NOTES

Effect of Moisture on Crystallite Orientation in Cellulose Fibers

To explain the nature of fine structure of some cellulosic fibers, the interaction of water molecules and cellulose molecules was indicated earlier.[1] Moisture absorption reduced the degree of crystallinity,[1] while the orientation of crystallites[2] along the fiber axis appeared to improve. These effects were much reduced when the fibers were polymer-grafted,[3] and water had no effect on the orientation of crystallites in the grafted fiber. These results were explained on the basis of a paracrystalline nature of fiber structure[1] in which 15% to 20% of the fiber material has been found to be capable of diffracting x-rays but amenable to the attack of moisture; as a result the contribution of these regions added to the continuous background scattering after moisture absorption.

To explain these effects further, a range of fibers including both poorly and highly oriented fibers were investigated here. Hermans' methods[4,5] as previously adopted[1,2] were followed. The intensity distribution curves as a function of the angular distance from the equator were drawn for both the (002) and composite $(101 + 10\bar{1})$ spots in the case of native fibers and $(10\bar{1})$ and (101) spots in the case of rayon fibers. The fibers were examined only in a very low humidity (dry) and high humidity (about 95% R.H. or moist) conditions.

TABLE I
Average Angle of Orientation α_m in Dry and Moist Conditions

	α_m	
Sample	Dry	Moist
Ramie	8°21′	8°15′
Ramie treated with 5% NaOH solution	9°10′	8°50′
Jute (white)	10°12′	9°21′
Jute (Tossa)	10°14′	9°4′
Jute (white)	11°0′	10°0′
Jute (Tossa) delignified	11°12′	10°22′
Mesta	11°52′	10°48′
Mesta delignified	11°52′	10°37′
Rayon	18°54′	16°34′
Sisal	22°27′	21°06′

The results are given in Table I, and in Figure 1 the values of the angles of orientation in the dry state are plotted against the difference of the angles of orientation in the two states. The figure indicates that the reduction in the average angle of orientation gradually increases with the increase in angle of orientation, but sisal seems to be an exception to this rule. The change in the angle of orientation with moisture absorption was explained[2] by assuming that in a fraction of the fiber material, the arrangement of molecules was of varying degrees of perfection, which added to the coherence of x-ray reflection in the dry state but did not do so when deranged by the action of moisture. The present series of results may also be explained if it is further assumed that this derangement increases as the average deviation of the crystallites increases, and accordingly the reduction of the angle of orientation increased with the angle orientation.

In the case of sisal, the change was not as much as was the general trend of other fibers shown in Figure 1. Although Hermans' angle is a general parameter which is applicable to any cellulose fibers, its meaning differs in a spiral fibrillar structure. Sisal being a fiber of high spirality, the average orientation angle is the resultant of spirality of the

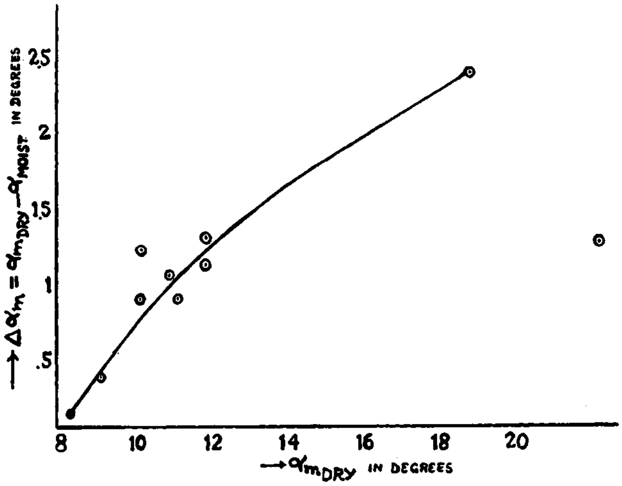

Fig. 1. Curve showing relation between the angle of orientation in the dry state and the difference of the angles in the dry and moist states.

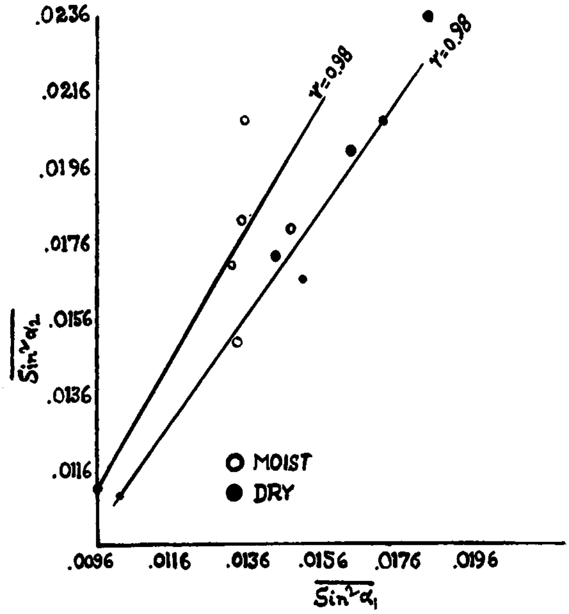

Fig. 2. Relation between orientation angles of (101) + (101) and (002) planes.

fibrils and the dispersion of crystallites within the fibrils. The action of water might be thought to be mainly on the latter component. The latter part being small in the case of sisal fiber, the effect of moisture was small, although the average angle of orientation was high. This was corroborated by the results of rayon filaments, in which the spirality is practically nil, and the high average angle of orientation is mainly due to the dispersion of crystallites; in this case the change in orientation angle is more or less consistent with what it should be from a consideration of other fibers.

Relations between the angles of orientation obtained from the (002) and $(101 + 10\bar{1})$ arcs are shown in Figure 2. In Figure 3, the average orientation is plotted against the difference in the orientation of the two planes in the dry and moist states. It was found that in all the cases there is a difference in the distribution of intensities along the arcs of the equatorial interferences (002) and the $(101 + 10\bar{1})$ planes. It was found that the composite $(101 + 10\bar{1})$ plane is less perfectly oriented and has a greater average angle of orientation than the other. This observation is also shown in Figure 2. This is true both for the dry and moist states. The relative trends in the orientation of the (002) and $(101 + 10\bar{1})$ planes are, however, similar in both conditions.

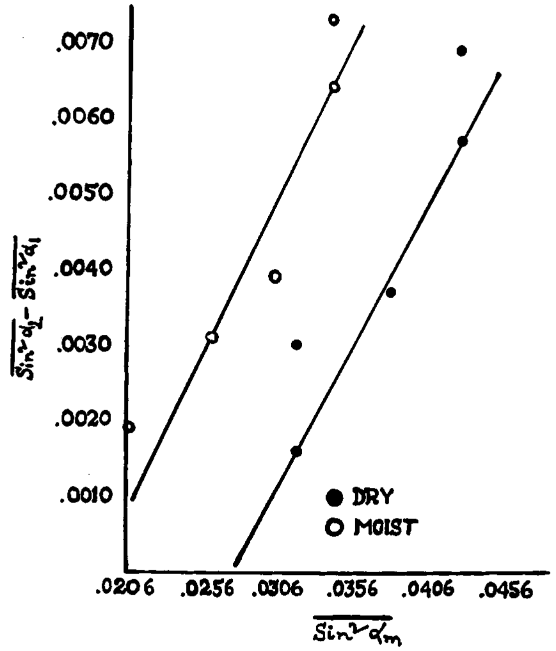

Fig. 3. Relation between average angle of orientation and the difference of the angles of orientation of (002) and (101 and $10\bar{1}$) planes.

From Figure 3 it is found that the difference in the orientation of the (002) and $(101 + 10\bar{1})$ plane is more in the moist state. This might be due to the fact that the plane $(101 + 10\bar{1})$ containing the maximum number of hydroxyl groups per unit area is more sensitive to the action of moisture, and so its effect on the orientation of this plane is more pronounced. A fairly good correlation, 0.98, is found to exist between the orientations of the (002) and $(101 + 10\bar{1})$ plane in both conditions.

The author is deeply grateful to Dr. S. B. Bandyopadhyay, Director, for his guidance and to the Indian Council of Agricultural Research for providing facilities for this work.

References

1. P. K. Ray, *Text. Res. J.*, **37**, 434 (1967).
2. P. K. Ray, *J. Appl. Polym. Sci.*, **11**, 2021, (1967).
3. P. K. Ray, *J. Appl. Polym. Sci.*, **12**, 1787, (1968).
4. P. H. Hermans and A. Weidinger, *J. Appl. Phys.*, **19**, 491 (1948).
5. P. H. Hermans, *Contribution to the Physics of Cellulose Fibres*, Elsevier Amsterdam, 1946.

P. K. Ray

Jute Technological Research Laboratories
Indian Council of Agricultural Research
Calcutta 40, India.

Received April 28, 1970
Revised October 9, 1970