JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 2021-2028 (1967)

On the Crystallite Orientation in Jute and Mesta Fibers Under Different Moisture Conditions

P. K. RAY, *Technological Research Laboratories, Indian Council of Agricultural Research, Calcutta 40, India*

Synopsis

The Hermans' average angle of orientation, the angle at 40% intensity, and the Hermans' orientation factor have been studied in raw and delignified jute and mesta fibers under different moisture conditions. It is observed that the average orientation of micelles in these fibers improves on moisture absorption and further improves when the moist fiber is subjected to tension, and that the action of water is more pronounced in delignified jute fibers. The derangement of a fraction of the regions, contributing to the x-ray pattern of these fibers, and the releasing of internal stresses have been cited here as possible causes of the phenomenon.

Introduction

Crystallite orientation in cellulose fibers has engaged the attention of many workers, since some of the physical properties of these fibers depend on it. In fibers such as jute and mesta the crystallites (or the crystalline areas) are uniaxially orientated; that is, the *b* axis of the crystallites makes a small angle with the fiber axis. The x-ray diffraction spots are drawn out into an arc to an extent depending on the degree of dispersion of the crystallites from the fiber axis. The average angle of orientation is generally measured from the distribution of intensity of x-ray reflections along the diffraction arc. Sisson[1] and Berkeley and Woodyard[2] found a correlation between the angle at 40% intensity and the strength for the different varieties of cotton. Banerjee et al.,[4] found that the orientation in jute deteriorates on delignification and thus concluded that a part of the lignin helps to keep the cellulose crystallites in regular orientation. Sen and Woods[5] studied the orientation factor of jute and ramie. Sen and Chaudhury[6] found that the orientation factor and the angle at 40% intensity have some correlation with the intrinsic strength of jute fibers. Gupta[7] found that the orientation in jute deteriorates on NaOH treatment. Kar and Basu[8] measured the orientation factor in raw and treated mesta fibers and found that the crystallites retain their orientation on delignification but do not do so on strong alkali treatment. Chakraborty[9] measured the orientation factor of jute at different stages of growth of the jute plant. Thus, different workers have studied the orientation of the crystallites in jute and mesta, but a study of the action of water on the crystallite orientation in these fibers has not been reported, and it was with this object in view that the present work was undertaken.

Experimental

Bundles of raw jute (*Corchorus capsularis* and *Corchorus olitorius*) and mesta fibers were combed, to ensure parallelism, and were mounted and kept taut in a stretching frame. For the examination of moisture-free samples they were conditioned over P_2O_5 for 4 days in a vacuum desiccator and for 2 days in a closed Perspex camera chamber, also kept at the same humidity, and dry air was slowly passed through the chamber during x-ray exposure. The sample was then left for 4 days in room conditions, which varied from 55 to 70% relative humidity for different samples, and it was then exposed to x-rays. For examination in moist condition the air in the chamber was kept saturated with water vapor for the same period, before the photographic film was introduced; x-ray exposure was made, and air, saturated with water vapor, was slowly passed through the chamber during x-ray exposure. For the examination of moist fiber under tension about three fourths of the breaking tension was applied to the fiber bundle by stretching it to the extent of 1.5% which is approximately three fourths of the breaking extension.

For delignification according to the method of Saktar et al.[10] clean fibers free from bark were taken from these samples and were cut into pieces of 1 cm. length and extracted in a Soxhlet with alcohol–benzene (1:1) for 6 hr. The samples were then air-dried. Holocelluloses were prepared by treating 1 g. of each of these samples with 50 $cm.^3$ of 0.7% sodium chlorite (Textone), acidified with 0.2 $cm.^3$ of glacial acetic acid, on a boiling water bath for 2 hr. with occasional stirring for complete oxidation. The samples were then washed with water and suspended in sulfur dioxide solution for 10 min. These were then washed free from acid and dried at 75°C. in a steam oven and then over P_2O_5 in a vacuum desiccator. Then similar experiments were carried out with these delignified samples. These delignified samples were then treated with 5 and 9.3% NaOH solution; they could not, however, be examined for orientation measurement, because they fragmented, but they were used for studying the degree of crystallinity under moisture conditions, and the results will be published in due time. The treatment was confined to concentrations of up to 9.3%, since the crystalline structure was found to remain unaltered at such concentrations.

Filtered CuK_α radiation was used with a specimen film distance of 10 cm., and the specimen size, exposure time, and photographic technique were standardized as far as was possible. The x-ray film was mounted on a rotatable holder fixed to the stage of the photometer, so that the rotation, which could be made in steps of 2.5° of arc, took place about the center of the photograph. At each setting the film was scanned radially by traversing the holder, and the intensity of the transmitted light was recorded for the clear film and for the position of maximum blackening in each reflection, i.e. (002) and composite (101) and ($10\bar{1}$) spots.

Results and Discussions

The intensity distribution curves as a function of the angular distance from the equator were drawn for the Debye-Scherrer arcs of (002) and composite (101) and (10$\bar{1}$) spots. Some of these curves are reproduced in Figures 1 and 2. The peak intensity in all cases was taken as unity. These intensity distribution curves represent the statistical spatial distribution of the paratropic planes of the crystallites in the fibers, and they may be designated by $I' = F'(\alpha_1)$ for (002) reflection and $I'' = F''(\alpha_2)$ for composite (101) and (10$\bar{1}$) reflections, where α_1 and α_2 refer to the angular distance from the equator. The Hermans' average angle of orientation α_m and the Hermans orientation factor f_x were found from the following relations:

$$\sin^2 \alpha_m = \overline{\sin^2 \alpha_1} + \overline{\sin^2 \alpha_2}$$

$$f_x = 1 - (3/2\overline{\sin^2 \alpha_1} + \overline{\sin^2 \alpha_2})$$

where

$$\overline{\sin^2 \alpha_1} = \int_0^{\pi/2} F'(\alpha_1) \sin^2 \alpha_1 \cos \alpha_1 \, d\alpha_1 \Big/ \int_0^{\pi/2} F'(\alpha_1) \cos \alpha_1 \, d\alpha_1$$

$$\overline{\sin^2 \alpha_2} = \int_0^{\pi/2} F''(\alpha_2) \sin^2 \alpha_2 \cos \alpha_2 \, d\alpha_2 \Big/ \int_0^{\pi/2} F''(\alpha_2) \cos \alpha_2 \, d\alpha_2$$

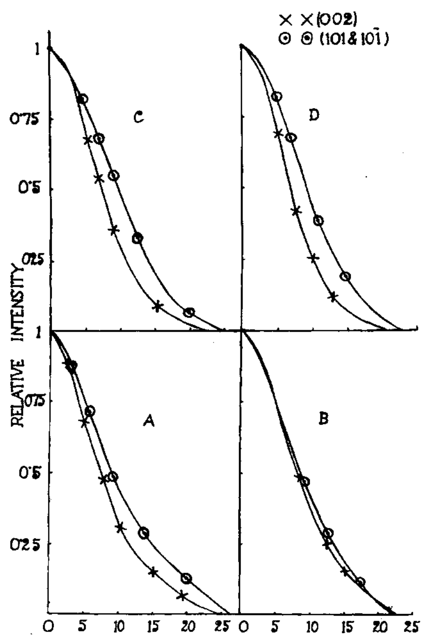

Fig. 1. Intensity distribution curves as a function of angular distance for raw mesta fiber: (*A*) dry, (*B*) room condition, (*C*) moist, (*D*) moist under tension.

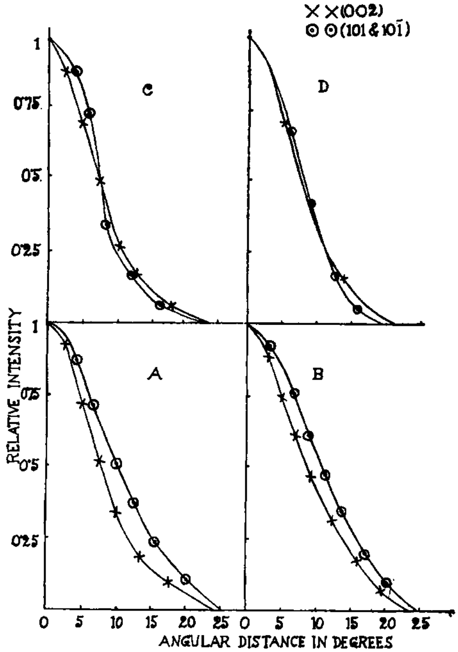

Fig. 2. Intensity distribution curves as a function of angular distance for delignified mesta fiber: (*A*) dry, (*B*) room condition, (*C*) moist, (*D*) moist under tension.

The distribution curves of both the paratropic planes did not coincide in any of the cases, and it was observed in general that the (002) plane is less disoriented than the composite (101) and (10$\bar{1}$) plane. Therefore the average angle of orientation was calculated from both the distribution curves.

The values of $\overline{\sin^2 \alpha_1}$ were determined from the relative intensity I curves (Fig. 1) by plotting $I \sin^2 \alpha_1 \cos \alpha_1$ and $I \cos \alpha_1$ against the angular distances, integrating graphically the areas under these curves, and finally taking the ratio of the integrals.

From the graphs of I versus α the values of the angle α of the intensity corresponding to 40% of the maximum intensity was also found from the distribution curves, and the values given are the mean of those found from the (002) and the (101) and (10$\bar{1}$) graphs.

From Tables I and II it is found that the intercrystalline adjustment improves with absorption of water for all the samples. The Hermans' average angle of orientation and angle at 40% intensity decrease at higher humidities for all the samples. The orientation further improves when the moist fibers are subjected to tension and the change in orientation with tension is more in mesta, and this may be due to the fact that the crystallites in mesta are deviated more from the fiber axis than those in jute, as shown in Table I, so that mesta shows the greater extensibility, which manifests itself in the drawing of chain molecules more to the fiber

TABLE I

Angle α at 40% Intensity, $\overline{\sin^2 \alpha_1}$, $\overline{\sin^2 \alpha_2}$, Average Angle of Orientation α_m, and Orientation Factor f_x of Raw Jute and Mesta Fibers

Sample	Humidity	α	$\overline{\sin^2 \alpha_1}$	$\overline{\sin^2 \alpha_2}$	α_m	f_x
Jute (Tossa)	Dry	9°50′	0.0150	0.0166	10°14′	0.952
Corchorus	Room	9°45′	0.0140	0.0160	9°58′	0.955
olitorius	Moist	9°0′	0.0133	0.0150	9°41′	0.957
	Moist under tension	8°20′	0.0107	0.0123	8°43′	0.965
Jute (white)	Dry	9°50′	0.0143	0.0173	10°12′	0.952
Corchorus	Room	9°50′	0.0140	0.0161	10°0′	0.955
capsularis	Moist	9°0′	0.0117	0.0148	9°21′	0.960
	Moist under tension	8°10′	0.0105	0.0125	8°43′	0.968
Mesta	Dry	10°0′	0.0177	0.0246	11°52′	0.936
	Room	9°45′	0.0171	0.0180	10°49′	0.947
	Moist	9°0′	0.0133	0.0167	9°58′	0.955
	Moist under tension	8°40′	0.0111	0.0134	9°0′	0.963

TABLE II

Angle α at 40% Intensity, $\overline{\sin^2 \alpha_1}$, $\overline{\sin \alpha_2}$, Average Angle of Orientation α_m, and Orientation Factor f_x of Delignified Jute and Mesta Fibers

Sample	Humidity	α	$\overline{\sin^2 \alpha_1}$	$\overline{\sin^2 \alpha_2}$	α_m	f_x
Jute (Tossa)	Dry	10°0′	0.0171	0.0208	11°12′	0.943
Corchorus	Room	9°40′	0.0171	0.0180	10°48′	0.947
olitorious	Moist	9°40′	0.0147	0.0180	10°22′	0.950
	Moist under tension	8°0′	0.0095	0.0107	8°22′	0.969
Jute (white)	Dry	10°0′	0.0163	0.0200	11°0′	0.945
Corchorus	Room	9°50′	0.0151	0.0180	10°30′	0.950
capsularis	Moist	9°20′	0.0131	0.0170	10°0′	0.955
	Moist under tension	8°0′	0.0112	0.0122	8°40′	0.964
Mesta	Dry	10°42′	0.0183	0.0240	11°52′	0.936
	Room	10°5′	0.0177	0.0222	11°25′	0.941
	Moist	9°0′	0.0134	0.0182	10°37′	0.949
	Moist under tension	8°0′	0.0103	0.0131	8°48′	0.964

axis than in their respective dry conditions. The orientation deteriorates on delignification, appreciably so in jute, and the result corroborates the earlier observations of Banerjee et al.[4] and Gupta,[11] who observed a similar decrease in orientation factor in jute in the absence of cementing material lignin. The orientation in mesta is not found to change on delignification, unlike that in jute. This may be due to a lower lignin content of mesta than of jute, and it may be concluded that lignin in mesta does not help as effectively as it does in jute to keep the cellulose crystallites in regular orientation. The action of water in improving orientation is more pronounced in delignified jute samples. This may be explained if we assume that water molecules tend to align the crystallites along the fiber axis. In the absence of constraining forces due to the binding material, lignin, water has a greater tendency to align the crystallites along the fiber axis, but this tendency in the delignified state of the jute samples cannot outweigh the disorientation already caused by delignification.

The results may be explained in conjunction with a previous finding of the writer,[12] that the degree of crystallinity decreases with moisture absorption. It was assumed at that time that an arrangement of a fraction of fiber material of varying degrees of perfection, adding to the coherence of x-ray reflections, is deranged by the action of moisture. It may be presumed that the average degree of alignment in this region is worse than that in the other regions. Thus, when this fraction ceases to add to x-ray intensity in the moist condition, the value of the observed orientation is higher.

The presence of water in the amorphous regions releases internal stresses in the long-chain molecules anchored to the crystalline regions, and thus helps the crystallites to align themselves along the fiber axis.

The author is deeply grateful to S. B. Bandyopadhyay, Head of the Physics Section, for his guidance and to R. K. Sen, Reader, Indian Association for the Cultivation of Science, Jadavpur, for many helpful suggestions. He is also indebted to the Indian Council of Agricultural Research for providing facilities for this work.

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Résumé

L'angle moyen d'orientation de Hermans, l'angle à 40% d'intensité et les facteurs d'orientation d'Hermans ont été étudiés sur de la jute brute et délignifiée et sur des fibres mesta dans différentes conditions d'humidité. On a observé que l'orientation moyenne des micelles dans ces fibres s'améliore par absorption d'humidité; èlle s'améliore en outre lorsque la fibre mouillée est soumise à une tension; on constate que l'action de l'eau est plus prononcée sur les fibres de jute délignifiée. La perturbation apporée dans certaines régions contribuant au diagramme de rayons-X de ces fibres et le relâchement des tensions internes sont cités comme causes possibles du phénomène observé.

Zusammenfassung

Der Herman'sche mittlere Orientierungswinkel, der Winkel bei 40% Intensität, und der Herman'sche Orientierungsfaktor wurden an Rohjutefasern, an delignifizierten Jutefasern und Mestafasern bei verschiedenem Feuchtigkeitsgrad untersucht. Die mittlere Mizellorientierung verbessert sich in diesen Fasern bei Feuchtigkeitsaufnahme und wird bei Einwirkung einer Spannung auf die feuchte Faser noch besser; die Wirkung des Wassers tritt in der delignifizierten Jutefaser stärker hervor. Der Ordnungsverlust eines Teiles der zum Röntgendiagramm dieser Fasern beitragenden Bereiche und die Aufhebung innerer Spannungen werden hier als mögliche Ursachen dieser Erscheinung angegeben.

Received February 16, 1967
Revised April 5, 1967
Prod. No. 1613