that an increase in the volumetric fraction increases the tensile and flexural properties of composites.[24] Venkateshwaran *et al.* investigated the tensile properties of hybrid natural fiber reinforced composites. They used banana/sisal in different ratios by maintaining a 40% vol. ratio with the matrix, and compared the experimental tensile strength with that predicted by the rule of hybrid mixture (RoHM).[25] Ramesh *et al.* evaluated the mechanical properties of sisal-jute-glass fiber reinforced composites. The composites were tested in terms of tensile, flexural and impact strengths, as well as interfacial properties. They analyzed the internal structure of composites using a scanning electron microscope (SEM).[26]

Jawaid *et al.* studied the effect of jute fiber and oil palm fiber reinforced epoxy composites. The composites were tested in terms of their damping and tensile properties and were found suitable for applications in the automobile and building industries.[27] Sanjay *et al.* studied the mechanical properties of banana/glass fiber reinforced composites. They conducted tensile, flexural, impact and hardness tests on the composites. They also investigated the water absorption tendency for pure glass fiber composites and pure banana fiber composites.[28] Gunti *et al.* investigated the mechanical and degradation properties of jute, sisal and elephant grass reinforced composites. The fibers were treated by mercerization and bleaching processes. They added treated and untreated fibers to polylactic acid (PLA), in different weight ratios, through the injection process, and compared the mechanical properties, water absorption ability, thermal degradation, soil burial degradation and enzymatic degradation of the composite combinations. Their results showed that chemical treatment increases the flexural property of the composites and decreases their thermal degradation.[29] Wu *et al.* fabricated kenaf fiber-reinforced composites and tested them in terms of mechanical properties. They additionally investigated the energy consumption and environmental impact of kenaf fiber composites and compared them with glass fiber composites. They suggested possible replacement of the automotive glass-fiber sheets with natural fiber reinforced composite sheets.[30] Baley *et al.* investigated the compressive and tensile behaviors of flax and jute fiber reinforced composites. The fibers were treated with a coupling agent, reinforced with matrix, tested under compressive and tensile conditions, and were found suitable for application in low weight structures.[31] Sanjay *et al.* reviewed different characteristics and properties of natural fiber reinforced composites. Natural fiber reinforced composites were discussed with regard to their tensile, flexural, impact, inter-laminar, thermal and hardness behaviors and compared with synthetic fiber reinforced composites. Also, their water absorption capabilities, thermal and tribological properties were considered. The results showed that chemical treatment increases the thermal resistance of the fiber used for reinforcement of the polymer. The fiber matrix adhesion and inter-laminar delamination properties were also analyzed.[32]

Alaaeddin *et al.* investigated the physical and mechanical properties of sugarcane fiber reinforced composites. Short sugarcane fiber was added to polyvinylidene fluoride using the injection molding process and then the mechanical and physical properties of the composites were analyzed.[33-34] Navaneethakrishnan *et al.* analyzed the structural properties of natural fiber reinforced composites. They attempted to reinforce polymer matrix with sisal and luffa fibers by the compression molding process. They conducted tensile, impact and flexural experiments.[35] Cavalcanti *et al.* performed the mechanical characterization of intra-laminar natural fiber reinforced composites. They used alkaline treated and untreated jute, sisal and curaua fibers as reinforcement for composites. They investigated the effect of alkaline treatment of the fibers on the mechanical properties of the composites by tensile and flexural tests.[36] Adeniyi *et al.* reviewed coir fiber reinforced composites and their applications. Coir fiber is abundantly available as a waste by-product and hence it can be used with different resin matrices for different applications. Coir fibers were treated with an acid-alkaline solution to increase the α-cellulose content and thus the thermal stability and mechanical properties of fiber increased. When treated coir fibers were used as reinforcement of an epoxy matrix, the results showed improved mechanical properties, compared to untreated coir fibers. Coir fiber has good cellulose content and so it can be used for structural applications.[37] Senthilkumar *et al.* evaluated the mechanical and vibration properties

of pineapple leaf fiber (PALF) reinforced composites. They prepared the PALF polyester composites by the hand lay-up process and then compressed the materials using a compression testing machine. They analyzed the tensile, flexural and vibration results and found that an increase in PALF reinforcement increases the mechanical strength and reduces the damping ratio of the composites. They suggested that 45 wt% PALF composites are better suited for structural applications.[38] Along with structural applications, cellulose microfibril reinforced composites were used for making thin films, bags and other packaging applications.[39]

From the literature survey, it can be concluded that limited attempts have been made by researchers regarding the optimization of chemical treatment and fiber size to improve the mechanical properties of natural cellulose microfibril reinforced composites. Response surface methodology (RSM) is a powerful statistical-based technique for modeling complex systems, evaluating the simultaneous effects of several factors and obtaining optimum conditions for a desirable response using Derringer's design function methodology.[40-41] Also, other authors have applied the Box-Behnken Design (BBD) for modeling the optimum tensile and flexural properties of composites.[42-43]

Hence, in this study, the Box-Behnken response surface design (BBD) was used to investigate the tensile strength of cellulose microfibril reinforced composites and to obtain the optimized desirable values of the parameters of interest. The influence of key independent variables, such as NaOH% (w/w), fiber diameter (µm) and fiber volume% (w/w), on the tensile stress and tensile modulus (dependent variables) of the developed composites were investigated.

EXPERIMENTAL

Raw materials

Raw banana stem fibers were purchased from local suppliers (ECO Green unit, Coimbatore, TN, India) and ground to micron size to be used as filler. The chemicals used for the extraction of cellulose microfibrils: NaOH, HCl and demineralized water, were purchased from SRL chemicals, Sigma Aldrich and NICE Chemicals. Epoxy LY556 and hardener HY951 were purchased from S.M. Composites, Chennai, TN, India.

Chemical treatment of fibers

Raw banana fibers were cut to 4-5 mm length and prewashed with demineralized water to remove dirt and impurities. Then, the fibers were air-dried for two days to remove excess moisture. Fully dried banana fibers were powdered by the pulverizing process (Saral Pulverizer, Gujarat, India) and size separation was performed using a sieve shaker. Figure 1 describes the procedure for the chemical treatment of powdered banana fiber to prepare cellulose microfibrils for reinforcement of epoxy composites.

The chopped banana fibers were pretreated with different w/w percentages of a sodium hydroxide (NaOH) solution for 2 hours, as shown in Table 1. Then, the fibers were washed several times with distilled water. The pretreated banana fibers were hydrolyzed using a 1M HCl solution at 80 °C ± 5 °C for 2 hours. Then, the fibers were washed several times with demineralized water.

The acid hydrolyzed fibers were treated again with a 2% (w/w) NaOH solution for 2 hours at 60 °C ± 5 °C. The acid-alkali treated fibers were washed several times with demineralized water until the pH reached 7. These acid-alkali treated fibers had higher content of cellulose microfibrils and less pectin, hemicelluloses and lignin.

Morphology of microfibrils

The surface morphology of untreated and chemically treated cellulose microfibrils was examined using a ZEISS EVO18 Scanning Electron Microscope (ZEISS Microscopy, NY, USA). The microscope was operated at 10 kV to observe the microfibrils. The microfibrils were placed on metal stubs by using double-faced tape and the surface was coated by gold using a QUORUM Sputter Coater.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis is used to perform the thermal degradability of untreated and treated microfibrils. The samples of 200 mg were placed in a platinum pan of SDT Q600 (TA Instruments, USA) and their thermal behavior was analyzed from ambient temperature to 800 °C, at a heating rate of 10 °C/min, in a nitrogen environment at a flow rate of 25 mL/min.

Experimental design

A three-level three-factor Box-Behnken Design (BBD), requiring 15 experiments, was employed in this study. The fractional factorial design, consisting of 3 factors, has to be placed with equally spaced values as -1, 0, +1. The variables and their levels selected for this study were as follows: NaOH (15, 17.5 and 20 in % w/w), fiber diameter (250, 375 and 500 µm) and fiber volume (2, 4 and 6 in % w/w), as shown in Table 1. The data obtained were fitted to a second-order polynomial model, as shown in the next equation:[41]

$$Y = \beta_0 + \sum_{i=1}^{k}\beta_i X_i + \sum_{i=1}^{k}\beta_{ii} X_i^2 + \sum_{i=1}^{k}\sum_{j=1}^{k}\beta_{ij} X_i X_j + \varepsilon$$

where Y is the response (tensile stress and tensile modulus); β_0, β_i (i = 1, 2, 3, 4) and β_{ij} (i = 1, 2, 3, 4; j = 1, 2, 3, 4) are the model coefficients, and X_i and X_j are the coded independent variables. BBD was applied to

the experimental data using the Design Expert statistical software, version 11.

Preparation of samples

Table 2 shows the order of the experiment to be followed to prepare the samples according to BBD. Tensile test samples were prepared according to ASTM D3039/D3039-17.[44] The dimensions of the tensile samples were 250 mm x 25 mm x 2.5 mm.

The cellulose microfibrils were prepared according to Table 2, mixed with epoxy resin and stirred mechanically for 45 minutes to obtain their uniform dispersion in the epoxy. Then, 10% v/v hardener was added to the epoxy/filler mixture and stirred for 10 minutes. The mixture was transferred to a tensile testing mold for curing. The samples were cured for 4 hours and the samples were left undisturbed for 1 day for complete curing. For each combination, triplicate samples were prepared for testing. 45 specimens were prepared based on the BBD model. Also, triplicate pure epoxy samples of the same dimension were prepared for comparison purposes.

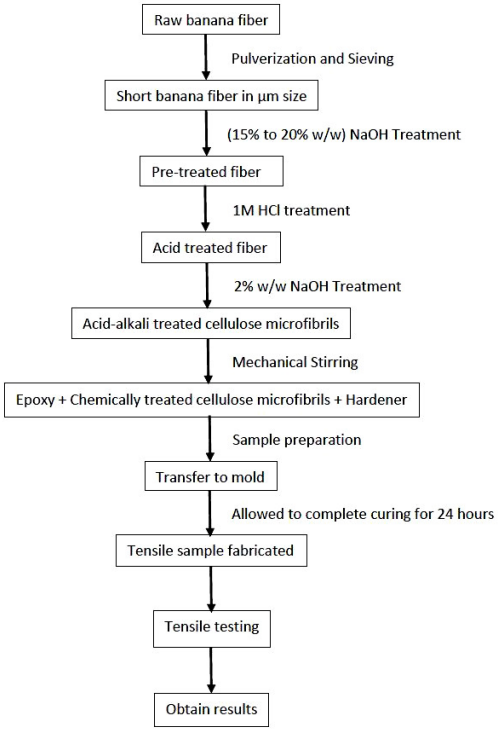


Figure 1: Process flowchart for tensile sample preparation

Tensile testing method

The specimens were tested using a computerized INSTRON 8801 machine (INSTRON, Norwood, MA, US) by clamping both specimen ends using grippers and axial load was applied gradually. The strain rate of 1 mm/min was maintained at room temperature (25 °C). During testing, the machine recorded all the values automatically.

Data analysis

The experimental data obtained by testing were analyzed using the Design Expert analytical software, version 11.

Table 1
Levels and codes chosen for Box-Behnken Design

Factor	Variables	Coded levels of variables		
		-1	0	+1
X_1	NaOH% (w/w)	15	17.5	20
X_2	Fiber diameter (µm)	250	375	500
X_3	Fiber volume% (w/w)	2	4	6

Table 2
Box-Behnken Design with actual/coded values for three size fractions

Run no.	NaOH% (w/w)	Fiber diameter (μm)	Fiber volume% (w/w)
1	20 (+1)	375 (0)	6 (+1)
2	15 (-1)	375 (0)	2 (-1)
3	17.5 (0)	375 (0)	4 (0)
4	15 (-1)	250 (-1)	4 (0)
5	20 (+1)	500 (+1)	4 (0)
6	17.5 (0)	500 (+1)	2 (-1)
7	17.5 (0)	500 (+1)	6 (+1)
8	17.5 (0)	375 (0)	4 (0)
9	17.5 (0)	250 (-1)	2 (-1)
10	17.5 (0)	250 (-1)	6 (+1)
11	15 (-1)	375 (0)	6 (+1)
12	20 (+1)	375 (0)	2 (-1)
13	17.5 (0)	375 (0)	4 (0)
14	20 (+1)	250 (-1)	4 (0)
15	15 (-1)	500 (+1)	4 (0)
Pure epoxy (16)	0	0	0

The main methodology involved getting tensile results (*i.e*. tensile stress and tensile modulus were fed), performing the analysis of variance (ANOVA), generating the regression equation through regression analysis and plotting 3D contour plots between dependent and independent variables to establish optimum conditions for tensile stress and tensile modulus.

RESULTS AND DISCUSSION

Morphology of microfibrils

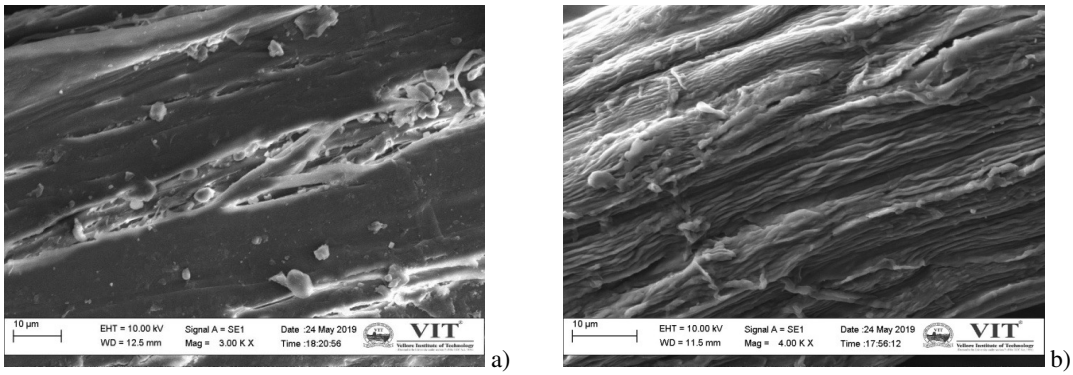
Figure 2 (a) shows the SEM micrograph of untreated fiber. In the raw fiber, α-cellulose, hemicelluloses and lignin are bonded to each other forming a compound structure. α-Cellulose has high Young's modulus, compared to other elements. Hence, chemical treatment is carried out to extract the α-cellulose from the raw fiber. Figure 2 (b) shows the SEM image of banana fiber treated with 17.5% (w/w) NaOH, 1M HCl solution and 2% (w/w) NaOH solution. Figure 3 shows the cellulose microfibrils of 2.43 μm in diameter and 19.54 μm length.[45] The pretreatment helped increase the surface area of fibers, exposing the polysaccharides to acidic medium. Acid treatment hydrolyzes the polysaccharides into simple sugars and solubilizes hemicelluloses. Alkali treatment dilutes the remaining pectin, lignin and hemicellulose.[2] Untreated banana fibers have primary cell walls, wax, dust and other foreign particles. These unwanted contents do not bond with the matrix and hence reduce the mechanical strength of the composites. During chemical treatment, these unwanted materials are removed one by one and α-cellulose is exposed to the matrix, leading to good bonding in composites. This increases the mechanical strength of cellulose microfibril reinforced composites, compared to that of untreated banana fiber reinforced composites.[46]

Thermostability analysis of microfibrils

Cellulose microfibrils are considered to be a promising candidate for reinforcement of polymer materials. Most commercially used polymers can withstand temperatures over 250 °C. Thus, cellulose microfibrils must withstand this operating temperature as well to be suitable for such application. Thermogravimetric analysis was used to study the thermal stability of cellulose microfibrils.[9]

Figure 3 shows the thermogravimetric curves for untreated banana fiber and chemically modified cellulose microfibrils treated with 17.5% (w/w) NaOH, 1M HCl solution and 2% (w/w) NaOH solution. It can be noted from the curves that, from 200 °C to 300 °C, the raw untreated fiber lost almost 40% of its weight, whereas the acid-alkali treated cellulose microfibrils lost only about 10%. This indicates an improvement in the thermal stability of the acid-alkali treated cellulose microfibrils, which was 3 times higher than that of the untreated fiber.[32-34] From 300 °C to 400 °C, the acid-alkali treated cellulose microfibrils entered a slow and steady weight loss phase, whereas untreated fibers lost weight rapidly. It is evident that the chemically treated fibers have higher thermal resistance, making them suitable for reinforcing

composites. Untreated fibers contain more soluble sugars, compared to chemically treated cellulose microfibrils. These soluble sugars degrade early in the decomposition process. Hence, untreated banana fibers started decomposing at a temperature of around 230 °C, while chemically treated CMFs could withstand up to 360 °C, without significant weight loss.[47-48] Both samples were analyzed up to 800 °C and their residues ranged from 19% to 22%.



a) b)

Figure 2: SEM images of a) untreated banana fibers, b) 17.5% (w/w) NaOH, 1M HCl, 2% (w/w) NaOH treated cellulose microfibrils

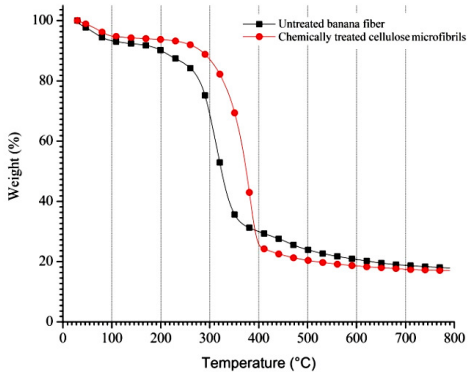


Figure 3: TGA curves of untreated banana fiber and 17.5% (w/w) NaOH, 1M HCl, 2% (w/w) NaOH treated cellulose microfibrils

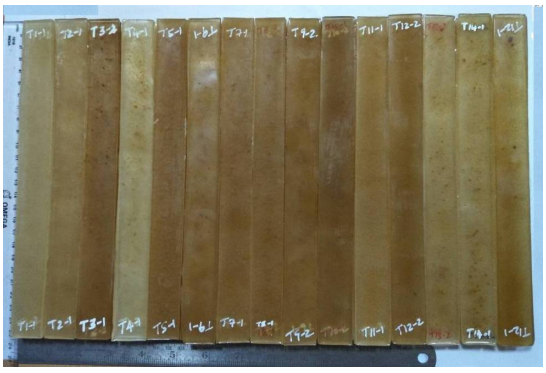


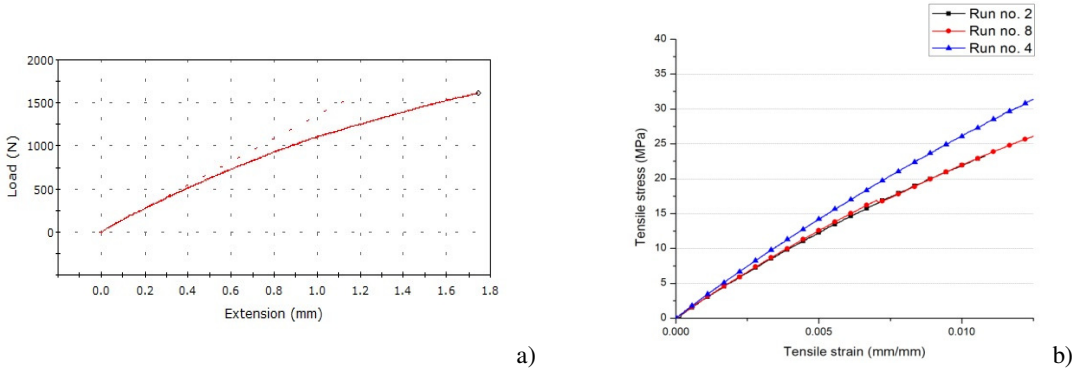
Figure 4: Tensile samples prepared according to ASTM D3039/D3039-15

Tensile test analysis

Tensile specimens prepared according to ASTM standards are shown in Figure 4. The tensile sample was fixed between the top and bottom grippers of the INSTRON machine, ensuring no slip occurred during testing. During testing, an axial load was applied gradually on the specimen and the corresponding readings were recorded. Tensile load, tensile stress and tensile modulus graphs were retrieved from the machine after the experiment. Figure 5 (a) shows the tensile load–extension graph. Figure 5 (b) shows the tensile stress–strain curves for 3 different NaOH treated CMF reinforced epoxy composite samples. The curve of run no. 2 represents the CMF treated with 15% (w/w) NaOH, 1M HCl and 2% (w/w) NaOH solutions. The curve of run no. 8 represents the CMF treated with 17.5% (w/w) NaOH, 1M HCl and 2% (w/w) NaOH solutions. Finally, the curve of run no. 4 represents the CMF treated with 20% (w/w) NaOH, 1M HCl and 2% (w/w) NaOH solutions. From the graph, it is clear that the 20% (w/w) NaOH treated CMFs performed better than the other two. It seems that an increase in the NaOH concentration increases the surface area of the

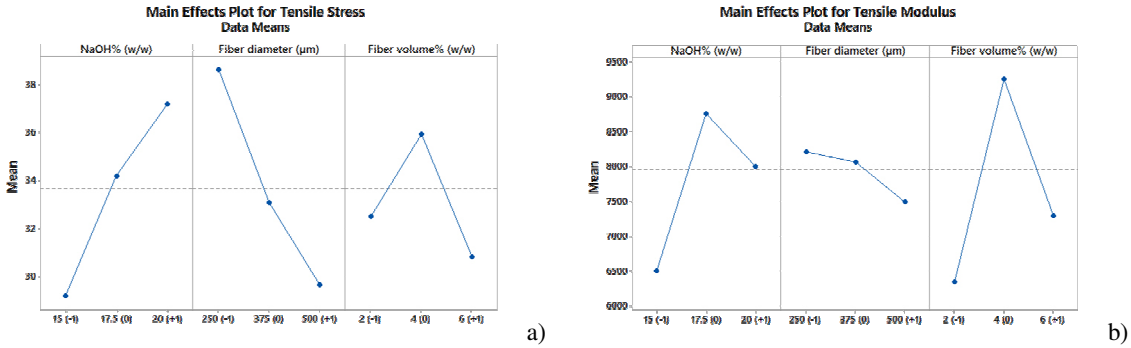
fiber, by solubilizing more lignin and pectin in the successive chemical treatments. The increase in the surface area enhances the bonding between the CMFs and the resin, thus, the mechanical strength of the composite is increased. Figure 6 shows the main effects plots for tensile stress (a) and tensile modulus (b) of the composites. It may be noted that the increase in the pretreatment NaOH% increases the tensile stress, while it initially increases and then decreases the tensile modulus. As regards the other two parameters, *i.e.* fiber size and fiber volume, the graph shows the same trend for both tensile stress and modulus.

Table 3 shows the values of tensile stress and tensile modulus for all the samples, with mean and standard deviation values. Standard deviation values show that there is very little variation among the trials and hence the results are consistent for all the samples. Table 4 shows experimental and predicted values of tensile stress and tensile modulus for 15 samples, obtained from the INSTRON machine and Design Expert software, respectively. The tensile stress and tensile modulus values of the pure epoxy sample are also included for the sake of comparison. From Table 4, it is evident that the epoxy reinforced with 20% NaOH treated filler (run no. 14) shows higher tensile stress and modulus, compared to the other samples.



a) b)

Figure 5: Sample tensile load–extension graph obtained from INSTRON (a), tensile stress–strain graph for samples containing differently treated fibers (b)



a) b)

Figure 6: Main effects plots for tensile stress (a) and tensile modulus (b)

Model fitting and ANOVA

The main effects of NaOH% (w/w), fiber diameter and fiber volume can be analyzed using the regression equations. Equations 2 and 3 show the quadratic polynomial regression equations for tensile stress and tensile modulus, respectively:

$$Tensile\ stress = 21.3092 + 1.594A - 0.075B + 4.337C + 0.0095BC - 1.0486C^2 \quad (2)$$

$$Tensile\ modulus = -92274.84 + 10117.77A + 5472.95C - 280.5A^2 - 654.23C^2 \quad (3)$$

where A – NaOH% (w/w), B – fiber diameter (µm), C – fiber vol% (w/w). From Equation 2, it is clear that fiber vol% (w/w) plays an important role in tensile stress, while Equation 3 indicates that NaOH% (w/w) plays an important role in tensile modulus. An increase in fiber vol% (w/w) and NaOH% (w/w) will raise the tensile stress and tensile modulus, respectively.

Table 3
Complete tensile stress and tensile modulus results with mean and standard deviation

Run no.	Tensile stress (MPa)					Tensile modulus (MPa)				
	Trail 1	Trail 2	Trail 3	Mean	Standard deviation	Trail 1	Trail 2	Trail 3	Mean	Standard deviation
1	28.628	40.416	31.996	33.68	6.072	5821.395	8218.440	6506.265	6848.70	1232.667
2	24.553	30.038	23.769	26.12	3.416	4934.314	6036.661	4776.836	5249.27	686.4311
3	30.821	43.512	34.447	36.26	6.537	9053.426	13159.050	9369.244	10527.24	2284.678
4	31.102	43.908	35.761	36.59	6.596	6949.779	9811.452	7767.400	8176.21	1473.987
5	33.652	41.170	32.578	35.80	4.681	7679.631	9395.293	7434.536	8169.82	1068.343
6	21.861	31.775	22.624	25.42	5.517	5366.073	7799.525	5553.262	6239.62	1354.156
7	24.404	34.452	27.275	28.71	5.176	7233.968	10212.660	8085.023	8510.55	1534.261
8	30.821	43.512	34.447	36.26	6.537	9895.606	12106.326	9579.788	10527.24	1376.615
9	35.071	50.975	36.294	40.78	8.850	5691.532	8272.575	5890.073	6618.06	1436.287
10	30.218	42.660	33.773	35.55	6.409	7064.393	9973.260	7895.498	8311.05	1498.296
11	23.848	29.176	23.087	25.37	3.318	5175.555	6331.797	5010.378	5505.91	719.9912
12	32.413	47.113	33.544	37.69	8.180	6229.092	9053.913	6446.386	7243.13	1571.943
13	30.821	43.512	34.447	36.26	6.537	9053.426	13159.050	9369.244	10527.24	1897.825
14	38.991	47.702	37.747	41.48	5.424	9150.139	11194.319	8858.113	9734.19	1272.911
15	24.673	35.863	25.534	28.69	6.226	6066.741	8817.938	6278.372	7054.35	1530.973

Table 4
Experimental and predicted values of tensile stress and tensile modulus of composites and of pure epoxy

Run no.	Tensile stress (MPa)				Tensile modulus (MPa)			
	Experimental	Predicted	Residual error	%Error	Experimental	Predicted	Residual error	%Error
1	33.68	34.81	-1.130	-3.35	6848.70	7168.77	-320.07	-4.67
2	26.12	28.77	-2.650	-10.14	5249.27	4709.72	539.55	10.27
3	36.26	35.98	0.276	0.76	10527.24	10309.23	218.01	2.07
4	36.59	36.60	-0.007	0.02	8176.21	7804.89	371.32	4.54
5	35.80	35.37	0.428	1.12	8169.82	9307.41	-1137.59	-13.92
6	25.42	25.77	-0.355	-1.39	6239.62	7214.06	-974.44	-15.62
7	28.71	28.61	0.100	0.35	8510.55	8170.59	339.96	4.03
8	36.26	35.98	0.275	0.76	10527.24	10309.23	218.01	2.07
9	40.78	39.73	2.052	5.03	6618.06	7214.06	-596.00	-9.21
10	35.55	33.04	2.514	7.06	8311.05	8170.59	140.46	1.69
11	25.37	26.84	-1.473	-5.75	5505.91	5666.25	-160.34	-2.92
12	37.69	36.74	0.953	2.53	7243.13	6212.24	1030.89	14.23
13	36.26	35.98	0.276	0.76	10527.24	10309.23	218.01	2.07
14	41.48	44.57	-3.092	-7.45	9734.19	9307.41	426.78	4.38
15	28.69	27.40	1.293	4.53	7054.35	7804.89	-750.54	-10.64
16	32.04		---		4337.98		---	

Table 5 shows the ANOVA for the tensile stress quadratic model. The model p-value is <0.0001, which shows the significance of the model. The p-values of other factors, such as A, B, BC, C^2, reached <0.05. The predicted R^2 value is 0.9224, which is very close to the adjusted R^2 value of 0.8871. The difference between the predicted R^2 value and the adjusted R^2 value is less than 0.2, and hence the model is significant.

Table 6 shows the ANOVA for the tensile modulus quadratic model. The model p-value is <0.0001, which shows the significance of the model. The p-values of other factors, such as A, A^2, C^2, reached <0.05. The predicted R^2 value is 0.9045, which is close to the adjusted R^2 value of 0.8726. The difference between the predicted R^2 value and the adjusted R^2 value is also less than 0.2, and hence the model is significant.

Figure 7 (a) presents the predicted *vs*. actual values of tensile stress. The points in the graph are close to the line and grouped, which indicates that the predicted and actual values are close to each other. Figure 7 (b) shows the predicted *vs*. actual values of tensile modulus. The points in the graph are a bit scattered. The variation between

the predicted values and the actual ones is a bit wider, but the points are still within the range.

Effects of parameters

In BBD, three factors at three levels were utilized to study the influence of NaOH, fiber size and fiber volume on the tensile stress and tensile modulus of chemically treated cellulose microfibril reinforced epoxy composites. The 3D response surface plots were developed to show the main and the interactive effects of the independent and the response variables. These graphs are easy to understand and very useful to intercept the numerical values graphically. The graphs are generated between two independent variables, keeping one variable constant for better understanding the effects of the variables and also to find the optimum conditions. Figure 8 (a) shows the response surface plot effect of fiber diameter and fiber volume on the tensile stress by keeping the percentage of NaOH constant at 17.5% w/w. According to the graph, the maximum tensile stress is reached at a fiber diameter of 250 microns and a fiber volume of 4% w/w ratio.

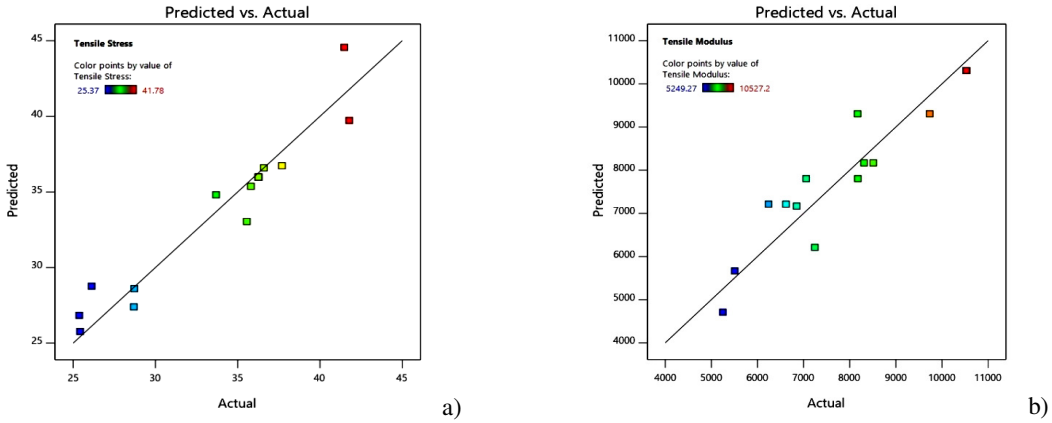
Figure 8 (b) shows the response surface plot effect of NaOH and fiber diameter on the tensile modulus, while keeping the fiber volume at a 4% w/w ratio. According to Figure 8 (b), the maximum tensile modulus is attained at 18.5% w/w of NaOH. The fiber diameter does not have any influence on the tensile modulus, whereas the fiber volume should be at a 4% w/w ratio. The surface plot effects indicate that a higher NaOH percentage increases the surface area of natural fiber.

Table 5
ANOVA results of the quadratic regression model for tensile stress

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model	400.72	5	80.14	26.13	< 0.0001	significant
A-NaOH	127.04	1	127.04	41.43	< 0.0001	
B-Fiber diameter	169.10	1	169.10	55.14	< 0.0001	
C-Fiber volume	7.41	1	7.41	2.42	0.1483	
BC	22.66	1	22.66	7.39	0.0200	
C^2	74.51	1	74.51	24.30	0.0005	
Residual	33.73	11	3.07			
Lack of fit	33.73	7	4.82			
Pure error	0.0000	4	0.0000			
Cor. total	434.45	16				
R^2	0.9224					
Adjusted R^2	0.8871					
Predicted R^2	0.6941					

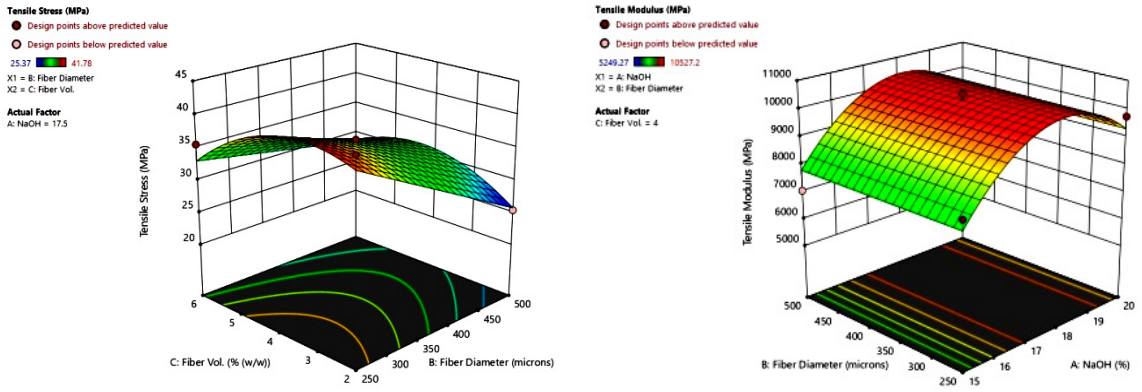
Table 6
ANOVA results of the quadratic regression model for tensile modulus

Source	Sum of squares	df	Mean square	F-value	p-value	Remarks
Model	5.052E+07	4	1.263E+07	28.40	< 0.0001	significant
A-NaOH	4.515E+06	1	4.515E+06	10.15	0.0078	
C-Fiber volume	1.830E+06	1	1.830E+06	4.11	0.0653	
A^2	1.298E+07	1	1.298E+07	29.18	0.0002	
C^2	2.891E+07	1	2.891E+07	65.01	< 0.0001	
Residual	5.337E+06	12	4.448E+05			
Lack of fit	5.337E+06	8	6.671E+05			
Pure error	0.0000	4	0.0000			
Cor. total	5.586E+07	16				
R^2	0.9045					
Adjusted R^2	0.8726					
Predicted R^2	0.7754					



a) b)

Figure 7: Graphs of predicted *vs*. actual values for tensile stress (a) and tensile modulus (b)



a) b)

Figure 8: Response surface plots showing (a) the effects of fiber diameter and fiber volume, as well as their interactive effect, on tensile stress for 17.5% (w/w) NaOH, and (b) the effects of NaOH and fiber diameter, as well as their interactive effect, on tensile modulus for 4% (w/w) fiber volume

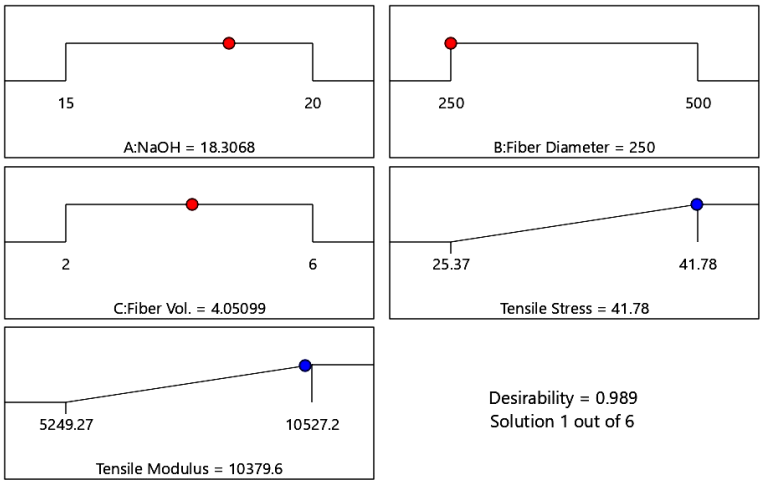


Figure 9: Desirability ramp for optimization

This increase in the surface area aids the matrix to penetrate well and create very good bonding with the natural fiber. Further, chemical treatment increases the chance of exposing more cellulose fibrils to the matrix material, which, in turn, increases the mechanical strength of the cellulose fibril reinforced composites.

Optimization and verification of the model

Derringer's desirability function was employed as optimization methodology to find the optimum conditions to achieve maximum tensile stress and modulus values.[49] 'Maximum level' and 'high importance' data for tensile stress were fed into the software, which provided the optimized conditions. Figure 9 shows the desirability ramp for optimizing the input variables to obtain the maximum outcome. According to Figure 9, it is recommended to set the input variables of NaOH to 18.31% w/w ratio, fiber diameter to 250 µm and fiber volume to 4.05% w/w ratio in order to obtain the maximum outcome for tensile stress of 41.78 MPa and tensile modulus of 10380 MPa. Table 7 shows six combinations of solutions with the desirability factor. From Table 7, the desirability of the ramp with 0.989 was selected as the optimized combination out of the six combinations proposed.

Table 7
Final settings for the optimal parameters derived by the software

Number	NaOH	Fiber diameter	Fiber volume	Tensile stress	Tensile modulus	Desirability	Remarks
1	18.309	250.001	4.053	41.780	10379.589	0.989	Selected
2	18.329	250.001	4.070	41.780	10379.225	0.989	
3	18.288	250.005	4.034	41.780	10379.194	0.989	
4	18.348	250.000	4.087	41.781	10378.163	0.989	
5	18.383	250.649	4.105	41.780	10373.683	0.989	
6	18.426	250.001	4.090	41.900	10363.111	0.988	

CONCLUSION

In the present study, the Box-Behnken Design method was employed to obtain optimized process parameters. The three-parameter, three-level model was used and the variables considered for this study were NaOH% (w/w), fiber diameter (µm) and fiber volume% (w/w). Triplicate specimens were prepared and tested using the INSTRON 8801 machine. Tensile stress and tensile modulus results were tabulated, analyzed and optimized using Design-Expert software. The experimental values and predicted values were found to be in good agreement, with high R^2 values of 92.2% for tensile stress and of 90.4% for tensile modulus obtained by ANOVA. The effect of the variables on tensile stress and tensile modulus was clearly explained with the help of 3D response surface graphs. The optimum tensile stress and tensile moduli were 41.78 MPa and 10380 MPa, respectively, using the optimized values of NaOH% (w/w), fiber diameter (µm) and fiber volume% (w/w) of 18.31, 250 and 4.05, respectively. The desirability ramp values and the combination solution tables were also presented. This study proves that the Box-Behnken Design can be successfully applied to model cellulose microfibril reinforced polymer composites, providing optimized results within a short period of time and with a minimal number of experimental runs.

ACKNOWLEDGMENT: The authors are very grateful to the Vellore Institute of Technology, Vellore Campus, India. This work was financially supported by the Institution of Engineers (India) IEI [DR2019005].

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