Sorption Behavior and Crystallinity of Jute Fiber at Higher Alkali Treatments

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

Synopsis

Moisture regain of jute fiber was studied at different alkali concentrations and temperatures. It was found that the moisture regain increased up to 4.5*N* alkali treatment and then leveled off. Variation in swelling temperature had no significant effect on moisture regain. Amorphous fraction calculated from Valentine's equation using sorption ratio was compared with infrared crystallinity. The accessibility was increased with decreasing crystallinity in alkali-treated jute fiber, where as in cyanoethylated jute fiber it increased with increasing the degree of cyanoethylation.

INTRODUCTION

Highly accessible cellulose was prepared[1] by swelling cotton with lower alkylamines at lower temperatures followed by cyanoethylation. By this method the crystallinity of cotton was markedly decreased. The fiber tenacity was not lowered, but elongation, water absorbancy, dyability, and luster were improved. Hermans,[2] Howsman,[3] and Valentine[4] have noted that the moisture regain of cellulose is linearly related to amorphous fraction, which is a readily accessible portion in cellulose. Valentine pointed out this relation enables the moisture sorption value to be used as a simple method and a reliable measure of amorphous fraction. Hirai et al.[5] found that the cotton fibers could considerably increase their accessibility or decrease their crystallinity by treatment with acrylonitrile subsequent to NaOH swelling. They also pointed out that a small quantity of cyanoethyl residue in cellulose prevents the recrystallization of decrystallized cotton during water washings and drying whereby remarkable high accessibility and low degree of cyanoethylation are permanently attained.

In order to improve the accessibility of jute, decrystallization of jute cellulose by swelling with different concentrations of alkali at various temperatures followed by cyanoethylation is being investigated. Since jute is a heterogeneous polymer of α-cellulose, hemicellulose, and lignin, the structure of these components is different and there might be variation in moisture absorption. Though hemicellulose and lignin are amorphous in nature, the crystallinity of α-cellulose is predominant and tends to lower the absorption power of jute fiber. If the crystallinity of jute fiber cellulose is markedly decreased, the amorphous portion in total fiber will increase and thereby moisture regain will be more. It is interesting to study the accessibility of this

Journal of Applied Polymer Science, Vol. 39, 553–559 (1990)
 CCC 0021-8995/90/030553-07$04.00

lignocellulosic fiber in relation to moisture regain and infrared ratio at crystalline region.

In the present paper we reported the moisture regain and crystallinity of jute fiber treated with NaOH and KOH at different concentrations and temperatures. A comparative study with cyanoethylated jute samples is also discussed to know the change in degree of accessibility.

EXPERIMENTAL

Jute fiber (C. capsularies) was combed, cut into 10 cm length, made into small bundles of 1 g each, and tied loosely at one end. Each bundle was defatted with benzene-alcohol (2:1) before treatment. The composition of jute fiber is as follows[6]: α-cellulose 60.7%; lignin 12.5%; pentosans 15.6%; ash 0.79%; fat and wax 1.09%; nitrogenous matter 1.87%; acetyl value 3.5%, and polyuronide 4.8%.

Treatment with Alkali. The fiber bundles were immersed in alkali at different concentrations at various temperatures for 30 min. Treatment was done with NaOH and KOH separately. The fibers were washed with water and then immersed in 5% acetic acid for 5 min and again washed with water and then air dried.

Cyanoethylation. Jute fiber bundles were immersed in alkali at room temperature for 30 min, squeezed to about 70% weight pickup, and immersed in acrylonitrile (5 ml) at 60°C for 5 min with constant stirring in a water bath. Excess acrylonitrile was decanted and washed with acetone and then kept in 5% acetic acid for 10 min. Finally the fibers were washed with water and then air dried.

Moisture Regain. After being vaccum dried over P_2O_5 for 5 h at 40°C, the fibers were conditioned at 30°C and 75% RH (over a saturated solution of magnesium acetate) for 72 h until constant weight reached. The samples were dried at 110°C until reaching constant weight. The moisture regain was calculated on the basis of oven dry weight.

Nitrogen Analysis. Nitrogen content of the cyanoethylated jute fiber was estimated by semimicro Kjeldahl method.

Infrared Spectra. Infrared spectra of jute was obtained with Shimadzu IR 440 spectrophotometer by using KBr pellet technique. Fiber samples were cut into small pieces before mixing with KBr.

RESULTS AND DISCUSSION

Loss in Fiber Weight

It is known that hemicellulose is associated with polyuronic acid in wood and can be extracted with dilute alkali. Jute fiber which contains cellulose, hemicellulose, and lignin, when treated with alkali the liable hemicellulose dissolved along with other soluble components. It results in a loss in weight. This weight loss depends on the strength of alkali used. Figure 1 shows the effect of alkali concentration on weight loss. The swelling was carried out with 1.0, 3.0, 4.5, 6.5, and 8.0*N* NaOH and KOH solutions at 10°C, 20°C, and room temperature (38°C). In all cases the weight loss is increased with temperature and concentration up to 4.5*N*. Beyond this strength the loss in weight tends to

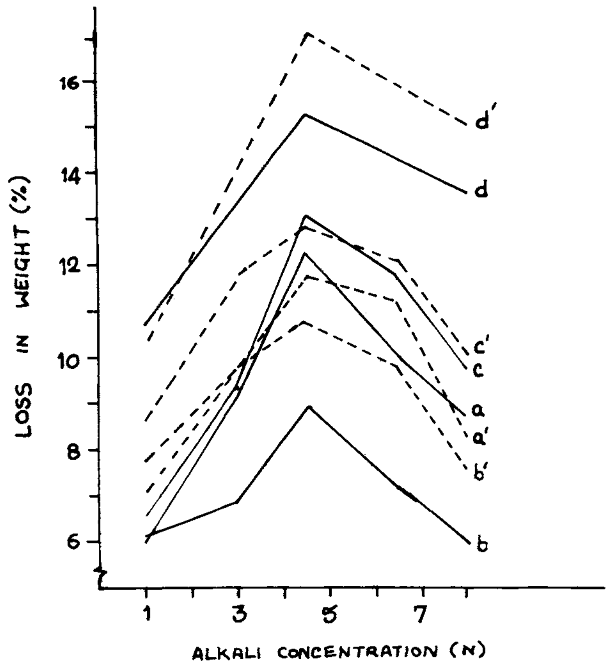

Fig. 1. Effect of alkali treatment on weight loss: NaOH (—) and KOH (---) at: (a) 10°C; (b) 20°C; (c) room temp; (d) 50°C.

decrease. The reason attributed for decrease in weight loss at higher alkali concentrations might be due to the increased thickness of the cell wall, which does not allow the alkali ions to penetrate further into the soluble portion of jute fiber, thereby resulting in a decrease in the dissolution of hemicellulose and other soluble materials.

Moisture Regain and Accessibility

Since the cellulosic fibers are hygroscopic, we can evaluate the accessibility and crystallinity from moisture regain data. According to the present theory of sorption,[3] the absorption of water by cellulose is caused by hydrogen bonding of water molecules to the accessible hydroxyl groups, which act as sorption sites. Since the holocellulose of jute fiber consists of both amorphous and crystalline regions, it is possible to say that the accessible hydroxyl groups may be either in the amorphous region or on the surface of the crystalline area. The percentage of hydroxyl groups on the surface of the crystal will increase with decreasing crystal size, and therefore the total amount of sorbed water will also increase with decreasing crystal size or increasing amorphous portion. Interpretation of sorption power in terms of amorphous cellulose is best expressed in the concept of accessibility, which is defined as the fraction of total cellulose in which the hydroxyl groups are freely available for reaction under certain conditions such as temperature, concentration, and time.

Figure 2 shows the linear relation of sorption ratio with accessibility. The accessibility was calculated from moisture regain data using Valentine's equa-

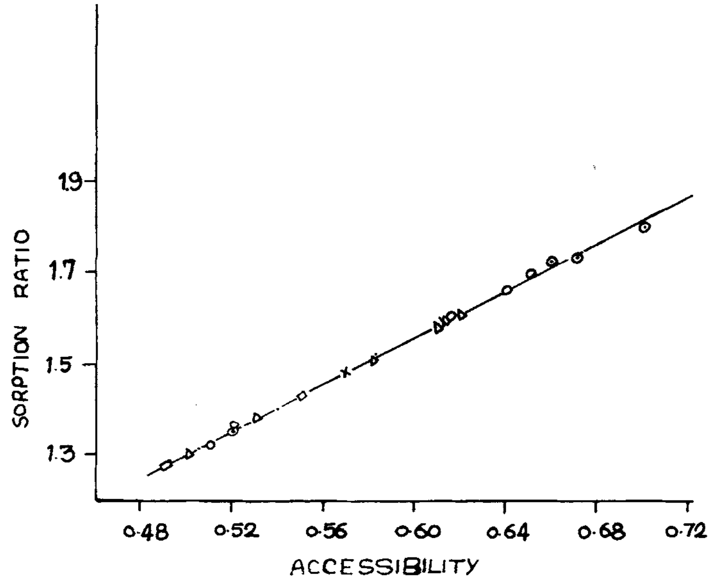

Fig. 2. Relation between sorption ratio and accessibility. Swelling with NaOH at (⊙) 10°C, (○) 20°C, (△) room temp, KOH at (□) 10°C, (×) 20°C, and (·) room temp.

tion $F_{am} = SR/2.6$, where SR is the sorption ratio (the ratio of the moisture sorption of the experimental sample to that of the standard or raw at the same relative humidity). It may be noted from the linear relation that the absorption of water takes place mainly in the amorphous region and consequently the crystalline region absorbs a small amount of water. This amount is smaller for the crystalline region of cellulose I than for that of cellulose II. This is shown in Figure 3 where moisture regain increases with increasing alkali strength up to 4.5N and then almost constant. At this concentration of alkali treatment the transition takes place from cellulose I to cellulose II, which resembles amorphous cellulose. Jeffries[7] pointed out that the difference in ratio of regain to amorphous content between cellulose I and cellulose II is a reflection of differences in sorption behavior, thus the structure of the amorphous region. The low moisture absorption at lower alkali treatments might be due to the stronger intermolecular hydrogen bonding in the amorphous region of cellulose I compared to that of cellulose II.

Cyanoethylation

When the hydroxyl protons are substituted by cyanoethyl groups the accessibility towards moisture (see Fig. 4) is increased with increasing the degree of cyanoethylation. Though the affinity of cyanoethyl groups is very less towards the water molecule, the increase of moisture regain in the region of higher degree of cyanoethylation might be due to the decrease in the crystallinity of cellulose. Figure 4 shows the effect of alkali concentration on the degree of cyanoethylation. There is a decrease in nitrogen content beyond 4.5N alkali treatments. This might be due to the higher concentration of alkali and high temperature the cyanoethylation tends to reverse reaction,[8] so

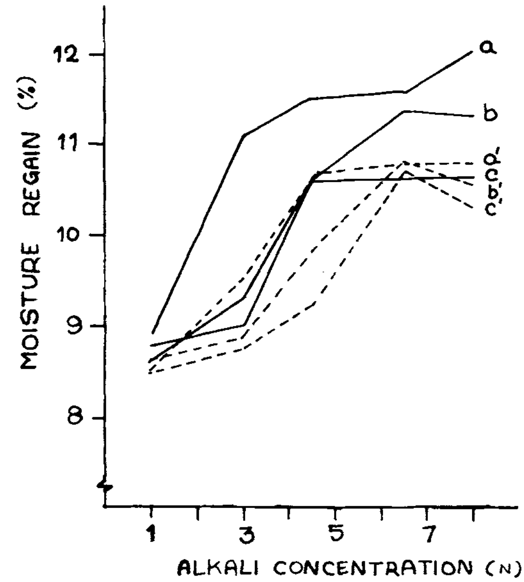

Fig. 3. Relation of moisture regain with alkali concentration: NaOH (—) and KOH (---) at: (a) 10°C; (b) 20°C; (c) room temp.

that decyanoethylation may occur as shown below:

$$\text{Cell—O—CH}_2\text{CH}_2\text{C}\equiv\text{N} \xrightarrow{\text{NaOH}} \begin{cases} \text{Cell—O—CH}_2\text{CH}_2\text{COONa} & \text{minor product} \\ \text{Cell—OH} + \text{CH}_2\text{=CH—C}\equiv\text{N} & \text{major product} \end{cases}$$

Crystallinity from IR Study

As a measure of crystallinity, the infrared ratio at 1372 cm^{-1}/2900 cm^{-1} is adopted according to Nelson and O'Connor.[9] Figure 5 shows the relation between crystallinity and amorphous fraction. The linear relation of decreasing crystallinity with increasing accessibility leads to the conclusion that the decrystallization proceeds with increasing alkali strength during swelling. This is observed in Figure 3 by increasing moisture regain with alkali strength. Replacements of hydroxyl protons by cyanoethyl groups also shows the order of increasing accessibility with decreasing IR ratio but at lower values. The increased moisture regain along with the degree of cyanoethylation raises an uncertain explanation whether there is a possibility for conversion of cellulose II into cellulose I or the formation of accessible crystalline cellulose II. We can

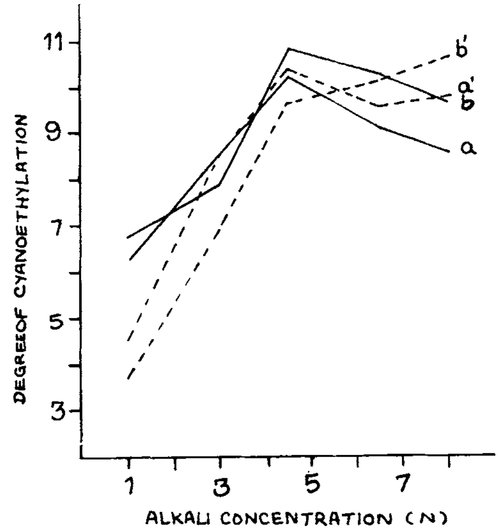

Fig. 4. Effect of alkali strength on degree of cyanoethylation: (a) NaOH and (b) KOH; the dotted lines show the moisture regain data of cyanoethylated jute at respective alkali treatments.

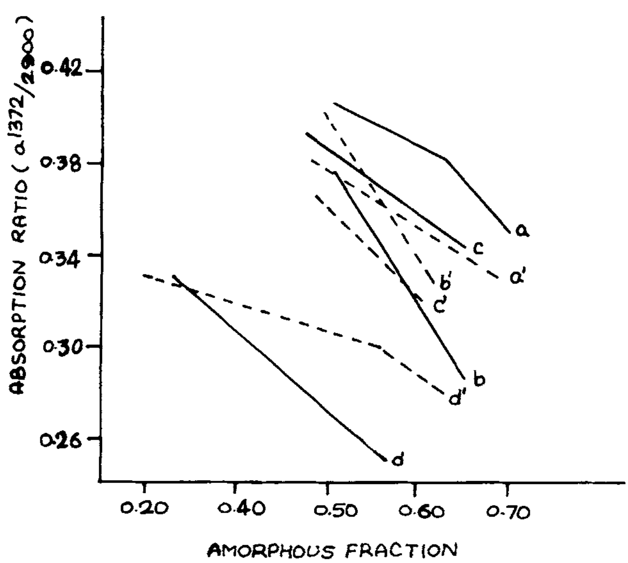

Fig. 5. Relation of amorphous fraction with infrared crystallinity: NaOH (—) and KOH (---) at: (a) 10°C; (b) 20°C; (c) room temp; (d) cyanoethylated jute at 60°C.

observe a marginal decrease in crystallinity for cyanoethylated samples in Figure 5.

CONCLUSIONS

The moisture regain of jute fiber increases with alkali treatment up to 4.5 N and then levels off. The swelling temperature has no significant effect on moisture regain. The degree of cyanoethylation also increases up to 4.5N

alkali treatment. The decreased moisture regain at a lower degree of cyanoethylation might be due to stronger intermolecular hydrogen bonding in the amorphous region of jute cellulose. The accessibility of modified jute treated at higher alkali strengths increases with decreasing crystallinity as measured from moisture regain data and infrared ratio.

The authors are thankful to Dr. S. N. Pandey, Director, Jute Technological Research Laboratory, for his keen interest and for permission to publish the work. They are also thankful to Indian Council of Agricultural Research for providing facilities for this work.

References

1. W. Tsuji, A. Hirai, and M. Hosono, *J. Appl. Polym. Sci.*, **20**, 2837 (1976).
2. P. H. Hermans, *Contributions to the Physics of Cellulose Fibers*, Elsevier, Amsterdam, 1946.
3. J. A. Housman, *Text. Res. J.*, **19**, 152 (1949).
4. L. Valentine, *Chem. Ind.*, **3**, 1279 (1956).
5. A. Hirai, W. Tsuji, R. Kitamaru, and M. Hosono, *J. Appl. Polym. Sci.*, **20**, 3365 (1976).
6. A. Majumdar, S. Samajpati, P. K. Ganguly, D. Sardar, and P. C. Das Gupta, *Text. Res. J.*, **50**, 575 (1980).
7. R. Jeffries, *J. Appl. Polym. Sci.*, **8**, 1213 (1964).
8. *Encyclopedia of Chemical Technology*, Wiley-Interscience, New York, 1965, Vol. 6, p. 653.
9. M. L. Nelson and R. T. O'Connor, *J. Appl. Polym. Sci.*, **8**, 1311, 1325 (1964).

Received November 1, 1988
Accepted November 7, 1988