Influence of Alkali Treatment on the Fine Structure and Morphology of Bamboo Fibers

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ABSTRACT: Bamboo fibers in the form of strips and dust were treated with NaOH solution of varying concentration (10, 15, and 20%). These treated and untreated samples were then subjected to FTIR and morphological studies. Again XRD study was carried out on those treated and untreated bamboo samples in both strip and dust form. It was found that during alkali treatment a lattice transformation from cellulose-I to cellulose-II took place. It is observed from IR index value that the conversion is maximum in between 15 and 20% of alkali treatment. Swelling in NaOH introduces considerable changes in crystallinity, orientation angle, etc. Degree of crystallinity and crystallinity index for bamboo strips increases with increasing treatment concentration of alkali and falls off after 15% alkali concentration. This is also supported by *d*-spacing value. Orientation factor f_x was calculated from the FWHM and it was found that f_x value has been increased from 0.9879 to 0.9915 for 15% alkali treated and again lowered to 0.8522 for 50% alkali treated samples. Same observation of X-ray study was obtained for dust samples but at an earlier concentration. Morphological study of bamboo dust with scanning electron microscope indicates fibrillation at higher alkali concentration. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5050–5056, 2006

Key words: crystallization; FTIR index; morphology; orientation; fibers

INTRODUCTION

For a better utilization of natural fibers as reinforcements in composites, information on the structure, properties, and their interrelationships is essential. Among the natural fibers, bamboo fiber can be suitably used due to its high strength property, easy availability at low cost, especially in the eastern regions of India.

For lingo-cellulosic fiber to be effective reinforcing constituents, it is essential that the fiber and the resin matrix have a good compatibility and bonding. To make them suitable reinforcing agent with adequate bonding characteristics for general application, various chemical treatments have been carried out with the natural fibers. Among the many convenient surface treatments employed, the most economically viable one is the alkali treatment.

The process of alkali treatment of natural fiber is known as mercerization. According to ASTM D 1695, this is the process of subjecting a vegetable fiber to the action of a fairly concentrated aqueous solution of a strong base so as to produce great swelling with resultant changes in fine structure, dimensions, morphology, and mechanical properties.[1] Several studies have been reported on the effect of mercerization on the fine structure and mechanical properties of natural fibers.[2–6] Ray and Sarkar observed increase in crystallinity of jute fiber with increase in time of alkali treatment (5% alkali solution) and same was obtained with coir and flax fiber also.[6–8] Although, there are many views on effects of alkali treatment on various natural fibers, information and its explanation for bamboo is scanty.

An attempt has therefore been made, to investigate the changes occurring in fine structure of bamboo fiber due to treatment with different concentration of alkali solution (10, 15, 20, and 50%). The fibers were then characterized using FTIR, scanning electron microscope and X-ray diffraction study.

EXPERIMENTAL

Bamboo belonging to the variety Bamboosa Balcua were supplied by FOSET (Forum of Scientist, engineers and Technologists), West Bengal. It was supplied in the particulate form (30–36 mesh size) and also in strip form with an average dimension of $100 \times 15 \times 1.5$ mm^3. This specimen is used through out the study.

Alkali treatment

Bamboo fibers (both in strips and dust form) were soaked in caustic soda solution with varying concen-

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TABLE I
Table for Sample Designation

Concentration of alkali solution used for treatment of bamboo (%)	Sample designation
Untreated	B-0
10	B-10
15	B-15
20	B-20
50	B-50

tration (10, 15, 20, and 50%) (Table I) at ambient temperature, maintaining a liquor ratio of 15 : 1. The fibers were kept immersed in the alkali solution for 1 h. Then the fibers were copiously washed with distilled water to remove any traces of alkali sticking to the fiber surface and subsequently neutralized with 2% sulfuric acid solution. The neutrality was checked with litmus paper. Then the fibers were dried in a hot air oven at 105°C.

TESTING

X-ray crystallinity

The powder diffractogram of untreated and treated bamboo were obtained by using a Philips PW 1710 X-ray diffractometer, employing Ni filtered CuKα radiation. Total crystallinity and amounts of cellulose I and cellulose II wherever required were computed according to Sreenivasan et al.[2]

Full width half maximum peak width (FWHM)

This is the difference in angle across the peak where the intensity is 50% of the maximum value. It indicates the order of arrangement or crystallinity of structure.

Hermans' orientation factor (f_x)

It is calculated by the equation

$$f_x = 1 - 3/2\ \sin^2 \alpha,$$

and for mercerized fibers constituting a major lattice of cellulose II:

$$f_x = 1 - 7/2\ \sin^2 \alpha,$$

where α is the mean orientation angle.[2] (Value of $\sin^2\alpha$ is obtained during analysis direct from instrument.) This orientation angle takes into account the spirallity of crystalline fibrils. Hermans' orientation factor is linearly related to some physical properties, e.g., modulus of sample.

Crystallinity index

Percentage crystallinity index (%CrI) expresses the relative degree of crystallinity. The equation used to calculate the CrI was modified by Segal et al.[8] in the following form:

$$\mathrm{CrI} = [(I_{002} - I_{\mathrm{am}})/I_{002}] \times 100$$

where I_{002} is the maximum intensity (in arbitrary units) of the 002 lattice diffraction and I_{am} is the intensity of diffraction in the same as $2\theta \sim 18^\circ$. For mercerized fiber Ingersoll et al. used the intensity of $1\bar{0}1$ plane, $I_{1\bar{0}a1}$ as this gives the maximum intensity value for mercerized fiber,[9] i.e., for cellulose II.

Degree of crystallinity

Theory predicts that the total intensity of X-ray scattered by a given material is independent of the state of order. This suggests that if one could partition the scattering into scattering arising from the crystalline component and scattering arising from the amorphous component; it would be possible to measure the mass fraction of crystalline material, i.e., the degree of crystallinity. Ruland, in 1961, proposed a method for achieving this partitioning.[10] More commonly, approximately, calibrated methods of measuring crystallinity, W_c, are employed where

$$W_c = I_c/(I_c + KI_a)$$

where $K = 0.884$ and the range of intensities is 10–32° in 2θ.[11]

Infrared spectroscopic study

IR spectra of finely cut bamboo fibers were recorded using a JASCO FTIR (JSM4200) IR spectrophotometer in a KBr matrix. IR index values, obtained with normalizing the absorbance peak at 609 and 2922 cm^{-1}, have been used to indicate removal of hemicellulose with alkali treatment. The IR index values based on the absorbance peaks at 893 and 2922 cm^{-1} have been used to analyze the conformational changes occurring during treatment.

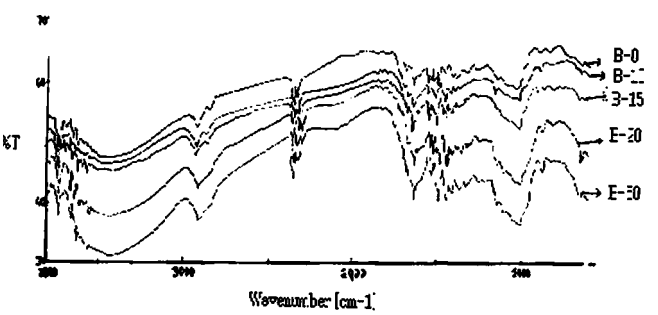

Figure 1 FTIR spectra of untreated and alkali treated bamboo dust.

TABLE II
Data from FTIR Spectra of Untreated and Alkali Treated Bamboo Dust (Transmittance in cm^{-1})

Probable assigned peaks (cm^{-1})	B-0	B-10	B-15	B-20	B-50
=OH stretching vibration	3300–3800	3100–3800	3200–3800	3300–3800	3400–3800
=CH stretching vibration cell/ hemicellulose	2921.63	2922.59	2922.59	2922.59	2922.59
=OH stretching vibration of inter- and intramolecular H-bonding	2853.17	2852.2			
>CO stretching of carboxylic acid or ester	1733.69	1733.69	1733.69	1733.69	1732.73
Absorbed water	1636.3	1636.3	1636.3	1636.3	1636.3
>C=C stretching vibration of lignin	1608.34	1608.34	1612.2	1612.2	1612.2
Lignin component	1464.67–1530.24	1464.67–1530.24	1464.67–1530.24	1464.67–1530.24	1464.67–1530.24
$>CH_2$ bending in lignin	1436.71	1436.71	1436.71	1436.71	1436.71
$>CH_2$ and $=CH_3$ bending	1419.3	1419.35	1419.35	1419.35	1419.3
=CH bending	1384.64	1382.71, 1387.53	1383.68, 1387.53	1383.68, 1386.57	1383.68, 1386.57
>CO stretching of acetyl ring	1363.43–1339.32	1369.21–1320.04	1368.25–1319.97	1368.25–1319.17	1363.43–1319.07
Antisymmetric bridge C=O=C stretching	1160.94	1161.9	1163.83	1158.04	1159.97
>CO/C=C stretching vibration	1044.26	1032.33	1025.3	1019.8	1017.26
β-glucosidic linkage	896.73	896.73	897.7	897.91	897.73
Out-of-plane bending vibration of intermolecular H-bonded =OH group	680.74, 669.17	689.427, 669.17	693.284, 669.17	669.17	669.17
Torsional vibration of pyranose ring	602.64–516.83	605.539–512.008	606.5–511.04	609.39–513.93	609.39–513.93

Morphology

Morphology studies were undertaken in a scanning electron microscope (Jeol JSM 5200) akter suitable gold coating on the treated and untreated bamboo samples in the particulate form.

RESULTS AND DISCUSSIONS

Figure 1 represents the IR spectrums of untreated and alkali treated bamboo samples. The significant transmission bands observed and the corresponding probable assignments responsible for the bands are given in Table II.

It was observed, that the peak area due to OH stretching vibration within the region 3100–3800 cm^{-1} increased considerably with increase in alkali concentration. It indicates that with increase in alkali concentration more and more alkali sensitive material has been removed resulting increasing number of —OH grs. A band at 2853.17 cm^{-1} in the untreated bamboo attributed to the —OH stretching vibration of inter and intramolecular H-bonding present among cellulose, hemicellulose and lignin molecules of bamboo fiber making the total structure as a network. With increasing treatment concentration of alkali the network structure were gradually destroyed and completely disappeared beyond 10% alkali concentration. Peak at 1733.69 cm^{-1} is ascribed to the >CO stretching of carboxylic acid or ester present in the bamboo.

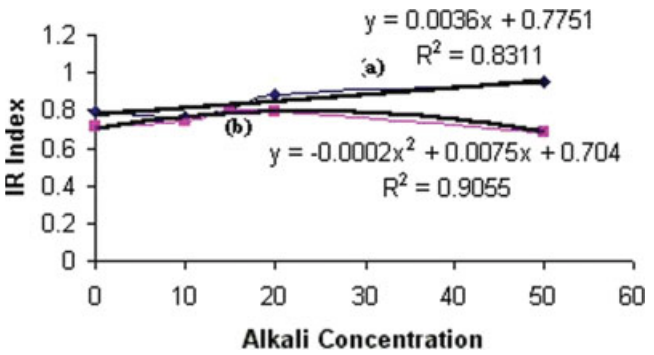

Figure 2 Plot of IR index values as obtained from FTIR spectra of untreated and alkali treated bamboo dust versus concentration of alkali solution; (a) for 609 cm^{-1}, (b) for 893 cm^{-1}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

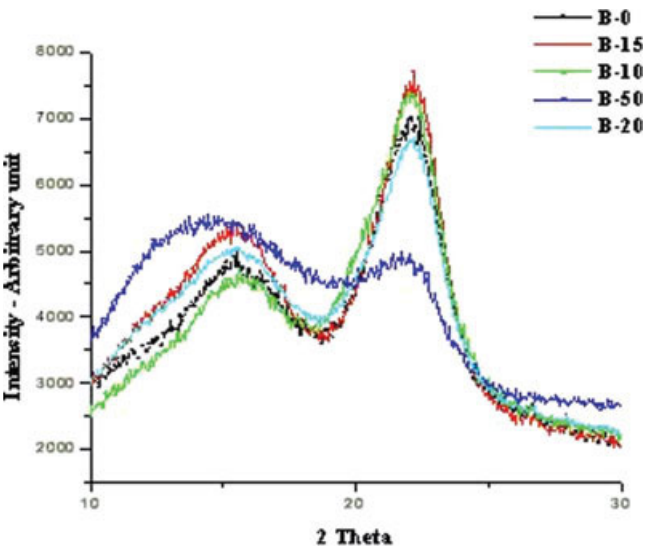

Figure 3 XRD study of untreated and alkali treated bamboo strips. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

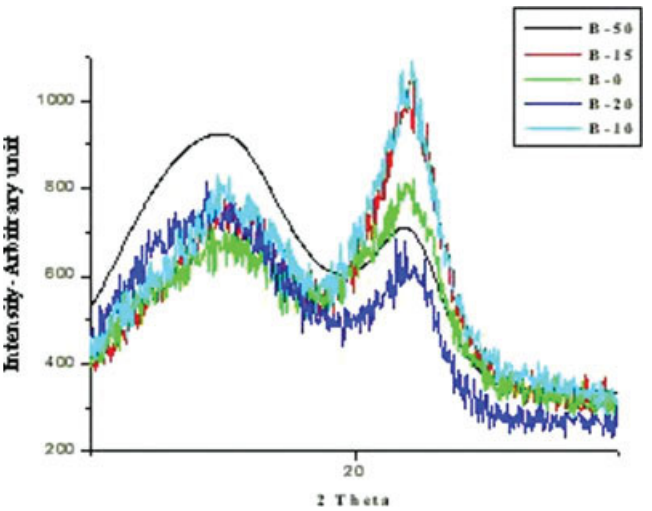

Figure 4 XRD study of untreated and alkali treated bamboo dust. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The peak intensity is gradually reducing as the concentration of the particular group has been reduced due to removal of hemicellulose. The short peak at 1636.3 due to absorbed water has been intensified with higher alkali treatment indicating a higher amount of absorbed water. FTIR spectra for parent and treated bamboo in the region beyond 1636.3 to 1160 cm^{-1} are almost similar and are due to various characterists of specific groups as indicated in Table II. There is a lower shift at the peak 1044.26 cm^{-1} (C—O/C—C stretching vibration) probably due to change in molecular orientation.er present in the parent bamboo. The strong band at 893.73 cm^{-1} due to β-glucosidic linkage in untreated bamboo underwent a shift to higher wave numbers in the treated fibers. This is due to the rotation of glucose residue around the glucosidic bond.[12] The bands at 680.74 and 669.17 cm^{-1} are due to an out of plane bending vibration of an intermolecular H-bonded —OH group. The peak at 680.74 cm^{-1} has been disappeared after sample B-15 is probably due to the gradual depletion of hemicellulose with increasing alkali treatment. The bands at and beyond 669.17 cm^{-1} corroborate clearly with the discussion of Blackwell et al.[13]

Figure 2 shows the plots of IR indices based on the absorbance values of the peaks at 893 and 609 cm^{-1} with respect to the absorbance peak at 2922 cm^{-1}. The intensity change in the 609 band is influenced by the torsional vibration of pyranose ring. The increase in the value of IR index with the increasing alkali treatment indicates that the removal of cementing material from bamboo allows the pyranose ring to undergo more torsional vibration.

The IR index values for the peak at 893 cm^{-1} are maximum for the sample, B-15 and then fall off. The values at 15 and 20% alkali treatment are comparable. The intensity for this peak is influenced by conformational changes occurring during conversion of cellulose-I to cellulose-II.[2] It is observed that the conversion is maximum in between 15 and 20% alkali treatment.

Figures 3 and 4 show the X-ray diffractograms for the native and mercerized bamboo samples both in strip and dust form respectively. Swelling in NaOH introduces considerable changes in crystallinity, orientation angle, etc. All the parameters, which have undergone a change after mercerization, are given in the Tables III and IV.

Sodium hydroxide when reacts with cellulose forms stable compound, sodium cellulosate or soda cellulose by replacement of the ionizable hydrogen in the —OH groups of cellulose with Na+ ions. A sodium polyalcoholate is formed which is in equilibrium with the steeping solution.[14] When the soda-cellulose compound is completely destroyed, by subsequent washing with distilled water and neutralization with H_2SO_4, a lattice transformation from cellulose-I to cellulose-II results. Cellulose-I contains two coexisting phases cellulose-I_α (triclinic) and cellulose-I_β (monoclinic) in varying proportions dependent on its origin. It can be recrystallized from base to a thermodynamically more stable structure, which consists of two different types of anhydroglucose unit in back-bone structures; The chains consisting of —A—A— or —B—B— type repeat unit.[15]

TABLE III
Data from XRD Study of Untreated and Alkali Treated Bamboo Strips and Dust

	Crystallinity (%)		Degree of crystallinity		Amorphous (%)		Cellulose-I (%)		Cellulose-II (%)	
Sample	Strip	Dust	Strip	Dust	Strip	Dust	Strip	Dust	Strip	Dust
B-0	45.57	43.54	0.6751	0.667	54.43	56.46	45.57	43.54	0	0
B-10	50.1	45.84	0.6939	0.6762	49.9	54.16	35.46	38.23	14.64	7.6
B-15	51.48	44.82	0.6955	0.651	48.2	55.18	34.03	31.01	17.85	14.81
B-20	47.55	41.6	0.6846	0.634	52.55	58.4	29.71	8.52	17.84	33.08
B-50	17.82[a]	18.51[a]	0.5792	0.5309	82.18	81.49	1.94	1.71	15.88	16.8

[a] $I_{max} = I_{101}$, in all other cases $I_{max} = I_{002}$.

TABLE IV
Data from XRD Study of Untreated and Alkali Treated Bamboo Strips and Dust

	FWHM		Herman's orientation factor (f_x)		Mean orientation angle		d-spacing	
Sample	Strip	Dust	Strip	Dust	Strip	Dust	Strip	Dust
B-0	5.1482	5.2294	0.9433	0.9425	11.20	11.28	4.0188	4
B-10	4.81	4.8500	0.9447	0.9444	11.06	11.09	4.0131	3.98
B-15	4.3136	4.6335	0.9448	0.9455	11.05	11.04	4.01	4
B-20	4.9117	16.4042	0.9459	0.8727	10.94	10.99	4.025	4.02
B-50	18.2896	16.3893	0.8748	0.8767	10.89	10.84	4.073	4.03

The extent of conversion depends on the experimental conditions. Much of the swollen cellulose frequently does not recrystallize, resulting in a large fraction of disordered (amorphous) cellulose, which can be detected with X-ray diffraction.

Figure 3 shows, that in case of bamboo strips increasing with alkali treatment %CrI is increasing, because of the removal of the cementing material which leads to a better packing of cellulose chains. The fact is also supported from the trend of d-spacing values of lattice. For B-50 sample the crystallinity is due to cellulose-II structure. Degree of crystallinity follows the same trend of %CrI. In the X-ray diffractogram the low resolution of peaks is indicative of less crystalline perfection and of the presence of large amounts of noncellulosic matter. The resolution of the peaks improves after alkali treatment and the diffractogram shows the signs of better crystalline order than the control up to 15% alkali treatment beyond that the crystallinity falls off. It is found that the lattice transformation takes place faster than the recrystallization process after 15% alkali concentration. The intensities were then normalized and the amounts of cellulose-I and cellulose-II in the control and treated samples were calculated by following standard methods.[16] This confirms that with increasing concentration of alkali solution percentage of cellulose-II increases and maximum amount of cellulose-II is obtained with 50% alkali solution for strips samples.

The decreased FWHM value is also indicative of a higher crystallinity or better-ordered arrangement of fibers. Treatment up to 15% alkali solution induces conversion of cellulose-I to cellulose-II with the treated fibers showing increasing crystallinity. Beyond this, higher alkali solution promotes further lattice conversion to cellulose-II but at the same time the FWHM value increases markedly indicating randomness in the structure, which is also reflected in increased amount of amorphous cellulose.

Orientation factor f_x is calculated from the mean orientation angle, α value and it has been found f_x value has been increased from 0.9433 to 0.9459 for B-20 sample. It has been lowered to 0.8748 for B-50 sample. It is known that f_x is linearly related to modulus and in another work[17] we have reported that the modulus of bamboo strips increases up to 20% alkali treatment and then it was decreased from 25% alkali treatment and onwards. For dust samples same observation is true but at an earlier stage. It was found that orientation factor (calculated against 002 plane) dropped suddenly at an

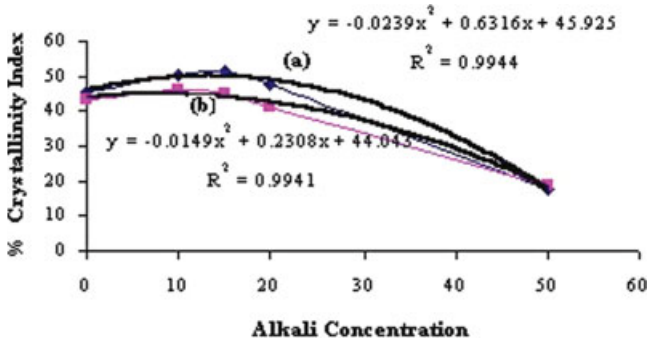

Figure 5 Plot of % crytallinity index values as obtained from XRD study of untreated and alkali treated bamboo strips and dust versus concentration of alkali solution; (a)- for bamboo strip sample, (b)- for bamboo dust samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

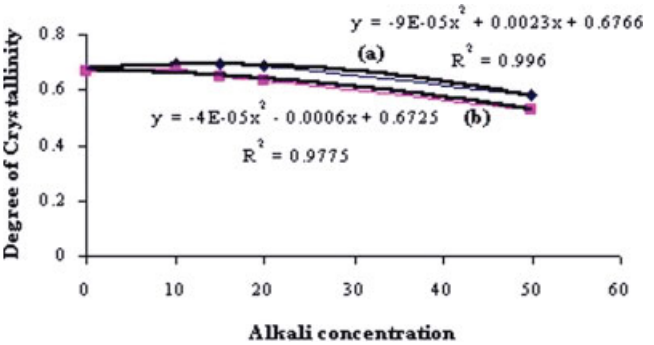

Figure 6 Plot of degree of crystallinity values as obtained from XRD study of untreated and alkali treated bamboo strips and dust versus concentration of alkali solution; (a)- for bamboo strip sample, (b)- for bamboo dust samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

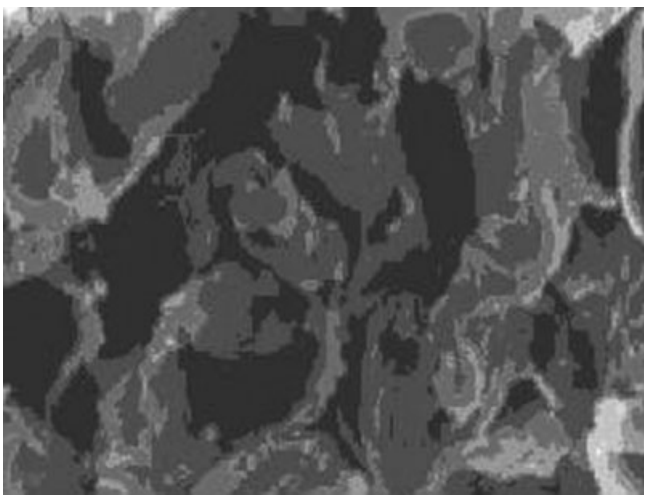

Figure 7 Scanning electron micrograph of untreated bamboo dust.

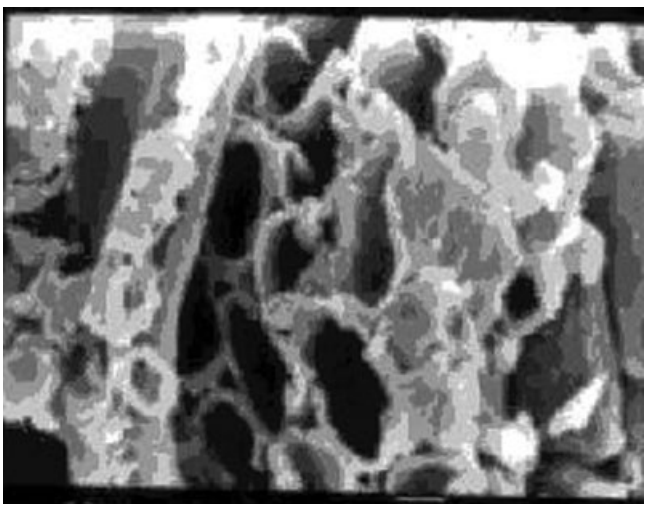

Figure 9 Scanning electron micrograph of 20% alkali treated bamboo dust.

alkali concentration where mercerized fiber predominates.

Mean orientation angle obtained from the data are also given. This parameter is indicative of spiral angle (the angle at which the fibril spirals around the axis of the fiber). The decrease in orientation angle is resulted from an increased orientation of fibrils with respect to the fiber axis. There is not any marked difference in orientation angle due to alkali treatment.

From Figure 4 it has been cleared that the same observation is true for mercerized bamboo dust samples but reached at an earlier concentration as during alkali treatment the dust samples provide a larger surface area for leaching out the cementing materials. In this case, cellulose-II is maximum for B-20 samples and in presence of strong alkali the glucosidic bond cleavage of cellulose leads to increase in amount of amorphous cellulose.

Changes in fine structure were also observed from scanning electron micrographs (SEM) of treated and untreated bamboo dust samples as shown in Figure 5–10. Bamboo is a lignocellulosic composite fiber, which consists of crystalline α-cellulose and amorphous cementing material hemicellulose and lignin. Figure 7 indicates that the morphology for untreated sample is more homogeneous than the others showing better bonding in between α-cellulose and the matrix. The fiber lumen is not so well defined. Whereas after alkali treatment the fibers are becoming more and more convoluted and the lumens are well defined with increasing alkali treatment. The matrix is disturbed due to removal of noncellulosic

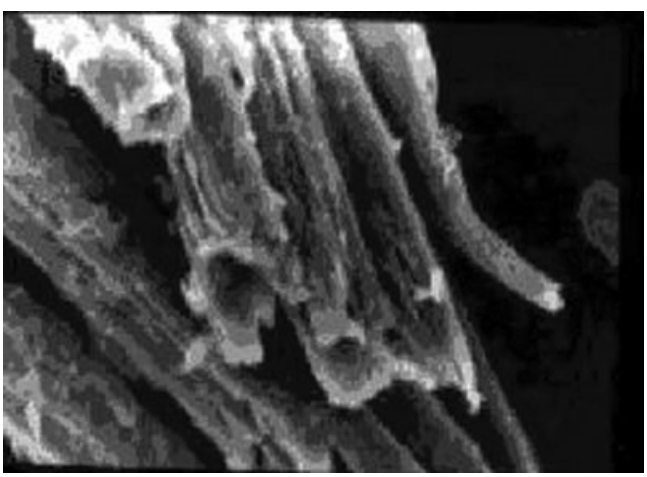

Figure 8 Scanning electron micrograph of 10% alkali treated bamboo dust.

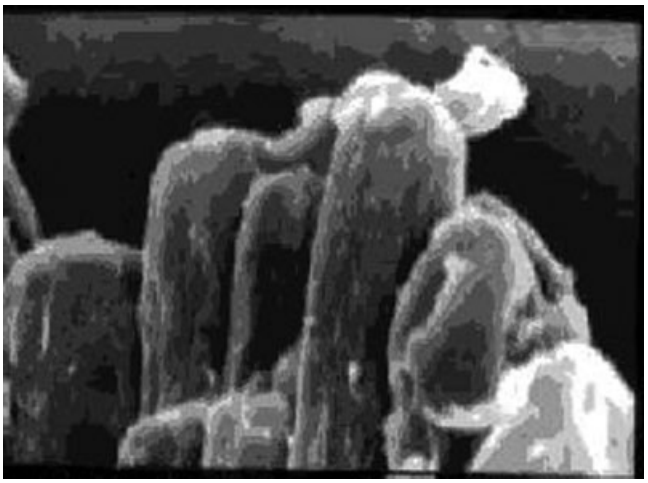

Figure 10 Scanning electron micrograph of 50% alkali treated bamboo dust.

material showing a sign of debonding. It is well known that alkali reacts with hemicellulose faster and then with lignin also the SEM pictures reveals continuously diminishing binding material from B-0 sample onwards.

CONCLUSIONS

1. IR spectra indicate that with higher alkali treatment the conformational change from cellulose-I to cellulose-II is favored.
2. X-ray diffractograms reveals that alkali treated samples have higher crystallinity and orientation angle up to B-15 samples for bamboo strips and B-10 samples in case of bamboo dust samples and then fall.
3. Bamboo, itself is a composite made of cellulose reinforcement embedded in hemicellulose and lignin matrix. Mercerization leads to fibrillation by removing cementing material.

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