

The Effect of Methods of Drying on the Fine Structure, Density, and Some Mechanical Properties of Jute and Allied Fibers

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Synopsis

The degree of crystallinity and crystallite orientation in jute, mesta, and roselle fibers have been studied by x-ray diffraction. Removal of water, indirectly, has been carried out by alternate immersion in methanol and benzene. It has been found that an increase in crystallinity and a decrease in crystallite orientation take place in these fibers as a result of direct drying, presumably because of the formation of an increased number of hydrogen bonds associated with direct drying. Density, tenacity, and rigidity of the fiber in the two drying conditions are in agreement with the x-ray results.

INTRODUCTION

A knowledge of the molecular arrangement in textile fibers is of great importance in explaining the behavior of these fibers when used under different conditions. X-Ray studies of fibers like jute, mesta,^{1,2} etc., at different humidity conditions have brought forth some new ideas regarding the fine structure of these materials. It has been suggested that incursion of moisture into the dry fiber tends to bring about some derangement in the molecular order, the effect increasing with increasing amount of water molecules inside. To check this idea, experiments were planned for removing the moisture without disturbing the arrangement of the molecular chains, by a process of drying the fiber indirectly in which moisture could be replaced by an inert molecule to be removed later by evaporation. In the normal drying process, it was thought that the deranged molecules get a chance of improving their arrangement through hydrogen bonding as the layer of water molecules is thinned. A comparative study of directly and indirectly dried fibers in respect of fine structure and their physical properties was also proposed.

Several workers have compared different properties of directly and indirectly dried cotton and other cellulosic fibers. Heyn³ has observed in case of fresh cotton from unopened boll that a crystallization process takes place during the direct drying of the wet fiber and is prevented when the fiber is dried indirectly. Kouris et al.⁴ observed a lower value in crystal-

linity when cellulose fibers from soft wood were dried from benzene, to which the fibers were accommodated by a series of solvent exchanges. Solvent-exchanged fibers showed an increase in reactivity toward various reagents. Mark et al.⁵ also found an increased accessibility of cotton linters to HIO_4 solution. Vanden Akker⁶ and Broughton and Wang⁷ demonstrated that the strength of paper handsheets dried by solvent exchange was considerably lower than the strength of normally air-dried sheets. The method of drying was thus found to influence the degree of order and thus to affect the physical properties of cellulose fibers.

In the present work, fine structure of jute, mesta, and roselle under different drying conditions has been studied by x-ray method. The influence of drying conditions on the density and some mechanical properties has also been studied.

EXPERIMENTAL

Methods of Drying

For direct drying, the moist fiber bundle was kept in a vacuum desiccator over P_2O_5 for two days, and in the camera chamber containing P_2O_5 for another two days when it was considered ready for exposure.

For indirect drying, the bundle was kept moist in water for 6 hr and then inside a desiccator containing distilled water for 18 hr; the bundle was then kept in dry methanol, changing the methanol several times at 2-hr intervals; thereafter the bundle was washed with several changes of benzene. It was then kept overnight over P_2O_5 in a vacuum desiccator in which small pieces of paraffin wax were kept in a Petri dish to absorb the benzene vapors. The bundle was then transferred to the closed chamber containing P_2O_5 and exposed to x-rays. Air scatter was recorded for each drying condition on the unexposed quadrant of the film.

Fine Structure by X-Ray Method

The experiments were based on the method of Hermans and Weidinger⁸ with suitable modifications. Ni-filtered CuK_α radiation from a Philips x-ray tube was used. A thin paste of aluminum hydroxide and pure gypsum was used as a standard sample inside a Goppel camera. A lead sector was placed between the Goppel camera and the x-ray film to cover the two opposite quadrants. A Perspex chamber enclosed the specimen, disc, etc. Petri dishes containing P_2O_5 were kept inside the chamber. The fiber sample 2.5 cm in length and 19 mg in weight was made into a parallel bundle and mounted in a stretching frame. For the measurement of the degree of crystallinity, two-dimensional randomization was obtained by rotating the film. Randomization in three dimensions as obtained in Hermans and Weidinger's pellets⁸ could not be effected, because such pellets collapsed in subsequent treatments. However, this would not vitiate the results as the same bundle of fibers was used under the two drying condi-

tions in case of a particular fiber specimen. For orientation measurement, the same bundle was used keeping the film stationary. All x-ray photographs were taken on moisture-free fiber bundles.

RESULTS

For the determination of the degree of crystallinity, the crystalline area above the background line of the intensity curve was found following the method of Hermans and Weidinger⁸ as described in a previous paper.¹ The value 74% for the degree of crystallinity for ramie was taken as a standard.

The figures for the degree of crystallinity were found by comparing the crystalline area of ramie with that of the respective fibers.

The crystallite orientation was found after Hermans,⁹ taking into consideration the intensity distribution curves of both the (002) and (101) and (10 $\bar{1}$) spots.

Effect of Benzene Included in the Structure of Indirectly Dried Fibers.

Bell¹⁰ has shown that about 2% benzene is retained by jute fiber, whereas Marchessault et al.¹¹ have found that 1.5% benzene is retained by softwood sulfite pulp. In case of our samples, we have found by the gravimetric method that 1.5% to 2% benzene is retained by indirectly dried samples compared to oven-dried samples.

Mass Spectrometry Analysis of Indirectly Dried Samples. The samples were taken in small glass ampoules which were first evacuated and then left connected to the mass spectrometer for 10 min. No trace of benzene was found at room temperature. The test was carried out with a Type MS3 mass spectrometer of Associated Electrical Industries Ltd., U.K.

Probably traces of benzene could not be detected by the mass spectrometer because the samples were already dried over vacuum, and about 2% benzene locked in the structure could not be removed by further evacuation and hence could not be detected by the mass spectrometer. Thus, the maximum amount of benzene retained is 2%.

Mass Absorption Coefficient. To see the effect of benzene in the indirectly dried fibers, measurements were made to determine any change in its x-ray absorption coefficients compared to that of the directly dried state. As described in the experimental part, the absorption measurements were made from the intensity of the standard sample in the Goppel camera with and without the fiber in the x-ray path.

From the difference in intensity from the standard sample, the absorption of the fiber sample was calculated using the relation⁸

$$\log(I_{\text{air}}) - \log(I_{\text{cell}}) = \mu_m \rho t$$

where I_{cell} , I_{air} = intensity of standard sample with and without the fiber bundle in position, respectively; μ_m = mass absorption coefficient of the fiber bundle (g/cm^3); and t = thickness of the fiber bundle (cm).

The resulting values of $\mu_m \rho t$ were 0.214 and 0.215 for jute, 0.214 and 0.216 for mesta, and 0.200 and 0.203 for roselle in directly and indirectly

dried states. These values indicate equal absorption within experimental error. Hence, no correction was applied to the observed peak height of the indirectly dried samples.

To see further the effect of benzene on x-ray intensity, we calculated the theoretical intensity of cellulose and benzene per molecule after Norman¹² for the whole region of observation. We then found the contribution toward integrated intensity of a mass of benzene one fiftieth of that of cellulose. It was found that it can affect the crystallinity figures by not even 1%, and hence it was not taken into account.

DENSITY AND SOME MECHANICAL PROPERTIES

To compare the density and mechanical properties of the fibers in the two states, pairs of fiber bundles were collected from adjacent portions of each of ten fiber reeds. This was done to eliminate the variations of the parameters within sample as far as possible.

For the measurement of fiber density, a density gradient column¹³ made with carbon tetrachloride and xylene was used. Fibers cut to 3-cm lengths and subjected to necessary drying treatment were kept in carbon tetrachloride for some time and then dropped inside the column. Each lot of fibers was left in the column for 24 hr before readings were taken. The results are given in Table III.

For the measurement of tenacity, each bundle of fibers was cut to 15-cm lengths and weighed to 300 mg at the same ambient conditions. One bundle from each pair was dried directly and another indirectly. They were then immersed in dry mineral oil to prevent absorption of moisture. The tensile strength, expressed in g/tex was measured by the J.T.R.L. fiber-bundle strength tester.¹⁴

The flexural rigidity was measured following a previous method¹⁵ with suitable adaptations. A fringe of 100 filaments each of length 2 cm was made in a width of 2 cm, so that the test length of the filaments in the fringe was 1 cm. A load of 200–300 mg was applied to bend the filaments such that the bending was confined to 1 to 2 mm. The following formula was used to determine the flexural rigidity F :

$$F = PL^3/3d \text{ (dynes.cm}^2\text{)}$$

where P = load applied for bending; L = test length of the filaments in the fringe, and d = vertical deflection of the plane of the fringe.

The modulus of torsional rigidity n was measured after Sen.¹⁶ The following formula was used to determine it:

$$n = 4\pi IL \frac{a^2 + b^2}{a^3b^3T^2} \text{ (dynes/cm}^2\text{)}$$

where I = moment of inertia of the pendulum bob about the fiber axis; L = length of the filament, which was taken to be 5 cm; a and b = semi-axes of the cross sections of the filaments, assumed to be elliptical, and T = time period of oscillations of the pendulum bob.

DISCUSSION

From Table I it is found that with samples from which the water has been removed in the indirect way, x-ray patterns with peaks of lower height and larger width, along with higher background intensity, are obtained compared to those from the directly dried samples. The magnitude of the change in the peak height does not, however, agree with the result of Heyn³ in case of mature cotton fiber where he got somewhat bigger change in peak height in benzene-dried fiber. The degree of crystallinity, calculated from the crystalline area, showed a consistent reduction when drying was carried out indirectly. From Tables I and II it is also found that the change in the degree of crystallinity and orientation for mesta is a bit higher than that for jute and roselle fibers.

These results may be clear when we consider the nature of actions of water and benzene on the molecular arrangement of the cellulose chains. Benzene is a poor swelling and a poor hydrogen-bonding medium, and therefore there will be no hydrogen bonding between hydroxyls between and within

TABLE I
Crystalline Area (*C*), Amorphous Height (*A*), Half-width (*W*), Peak Height (*H*), Degree of Crystallinity (*D.C.*), and Relative Intensity (*R.I.*)^a = $I_{002}/I_{101} \& 10\bar{1}$ of Fibers after Direct (*D*) and Indirect (*I*) Drying, all in Arbitrary Units

Fiber		<i>C</i>	<i>A</i>	<i>W</i>	<i>H</i>	<i>D.C.</i>	<i>R.I.</i>
Ramie	D	160	2.6	4.8	20.5	74.0	3.33
	I	134	4.6	5.0	17.4	61.6	3.48
Mesta	D	141	6.0	9.0	13.5	64.8	1.68
	I	114	6.8	9.5	12.5	52.4	3.12
Jute (Tossa)	D	129	7.0	8.0	10.0	59.3	2.00
	I	111	7.4	9.0	9.0	52.4	2.15
Jute (White)	D	125	7.5	7.6	9.5	57.5	2.30
	I	112	8.0	8.0	9.0	51.5	2.50
Roselle	D	76	4.0	7.0	7.5	34.9	1.87
	I	64	4.5	8.0	7.0	29.4	2.33

^a Ratio of the height of I_{002} peak to that of the $I_{(101 \& 10\bar{1})}$ peak both being measured above the background line.

TABLE II
Crystallite Orientation (α_m) of Different Fibers After Direct and Indirect Drying

Fiber	Crystallite Orientation α_m , degree and minutes	
	Direct	Indirect
Ramie	7°15'	7°08'
Mesta	11°44'	9°24'
Jute (Tossa)	10°16'	9°38'
Jute (White)	10°08'	9°28'
Roselle	9°53'	9°32'

TABLE III
Density and Some Mechanical Properties in the Directly (*D*) and Indirectly (*I*) Dried States

Fibers	Density, g/cm ³		Tenacity, g/tex		Flexural rigidity, dynes.cm ²		Torsional rigidity, (dynes/cm ² ,) × 10 ¹⁰	
	<i>D</i>	<i>I</i>	<i>D</i>	<i>I</i>	<i>D</i>	<i>I</i>	<i>D</i>	<i>I</i>
Jute (White)	1.475	1.457	15.7	14.3	4.0	3.0	.36	.20
Jute (Tossa)	1.478	1.471	18.7	16.8	5.5	4.0	.38	.27
Mesta	1.480	1.477	19.9	18.6	8.9	7.2	.30	.21
Roselle	1.455	1.445	9.3	8.0	6.8	5.9	.29	.18

the cellulose molecules in benzene drying. These results also agree with the findings of Kouris et al.⁴ in cellulose pulp where they observed that the mobility of the chains in benzene was greatly curtailed and there was little tendency for hydrogen bonding.

These results can also be explained in line with our previous findings^{1,2} that the degree of crystallinity decreases with humidity whereas the crystallite orientation improves. Here, also, we find from Table II that the micellar orientation improves as a result of indirect drying. So, due to the presence of moisture, the fiber assumes a structure which is characterized by the reduction of *D.C.* and improvement in the micellar orientation. When this moisture is removed by indirect drying, the molecular organization remains more or less unchanged, and as a result we obtain a structure similar to that with moisture. From the results on crystallite orientation, it appears that the molecules in some of the regions in the fiber cannot realign themselves in absence of hydrogen bonding in indirect drying, and these regions are likely to be of poorer orientation. As a result, contribution of those regions toward x-ray reflection being nil, the average orientation is better.

In case of indirect drying, we find a larger width of (002) peak. In the process of indirect drying, as is pointed out, water is removed by methanol and methanol by benzene, and finally benzene is removed. This process might introduce further stresses in the structure, and as a result the peak broadening might take place and it may also alter relative intensities, as is shown in Table I.

Lower density values in indirectly dried fibers in Table III also indicate that there is a general disordering of molecular packing in fibers in the indirectly dried state vis-a-vis fibers in the moistened condition.

From Table III it is also found that for all fibers the strength in the indirectly dried state is lower than that in the directly dried state. The effect of a decrease in crystallinity is thus found to outweigh that of increased orientation.

The torsional and flexural rigidity values in Table III show differences in the two states of drying more clearly, indicating large reduction in lateral cohesion between the chain molecules in the indirectly dried fiber.

Thus, the physical properties like density, tensile strength, as well as rigidity values of fibers in the two states of drying give clear indication that in the indirectly dried state the molecular arrangement is less ordered. This corroborates the x-ray findings that the degree of crystallinity of fibers is reduced when dried indirectly.

This also confirms the view that the introduction of moisture into the fiber reduces the molecular ordering, since indirect drying helps the fiber to retain its reduced ordering in moist condition even after drying.

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