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On the Degree of Crystallinity in Jute and Mesta Fibers in Different States of Purifications and Moisture Conditions

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Synopsis

The degree of crystallinity (DC) in different moisture conditions was studied for jute and mesta holo- and α-celluloses. As in the case of raw fibers the DC was found to decrease as humidity increased, but the rate of change was diminished in the present case. The lower rate is explained on the supposition that some of the regions previously accessible to water have, after removal of lignin and hemicelluloses, assumed more ordered states and are less accessible. The DC increased as lignin and hemicelluloses were removed and tended to approach that of ramie or cotton. The crystalline structure of jute α-celluloses was also found to be similar to that of ramie or cotton.

INTRODUCTION

It has been reported earlier[1] that for raw jute and mesta fibers the degree of crystallinity (DC) diminishes with the increase of moisture absorption. As these fibers are composed of impurities like lignin and hemicelluloses it was thought worthwhile to study the effects of these constituents on the action of moisture.

The average values of the chemical constituents of jute[2] and mesta[3] are as shown in Table I.

Staining tests[4] show that the lignin is not uniformly distributed in the fiber, its proportion being higher in the middle lamella than in the primary and secondary walls, which are mainly composed of cellulose and hemicelluloses. Astbury et al.[5] suggested a state of mixed crystallization of cellulose and lignin, and hemicelluloses in jute and other lignified fibers. Banerjee and Roy[6] pointed out that the crystalline structure of α-cellulose from jute is identical with that of ramie or other pure celluloses. Different workers[7–12] have studied the various effects of removal of lignin and hemicelluloses on the crystalline structure of jute. Sen and Hermans[9] found that the crystalline fraction in jute fiber goes on increasing with the gradual delignification and concluded that the percentage of cellulose crystallites in jute calculated on the basis of its α-cellulose content was the same as that in pure cellulose fibers.

In the present work the effect of moisture on the DC of jute and mesta fibers has been examined in the following stages of purification: (1) fiber

TABLE I

	Jute, %	Mesta, %
α-Cellulose	60.5	60.0
Lignin	13.3	10.1
Hemicellulose	23.0	28.0
Ash	1.6	0.7
Protein	1.6	1.2

after complete removal of lignin; (2) fiber after partial removal of hemicelluloses from delignified fiber; (3) fiber after almost complete removal of hemicelluloses from delignified fiber but with retention of cellulose I structure.

EXPERIMENTAL

Preparation of the Samples

Delignified Fiber or Holocellulose. Clean jute and mesta fibers free from bark were taken from those samples as previously reported[1] and bleached according to the method of Sarkar et al.[13] After extracting in a Soxhlet apparatus with alcohol–benzene (1:1) for 6 hr the samples were dried in air. One gram of each of these samples was then treated with 50 cc of 0.7% sodium chlorite (Textone) (acidified with 0.2 cc of glacial acetic acid) on boiling water bath for 2 hr with occasional stirring for complete oxidation. The samples were then washed with water and then suspended in sulfur dioxide solution for 10 min. These were then washed free of acid and dried at 75°C in a steam oven and then over P_2O_5 in a vacuum desiccator.

Partial Removal of Hemicelluloses from Delignified Fiber. Holocellulose thus prepared was first treated with 16 cc of 5% (w/v) NaOH at room temperature for 1 hr, filtered, washed with 50 cc of 5% NaOH, and again steeped in 16 cc of 5% NaOH and finally washed free from alkali with distilled water and dried at 100°C for 5 hr.

Complete Removal of Hemicelluloses from Delignified Fiber. After partial removal of hemicelluloses some samples were treated with 9.3% NaOH (w/w) (1:20) at room temperature for $1^1/_2$ hr. They were washed free from alkali and then dried at 75 to 80°C for 5 hr and then over P_2O_5 in a vacuum desiccator. Treatment has been confined to concentrations of up to 9.3%, since the crystalline structure usually remains unaltered at such concentrations.

Procedure

The experiments were based on the method of Hermans and Weidinger as reported earlier.[1] Ni-filtered CuKα radiation from a Philips x-ray tube, collimated down a distance of 5 cm through a lead glass capillary tube 0.5

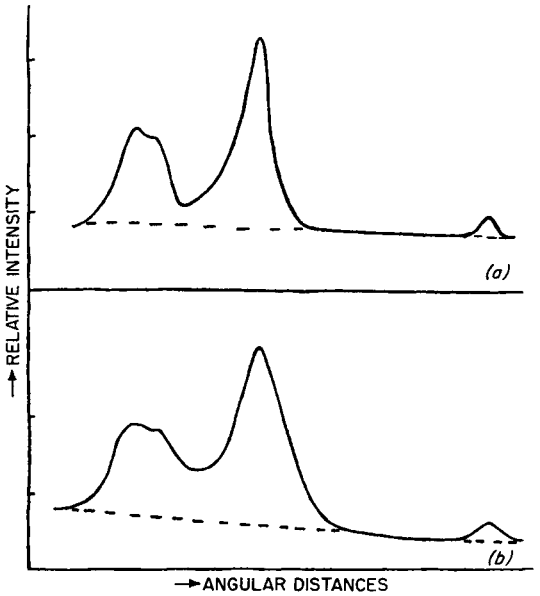

Fig. 1. Intensity distribution curves for tossa jute: (*a*) 9.3% NaOH-treated, moist; (*b*) 9.3% NaOH-treated, dry.

mm in diameter, passed through the fiber pellet. It produced diffracted rays; the undiffracted beam used as reference, fell on a silver foil. The foil was held within a Goppel cone of base diameter 2.3 cm covering the

TABLE II
Crystalline Area (*C*), Amorphous Height (*A*), Half Width (*W*), and Peak Height (*H*) for Delignified Fibers or Holocelluloses

Sample	Humidity[b]	Crystalline area (*C*)[a]	Amorphous height (*A*)[a]	Half width (*W*)[a]	Peak height (*H*)[a]	DC, %
Tossa jute	Dry	277	6.5	8.5	18	58
(*Corchorus*	Room	223	7	7	18	46
olitorius)	Moist	200	8	6	18	42
		275	6.8	8	19	57
White jute	Dry					
(*Corchorus*	Room	225	7	6.5	18	47
capsularis)	Moist	206	7.5	6	18	43
		281	8	7.5	21	59
Mesta	Dry					
(*Hibiscus*	Room	236	8.5	7.5	20	49
cannabinus)	Moist	205	9	6.5	20	43

[a] Arbitrary units.
[b] Dry ≈ 0%, room ≈ 65%, moist ≈ 100%.

central portion of a circular disk-type film holder. Between the cone and the x-ray film was placed a lead sector which covered two opposite quadrants. The disk along with the cone was rotated by a motor in a plane perpendicular to the x-ray beam which formed the axis of rotation. A Perspex chamber enclosed the entire space including the disk, specimen, and

TABLE III
Crystalline Area (C), Amorphous Height (A), Half Width (W), and Peak Height (H) for Delignified Fibers (Holocellulose after Partial Removal of Hemicelluloses

Sample	Humidity	Crystalline area (C)[a]	Amorphous height (A)[a]	Half width (W)[a]	Peak height (H)[a]	DC, %
Tossa jute	Dry	296	6.5	7	23	62
	Room	260	7.5	6	23	54
	Moist	240	8.5	5	24	50
White jute	Dry	290	6.5	7.5	24	60
	Room	255	7	6.5	23.5	53
	Moist	230	8	6	22	48
Mesta	Dry	297	7	7	23.5	62
	Room	265	7	6	23	55
	Moist	220	8	6	23	46

[a] Arbitrary units.

TABLE IV
Crystalline Area (C), Amorphous Height (A), Half Width (W), and Peak Height (H) for α-Celluloses

Sample	Humidity	Crystalline area (C)[a]	Amorphous height (A)[a]	Half width (W)[a]	Peak height (H)[a]	DC, %
Tossa jute	Dry	314	6	6.5	23	66
	Room	270	7	5.5	23	56
	Moist	250	7	5.0	24	52
White jute	Dry	320	6.5	6	22	67
	Room	275	6.0	5.5	22	57
	Moist	252	6.0	5.0	23	53
Mesta	Dry	330	7	7	29	69
	Room	288	7.5	5	28	60
	Moist	255	7.5	5	29	53

[a] Arbitrary units.

a part of the collimator. Trays containing requisite materials kept the atmosphere within the chamber at different humidities; air at respective humidities was also slowly passed through the chamber by a pump.

The intensity distribution curves, as shown in Figure 1, were drawn after reducing the intensity due to pellets to equal exposure and correction due to

air scattering and absorption in the pellets. The integrated intensity due to crystalline reflection was found by measuring the area c between the peaks and the background line, and the height A of the background line below the minimum between the (002) and the composite (101) and ($10\bar{1}$) peaks was taken as a measure of amorphous content. The DC was determined by comparing the crystalline areas of the samples with those of ramie, the values are given in Tables II–IV. Repeated determinations showed experiments that the DC values do not differ by more than 2%.

RESULTS AND DISCUSSION

Before discussing the results, it would be worthwhile to see how the increased quantity of absorbed moisture at high humidity might affect the incoherent scatter of x-rays.

For this purpose Water in a polyethylene cylinder, equal in diameter (1 mm) to the fiber pellet was used to scatter an x-ray beam and the scattering corrected by reference to that of an empty polyethylene cylinder. The increased area under the intensity diagram was very small; on considering the mass of absorbed moisture to be less than 30% of the mass of the pellet, the increase in amorphous area due to absorbed moisture was calculated. It was found that the error incurred in the estimate of the degree of crystallinity was not likely to exceed 1%. This correction was thought to be negligible in comparison to other sources of error in such methods of estimation. As such, this was not mentioned in the earlier paper.[1]

Delignified Fibers of Holocelluloses

Some of the photographs of the treated fibers are shown in Figure 2. A comparative study of the photographs of holocelluloses and α-celluloses indicates that the background is clearer than those of raw fibers reported in the previous paper.[1] Though maintaining the same trend, the rate of change in the degree of crystallinity (DC) with the change of humidity in holocellulose is less than what it was in the raw fiber.[1] The values for the half width in Table II show that the diffraction patterns of delignified fibers also become sharper than those of raw fibers,[1] and that the sharpness also maintains the same trend of change with humidity as in raw fibers.[1] The values for the degree of crystallinity in delignified fibers are somewhat higher than those for the respective raw fibers.[1] It is thought that lignin[11] hinders the packing of the cellulose chains; as such, the increase in DC might be considered to be an effect of better packing brought about by the removal of lignin. It is well known that lignin is distributed throughout the body of the jute cell[9] and part of the lignin lies in the noncrystalline region. Therefore, any influence in the noncrystalline regions restricting the chains' ability to fit together into the state of higher organization may extend by virtue of the structural continuity into the crystalline regions, and with the removal of lignin this restriction is also removed.

Delignified Fiber after Partial and Complete Removal of Hemicelluloses by Alkali Treatments

Tables III and IV show that the changes taking place in the DC of holocelluloses treated with 5% and 9.3% NaOH solution, with the changes in humidity are of the same nature, but in these cases the rate of change is less than that in raw or delignified fibers. Further, the values for the DC are higher than those in the delignified state. The diffraction pattern (Fig. 2) of the samples treated with 9.3% aqueous NaOH, which extracts most of the hemicelluloses, leaving the α-cellulose residue only, shows that these samples have a crystalline structure similar to that of ramie or cotton; this agrees with the findings of Chaudhury and Sen.[12]

The decrease in the DC with increasing humidity for delignified fibers and alkali-treated holocelluloses also may be explained in a similar way, as done in the case of raw fibers in terms of paracrystallinity. But here the effect

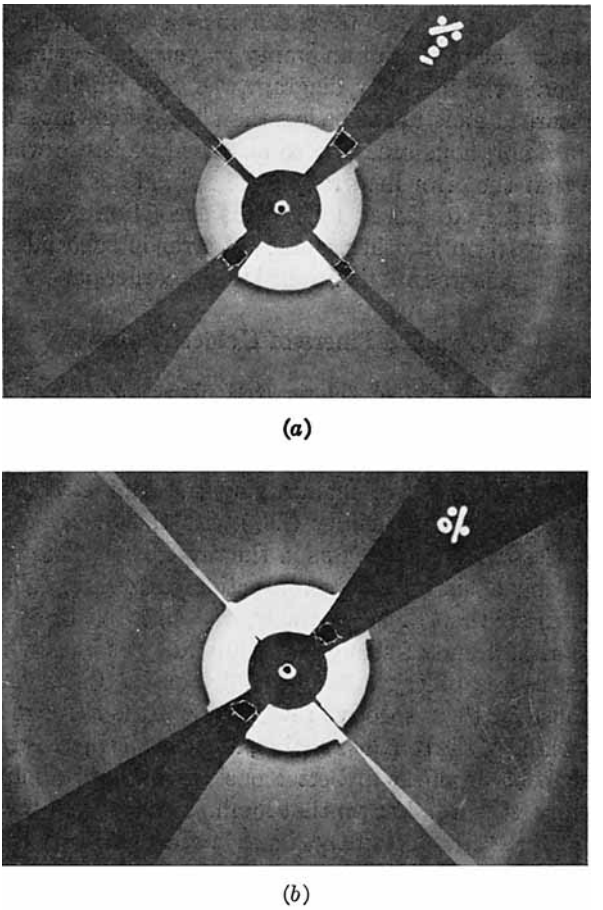

Fig. 2. X-Ray photographs of 9.3% NaOH-treated tossa jute: (*a*) dry; (*b*) moist. One pair of quadrants shows cellulose pattern and the other pair shows air scattering.

of the removal of lignin and hemicelluloses is superimposed on that of water, and both influence the extent of the change. A gradual decrease in the rate of change of the DC with humidity (Tables II–IV) occurs as the samples are increasingly purified by the removal of the noncellulosic incrustants, and ultimately the values of DC for α-cellulose in the dry state in Table IV tend towards the values for ramie or cotton.

It is well known that hemicelluloses are the main absorbent of water and with the removal of hemicelluloses the absorption will be less as shown in Table V, and as a result, the rate of diminution of the DC with humidities diminishes in the case of α-celluloses in Table IV. Again with the removal of hemicelluloses some of those regions affected by water in the raw state have now assumed a better organized state, and as a result, water cannot enter those regions to effect any change in the DC, hence the decrease in the rate of diminution of DC in the purified samples.

TABLE V
Sorption data at Various Sample Humidities

Sample	Sorbed, %		
	Dry	65% RH	99% RH
Jute holocellulose	0	9.90	32.19
Jute holocellulose treated with 5% NaOH	0	8.09	29.04
Jute holocellulose treated with 9.3% NaOH	0	7.86	29.00
Mesta holocellulose	0	9.47	32.56
Mesta holocellulose treated with 5% NaOH	0	8.17	30.91
Mesta holocellulose treated with 9.3% NaOH	0	7.80	28.63

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