

Structural Features of Cellulosic Change in Alkali-Treated Jute Stick: An Infrared Absorption Study

S. S. REDDY, *Jute Technological Research Laboratories, Indian Council of Agricultural Research, 12 Regent Park, Calcutta 700 040, India*

Synopsis

The cellulosic change has been discussed in terms of absorption ratio of certain infrared bands. It is shown that the absorption of O—H and C—H stretching frequencies decreases up to 25% alkali treatment and the absorption of β -glucosidic band increases with increasing alkali strength in swelling. The anomalous behavior in the absorption of these bands at 18% alkali treatment might be due to partial mercerization. A new type of hydrogen bonding is proposed where C₆ hydroxyl groups are involved in a bifurcated six-membered hydrogen bonding system giving more crystalline nature to mixed lattice of cellulose. The O₂ hydroxyl proton forms hydrogen bond with O₃ of the same unit and with O₂H of its antiparallel chain. It is also noted that the presence of lignin has no significant effect on cellulosic transition.

INTRODUCTION

Jute stick is a multicomponent polymer of α -cellulose, hemicellulose, and lignin, which are associated with each other in a manner not clearly known. In order to study the structural features in jute stick during pulping, we have undertaken the present work of IR studies for investigating the morphology of cellulose during its modification. Nelson and O'Connor¹ reported that the alkalization of cellulose causes transition from cellulose I to cellulose II. They also noted a decrease in the intensity of CH₂ wagging motion at 1425 cm⁻¹ and an increase in the intensity of β -glucosidic band at 895 cm⁻¹ during this transition.

It has been reported that the IR spectra of cellulose II and amorphous cellulose showed some similarities at 1420, 1111, and 895 cm⁻¹. The region between 1400 and 1200 cm⁻¹ would be affected by amorphous content. The mixture of cellulose II with cellulose I does not change the relative intensities appreciably whereas mixture of amorphous cellulose does.¹

In the previous paper² we reported the broad band at 1440–1430 cm⁻¹ due to COO⁻ of 4-O-methyl-D-glucuronoxylan of hemicellulose. The broadening of the region 1400–1300 cm⁻¹ is due to amorphous content. The removal of Na⁺ ions by acid and water washings in the control sample brought the appearance of all the bands in the crystalline region.

In the present paper the change of absorption ratio with alkali concentration was discussed. Hurtubise³ calculated the I_0/I values and lateral order index for cotton, spruce, birch, and other celluloses and reported that the absorption decreases with increasing alkali strength in swelling. Nelson and O'Connor

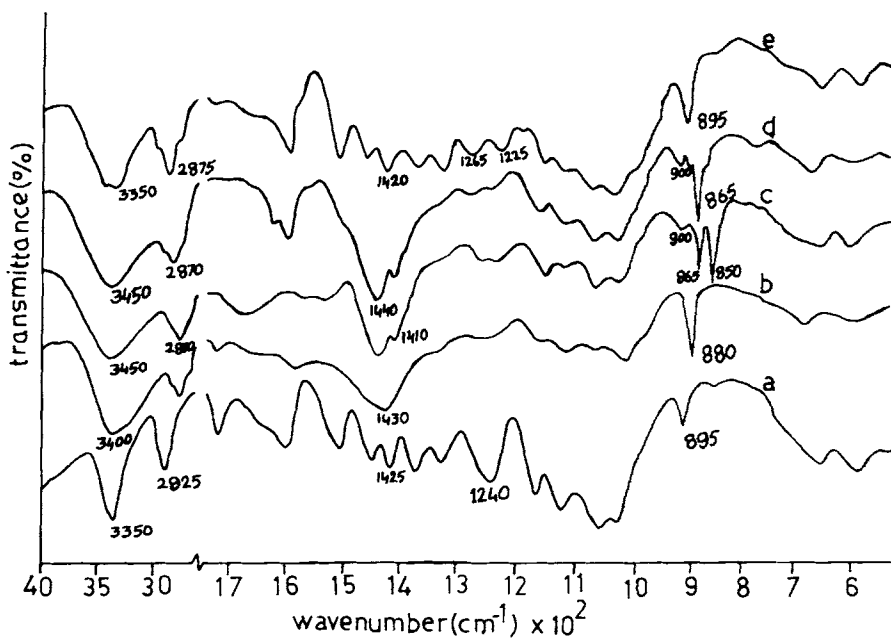


Fig. 1. Infrared spectra of jute stick: (a) untreated (b) 12%; (c) 18%; (d) 30% alkali treated; (e) control sample.

proposed a new absorbance ratio $1372/2900\text{ cm}^{-1}$ which can be used to measure the crystallinity and concluded that the crystallinity index decreases with increasing the strength of alkali during mercerization. In the present work the band at 1372 cm^{-1} is not clearly noticed in the spectra of alkaline jute stick so that the band at 880 cm^{-1} was taken into account.

EXPERIMENTAL

Jute stick was crushed into 80–100 mesh size and extracted with ethanol–benzene (1 : 2). The chemical constituents of the defatted sample estimated by Tappi standard methods⁴ are as follows (in percentage): α -cellulose 41.10; pentosan 24.60; lignin 22.85; uronic anhydride 7.40; fat and wax 1.82; ash 1.28.

Alkalization of Jute Stick. Alkalization of jute stick was carried out at different concentrations of alkali by immersing the material into an emulsion of NaOH–benzene (1 : 1) and vigorous stirring was continued for 1 h at room temperature and then centrifuged. The benzene present in the cake was evaporated and the alkaline material thus obtained was air dried for further study. Control samples were prepared by washing the alkaline jute stick with acetic acid (10%) and water several times until it is neutral to litmus.

Infrared Spectra. Infrared (IR) spectra of the above samples were taken on Shimadzu IR-440 spectrophotometer using KBr pellet. The alkaline jute stick powder was severely dried under vacuum at 65°C for 72 h.

RESULTS

Infrared spectra of alkaline jute stick and control samples are shown in Figure 1. The important bands affected on alkali treatment are 3350, 2925,

1420, 1375, 1320, 1240, and 895 cm^{-1} . The O—H stretching band at 3350 cm^{-1} in the spectra of untreated sample is shifted to $3450\text{--}3400\text{ cm}^{-1}$ as a broad band and the C—H stretching band at 2925 cm^{-1} shifted to lower region to 2875 cm^{-1} with decreased intensity in the spectra of alkaline jute stick. The intensity of a strong band at $1440\text{--}1430$ due to COO^- frequency increased with increasing alkali strength during treatment. A shoulder peak at 1410 cm^{-1} in 18% and above alkali treatments might be due to CH_2 wagging motions. A strong band at 1240 cm^{-1} assigned to the C—O stretching mode of COO^- group of hemi-cellulose was eliminated on alkali treatment and the appearance of two medium bands at 1260 and 1225 cm^{-1} was probably due to C—H and O—H bending frequencies,⁵ respectively. The sharp band for β -glucosidic linkage of $\text{C}_1\text{—O—C}_4$ (C—H frequency)^{1,6} at 895 cm^{-1} is the one mostly affected by alkali treatment. Its position was shifted to lower region near to 880 cm^{-1} with doubled intensity. All the peaks in the crystalline region $1400\text{--}1300\text{ cm}^{-1}$ were broadened in the spectra of the alkaline sample. The shift observed in these bands to their original position in control sample is good evidence for cellulosic change.

DISCUSSION

Mercerization converts cellulose I first to alkali cellulose and, after washing, into cellulose II. During this intracrystalline swelling with alkali, the hydroxide ions generate the conjugate base of cellulose, allowing conversion into alkali cellulose. Since the hydroxyl protons are involved in hydrogen bonding in the crystalline lattice of cellulose I, a strong alkali solution is required to break these intermolecular hydrogen bonds. It has been reported⁷ that, at high concentration of sodium hydroxide swelling, a number of different addition compounds (alkali celluloses II) are formed in the cellulose lattice. The actual structure of these different alkali celluloses has not yet been established with certainty, but the majority of the investigators agree that alkali cellulose is an addition compound of the type $\text{Cell}(\text{OH}) \cdot (\text{NaOH})$ rather than true alcoholate of the form $\text{Cell}(\text{O}^- \text{Na}^+)$.

Both the swelling action of sodium hydroxide as well as the presence of sodium ions in the lattice are responsible for changes in the lattice. Changes in the IR spectra of mercerized sample as compared with that of untreated one can be attributed to the formation of rotational isomers due to rotation of CH_2OH groups around the $\text{C}_5\text{—C}_6$ bond⁸ and β -glucosidic rotation through $\text{C}_1\text{—O—C}_4$ linkage.

Due to the disruption of hydrogen bonds in the cellulose lattice I by strong alkali, the O—H stretching frequency shifted to higher region. The interaction of Na^+ ions with neighboring protons brought out changes in the C—H bending and stretching modes causing a lower shift with decreased intensity. It has been reported from the observations of the polarized spectra⁶ that the parallel band at 3350 cm^{-1} is due to intramolecular hydrogen bond of the type $\text{O}_3\text{H—O}'_5$ in cellulose I lattice. On the basis of the vibrational spectra it was concluded that every alternate C_6 hydroxyl group is involved in a hydrogen bond with the bridge oxygen atom of the next antiparallel chain in cellulose I. Once this type of intermolecular hydrogen bond is cleaved by alkali, the bridge oxygen atom is free to relax into a more distinct favorable conformation with a new set of

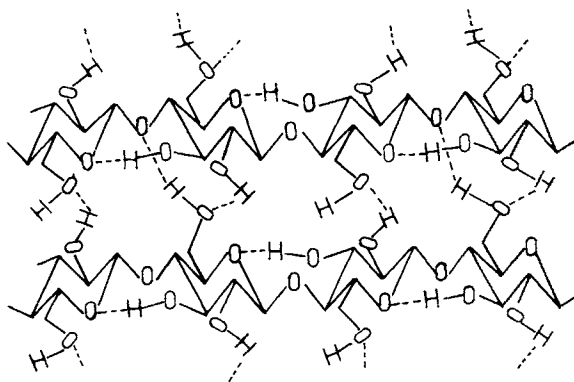


Fig. 2(a). Structure of cellulose I lattice.

hydrogen bonds. The probable scheme is given in Figure 2. Figure 2(b) shows the lattice of alkaline cellulose where C_2 and C_6 hydroxyl protons are replaced by Na^+ ions. The C_3O protons are not disturbed as these are involved in a stronger intermolecular hydrogen bond of the type $O_3H-O'_5$ which stabilizes the cellulose chain. But at high concentration of alkali treatment the $O_3H-O'_5$ bond is disrupted to provide higher absorption for free $O-H$ stretchings (Fig. 3). Though the $O-H$ absorption is also contributed by lignin (phenolic groups), the change in the frequency with alkali is considered to be mainly due to cellulosic hydroxyl groups. Once the $O_3H-O'_5$ bond is cleaved, the cellulose chain will relax through β -glucosidic rotation about the C_1-O-C_4 bond to give a more favorable conformation for cellulose II. In Figure 2(c), where all Na^+ ions are removed during acid and water washings, is shown a different set of hydrogen bonds similar to Liang and Marchessault's structure.⁶ They summarized that the O_2 hydroxyls are bonded in the 002 plane to the O_6 atom of adjacent chain similar to the case in cellulose I. During this change, it is assumed that the O_2 is bonded to O'_2H of another unit in the antiparallel chain and the

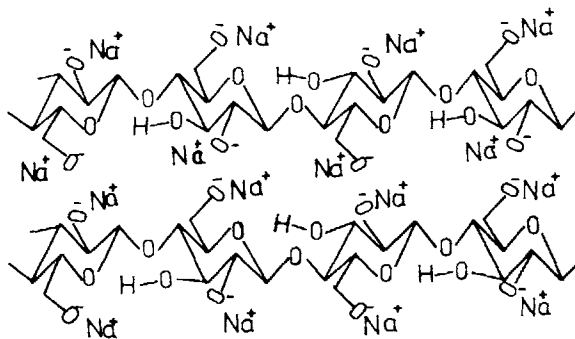


Fig. 2(b). Alkaline cellulose.

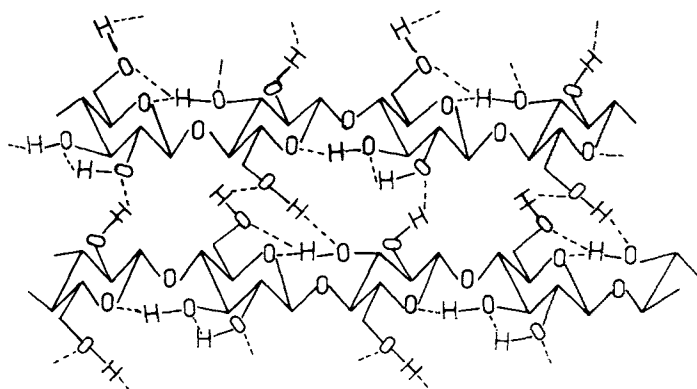


Fig. 2(c). Probable structure of cellulose lattice in control sample.

O_2H may also be bonded with O_3 atom of the same unit to give a five-membered hydrogen bond ring system below the chain. The O'_2H of the antiparallel chain may not be involved in the hydrogen bond with the O'_3 atom of the same unit as it (O'_3) is strongly bonded with the C_6 hydroxyl proton of the antiparallel chain and with the C'_6H hydroxyl proton of the next unit in the same chain, providing a more stable six-membered bifurcated hydrogen bonding system between these two chains [Fig. 2(c)]. Though the above structure has not yet

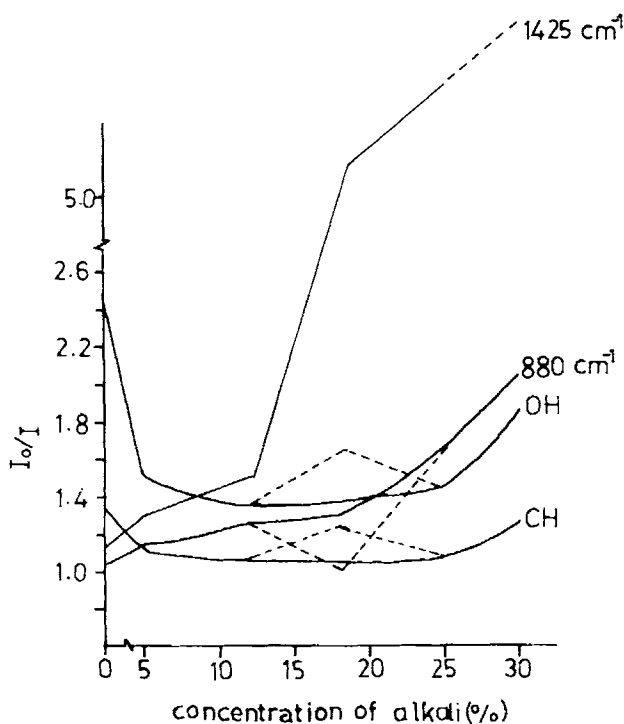


Fig. 3. Change of absorption of certain IR bands with alkali concentration.

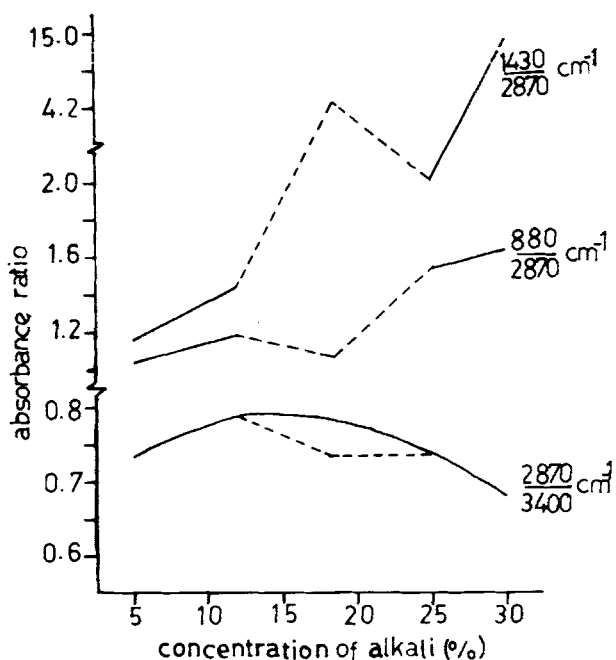


Fig. 4. Relation between absorbance ratio and alkali concentration.

been proved with certainty, the possibility of accessible crystalline cellulose II cannot be ruled out as the infrared spectra shows sharp bands in the crystalline region of cyanoethylated jute fiber the accessibility of which increases with increasing the degree of cyanoethylation at higher alkali treatment.⁹

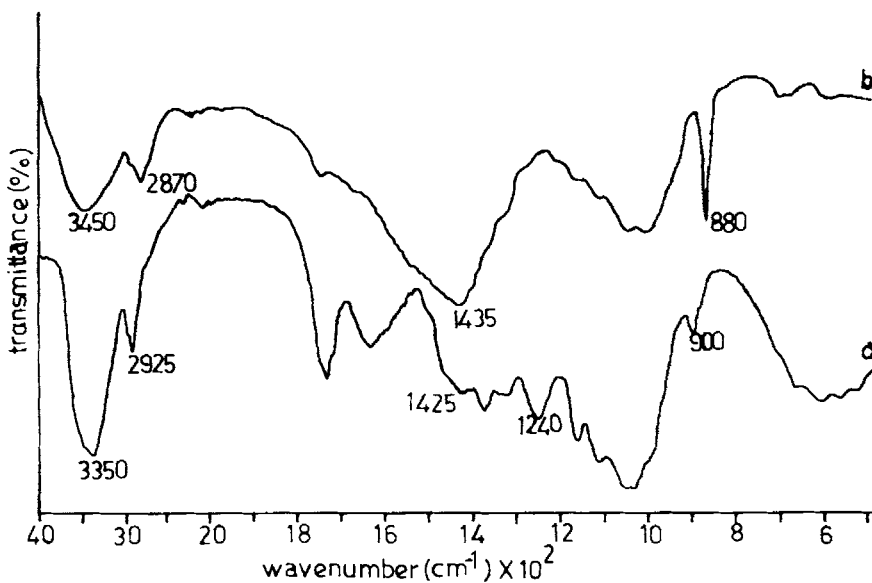


Fig. 5. Infrared spectra of (a) delignified jute stick and (b) alkaline delignified jute stick.

During this lattice change the C—H bond of the C₁—O—C₄ group requires less energy to vibrate and thus its frequency is lowered to 880 cm⁻¹ with doubled intensity. The presence of a shoulder peak at 1410 cm⁻¹ in 18% and above alkaline samples might be due to CH₂ bending frequency which shifted to a lower region on mercerization. The sodium ion of CH₂—O⁻Na⁺ in the cellulose lattice affects the vibrational modes of the C—H bond; as a result, a lower shift in stretching and bending frequencies is observed in the spectra of the alkaline sample. In the control sample the removal of sodium ions fetch the infrared positions more or less to the same position with different lattice structure. The strong band at 1240 cm⁻¹ in the untreated sample replaced by two medium bands on alkali treatment is remarkable evidence for cellulosic transition in jute.

The I_0/I values for certain important bands were calculated using convenient base lines. The variation of these values with alkali strength is given in Figure 3. The boat-shaped curve of C—H and O—H stretching frequencies indicates that the absorption decreases with increasing alkali strength in swelling up to a certain limit of concentration. The deviation at 18% alkali treatment by an increase in absorption is due to the formation of mixed lattice or an addition compound of the type Cell(OH)·(NaOH). At high concentration of alkali, the increased thickness of cell wall does not allow the sodium hydroxide ions to penetrate into the crystalline region of the cellulose lattice; hence, higher absorption values are obtained.

The I_0/I values for β -glucosidic band measured at 880 cm⁻¹ increases with increasing alkali strength. However, this value is lowered at 18% alkali treatment due to the formation of two additional peaks at 900 and 850 cm⁻¹. Barker et al.¹⁰ reported that these two bands arose due to van der Waals interaction between axial hydrogens on the C₅ atom with the bending vibration of C₁—H (equatorial) in α -isomer of glucose. The nonobservance of these two bands in the control sample shows the uncertainty of anomeric change.

Assuming that the lateral order index^{1,3}—the ratio of absorptivity at 1425 and 895 cm⁻¹ to that of 2925 cm⁻¹—is related to cellulosic transformation, we have calculated the absorptivity of 1430 and 880 cm⁻¹ with 2870 cm⁻¹ as standard (plotted in Fig. 4). It shows an increase in CH/OH ratio up to 12% alkali treatment and the absorption ratios of 1430/2870 and 880/2870 cm⁻¹ increase with increase in alkali strength. But at 18% alkali treatment a decrease in the absorption ratio for CH/OH and 880/2870 cm⁻¹ and an increase at 1430/2870 cm⁻¹ is observed. The formation of mixed lattice of cellulose I and cellulose II is considered to be responsible for this anomalous behavior. On correlating Figures 3 and 4, we can observe an increase in C—H and O—H absorption and a decrease in its ratio at this treatment. It can be pointed out here that the OH absorption is more than CH absorption might be due to cellulose II, where some of the intermolecular hydrogen bonds are cleaved. This is also confirmed by an increase in the absorption of β -glucosidic band and a decrease in its ratio.

To study the effect of lignin, the IR spectra of delignified jute stick was compared with that of untreated one (Fig. 5). The spectra of alkaline delignified jute stick is almost same with that of alkaline jute stick. The content of lignin in jute stick does not affect the structural changes in cellulose during mercerization.

CONCLUSIONS

The anomalous behavior of cellulose at 18% alkali treatment is evidenced by I_0/I values and absorption ratios of certain infrared bands. This is due to the presence of mixed lattice in jute cellulose. There is no effect of lignin on cellulosic change during alkali treatment.

The author wishes to express his thanks to Dr. S. N. Pandey, Director, JTRL, and to the Indian Council of Agricultural Research for providing facilities and for permission to publish the work.

References

1. M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1311 and 1325 (1964).
2. S. S. Reddy, S. K. Bhduri, and S. K. Sen, *J. Appl. Polym. Sci.*, to appear.
3. Fernard C. Hurtubise, *Anal. Chem.*, **32**, 177 (1960).
4. *Standard and Suggested Methods of Technical Association of Pulp and Paper Industries*, New York, 1971.
5. C. Y. Liang, K. H. Basett, E. A. McGinnes, and R. H. Marchessault, *Tappi*, **43**, 1017 (1960).
6. C. Y. Liang, in *Instrumental Analysis of Cotton Cellulose and Modified Cotton Cellulose*, Robert T. O'Connor, Ed., Dekker, New York, 1972, pp. 60-90.
7. E. H. Immergut, in *The Chemistry of Wood*, B. L. Browning, Ed., Wiley-Interscience, New York, 1963, p. 161.
8. *Encyclopedia of Polymer Science and Technology*, Wiley-Interscience, New York, 1965, Vol. 3, p. 166.
9. S. S. Reddy and S. K. Bhaduri, *J. Appl. Polym. Sci.*, **39**, 553 (1990).
10. S. A. Barker, E. J. Bourne, R. Stephens, and D. H. Whiffen, *J. Chem. Soc.*, **171**, 3468 (1954).

Received January 14, 1990

Accepted February 28, 1990