On the Degree of Crystallinity and Orientation in Polymer-Grafted Jute Fiber

It has been reported in previous communications[1,2] that in jute and mesta fibers the degree of crystallinity decreases[1] with the rise of humidity and that the orientation of micelles[2] improves with moisture absorption. With a view to examining more thoroughly this interaction of water molecules and cellulose molecules a similar study was undertaken with fibers grafted with polymers. This note is a report of this study.

Grafting was effected in two ways. Holocellulose prepared by a standard process[2] was grafted with acrylonitrile and with methyl methacrylate.

In the first case 4.2 g. of holocellulose taken in 200 ml. of water was treated with 8 ml. of acrylonitrile (AN) monomer and then 8 ml. of ceric ammonium nitrate at 25°C. for 2 hr. in nitrogen atmosphere. The treated samples were then washed with water. The samples were grafted up to 20% increase in weight.

In the second case 4.2 g. of holocellulose in 200 ml. of water was treated with 3 ml. of methyl methacrylate (MMA) monomer and then with 10 ml. of ceric ammonium nitrate at 20°C. for 2 hr. The grafted samples were then treated with acetone in a Soxhlet apparatus, and grafting was up to 30% increase in weight.

X-ray photographs were taken of the two grafted samples and the one holocellulose sample as control. The experiments were based on the method of Hermams and Weidinger as reported earlier.[1] Randomized pellets wre prepared with the samples of equal weights in each case. A silver foil inside a Goppel cone was used as reference material. Photographs were taken with rotation of the film. Corrections for air scattering and absorption in the pellets were made. The corrected intensity curves are shown in Figs. 1, 2, and 3, which are intensity distribution curves of holocellulose, holocellulose grafted with (AN), and holocellulose grafted with (MMA), respectively. The origin of these curves is taken at a fixed point from the center of the photographs. As reported earlier,[1] a straight line passing through an approximately linear portion of the intensity curve was taken to be a guide for drawing a line of demarcation between intensity due to crystalline scattering and that due to noncrystalline scattering.

TABLE I
Crystalline Area c, Amorphous Height A, Half-Width W, and Peak Height H of (002) Reflection in Arbitrary Units)

Humidity	c	Corrected c	A	W	H	D.C., %[a]
Holocell. control:						
dry	280	—	7.0	8	20.0	58
room	230	—	7.5	7	18.0	48
moist	200	—	9.0	6.5	19.0	41
Holocell. grafted up to 20% increase in weight						
dry	220	275	10.0	8.5	15.5	57
room	194	242	10.0	6.75	14.0	50
moist	180	225	10.5	5.75	14.0	47
Holocell. grafted up to 30% increase in weight						
dry	190	271	8.5	9.0	13.0	56
room	182	260	9.75	7.5	13.0	54
moist	166	237	10.0	6.0	11.5	49

[a] Rounded to two digits.

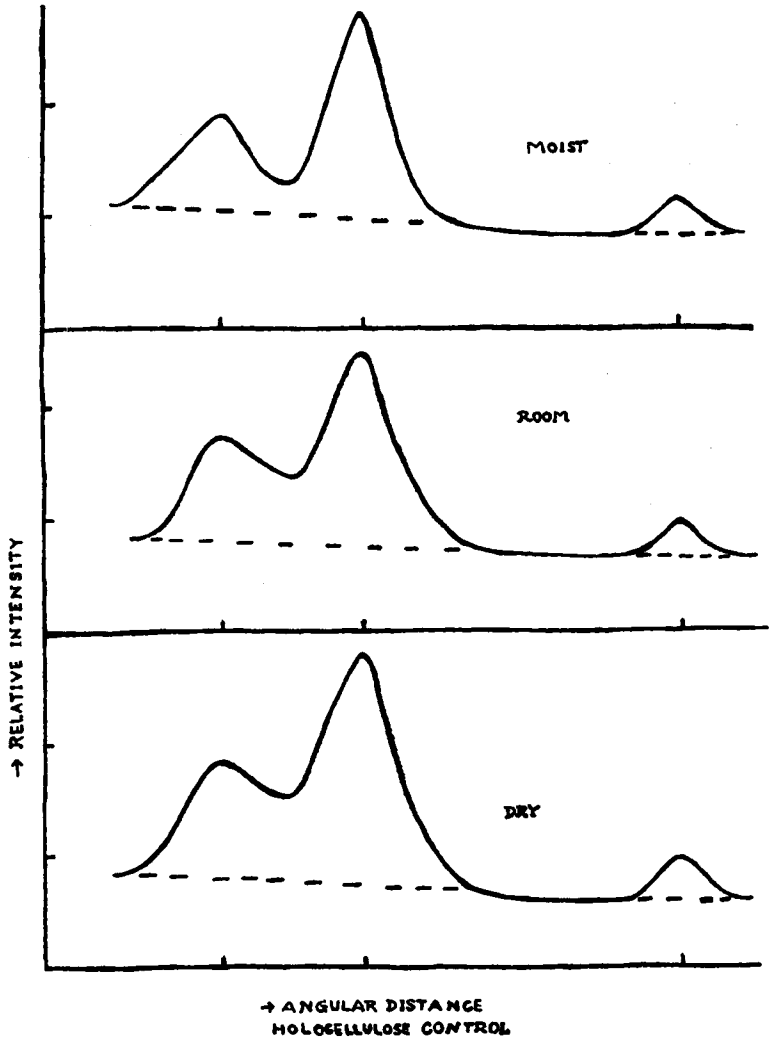

Fig. 1. Intensity distribution curves: holocellulose control.

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) + ($10\bar{1}$) peaks, was taken as a measure of amorphous content. The figures for the degree of crystallinity were found simply by comparing the crystalline area of the intensity curves for the samples with that for ramie. The crystalline area for the grafted samples was reduced to an equal amount of holocellulose. A crystalline area of 353 corresponded to a value for the degree of crystallinity of 74%, as reported earlier.[1] The peak height of the (002) plane and its half-width are shown in Table I. Crystallite orientation has been found by Hermans' method, as reported earlier.[2]

The results are tabulated in Tables I and II.

In Table I it is observed that the degree of crystallinities for the grafted fibers in the dry condition is practically the same as in holocellulose sample in the same condition.

Again, it is clear from Figures 1, 2, and 3 that the positions of the peaks remain the same, as a result of grafting, and the peaks are also not distorted, indicating that no structural change takes place in the process. The results show that copolymerization of the grafted material has taken place without any appreciable effect on the molecular arrangement of the fiber. Table I also shows that the change in the degree of crystallinities with humidity takes place at a lower rate than that of the holocellulose control and that the rate diminishes as the percentage of grafting increases. Possibly, as more and more

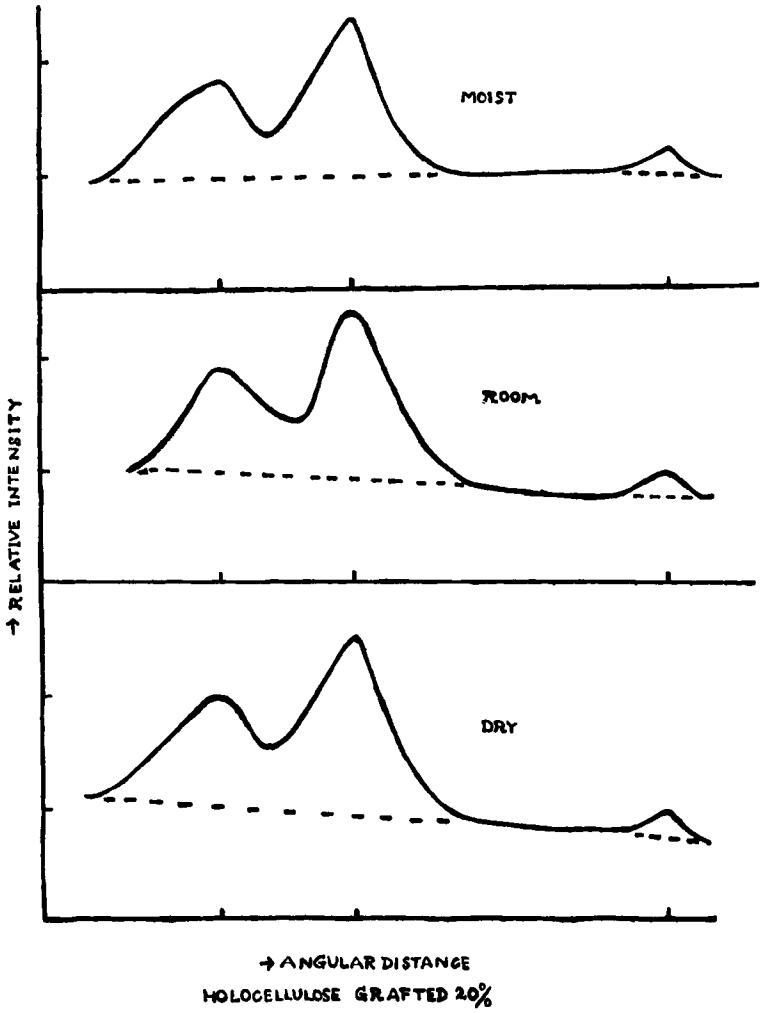

Fig. 2. Intensity distribution curves: hollocellulose grafted 20%.

grafting material is anchored in the fiber, the scope of entrance of the water molecules is limited and thereby the effect of water on the degree of crystallinity is diminished.

From Table II it is observed that not only do the crystallites retain their orientation in the grafted state, but also water has no effect on the orientation of the crystallites in the grafted fibers, unlike those in holocellulose, in which the orientation of the micelles apparently goes on improving with moisture absorption.

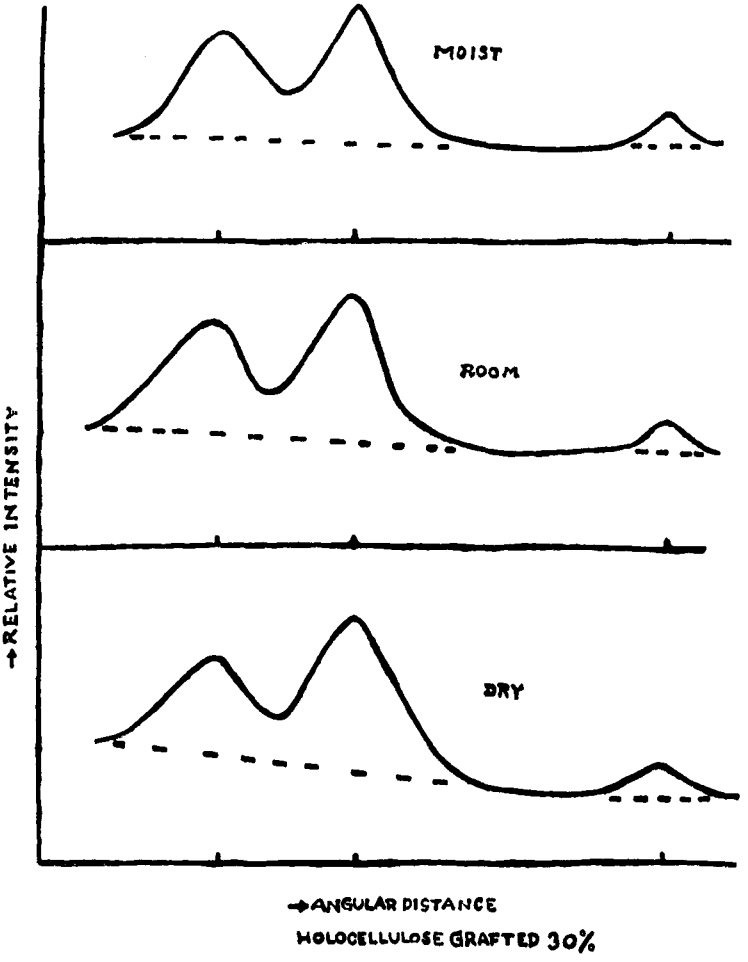

Fig. 3. Intensity distribution curves: hollocellulose grafted 30%.

From the orientation values in the moist fibers under tension it is seen that orientation is more sensitive to tension in holocellulose than in grafted fibers, and this proves that as a result of grafting the fiber assumes a more rigid structure; therefore, it is likely that on subsequent absorption of water the internal stresses in the long chain are not released, contrary to what is assumed to take place in holocellulose, and that the crystallites retain their orientation.

It was reported earlier[1,2] that the arrangement in some of the regions of varying degrees of perfection is disturbed by water and, since those regions do not contribute to x-ray reflections, the average orientation in holocellulose improves in the moist state. In the grafted condition the probability of the change of orientation due to this is minimized because, some of these regions having been already grafted, the scope for water to enter those regions and effect any change is largely reduced. It may also happen that in grafted fibers, the water-absorbing regions being small, the average effect of moisture on orientation could not be detected.

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TABLE II
Angle at 40% Intensity α,[a] $\overline{\sin^2}\ \alpha_1$, $\overline{\sin^2}\ \alpha_2$, Hermans' Average Angle of Orientation αm,[b] and Orientation Factor F_x

Humidity	α	$\overline{\sin^2}\ \alpha_1$	$\overline{\sin^2}\alpha_2$	α_m	F_x
Holocell. control					
dry	9°51′	0.0190	0.0200	11°23′	0.941
room	9°10′	0.0163	0.0183	10°43′	0.948
moist	9°0′	0.0141	0.0155	9°54′	0.955
moist under tension	8°45′	0.0123	0.0134	9°13′	0.961
Holocell. grafted with AN wt. increase 20%					
dry	10°40′	0.0186	0.0203	11°23′	0.941
room	10°35′	0.0172	0.0213	11°19′	0.942
moist	10°50′	0.0176	0.0210	11°20′	0.942
moist under tension	10°20′	0.0169	0.0176	10°42′	0.948
MMA, wt. increase 30%					
dry	10°30′	0.0173	0.0221	11°26′	0.940
room	10°40′	0.0165	0.0216	11°16′	0.943
moist	11°0′	0.0165	0.0228	11°25′	0.941
moist under tension	9°35′	0.0152	0.0206	10°54′	0.946

[a] P. K. Ray.[1]
[b] P. K. Ray.[2]

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