Decrystallization of Jute by Cyanoethylation

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SYNOPSIS

The cyanoethylation of jute fiber was studied at different reaction conditions. Moisture regain decreased significantly on cyanoethylation. Introduction of 5–6% nitrogen content on the fiber minimized the moisture regain capacity to 2.8%. A further increase in the nitrogen content increased the moisture regain. The effect of cyanoethylation on infrared absorption was studied. The absorbance curves of O—H and C—H stretching frequencies are parabolic in nature, whereas β-glycosidic and C—H bending absorption curves are almost linear with an increase in the degree of substitution. The cellulosic transition was indicated by the lattice conversion ratio, which showed an increase along with the degree of cyanoethylation. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The cyanoethylation of cellulosic and other high polymeric materials containing hydroxyl groups was first investigated and patented by Farbenin[1] in 1938. Segal et al.[2] studied the decrystallization of cotton cellulose to improve fiber elongation, water absorbancy, dyeability, and luster.[3] The method was based on swelling cotton fiber at low temperatures with low alkyl amines like ethylamine, followed by extraction with nonaqueous solvents such as chloroform and hexane. A different method was adopted by Tsuji et al.[4] to decrystallize cotton cellulose by impregnation with 18% alkali, followed by reaction with acrylonitrile. Thus, a small amount of cyanoethyl residue is introduced on the cellulose chain in the amorphous region of the fiber, which prevents recrystallization during water washings and drying. By this method, permanently decrystallized accessible cotton is obtained.

Although considerable work has been done by various workers[5] on decrystallization of cellulosic fibers, work in this line on lignocellulosic fibers like jute is scanty in the literature. Jute fiber, being multicomponent in nature, is known for its hygroscopic behavior. The major constituents of jute are cellulose, hemicellulose, and lignin. Cellulose alone contributes the major fiber crystallinity. The other components, viz., hemicellulose and lignin, along with a noncrystalline portion of cellulose, form the amorphous region in the fiber.

Ray[6] reported that in jute and mesta fiber the degree of crystallinity decreases with rise of humidity and that the orientation of micelles improves with moisture absorption. Dmitry and Gagarin[7] reported from their observations that as a result of cyanoethylation to a nitrogen content of 2–4% a new fiber formed that has most of the desirable properties of cotton, i.e., immune to microorganism attack, more resistance to heat and acid degradation, greater affinity toward dyes, and different stress–strain properties with low moisture regain, and, in some cases, improved electrical resistance properties.

In the present work, an attempt has been made to decrystallize jute fiber by pretreatment with various inter- and intracrystalline swelling agents followed by cyanoethylation with acrylonitrile. The accessibility and crystallinity of the cyanoethylated fiber is discussed.

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EXPERIMENTAL

Jute fiber was combed, cut into 10 cm lengths, made into small bundles of 1 g each, and tied at one end. Each bundle was defatted with benzene–alcohol (2 : 1) before treatment.

Swelling in Alkali and Other Reagents

The fiber bundles were immersed in a swelling agent at different concentrations at various temperatures for 30 min, then washed with dilute acetic acid and, finally, with distilled water until free from acid.

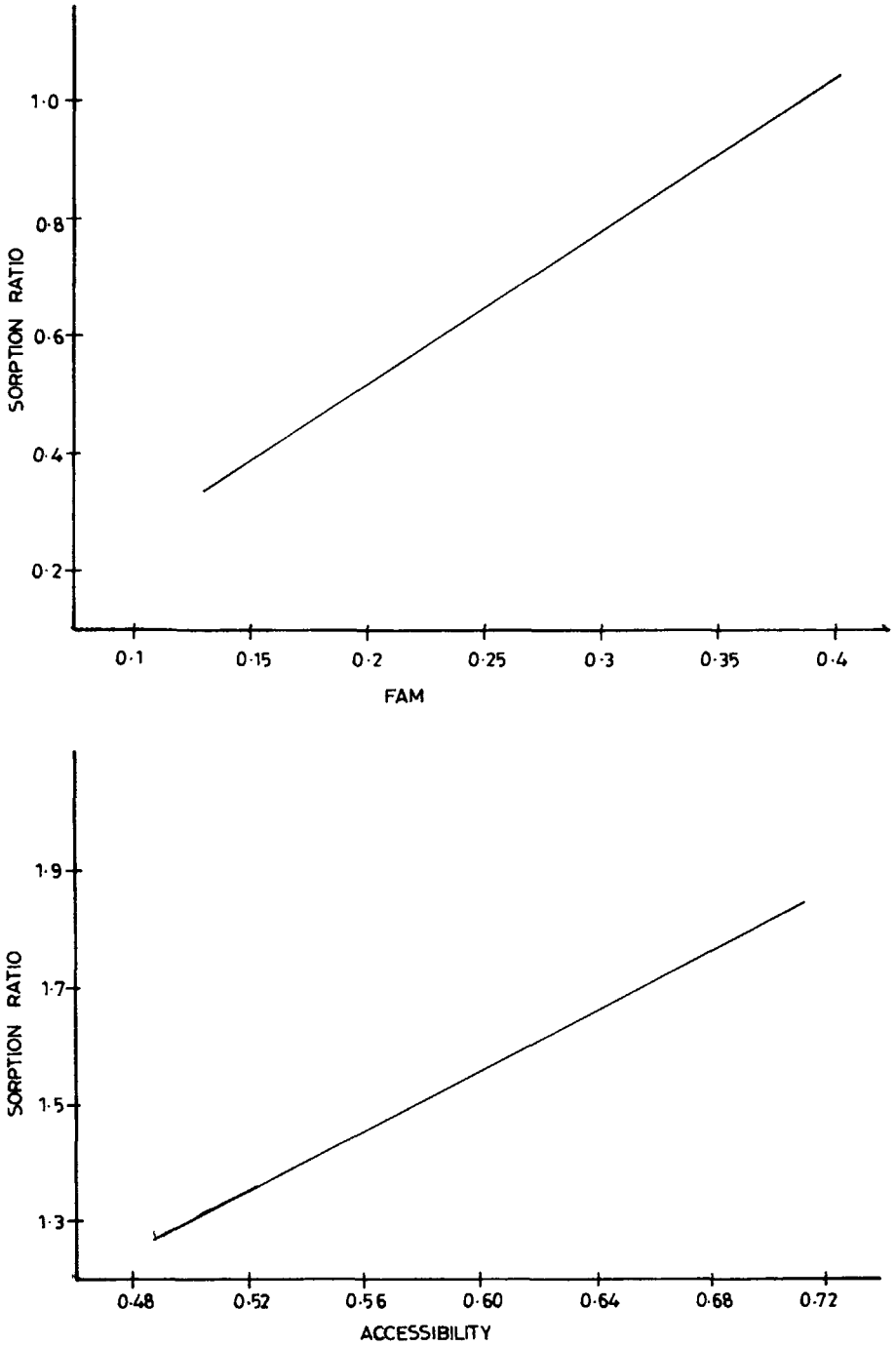

Figure 1 Relationship between sorption ratio and amorphous portion: (a) for alkali-treated fibers; (b) for cyanoethylated fibers.

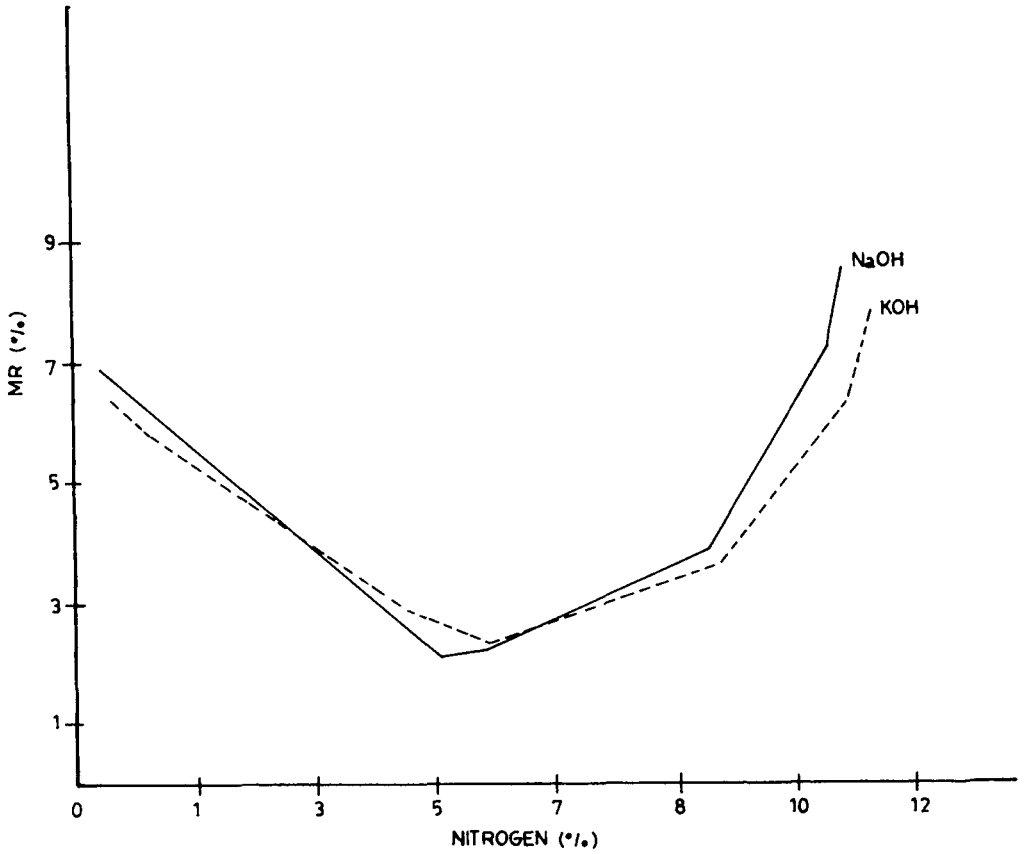

Figure 2 Effect of nitrogen content on moisture regain (MR).

Cyanoethylation

Jute fiber samples were swollen in various swelling agents at different temperatures, squeezed to about 70% weight pickup, and immersed in acrylonitrile (10 mL) at different temperatures for 30 min with constant stirring in a water bath. Excess acrylonitrile was decanted and the fibers were washed with acetone and then kept in dilute acetic acid for 5 min. Finally, the fibers were washed with distilled water and then air-dried.

Dual Treatment

Dual treatment was conducted on the fiber samples swollen in different swelling agents for 30 min, followed by alkali swelling and then etherification by acrylonitrile.

Moisture Regain (MR)

The fiber samples were dried in an oven at 110°C for 3–4 h and then kept in vacuum over P_2O_5 at 50°C overnight. The vacuum-dried samples were conditioned at 30°C for 72 h at 65% RH [over saturated $Mg(OAc)_2$ solution] until constant weight was reached. The conditioned samples were dried at 110°C and weighed. The MR was calculated on the basis of the oven-dry weight.

Nitrogen Analysis

Nitrogen content of the cyanoethylated samples was estimated by the semimicro-Kjeldahl method.

Infrared Spectra

Infrared spectra were obtained on a Shimadzu IR 440 spectrophotometer by using the KBr pellet technique.

X-ray Spectra

X-ray diffractograms of the fiber samples were taken on Philips PH-1710 X-ray diffractometer. The fibers were cut into small pieces before taking the spectra.

RESULTS AND DISCUSSION

Accessibility

The strong intracrystalline swelling agents such as NaOH and KOH disrupts the regular hydrogen bonding in the cellulose I lattice due to intrafibrillar swelling resulting in the cellulose II structure. Swelling causes decrystallization, which further increases the sorption capacity of the fiber. On cyanoethylation of the alkali-treated fiber, the sorptive capacity decreased to some extent due to the presence of nonhydrophilic cyanoethyl groups on the cellulose chain.

Since the MR is related to the amorphous content of the fiber, Valentine[8] established a relationship between the sorption ratio and the amorphous portion in the equation $F_{am} = SR/2.6$, where SR is the sorption ratio (the ratio of the moisture sorption of the experimental sample to that of a standard or raw one at the same relative humidity), which was perfectly followed by cellulosic fibers. In the present work, the relation between the sorption ratio and the amorphous portion is shown in Figure 1(a) for alkali-treated fibers and in Figure 1(b) for cyanoethylated fibers. Though the accessibility toward moisture initially decreased on cyanoethylation up to a certain level of increase in nitrogen content (6.5%), as shown in Figure 2, the overall effect of SR on F_{am} is linear, as shown in Figure 1(b).

On extrapolating the straight line to an amorphous portion of value 1.0 for Figure 1(a), the SR is 2.56, and for Figure 1(b), the SR is 2.6, which is in perfect agreement with Valentine's value. However, the validity of Valentine's equation for lignocellulosic fibers is yet to be established as hemicellulose and lignin also contribute to the amorphous portion in this fiber.

Effect of Various Swelling Agents on Moisture Regain (MR)

The effect of various swelling agents on moisture absorption at 10 and 40°C is given in the Table I. It is observed that the MR is decreased in urea, zinc chloride, and organic solvents like dimethylformamide and dimethylsulfoxide, whereas it increases on treatment with pyridine and ethylenediamine. It is assumed that the latter reagents, being more basic in nature, are effective in opening more accessible hydroxyl groups, resulting in higher MR.

On dual treatment with alkali and other swelling agents, the MR data indicate an increase in fiber accessibility. It is obvious that the alkali treatments alone increase the MR and that other swelling agents are not sufficient in strength to bring about the required cellulosic transition to increase the moisture absorption. In the case of cyanoethylation in the presence of swelling agents other than alkali, the MR decreases significantly due to blocking of the free hydroxyl groups by substituted cyanoethyl groups.

Table I Moisture Regain (MR) of Jute Fiber at Different Treatments

	MR (%) at			
Swelling Agent	10°C	40°C	40°C[a]	CE[b]
Urea (50%)	7.53	6.79	10.15	2.85
Dimethylformamide	7.22	6.13	9.91	3.22
Dimethylsulfoxide	7.72	6.07	9.65	3.38
Zinc chloride (65%)	7.63	6.91	11.05	4.13
Ethelenediamine (65%)	10.95	9.94	11.73	—
Triethylamine	9.25	8.55	10.57	—
Pyridine	10.45	10.97	11.85	—
NaOH[c]	10.83	11.13	—	2.75[b]
Untreated	8.45	8.78	—	—

[a] On dual treatment.
[b] 4.0% alkali swelling followed by cyanoethylation.
[c] Cyanoethylation at 40°C.

It has been reported[4] in the case of cotton that various swelling agents except ethylenediamine do not give much higher moisture absorption than does alkali. The acrylonitrile treatment increases the MR notably, suggesting the effect of cyanoethyl residues introduced on the cellulose prevented the recrystallization during water washings. However, the dual treatment (swelling and alkali) did not produce significant effects as compared to the NaOH treatment alone.

Effect of Cyanoethylation on Moisture Regain (MR)

Alkali-treated samples were immersed in acrylonitrile at different temperatures for a certain period

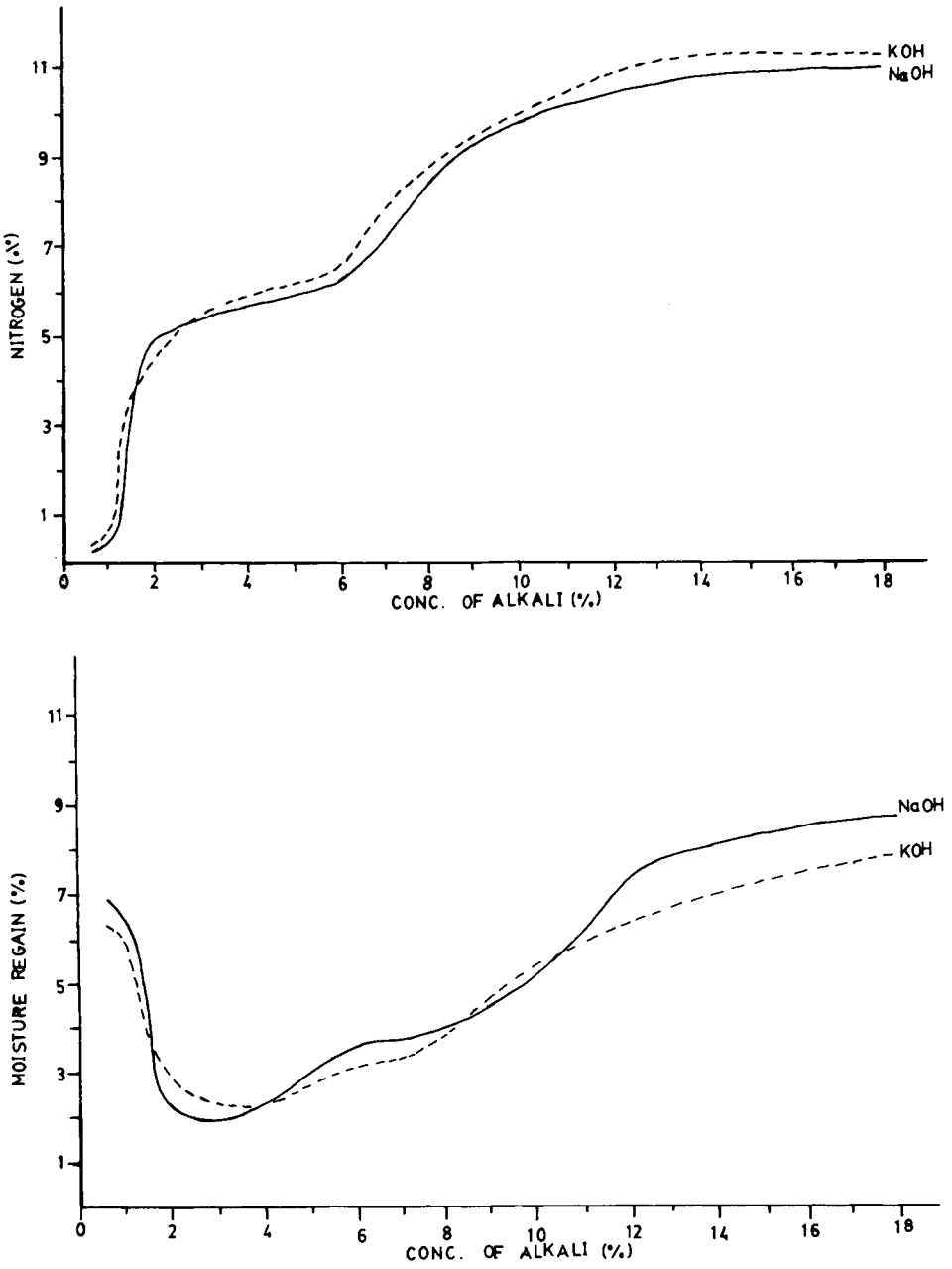

Figure 3 (a) Effect of alkali concentration on nitrogen content. (b) Effect of alkali concentration on moisture regain (MR).

of time. The relation between MR and degree of substitution (expressed as nitrogen content) is shown in Figure 2. There is a initial decrease in the MR up to 6.5% nitrogen content and then it increases with the degree of cyanoethylation. It can be seen in Figure 3(a) that the degree of cyanoethylation proceeds with alkali concentration, whereas the MR as shown in Figure 3(b) decreases initially up to 4.0% alkali concentration. A further increase in alkali strength increases moisture absorption.

Tsuji et al. reported[4] in cotton that the MR first increases, passes through maximum at about 6 mol % cyanoethylation, and then slightly decreases with increase in the degree of cyanoethylation. They reported that the increase in MR at a lower degree of cyanoethylation might be due to the cyanoethyl groups on the cellulose chain preventing recrystallization during water washings or drying. As a result, the accessibility toward moisture increases in the cotton fibers.

In case of jute with low cyanoethyl substitution,

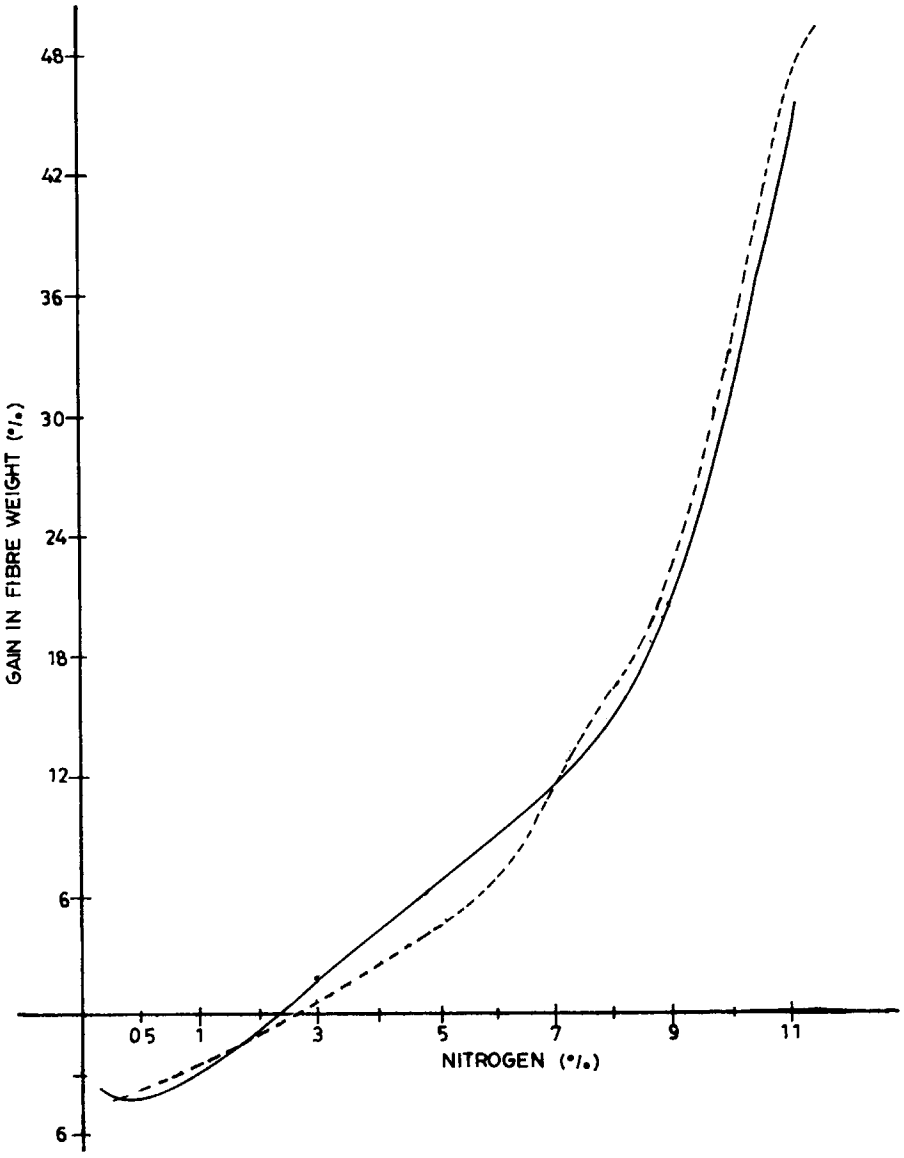

Figure 4 Effect of nitrogen content on fiber weight.

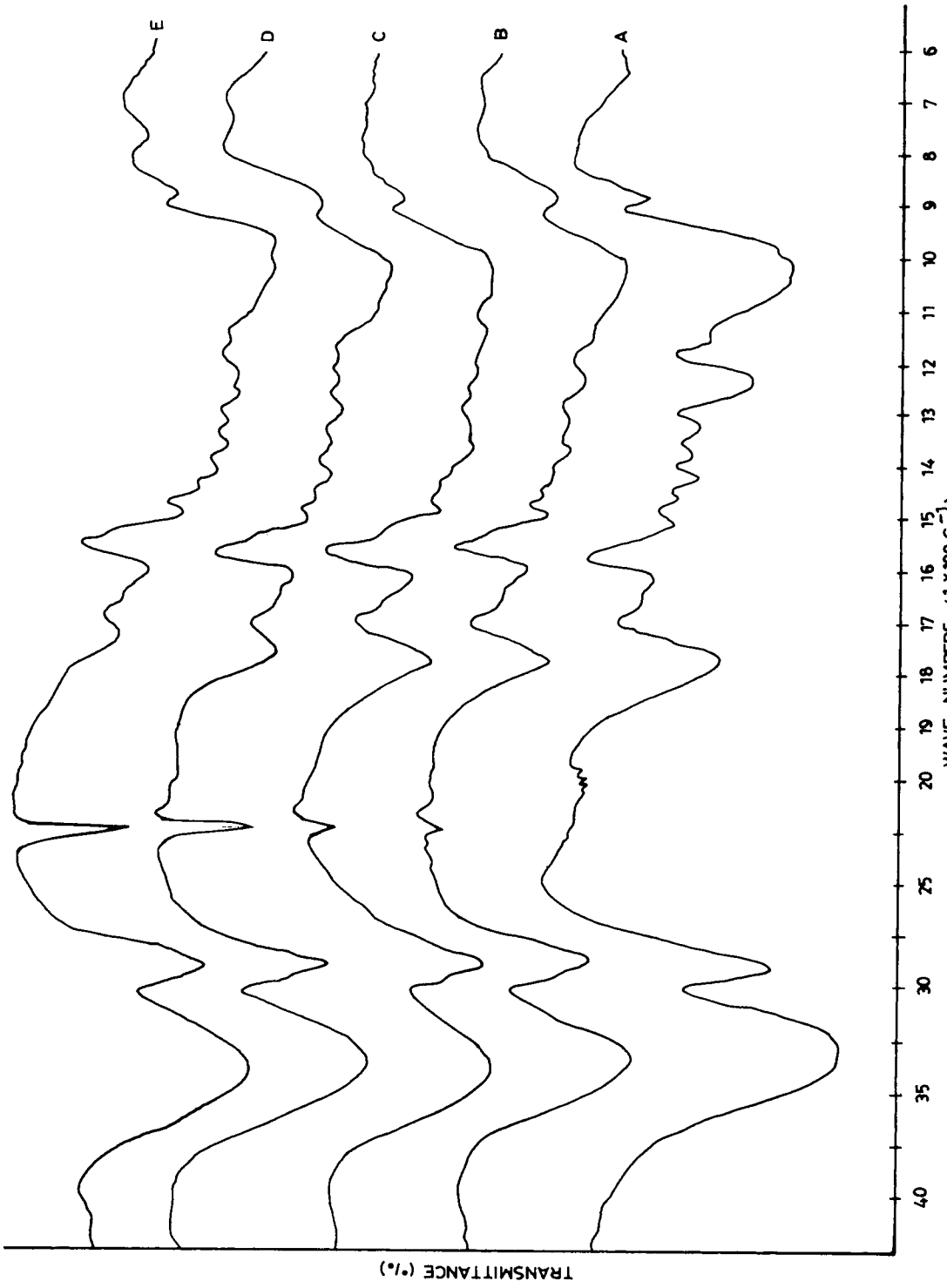

Figure 5 Infrared spectra of jute fiber: (a) untreated; (b–e) cyanoethylated, 0.4, 0.7, 5.1, and 5.85% nitrogen, respectively.

the initial decrease in MR at lower alkali treatment may be attributed to the partial removal of amorphous components, viz., lignin and hemicellulose, as well as insufficient swelling of fiber due to the lignin–carbohydrate complex. Tsuji et al.[4] also reported that aqueous alkali may be insufficient to allow a full hydrogen-bond rearrangement and that a reconversion of soda cellulose I to cellulose I may take place during water washings.

X-ray study on cyanoethylated jute also indicated an insignificant change in crystallinity at a lower degree of cyanoethylation. However, the increase in MR along with an increase in degree of cyanoethylation from an alkali concentration of 4.0% onward is due to decrystallization of the fiber. When cyanoethyl groups are introduced onto the cellulose chain swollen in alkali solution, a distended cellulose structure is obtained, and a hydrogen-bond rearrangement necessary for conversion of cellulose II takes place by decrystallization.

Weight Increase on Cyanoethylation

It is known that hemicellulose in wood is extracted with alkali. Jute fiber when treated with alkali or other swelling agents such as ethylenediamine or pyridine loses some weight due to dissolution of some

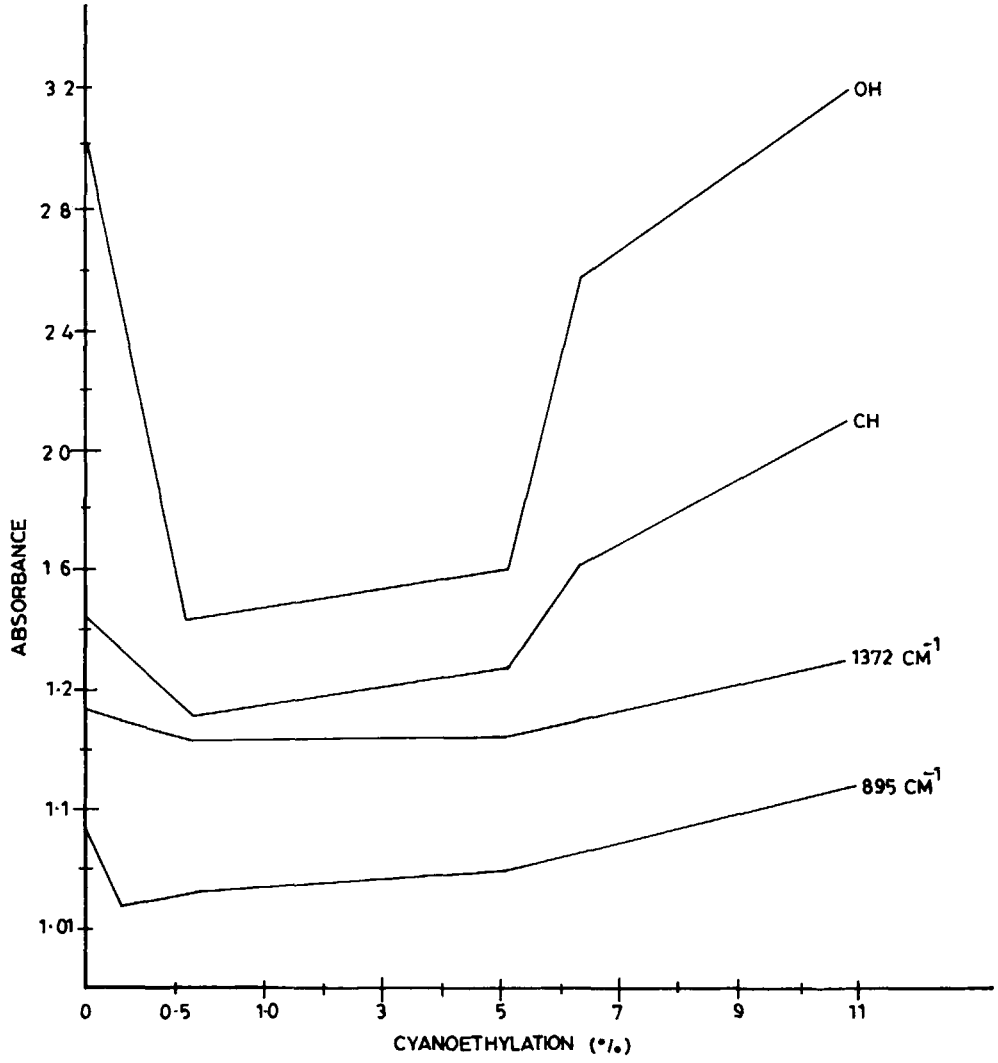

Figure 6 Change in the amount of absorbance (I_0/I) of certain infrared bands on cyanoethylation.

portion of the hemicellulose and other labile components. The weight loss depends on the strength of swelling agents used. On cyanoethylation, the fiber regains some weight due to the substitution of bulky cyanoethyl groups in place of hydroxyl groups. The weight increase is directly related to the degree of cyanoethylation. It is seen from Figure 4 that the increase in fiber weight is beyond 5.5% nitrogen content. The negative values in the fiber weight indicates more loss in weight by alkali treatment than that of gained on cyanoethylation.

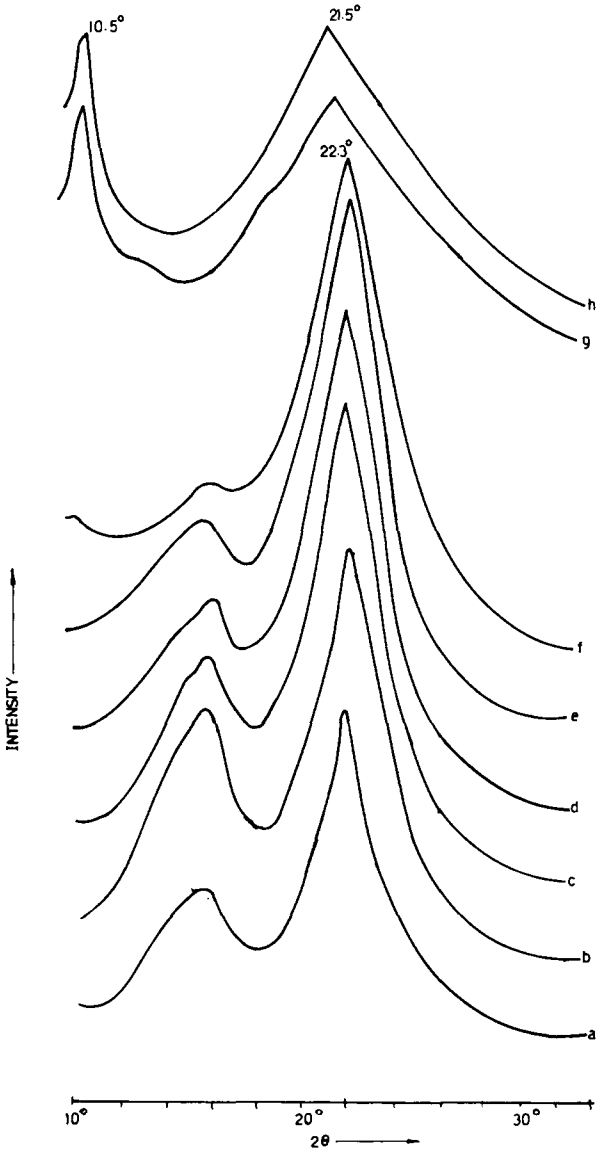

Figure 7 X-ray diffractograms of (a) untreated and (b–h) cyanoethylated (Table II) fibers.

Table II Crystallinity of Jute Fiber at Different Treatments

Sample	Alkali Concn (%)	Nitrogen (%)	Crystallinity (%)
a	Control	—	58.57
b	1.0	0.73	57.22
c	2.0	5.10	53.35
d	4.0	5.85	51.62
e	6.0	6.23	49.71
f	8.0	8.65	38.72
g	12.0	10.57	10.38
h	18.0	10.84	7.87

Effect of Cyanoethylation on Infrared Absorption

The IR spectra of cyanoethylated samples are shown in Figure 5. The evidence for cyanoethyl residue introduced by NaOH–acrylonitrile treatment is shown by a sharp C≡N stretching band at around 2240 cm^{-1}. The intensity of this band increases as cyanoethylation proceeds further.

To know the effect of cyanoethylation on the amount of absorption of various infrared bands, the absorbance (I_0/I) of the O—H, C—H, and β-glycosidic frequency at 895 cm^{-1} and the C—H bending frequency at 1372 cm^{-1} were calculated and plotted in Figure 6 against nitrogen content. The absorbance curves of O—H and C—H stretchings are more inclined to a "U" shape, whereas β-glycosidic and C—H bending frequency curves are stretched to linear.[9] A decrease in the absorption is noticed at a lower degree of cyanoethylation. However, an increase in the O—H and C—H stretching absorption curves at higher substitution might be due to decrystallization of cellulose where the hydroxyl groups are rearranged in a different hydrogen bonding required for formation of the cellulose II lattice. These data are corroborated by the observations in Figure 8 that showed an increase in the lattice conversion ratio at a higher degree of cyanoethylation. It is assumed that the increase in lattice conversion restricts the β-glycosidic rotation (C1—O—C4) and thus the C—H bending vibration, thereby decreasing its absorption in the crystalline region.

Crystallinity from X-ray Study

Figure 7 shows X-ray radial tracings of cyanoethylated samples with various degrees of nitrogen con-

tent. The crystallinity is given in Table II, which indicates decrystallization on increasing the percentage of cyanoethylation. The higher nitrogen content on jute cellulose prevented recrystallization that occurs during water washings or drying. For samples treated with 12% and above alkali followed by cyanoethylation, the 101 peak is not observed at 12°—instead, a sharp peak at 10.5° and a lower shift in case of the 002 peak with a decreased intensity at 21.5° is noticed. It is assumed that the lower shift in these two peaks might be due to higher substitution, resulting in higher amorphous content. The interference of cellulose I peaks with cellulose II peaks decreases as cyanoethylation proceeds to a higher degree.

The extent of conversion of cellulose I to cellulose II is related to $1 - I/I_{002}$,[10] where I_{am} is the intensity of the amorphous peak at $2 = 18°$, which due to the scattering of amorphous cellulose, and I_{002} is the intensity of the peak 002 of either cellulose I or cellulose II, whichever is predominant. Since the $\overline{101}$ peak for cellulose II overlaps with the amorphous region, Viego et al.[11] estimated the degree of lattice conversion (LC) using the ratio $(I_{am} + I_{101})/I_{002}$. In the present work, since the $10\bar{1}$ peak is not resolved, the LC ratio is calculated according to Segal's formula $1 - I_{am}/I_{002}$.[10] Figure 8 shows an increase in the LC ratio with nitrogen content. Beyond 6.5% nitrogen, the LC ratio increases rapidly, indicating cellulose II formation. It is assumed that the greater the degree of cyanoethylation, the greater the lattice conversion and, thus, more cellulose II. The lattice spacings also increase with increasing cyanoethyl content on the cellulose chain.

CONCLUSIONS

The accessibility of alkali-treated and cyanoethylated jute fibers was calculated from moisture regain (MR) data and applied to Valentine's equation, where a linear relation was obtained between sorption ratio (SR) and the amorphous portion (F_{am}). However, the validity of Valentine's equation to lignocellulosic fibers is yet to be confirmed. Quantitative IR study was made on the different degrees

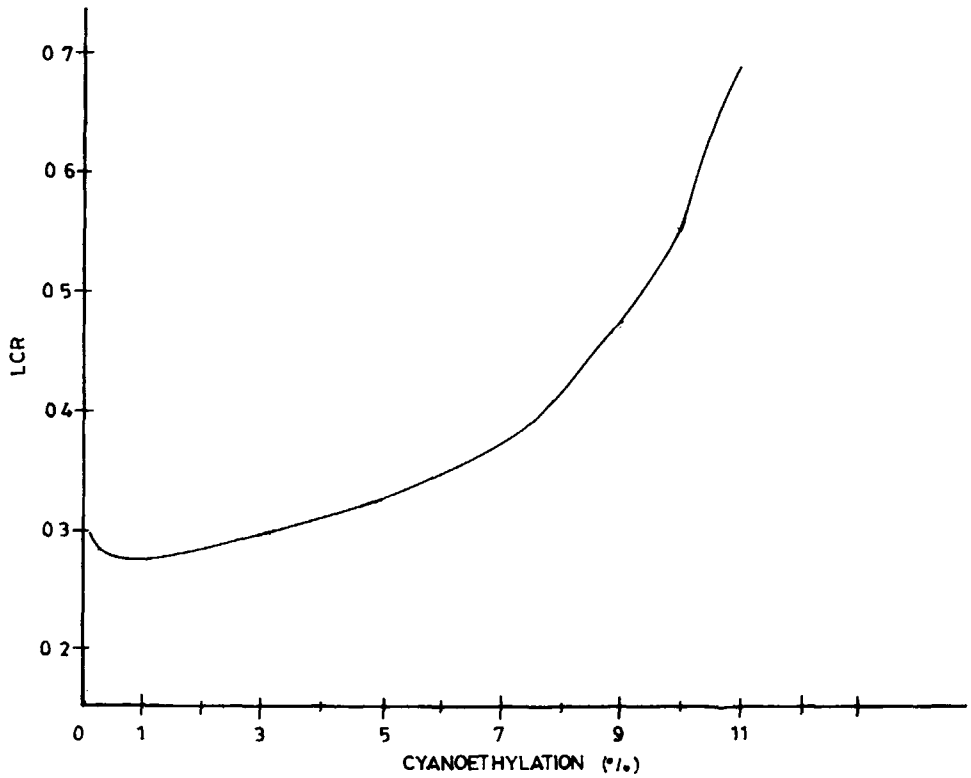

Figure 8 Effect of nitrogen content on lattice conversion (LC) ratio.

of cyanoethylation. A decrease of OH and CH stretching absorptions (I_0/I) was noticed at a lower degree of substitution. The I_0/I values for OH and CH stretching frequencies showed "U"-shape curves, whereas β-glycosidic and CH bending absorption curves are almost stretched to linear. X-ray study indicated an increase in lattice conversion on increasing the degree of substitution and, thus, resulted in more cellulose II formation.

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