Fibers and Polymers 2014, Vol.15, No.6, 1310-1320 DOI 10.1007/s12221-014-1310-9

Morphology and Mechanical Properties of Sisal Fibre/Vinyl Ester Composites

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(Received May 16, 2013; Revised January 3, 2014; Accepted January 11, 2014)

Abstract: Sisal fibres were subjected to a 2 % sodium hydroxide solution treatment for 2, 5 and 8 h at 35 °C. Change in chemical composition of the alkali treated fibres in comparison to that of the untreated fibres was evaluated. Fibres were characterized with respect to its FTIR, linear density, crystallinity, tenacity, modulus and % breaking strain. Tenacity of the fibres increased initially and then decreased as the time of alkali treatment was increased. Modulus of elasticity of the fibres increased with increase in alkali treatment time. Fibres lost breaking strain (%) gradually with increase in treatment time. Variation in mechanical properties of composites was studied with respect to the duration time of alkali treatment of fibres. The failure mode was particularly investigated before and after treatment for better understanding of the effect of alkali treatment.

Keywords: Mercerization, Sisal fibre composite, Vinyl ester, Fracture, Scanning electron microscopy

Introduction

The growing interest in the use of vegetable fibres as reinforcement of synthetic polymer matrices is mainly because of low cost, light weight, non-toxicity, high specific modulus, renewability, ease of handling and biodegradability of the fibres [1]. In addition to the traditional glass and carbon fibre reinforcement for structural composite fabrication, natural fibres, like jute, flax, hemp, tropical plants e.g. oil palms, coconut, pineapple, sisal etc. are also found to be suitable by the manufacturers. Sisal is a structural fibre, extracted from the huge, thick and stiff leaves of *Agave Sisalana* which is generally grown in Central America, Eastern and Western Africa and Eastern Asia. Fibre bundles, originally 45-90 cm in length, stiffen the leaves of the plant, consequently these are structural fibres and much more stiff and rough than the bast fibres like hemp or flax. Sisal is cheaper and lighter than synthetic fibres like E-glass or carbon fibre though its specific elastic modulus is somewhat lower than the synthetic fibres (Table 1). However being light weight natural fibres are becoming the choice of car manufacturers like Mercedes Benz, Toyota and Daimler Chrysler [2]. On the other hand, composite properties are dependent on the interfacial bond between the reinforcing fibres and the resin matrix. Alkali treatment or mercerization, being commercialized for cotton fibres for superior reactivity with dyes and uniform dye distribution [3,4], is tried for various other natural fibres to have improved bonding with matrix resin. Samal *et al.* reported that [5], treatment of jute fibres with 2 % NaOH solution for 1 hour caused 13 % improvement in the tenacity. In another study, done by Gassan and Bledzki with 25 % NaOH treated jute filled epoxy composites, maximum improvement of 120 and 150 % on the tensile strength and modulus of fibres respectively was shown when the treatment time was only 20 min [6,7]. In these cases, the composite properties were improved by 60 % with respect to that of untreated fibre composites. Sarkar [8] found that treatment of jute fibres with 1 % and 8 % Caustic Soda for 48 hours could improve the tensile strength of the fibres by 130 %. Rout *et al.* [9], after similar treatment of coir fibres, could achieve improvements by 35 % in tensile strength, 60 % in flexural strength and 69 % in impact strength. Ray and coworkers [10] have reported that alkali treatment of jute fibres caused increase in mechanical properties e.g. flexural modulus of the composites in comparison to that of the untreated fibre filled composites. Also with increase in treatment time the rate of change of properties reduced. Rao and coworkers [11] experienced that among jute and sisal fibre epoxy composites, the basic compactness in the physical structure of the fibre accounts for the moisture and resin absorption level in an un-impregnated (virgin) fibre while the chemical nature (cellulose content) appears to govern largely the absorption behaviour of an impregnated fibre in the composite.

Table 1. Fibre fineness and lignin content of sisal reinforcement

Sisal fibre	% Weight loss	Linear density, (dTex)	(yEr±) of Linear density	% Lignin	(yEr±) of lignin
UNF (Untreated)	-	90.33	2.7099	11	0.55
2MSisal2h (2 h alkali treated)	14.08	78.33	2.3499	5	0.25
2MSisal5h (5 h alkali treated)	15.07	67.33	2.0199	4.5	0.228
2MSisal8h (8 h alkali treated)	16.2	88.83	2.6649	4	0.2

However, most of the investigators showed the improvements in the composite properties due to alkali treatment and tried to correlate the trends observed with either the alkali concentration or duration time of alkali treatment. Therefore

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the most appropriate discussion could be made on the basis of the chemical nature of the fibres after treatment, as the bonding between the resin and reinforcement is much dependent on the interaction through the chemical groups present in both the constituents. Alkali treated sisal fibres use in composite fabrication with vinyl ester matrix is not yet tried though the jute fibre composites are widely studied [12]. Easy availability of this fibre in Chotanagpur plateau region of India has therefore provoked us to study the fibre in detail both in unmodified and modified form and to see its applicability as reinforcement for the thermosetting resin, vinyl ester which is stronger than unsaturated polyester and cheaper than epoxy resin [13]. Vinyl ester resin bonds very well to glass fibre but shows poor adhesion to Kevlar or C-fibre [14,15].

In the present work, the effects of treatment of sisal fibres with 2 % NaOH solution for short duration as 2, 5 and 8 h, on the mechanical properties of vinyl ester composites have been investigated. The alkali treated fibres were characterized in respect of mechanical properties like tenacity, % breaking strain and Young's modulus. Their percent weight loss upon alkali treatment was determined. Lignin content of both treated and untreated fibres was compared. Their surface character change was judged by measuring contact angle and surface energy. % Crystallinity of fibres was determined by X-ray diffraction (XRD). Also the composites, prepared by incorporation of these fibres in different percentage by weight, were evaluated in terms of tensile and flexural strength. Micro-structural examination was made to ascertain the tensile fracture behavior of the composites by scanning electron microscopy.

Experimental

Materials

Sisal fibres, as gifted by Chotanagpur Rope works Pvt. Ltd. (Mahilong, Ranchi), was originally procured from Kenya, Africa. The fibres were of pale brown silky appearance and 2-3 ft long. The fibres were wrapped in polyethylene bags and stored in 65 % RH and 25 °C temperature. General purpose vinyl ester resin (RPL 401) was supplied by REVEX PLASTICISERS (PVT.) Ltd., New Delhi, having specific gravity at 25 °C 1.05±0.01 and viscosity (Brookfield) 450±50 at 25 °C and gel time (15-20 mins) at 25 °C.

Methyl ethyl ketone peroxide (MEKP), Cobalt naphthenate and N, N-dimethylaniline were used as catalyst, accelerator and promoter respectively and these were procured from the resin supplier. Sodium Hydroxide (NaOH) was purchased from CDH, Mumbai.

Moulds

Glass moulds of rectangular shape were made by fixing beads on glass plates with an adhesive to get rectangular channels. Each mould had two channels so that two specimens of size 135×35×3 mm could be made at a time. An iron frame was used to tie the fibres with pin type fixtures across the glass mould so that the alignment of fibres could be kept fixed and straight on the glass mould during the hand layup processing.

Alkali Treatment

Sisal fibres were cut to 50 cm length and were soaked in a 2 % NaOH solution at 30 °C maintaining a liquor ratio of 15:1. The fibres were kept immersed for 2, 5 and 8 h. After the stipulated period of time the fibres were washed with fresh water to remove NaOH sticking to the surface (if any), neutralized with dilute acetic acid and finally washed with distilled water. A final pH of 7 was maintained in each case. These fibres were dried first in open air for 24 h followed by oven drying at 100 °C for 2 h.

Composite Preparation

Oven dried fibres were used. These fibres were then tied to the iron frame across the rectangular channels on the glass mould. Sisal-vinyl ester composites, containing untreated and alkali treated fibres were fabricated. The liquid resin, premixed with the accelerator, promoter and catalyst (each by 2 % weight of resin) was spread over the aligned fibres. After the flow of resin was found to cease, a transparency sheet was put over it, a certain weight (5 kg) was placed on it and clamped. It was kept there for 24 hours and then oven dried at 100 °C for 2 hours. Composites with five different loading (10, 15, 20, 25 and 30 % by weight) of untreated and treated sisal fibres were prepared for investigation. Since the density of raw fibre (1.28 gm/cc) was different than that of resin (1.013 gm/cc), the fibre wt% and vol. % values in the composites were different. To keep standard comparison, all the properties of composites were evaluated in respect of fibre wt. %. Sample nomenclature followed in present study has been given in Table 1.

Characterization

Characterization of Fibres

The fibres, after soaking in 2 % sodium hydroxide solution, for different time period, were checked for their weight change. The loss in weight was calculated in respect of a fixed amount of dry and cleaned fibre (W_1). The % weight loss was calculated as:

$$\%\ \text{Fractional Weight Loss} = \frac{W_1 - W_2}{W_1} \times 100 \qquad (1)$$

The weight of fibre after alkali treatment was W_2.

Lignin content of fibre was determined by chemical analysis following standard procedure, [TAPPI T222 om-88, 1999]. Lignin determination was done by solubilising all the constituents other than lignin by the action of 72 % sulphuric acid. 1 gm of the milled sisal sample was treated with acid at room temperature for 4 hours under constant stirring, followed by dilution to 3 % acid concentration and then boiled for 4 hours under reflux. The insoluble residue was filtered, washed till neutral pH and dried in an oven at 105±3 °C to constant weight.

Raw and alkali treated sisal fibres were analyzed by FTIR spectroscopy, (SHIMADZU, Japan, IR Prestige-21) at room temperature in the wavelength range of 4000-400 cm^{-1} and using finely divided solid samples in the form of KBr pellets. Transmittance values at specific peak position were recorded for comparison.

Crystallinity of fibres after and before alkali treatment was studied by Rigaku Miniflex, Japan, at room temperature and with fine powder of the sample. The XRD patterns were recorded with a step size of 0·03 ° on a 10-30 ° range with a scanning rate of 1 °/min. Line focus Kb filtered CuKα radiation from an X-ray tube (operated at 30 kV and 15 mA) and was collimated and the diffracted beam from the sample was passed through variable divergence slit, scattering at 4.2 ° and receiving slit of 0·3 mm. Crystallinity of the samples were determined with respect to the standard data (2θ &d-value) reported in ICDD card (no.03-0226) for polymorphic cellulose at (002) compiled by JCPDS.

The crystallinity index (CrI) of the fibres was calculated according to the Segal empirical method as follows [16]

$$CrI(\%) = \frac{(I_{002}-I_{am})}{I_{am}} \times 100 \tag{2}$$

where I_{002} is the maximum intensity of the 002 lattice reflection of the cellulose crystallographic form (I) at $2\theta\sim$ 22·365 ° and I_{am} is the intensity of diffraction of the amorphous portion at $2\theta\sim$20·7 °.

Optical contact angle and surface energy were measured by the instrument from Data Physics OCAH 230, Germany at room temperature using water as medium. The measurements were based on the Young's equation [17],

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV}\cos\theta \tag{3}$$

Where, γ=surface tension, SV=solid vapour interface, SL= solid liquid interface, LV=liquid vapour interface and θ= contact angle.

Fibre fineness was determined in terms of average linear density of the fibres according to ASTM D1577-07 expressed in mg/10 m (dtex) as below [18].

$$\text{Linear density, dtex} = \frac{W}{LN} \tag{4}$$

Where, W is the weight (mg) of N number of staple fibres of length L (m). The linear density was determined from the weight of 100 single fibres of 60 mm length each.

Breaking strain and modulus of fibre were determined according to ASTM D3822-07 method by Universal Testing Machine by Instron 3677. Tenacity i.e. the tensile stress, when expressed as force per unit linear density of the unstrained fibre, was calculated according to ASTM D 2256-07. Fifty single fibres, both treated and untreated, were tested after each treatment and the mean values were taken.

Characterization of Composites

A composite material can be divided into two components, fibre and matrix generally. Ideally the sum of the volume fraction of fibre (V_f) and that of matrix resin (V_m) should be one assuming there is no porosity. However if there is porosity as is found in reality, the sum of the two exceeds one and the volume fraction porosity (V_p) can be calculated as,

$$V_p = (V_f + V_m) - 1 \tag{5}$$

The composite volume V_c of the specimens was calculated based on the average length (l), thickness (t) and breadth (b) of it. The fibre weight (W_f) in the composite of the above dimension was determined from the weight of the fibre, W_{fi}, tied on the frame before composite preparation, and the initial fibre length l_{fi}. The fibre length was reduced from l_{fi} to l_c, as the composites were cut into specimen length where the subscript f denotes fibre. W_f was calculated using the following relation [19].

$$W_f = W_{fi} \times \frac{l_c}{l_{fi}} \tag{6}$$

The matrix weight, W_m, was calculated based on difference between the composite weight (W_c) and W_f, considering total absence of solid impurity. The volume fraction of the matrix and that of the fibres in the composites were calculated based on the densities of the matrix, ρ_m and that of fibre, ρ_f (Table 4) using the following relations:

$$V_f = \frac{W_f}{V_c \rho_f} \tag{7}$$

In the present work the composite specimens were cut according to ASTMD 2344 for the determination of volume fraction porosity.

Tensile properties of the composites were determined according to ASTM D638-10 by Universal Testing Machine of INSTRON 3366. Testing of rectangular specimens of size 60×13×3 mm was carried out at a crosshead speed of 2 mm/min and a gauge length of 20 mm. The tensile modulus and toughness values were given by the machine itself. Five specimens were tested for each set of samples and the mean values were reported.

Composites with treated and untreated fibres were tested for their flexural strength under three point bend tests in the same INSTRON 3366 machine according to ASTM D 790M-10. Test specimens were of dimension 60×10×3 mm. A span of 40 mm was employed maintaining a cross head speed of 2 mm/min. Flexural strength and modulus were obtained according to the following equation:

$$\text{Flexural strength} = \frac{3PL}{2bd^2} \tag{8}$$

Where P=load, L=the span, b=breadth and d=thickness of the specimen. The slope of the initial straight line portion of the load-displacement curve is denoted by *m*.

Morphology of the composites with untreated and alkali treated fibres was studied with samples after tensile testing and gold coating on the fractured surface. Scanning electron microscope by JEOL, Japan JSM-6390LV, was used. Magnification was X200.

Results and Discussion

Effect of Alkali Treatment on Sisal Fibre

Loss in weight was observed after alkali treatment of the fibres, shown in Table 1, due to dissolution of mainly hemicellulose along with some lignin and pectin content [20,21] which was further convinced by the FTIR study. Figure 1 shows the variation in lignin content of the fibres after alkali treatment with the time of treatment. Due to weight loss, as shown in Table 1 linear density changes of treated fibres, compared to that of untreated fibres, are found. Figure 2 shows decrease in linear density of the fibres from 78.33 dTex to 67.33 dTex when treated between 2 and 5 hours whereas that of untreated fibres was 90.33 dTex. With increase in alkali treatment time further increase in linear density may be due to reorganization of cellulose chains in fibres.

Summary of the FTIR results, including the significance of the bands, the ratios of absorbance maxima of individual bands and that of 2900 cm^{-1} band (Av/A_{2900}) are recorded in Table 2. The 2900 cm^{-1} is assigned to C-H stretching in methyl and methylene groups. The 3350 cm^{-1} band, ascribed to H-bonded H-O stretching [22] has slightly increased absorbance intensity ratio for the alkali treated sisal samples compared to untreated fibre indicating almost constant α-cellulose contents even after mercerization of the natural fibres with probability of reorientation of chains.

The band near 1735 cm^{-1} corresponding to the C-O stretching of carboxyl and acetyl groups in hemicelluloses of the natural fibre [23], is prominent in untreated sisal fibre but is disappeared after alkali treatment. This can be explained on the basis of removal of mainly acetyl groups from hemicellulose after alkali treatment of the fibre [24]. At this point the slight increase in O-H stretching may be further clearly explained. The absorbance at 1455 cm^{-1} is ascribed to CH_3 deformation (asymmetric) in lignin. The intensity ratios are found to decrease after alkali treatment of the fibre. This may be due to the loss of lignin after alkali treatment. The band at 1370 cm^{-1}, corresponding to the C-H deforming (symmetric), may be

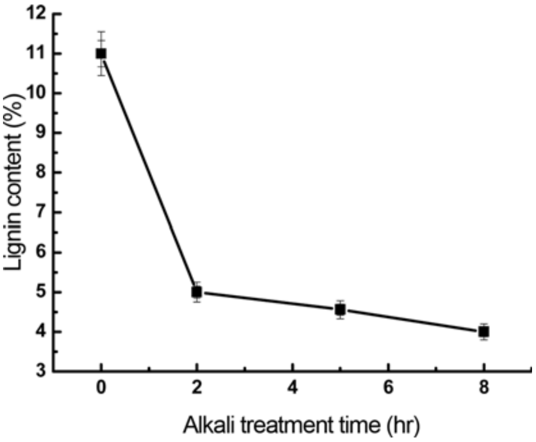


Figure 1. Loss in lignin content of sisal fibres after alkali treatment.

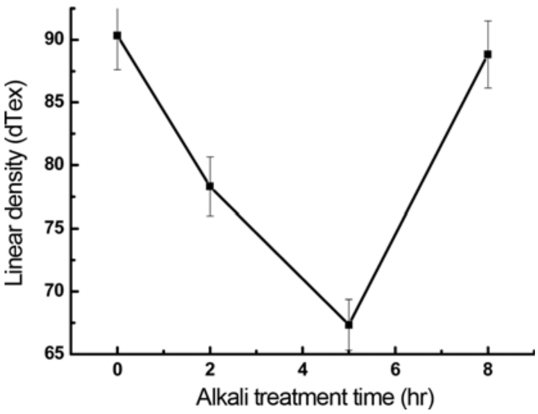


Figure 2. Variation in linear density of sisal fibres after alkali treatment.

Table 2. FTIR results of sisal fibres

Wavelength at peak (cm^{-1})	Assignment	UNF (Av/A2900)	2MSisal2h (Av/A2900)	2MSisal8h (Av/A2900)
3350	H-O stretching (H bonded)	1.025	1.067	1.061
2900	C-H Stretching in methyl and methylene	1	1	1
1735	C-O Stretching in carbonyl and unconjugated β-ketone	1.052	Nil	Nil
1455	C-H deformation and CH_2 bending	1.066	1.010	1.087
1370	C-H deforming (symmetric)	1.081	1.0183	1.017
1230-1240	C-O-C vibration in acetyl group	1.095	1.009	1.014
1030	Aromatic C-H in plane deformation	1.111	Nil	Nil
830	Aromatic C-H out-of-plane vibration	0.964	Nil	Nil

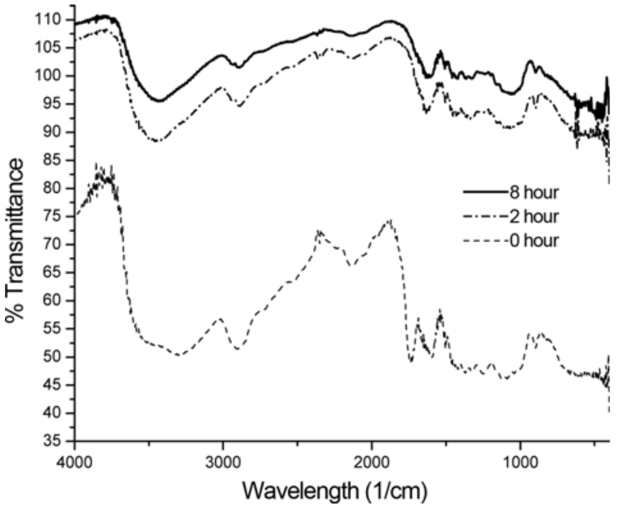


Figure 3. FTIR spectra of sisal fibres.

attributed to lignin, α-cellulose, or xylan and is found with higher intensity ratio for raw sisal in comparison to the alkali-treated one. The band at 1030 cm^{-1}, assigned to C-O stretching vibration in lignin is found to diminishing intensity ratio in alkali-treated fibre which may be ascribed to the loss of lignin from the fibre after alkali treatment. The 830 cm^{-1} band which is assigned to the aromatic C-H out of phase vibration in lignin is decreased in alkali treated fibres.

For the untreated natural fibres, hemicellulose and lignin remain dispersed in the inter-fibrillar region separating the cellulose chain from one another [25]. Moreover the cellulose chains possess intermolecular hydrogen bonding and therefore remain always in a constrained state. Removal of hemicellulose and lignin after alkali treatment reduces internal constraint leading to a closer packing of the cellulose chains with lesser hydrogen bonding and improved wet ability as is revealed from the contact angle measurement (Figure 4). Surface energy of the alkali treated fibres increased with increase in mercerization time suggesting improvement in the polarity of the surface required for better matrix-to resin adhesion. Mechanical properties of fibres are narrated in Table 3. *Tenacity* of mercerized fibres is increases with increase in alkali treatment time (Figure 5) from 0 hours to 8 hours by approximately 71 %. Deviation from the increasing trend is observed for 8 hour treated fibres which may be explained in the similar way as is done for their linear density variation. Modulus of elasticity of sisal fibres (Figure 6) increased with

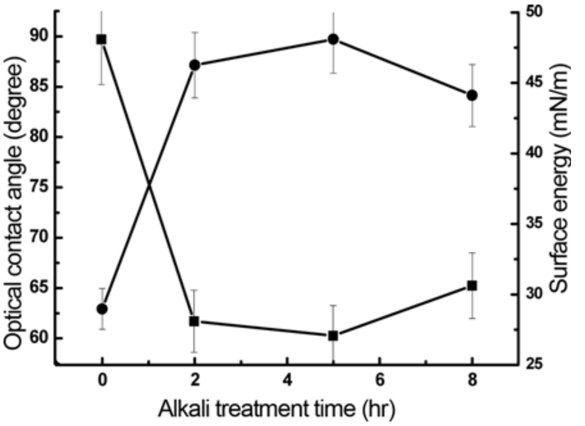


Figure 4. Variation of optical contact angle and surface energy of sisal fibres with alkali treatment time.

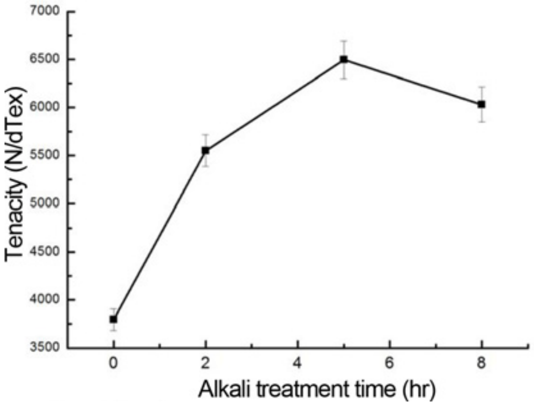


Figure 5. Variation of tenacity of sisal fibres with alkali treatment time.

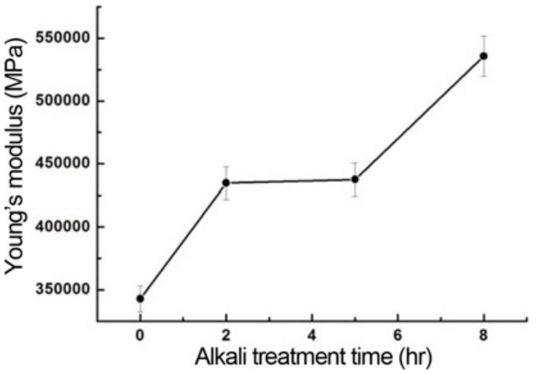


Figure 6. Variation of Young's modulus of sisal fibres with alkali treatment time.

Table 3. Mechanical properties of sisal fibre

Type of fibre	Young's modulus (MPa)	(yEr±) of Young's modulus	Strain at break (%)	Tenacity (N/dtex)	(yEr±) of Tenacity
UNF	342828.125	10284.84	9.167	3795.285	113.8587
2MSisal2h	434703.781	13041.09	5.416	5549.640	166.4892
2MSisal5h	437412.719	13122.36	5.000	6496.550	194.8965
2MSisal8h	535789.188	16073.60	4.583	6031.624	180.9486

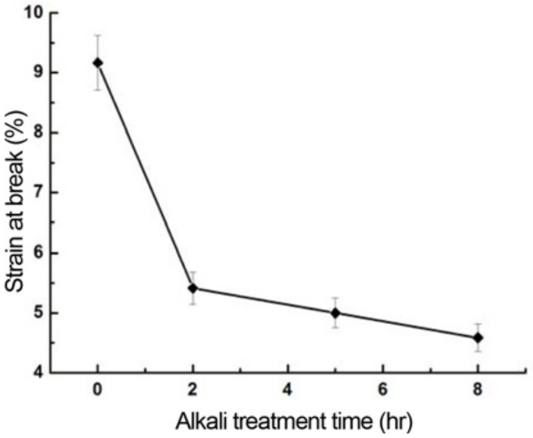


Figure 7. Variation of strain at break of sisal fibres with alkali treatment time.

Table 4. X-ray diffraction results of sisal fibres with and without alkali treatment

Parameter	Untreated fibre (UNF)	2MSisal2h	2MSisal8h
Peak position (2θ)	22.12	22.36	22.57
FWHM	0.141	0.176	0.106
d (A^o)	4.0152	3.9726	3.9361
I_{002} (counts/sec)	42	53	48
I_{am} (counts/sec)	9	10	9
CrI (%)	78.57	81.13	81.25

increases in time of alkali treatment whereas breaking strain (Figure 7) of treated fibres is found to decrease up to 50 % compared to that of the untreated sample after alkali treatment. The results shows that alkali treatment of fibres with 2 % alkali concentration has caused more stiff and brittle fibres as reported for Corchorus Capsularies by others [26].

The pattern of X-ray diffraction of the fibres (Table 4) show that the 002 peak is shifted slightly towards greater angle along with the decrease in d spacing indicating closer packing of the chains in treated fibres than in untreated sample. Crystallinity index for the fibres is found to increase upon alkali treatment and also with increase in soaking time.

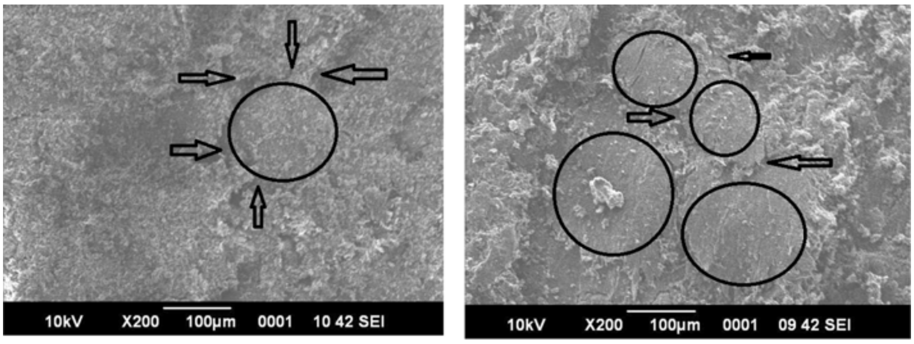
Effect of Alkali Treatment Time on Mechanical Properties of Composite

Composites with (2 % NaOH, 2 hours) alkali treated sisal fibres have shown less porosity fraction (Table 5) compared to that of raw fibre composites. Lower the volume fraction porosity of the composites better is the matrix- to-resin adhesion. Generally, in natural fibre composites due to hydrophilic character of the fibres matrix-to-polymer, adhesion is found to be poor. Incomplete wetting or impregnation often results in the formation of voids or air entrapment. Although the occurrence of voids has been frequently reported and recognized as a major problem in composites, the exact mechanism of void formation is not clear due to its complexity [27]. Alkali treatment of the sisal fibres has resulted decrease in porosity fraction giving indication of lesser void at the interface between the fibre surface and matrix although with increase in fibre loading porosity has increased. Morphology of the cross-sectional view of composites, prepared with 2, 5 and 8 hours alkali treated fibres, before tensile testing exhibited an interesting feature in this connection (Figure 8). For the composites with 2 hr alkali treated fibres, lesser number of pores were evidenced at the fibre/resin interface (marked with arrow) than in untreated fibre composite. However, 2AT8HRSF and 2AT5HRSF composites showed the fibre boundaries (marked with circle) being cemented by the resin in such a way that very less gaps are visible at the interface. Thus stronger fibre to fibre cohesion than fibre-to matrix adhesion for 2AT2HRSF in comparison to other composites may be inferred here.

Table 5. Fibre volume fraction porosity of composites

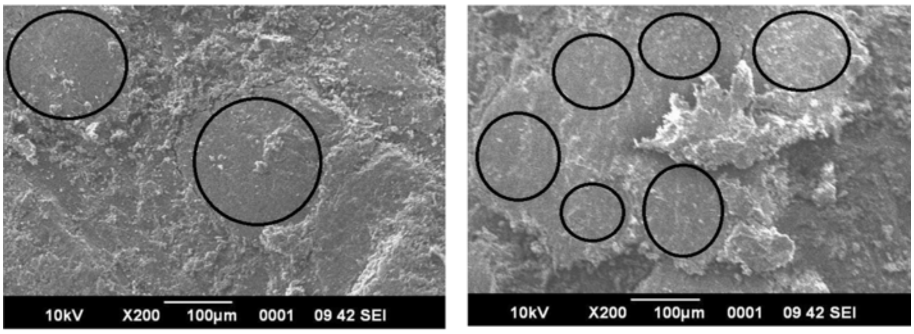
Fibre	Composite	ρ_f (gm/cc)	Weight of fibre (W_f) gm	Weight of matrix (W_m) gm	V_f	V_m	V_m+V_f	$V_p=V_m+V_f-1$
UNF	#UNF10	1.28	2.3	15.8	0.126	1.100	1.226	0.226
	UNF15		3.1	17.9	0.170	1.246	1.416	0.416
	UNF20		3.9	19.4	0.214	1.357	1.571	0.571
	UNF25		4.9	21.5	0.270	1.407	1.677	0.677
	UNF30		5.8	23	0.319	1.601	1.92	0.92
2MSisal2h	§M10	1.066	2.1	15.3	0.138	1.079	1.217	0.217
	M15		3.0	17.6	0.198	1.205	1.403	0.403
	M20		3.8	18.9	0.251	1.316	1.567	0.567
	M25		4.7	19.7	0.311	1.371	1.682	0.682
	M30		5.7	20.5	0.377	1.427	1.804	0.804

*§M10 indicates composites with modified fibre by 10 wt% etc.loading, #UNF10 indicates composites with unmodified fibre by 10 wt%, ρ_m=1.013 gm/cc, V_c=14.175 cc.



Untreated fibre

2hours alkali treated



5 hours alkali treated

8 hours alkali treated

Figure 8. Scanning electron micrograph of untreated and alkali treated sisal fibre reinforced composites with 15 wt% fibre loading.

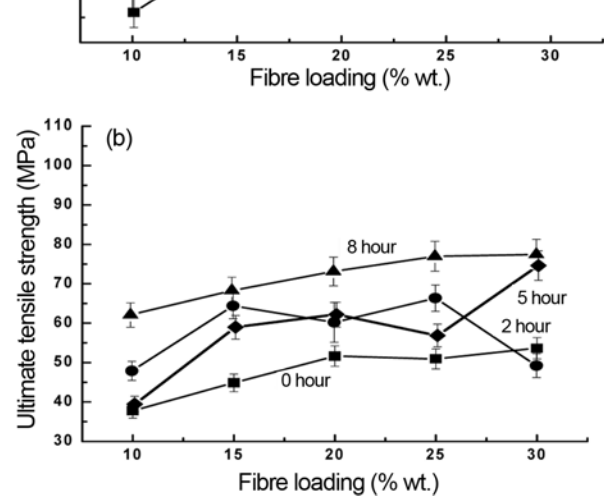


Figure 9. Variation in (a) Young's modulus and (b) tensile strength of sisal fibre reinforced vinyl ester composites with respect to Fibre loading.

Figure 9 represents the dependence of tensile modulus and strength of untreated fibre reinforced (UTFR) and treated fibre filled composites on alkali treatment time. For untreated fibre reinforced composites the mechanical strength varied according to the general rule of mixtures. Tensile modulus increased from 1895.5 MPa to 3108.7 MPa for them with increase in fibre loading. After alkali treatment of the sisal fibres for different duration time, tensile moduli of the composites became higher (5 hrs & 8 hrs soaking time) than that of untreated versions may be due to intrinsically increased matrix to fibre bonding and showed a gradually increasing trend with fibre content up to 20 % in all cases following the rule of mixtures. Such improved adhesion between fibre and resin may be attributed to the removal of lignin from the fibres thereby enhancing availability of polar hydroxyl groups for interaction with the vinyl ester resin surface. However no improvement was observed in case of tensile moduli for composites with fibres when treated for 2 hours may be due to the poor crystallinity of the fibres at this stage. Also when the volume fraction of reinforcement is greater than the critical quantity, tensile modulus of composites dropped because of poor adhesion at the fibre/resin interface in case of longer period mercerized fibres. Alkali treatment for 8 hours has improved the composite tensile strength significantly compared to untreated one with increase in fibre loading though the trend is not maintained in case of short period mercerization.

The experimental values of tensile modulus of sisal fibre reinforced vinyl ester composites with different fibre-volume fraction have been compared with existing theories of reinforcement [28]. According to the Rule-of-Mixtures (ROM), applicable to tensile property of composites based on rigid matrix and non rigid fibrous reinforcement, Young's modulus is calculated using the following equations:

Parallel model

$$M_c = M_f V_f + M_m V_m \tag{9}$$

Series Model

$$M_c = \frac{M_m V_f}{M_m V_f + M_f V_m} \tag{10}$$

Where M_c, M_f and M_m are the Young's moduli of composite, fibre and matrix, respectively. V_m and V_f are volume fractions of matrix and fibre respectively in the composites.

Halpin-Tsai Model

According to Halpin-Tsai, Young's modulus of the composites is given by

$$M_c = Mm\left(\frac{1+A\eta Vf}{1-\eta Vf}\right) \tag{11}$$

Where,

$$\eta = \frac{Mf/Mm-1}{Mf/Mm+A}$$

A function of fibre geometry, fibre distribution and fibre volume fraction, η is the relative moduli of the fibre and matrix [29].

In this case, it is assumed that the fibres in the unidirectional fibre composite are distributed uniformly in the matrix and the fibre/matrix interfacial adhesion is perfect i.e. iso-strain conditions exist for both matrix and fibre. Moreover the parallel model considers the alignment of fibres along the direction of the application of the load in contrast to that in case of series model where the fibre alignment is perpendicular to that of the load direction [30]. The Halpin-Tsai equation has been widely cited in the literature because it provides a fairly good prediction of transverse tensile modulus for continuous fibre composites. It is evident from the results shown here (Figure 10) that the experimental values of modulus of elasticity have similar trend in variation as is predicted by Halpin-Tsai and parallel model. Experimental modulus of (2 % 2 hour alkali) treated fibre reinforced composites are slightly higher than that predicted by Halpin -Tsai model giving significant justification of the treatment (Table 6).

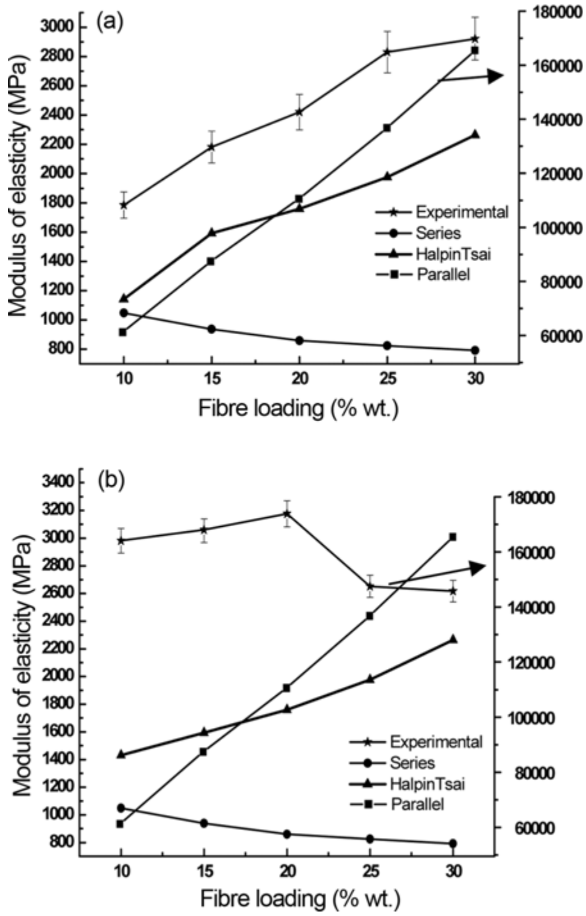


Figure 10. Comparison of experimental Young's modulus of the vinyl ester/sisal fibre composite (a) 2 hour and (b) 8 hour alkali treated fibre with that of theoretical value.

Table 6. Comparison of experimental modulus of elasticity of 2MSisal2h/vinyl ester composites with different theoretical models

Composite	Experimental modulus (MPa)	Series model modulus (MPa)	Halpin-Tsai modulus (MPa)	Parallel model modulus (MPa)
M10	1784.7	1047.84	1431.26	61209.47
M15	2181.1	938.188	1593.86	87434.20
M20	2420.2	858.996	1759.04	110599.0
M25	2830.2	824.458	1976.51	136743.5
M30	2921.4	792.027	2263.77	165497.3

The improvements apparently have occurred almost linearly in case of both flexural moduli (by 65 %) and flexural strength (by 100 %) (Figure 11) of composites with modified fibres (5 & 8 hrs treated) as the fibre loading is varied between 10 to 30 % by wt. in the matrix. However, flexural modulus of composites with untreated fibres is found higher than the composites with mercerized fibres at least up to 25 wt% loading though it does not maintain overall steady trend compared to the other composites. Also, these composites show anomalous trend in flexural strength with variation in fibre loading in them. This behaviour of composites may be explained in terms of poor matrix to fibre adhesion before treatment and higher fibre volume fraction porosity in composites [31]. Beyond a certain concentration of fibre in

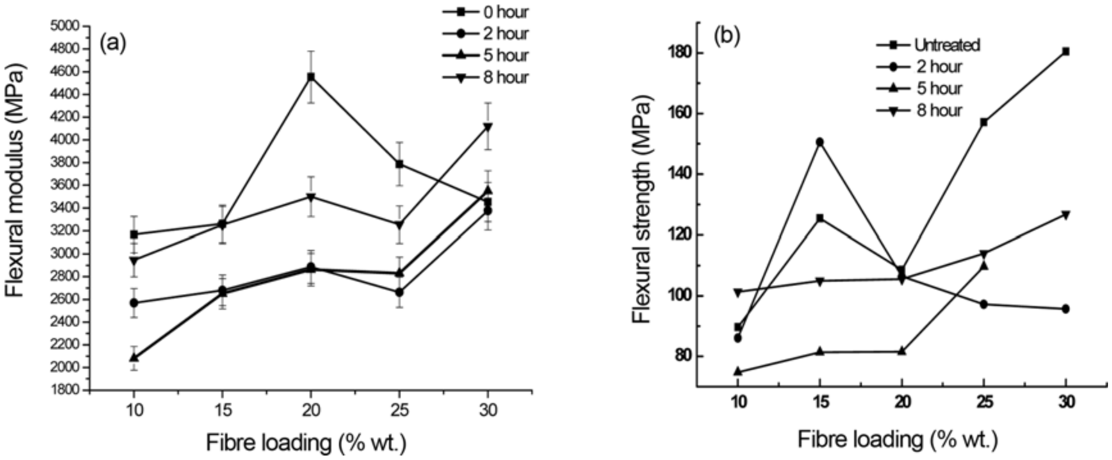
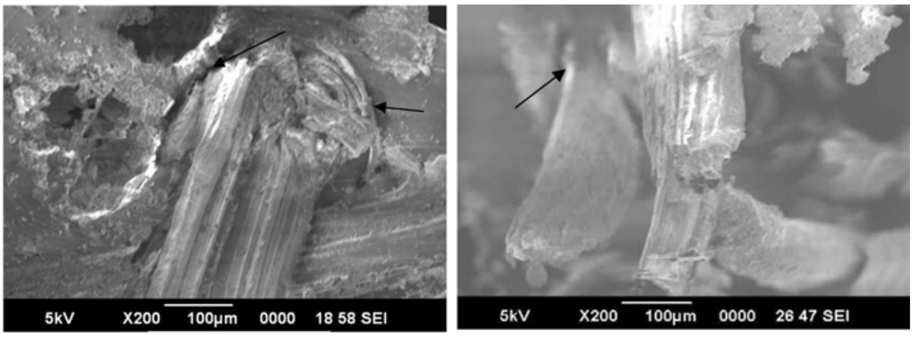
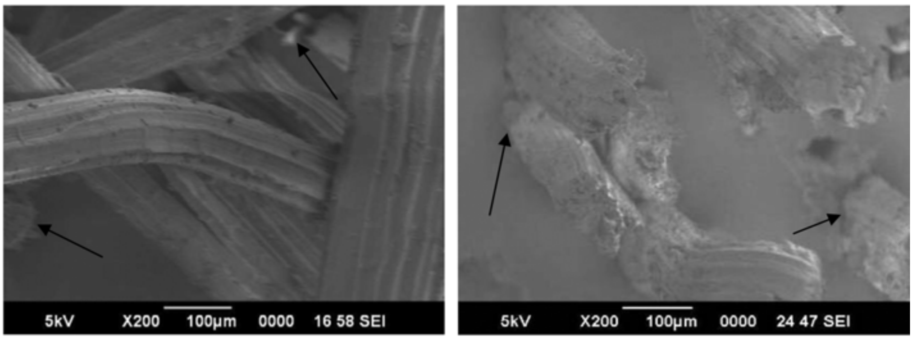


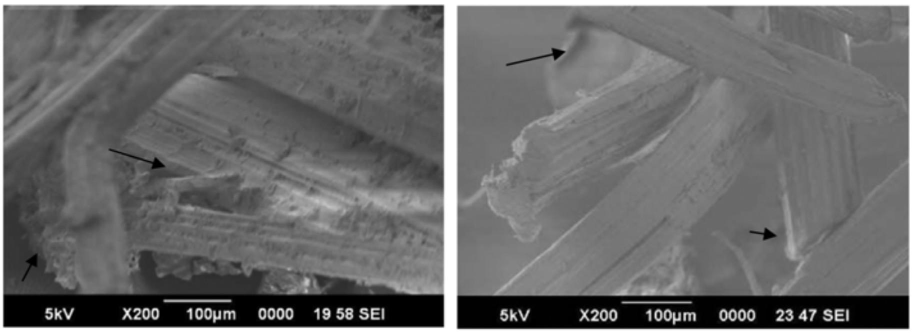
Figure 11. Effect of untreated and alkali treated sisal fibre content on (a) flexural modulus and (b) flexural strength.



Untreated 15 % sisal 15 % sisal treated



Untreated 25 % sisal 25 % sisal treated



Untreated 30 % sisal 30 % sisal treated

Figure 12. Scanning electron micrographs of the tensile fractured composites with comparable fibre loading.

the composites, with 2 hrs alkali treated fibres, loss in flexural strength is revealed may be due to the fibres acting as flaws in the matrix because of poor adhesion [32-35]. Longer treatment time has caused higher modulus with a linear increasing trend showing that alkali treatment has improved matrix-to fibre bonding. The composites prepared with fibres treated for 8 hours show maximum improvement in flexural and tensile toughness up to 25 wt% fibre loading.

Effect of Fibre Loading on Composite Properties

Scanning electron micrographs (Figure 12) of the composites with varying proportion of untreated fibre revealed the fracture behaviour in tensile testing. Even at 15 wt% fibre loading pull out of untreated fibres from the matrix leaving prominent holes back, has exhibited poor adhesion between fibre and matrix resin. On the other hand, with treated fibre composites of corresponding composition, fibre-pull-out seemed to be somewhat difficult rather twisting of fibres at the fractured surface before disintegration is clearly visible. Therefore inferior mechanical properties of the untreated fibre composites can be understood. With variation in the fibre loading from 15 to 25 %, fibre-pull-out tendency is decreased for both the variety of composite may be due to increase in fibre-to-resin ratio and higher porosity volume fraction. With treated fibre composite, sharp breaking of the fibres at the surface instead of total pulling out of them is evidenced, possibly because of better holding of fibre by the matrix. At 30 % loading again the similar fibre-pull-out behaviour is found for the composites with both treated and untreated fibres may be because of the insufficient matrix resin to bind the fibres properly.

Conclusion

Linear density of fibres decreased after alkali treatment due to loss in weight caused by dissolution of lignin. With increase in alkali contact time up to 8 hours increase in linear density of treated fibres was evidenced may be due to some changes in orientation of cellulose chains leading to recrystallisation. Decrease in contact angle and increase in surface energy was observed with increase in alkali treatment time due to increased polarity of fibre surface after treatment. Young's modulus of sisal fibres increased with increase in alkali treatment time up to 8 hr by 56.3 %. Tenacity of mercerized fibres was higher than that of untreated fibres and for alkali treatment time of 5 and 8 hours the values increased by 71 % and 58.6 % respectively. Breaking strain of treated fibres decreased approximately up to 50 % compared to that of the untreated sample after alkali treatment by 8 hrs. Thus after alkali treatment the fibres showed greater modulus and lesser strain at break i.e. the fibres became more rigid. After alkali treatment, sisal fibre surface became more polar and therefore fibre to-resin adhesion increased in composites resulting in lower porosity fraction. However with increase in fibre loading, porosity increased in the composites following the rule of mixing, i.e. beyond a certain critical concentration of fibre it behaves as flaws in the composite matrix rather as reinforcement.

Alkali treatment of fibres for 8 hours caused maximum improvement in properties and 2 hours treatment has been proved to be the least effective one. The improvement in properties apparently occurred almost linearly in case of both flexural moduli and flexural strength as the fibre loading was varied from 10 to 30 wt%. Tensile and flexural strength of the modified fibre reinforced composites became higher than that of untreated fibre versions due to intrinsically increased matrix to fibre bonding and showed a gradually increasing trend with fibre content up to 25 wt%. Heavy fibre-pull out and breakage was observed for composites reinforced with untreated fibres and with fibre content >25 %. The experimental values of modulus of elasticity of composites, 2MSisal2h and 2MSisal8h showed close proximity to the trend of the values predicted by Halpin-Tsai model. However 2MSisal2h composites showed steady increase in properties with increase in fibre loading from 10-30 wt% in comparison to that of 2MSisal8h composites while the highest values were not differing much due to variation in treatment time.

Acknowledgement

Authors would like to express their sincere thanks to Dr.R Bhar and Dr. P.Das Gupta, USIC, Jadavpur University, for carrying out X-ray diffraction of the sisal fibres.

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