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Properties of Ligno-cellulose Ficus Religiosa Leaf Fibers

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The native (untreated) and alkali treated fibers from the ficus leaves were analyzed by Fourier transform infrared (FTIR), Chemical, X-ray and Thermo gravimetric methods. The morphology of the fibers before and after alkali treatment was studied by scanning electron microscopic method. The FTIR and chemical analyses indicated lowering of hemi-cellulose content by alkali treatment of the fibers. The X-ray diffraction revealed an increase in crystallinity of the fibers on alkali treatment. The thermal stability of the fibers was found to increase slightly by alkali treatment. In order to assess the suitability of these fibers as reinforcement, their composites with styrenated polyester as matrix were prepared and their tensile and flexural moduli were determined. Though not much improvement in tensile modulus was detected, however flexural modulus of the composites was found to be enhanced more when alkali treated fibers were incorporated as reinforcement.

Keywords: Ficus leaf fibers, Crystallinity, Hemicellulose, Ligno-cellulose, Morphology, Thermo gravimetric analysis and Mechanical properties

INTRODUCTION

Natural fibers/fabrics have attracted worldwide attention as a potential reinforcement of composites because of their easy availability, as renewable resource, easy processability, low density, lightweight, non-abrasivity, non-hazardousness, recycling nature, low cost and above all environmental friendly characteristics. Thus, the usage of cheap plant and vegetable fibers/fabrics as reinforcement in making green composites is particularly significant from the economic point of view. The natural fibers/fabrics are lignocellulosic consisting á-cellulose as the main component along with hemicellulose and lignin as other components [1-3]. In this direction, many Green composites were developed using plant and vegetable fibers/fabrics [4-12] as reinforcement.

In the present work, we studied the properties of ficus leaf fibers to asses their suitability as reinforcement. The ficus species is native of India, Sri Lanka, Nepal, southwest China, Indochina and Vietnam. We studied some properties of these fibers such as chemical composition, spectral, thermal stability, X-Ray Diffraction (XRD) and morphology. Composites with styrenated polyester as matrix and ficus fibers as reinforcement were prepared and their tensile and flexural moduli were determined. The effect of alkali treatment on these properties was also studied and the results are reported in this paper.

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MATERIALS AND METHODS

Materials

Extracted ficus leaf fibers, sodium hydroxide pellets (Merk, India), benzene, sodium chlorite, acetic acid, sodium bisulphate and ethanol (S.d.fine-Chem, India), Styrenated polyester, Methyl ethyl ketone peroxide and Cobalt naphthanate were used as received.

Extraction of the Fibers from the Leaf

The ficus religiosa leaf fibers were extracted from the matured leaves and fallen leaves. These were dipped in water for three weeks, the green material from top and bottom of the layers was removed by smooth brush. The separated fibers were thoroughly washed with tap water, followed by distilled water and dried in the sun for one week. Then the fibers were kept in an hot air oven for 24 hours at 105-110 °C to remove the moisture. Some ficus leaf fibers were treated with 5% aqueous sodium hydroxide (NaOH) solution at room temperature, maintaining a liquor ratio of 30:1

and fibers were immersed in the alkali solution for 30 min to remove the hemicellulose and other greasy materials. Then the fibers were washed with water repeatedly and treated with dilute acetic acid to neutralise them. Finally the fibers were washed with distilled water before drying in hot air oven for a period of 24 hours.

Preparation of Composites

For making the composites, a glass mould covered by Teflon® sheet having dimensions of 160 X 160 x 3 mm was used. A 3 mm thick laminate was made from the polyester resin (mixed with styrene monomer), catalyst (methyl ethyl ketone peroxide) and accelerator (cobalt naphthanate) taken in the ratio of 100 and 1.5, 1.5 parts by weight respectively. Then the moulding box was loaded with the matrix mixture and ficus fibers in random orientation (with varying fiber content) and was placed at room temperature for 24 hours. The cured laminates were removed from the mould and post cured at 70 ^{o}C for three hours.

Instrumental Analysis

Morphology

The scanning electron micrograms of the surface of the fibers were recorded on a JEOL JSM 820 microscope (Akishima, Japan). The micrograms of the cross section of the fibers were also recorded. The fiber samples were gold coated before recording the micrograms.

Fourier Transform Infrared (FTIR) Spectral Analysis

The fibers were cryogenically cooled and powdered. These powders were diluted to 1% using potassium bromide (KBr) and pellets were prepared. The FTIR spectra of the native and alkali treated samples were recorded in the 4000-500 cm^{-1} region on a Perkin Elmer 16PC FTIR instrument with (Waltham, Massachusetts, U.S.A) 32 scans in each case at a resolution of 4 cm^{-1}.

Chemical Analysis

% of water which is the parts of water per 100parts of leaves, % of green material which is the parts of green material (chlorophyll, polysacharids etc.) per 100 parts of leaves, % of fibers which is the parts of dry fibers per 100 parts of leaves were evaluated in a two step procedure. In the first step, about ten preweighed leaves were heated to 105–110 °C for 24 hours to remove water and the weight loss was converted in to percent water content. In the second step, about ten preweighed leaves were soaked in distilled water for about three weeks to separate the fibers from leaves. The separated fibers were heated in a hot air oven maintained at 105-110 °C for 24 hours and their dry weight was determined. From this, the %dry fibers was subtracted from 100 to get the combined %green material and water and from this the %water as determined is step 1 was subtracted which yields the %green material in the leaves.

The chemical analysis of the native and alkali treated ficus leaf fibers was carried out as per the standard procedure [13, 14]. Extracted cleaned native fibers were finely chopped. The fine chopped fibers were dewaxed by using a mixture of Benzene/ethanol (2:1v/v) at 70 °C for 3hours. The dewaxed fibers were filtered, washed with ethanol for 30 min, dried and weighed. From this, the average %pectin and wax were calculated.

The dewaxed preweighed samples were boiled for two hours in 0.7% sodium chlorite solution (adjusted to pH 4 by using the buffer solution) by maintaining a fiber to liquor ratio of 1:50. Later they were washed with sodium bisulphate solution (5% w/v) and distilled water and dried at 105 °C in an hot air oven. In this step, the lignin was removed so that the lignin and holocellulose (hemicellulose and alpha (α)-cellulose) contents were calculated. From the isolated holocellulose, hemicellulose was removed by treating with 17.5% w/v aq. NaOH solution. The insoluble α-cellulose was filtered, washed thoroughly with distilled water and dried at 105 °C in a hot air oven. In this step, the components of the fiber were estimated. The same procedure also followed for 5% alkali treated fibers.

Thermo Gravimetric Analysis

The thermograms of the fibers were recorded on a Perkin Elmer TGA-7 instrument in nitrogen atmosphere at a heating rate of 10 °C /min in the temperature range of 50–600 °C.

X-Ray Analysis

The wide angle X-ray diffraction spectra of the fibers were recorded on a Rigaku Dmax 2500 diffractometer (Tokyo, Japan). The system has a rotating anode generator with a copper target and wide angle powder goniometer. The generator was operated at 40 KV and 150 mA. All the experiments were performed in the reflection mode at a scan speed of 4° /min in steps of 0.05°. All samples were scanned in 2θ range varying from 5^{o} to 50°.

Tensile and Flexural Properties

The tensile and flexural moduli of the matrix and composites were determined using an Instron-3369 universal testing machine. Specimens with dimensions 100 X 15 X 3 mm were employed. The tensile and flexural tests were conducted at crosshead speed of 5mm/min and 2mm/min respectively. In each case, 10 samples were tested and the average moduli reported.

RESULTS AND DISCUSSION

The photographs of the ficus tree, leaf, and leaf with fibers alone are presented in Fig. 1 (a), (b) and (c) respectively. The leaf belongs to Moraceae family with *Ficus religiosa L* species. Scanning electron micrograms of the surface and cross-section of the native and alkali treated fibers at different magnifications are shown in Fig. 2. From these micrograms it is evident that, on alkali treatment, surface of the fibers became rough. Further, the micrograms of cross-section of the fibers indicate that the fibers have multicellular structure. Each unit cell of fibers is composed of small particles of cellulose surrounded and cemented together with lignin and hemicellulose. Similar observation was made in the case of some other ligno-cellulose fibers also [15-17]. Alkali treatment tends to react with the cementing material hemicellulose, and increase the effective surface available for wetting by the resin.

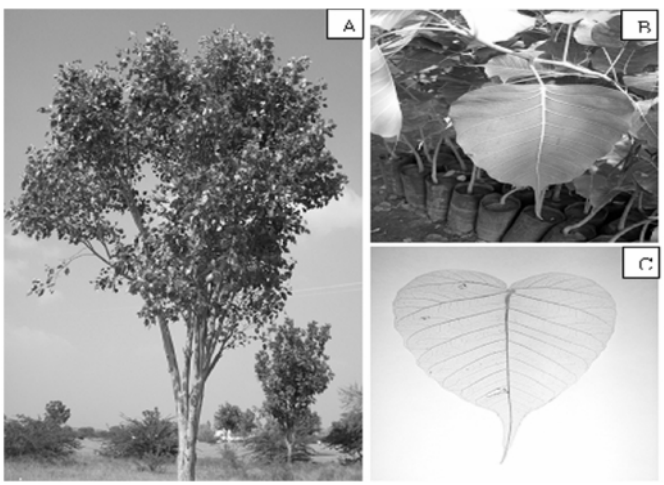

Figure 1: Photographs of (A) Ficus Tree; (B) Leaf; (C) Leaf with Fibers Alone

The composition of the fibers was estimated by chemical analysis as reported in recent literature [18] and as briefly described in the materials and method. Table 1 shows the chemical composition of both native and alkali treated dewaxed fibers. The chemical analysis of native and alkali treated dewaxed fibers (Table 1) indicates the presence of α-cellulose, hemicellulose and lignin. The average %pectin and wax was found to be 2.9 in the fibers.

Table 1
Chemical Analysis of Native and Alkali Treated Ficus leaf Fibers

Component	*Untreated*	*Alkali Treated*
% α-Cellulose	39.4	47.0
% Hemicellulose	34.2	12.6
Lignin	26.4	40.3

In order to confirm the changes in the composition on alkali treatment of the ficus leaf fibers, FT-IR technique was employed. Table 2 shows the characteristic absorptions of α-cellulose, hemicellulose and lignin fractions of the ficus leaf fibers. The FT-IR spectra of the native and alkali treated ficus leaf fibers are presented in Fig. 3. The band positions and their possible assignments of fibers are presented in Table 2. From Fig. 3 and Table 2, it can be observed that for alkali treated and native fibers, well defined bands at around 3435, 2930, 1740, 1631, 1510, 1459, 1430, 1380, 1319, 1257, 1159, 1120, 1050 and 878 cm^{-1}, are present in the spectra. But in the case of native fibers, additional bands at around 1740 and 1257 cm^{-1} are also present which correspond to hemicellulose [19]. On alkali treatment, these bands are found to be almost absent indicating the elimination of the hemicellulose to larger extent. The bands at around 3435 $cm^{-1}$and 2930 cm^{-1} correspond to α-cellulose whereas the remaining bands belong to lignin. Thus, the FT-IR studies suggest the reduction of the hemi cellulose content upon alkali treatment of the fibers. This is in support of the chemical analysis data of the alkali treated fibers as shown in Table 1.

The wide angle X-ray diffraction patterns of native and alkali treated fibers are shown in Fig. 4. The low angle reflections (15° and 22°) are broad whereas the reflection (30°) is sharp and intense. These reflections are attributed to amorphous (I_{am}) and crystalline components (I_{002}) arising from hemicellulose and á-cellulose respectively [20]. The crystallinity index of the fiber is determined [16] by using the following equation (1).

$$I_c = \frac{[I_{(002)} - I_{(am)}]}{I_{(002)}} \times 100 \qquad (1)$$

Where $I_{(002)}$ ($2\theta = 30°$) represents the intensity of crystalline peak while $I_{(am)}$ (average of $2\theta = 15°$ and

Table 2
Peak Positions and Assignments of Chemical Groups in the Native and Alkali Treated Ficus Leaf Fibers

Untreated Wavenumber (cm^{-1})	*Alkali Treated*	*Assignments*
3435	3416	OH-stretching of α–cellulose
2930	2917	Alkyl CH stretching
1740	– –	C=O stretching of hemi cellulose
1631	1630	C=C stretching of lignin
1510	1510	Aromatic skeletal vibration of benzene ring in lignin
1459	1458	CH deformation (methyl & methylene)
1430	1431	CH in plane deformation with aromatic ring stretching
1380	1371	CH bending of lignin
1319	1330	CH_2 wagging
1257	– –	CH bending of hemicellulose
1159	1160	Asymmetric C-O-C stretching of lignin
1120	1120	
1050	1049	Symmetric CO stretching of lignin
878	894	CH stretching (β-glycosidic linkages between the Monosaccharides)

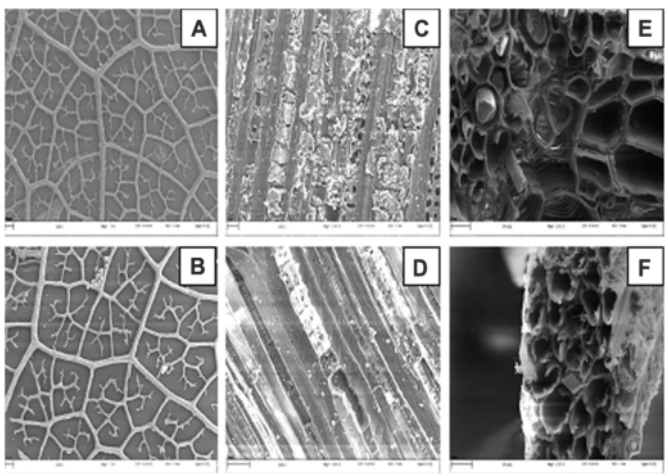

Figure 2: Scanning Electron Micrograms of Native and Alkali Treated Ficus Leaf Fiber

(A) Native fiber (78 X);

(B) Alkali treated fiber (75 X);

(C) Native fiber (1.99 KX);

(D) Alkali treated fiber (1.99 KX);

(E) Cross-section of native fiber (3.36 KX);

(F) Cross-section of alkali treated fiber (3.70 KX);

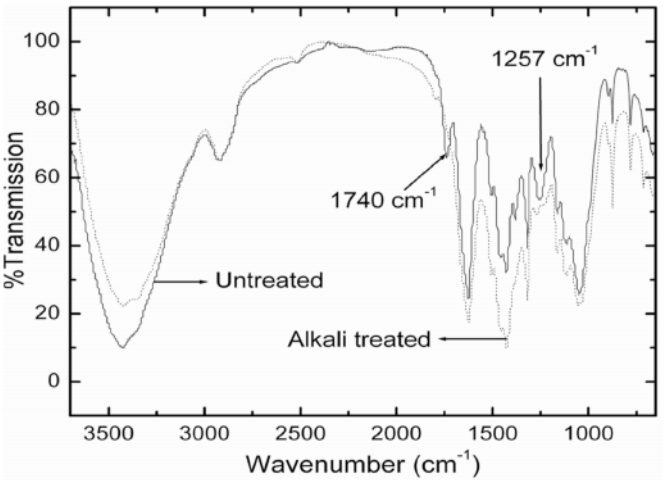

Figure 3: FT-IR Spectra of Native and Alkali Treated Ficus Leaf Fiber

22°) denotes intensity of the amorphous peak in the diffractograms. Accordingly, the calculated crystallinity values for native and alkali treated fibers are found to be 37.1 and 72.7 respectively. The increase in crystallinity of treated fibers is due to loss of amorphous hemicelluloses. It is in conformity with the results of FT-IR and chemical analyses.

The primary thermograms of the both native and after alkali treated fibers are presented in Fig. 5. Using these thermograms, the initial degradation temperature, 25% and 50% degradation temperatures, refractoriness (T*), inflection point (where the degradation rate is maximum) and integral procedural degradation temperature (IPDT) were calculated using the Doyle [21] method. These values are presented in Table 3. From the table, it is clearly evident that the initial degradation temperature and IPDT of the alkali treated fibers are slightly higher than those of the native fibers. Though the inflection point and refractoriness are found to be lowered slightly by alkali treatment, the %residue at 600 °C for alkali treated fibers is higher (38.9%) when compared to that of native fiber (31.6%). The char contents of ficus fibers are compared with those of other natural fibers/fabrics. These are presented in Table 4. From this table, it is evident that ficus leaf fibers are having highest char content. On the whole, it is evident that when the fibers were treated with alkali, the thermal stability is slightly enhanced. This may be due to the removal of amorphous hemi cellulose content from the fibers on alkali treatment. Further, these results indicate that alkali treated fibers can be used as reinforcement even in thermoplastic matrix materials whose processing temperature is below 280 °C.

Table 3
Thermal Degradation Parameters of Native and Alkali Treated Ficus Leaf Fibers

Degradation parameter	*Untreated*	*Alkali treated*
Initial degradation temperature °C	289	292
25% Degradation temperature °C	301	305
50% Degradation temperature °C	350	355
Inflection point °C	349	334
IPDT	242	232
Refractoriness	497	560

Table 4
% Char Content of Some Natural Fibers

S.No	*Fiber*	*% Char content*		*Ref*
		Untreated Fiber	*Alkali treated fiber*	
1.	Hildegardia	6	15	[22]
2	* Ridge gourd			
	A) Top layer	22.9	24.2	[1]
	B) Bottom layer	0.4	20.6	
3	Tamarind	12.9	25.3	[23]
4	Sterculia urens	2.4	15.0	[24]
5	Borassus			
	A) Fine Fiber	12.9	19.8	[25]
	B) Coarse fiber	18.4	18.4	
6	Ficus	31.6	38.9	Present work

* At 500 °C

As ficus leaf fibers are renewable and environmental friendly and have thermal stability, these can be considered as reinforcement in the preparation of thermoset and thermo plastic composites. In order to probe this further, the tensile and flexural moduli of composites of styrenated polyester reinforced with different loadings of untreated and alkali treated fibers are presented in Fig. 6 and Fig. 7 respectively. From Fig. 6, it is clearly evident that the tensile modulus of the composites increased marginally with fiber content. However, the modulus is found to be higher when alkali treated fibers were incorporated in the composites. From Fig. 7, it is clearly evident that with fiber content up to 6% fiber loading the flexural modulus increased and afterwards it decreased. These observations reveal that 6% fiber loading is optimum and beyond this the wetting problems arise. We have observed that 8% is the maximum fiber loading that is possible in making these composites. The improvement in tensile and flexural moduli when alkali treated fibers were incorporated in the composites may be attributed to

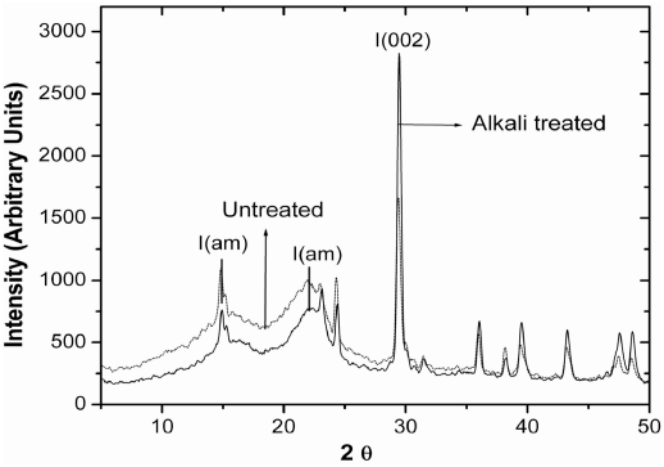

Figure 4: X-Ray Diffractograms of Native and Alkali Treated Ficus Leaf Fiber

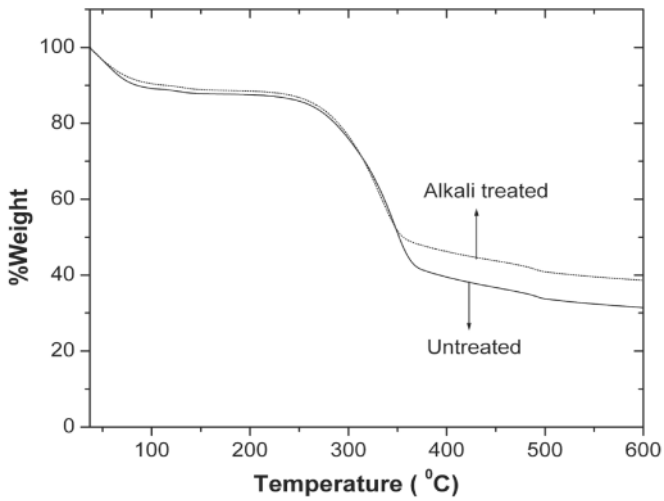

Figure 5: Primary Thermograms of Native and Alkali Treated Ficus Leaf Fiber

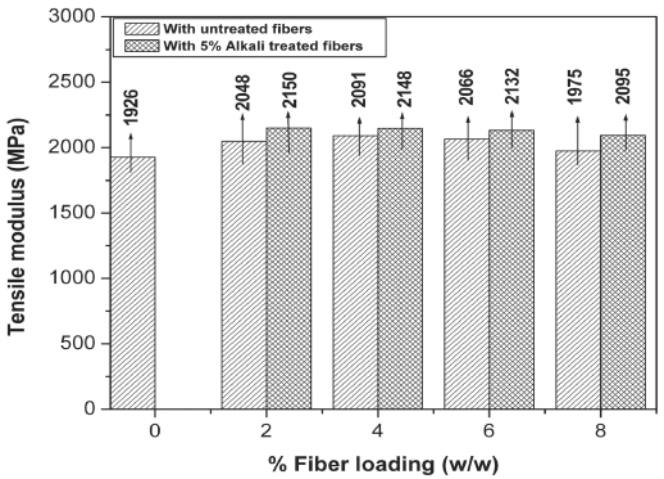

Figure 6: The Tensile Moduli of Styrenated Polyester Reinforced with Different Contents of Untreated and Alkali Treated Ficus Leaf Fibers

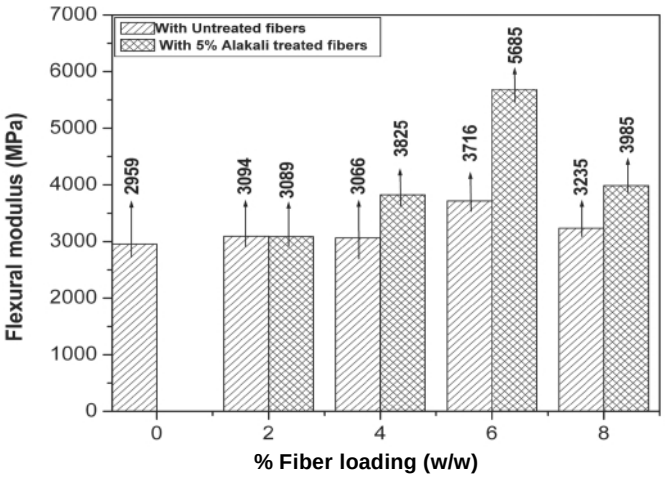

Figure 7: The Flexural Moduli of Styrenated Polyester Reinforced with Different Contents of Untreated and Alkali Treated Ficus Leaf Fibers

the improved crystallinity leading to higher strength and surface roughening (Fig. 2 A, B, C and D) facilitating better bonding between the reinforcement and the matrix. As both the fibers and matrix are having polar groups in their molecules, such a bonding is expected.

CONCLUSIONS

The ficus leaf fibers extracted from ficus leaves were analyzed by SEM, FTIR, XRD and TGA techniques. The amorphous hemicellulose was found to be eliminated to large extent on alkali treatment. Due to this, the crystallinity of the alkali treated fibers was found to increase. The flexural modulus of polyester was increased when these fibers were incorporated as reinforcement. Basing on the thermal stability, the renewablity and environment friendly natures, ficus leaf fibers can be favorably considered as reinforcement in green composites.

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