The Influence of Gum on the Crystalline Structure in Ramie Fiber

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Synopsis

The fine structure of decorticated and degummed ramie fibers was studied by x-ray and optical methods. It has been found that while crystallinity increases, crystallite orientation deteriorates with gradual removal of gum. Optical orientation falls at a more rapid rate, indicating that the major part of the gum resides in the amorphous regions and these regions are more sensitive to the process of extraction of gum.

INTRODUCTION

Ramie fiber is characterized by high crystallinity. The x-ray and optical properties of the fiber had been the subject of study of many workers[1-12] in the past. Hermans[1] studied the crystallinity by x-ray method and obtained a value for crystallinity in ramie of 70% in the native state and 50% in the mercerized state. Warwicker[2] observed a decrease in the crystallite orientation of the fiber when treated with caustic soda. However, Viswanathan[3] found no change in crystallinity in native and mercerized states of the fiber if a "disorder function," as enunciated by Ruland,[4] was taken into consideration while calculating the crystalline parameters. On the other hand, Kulshreshtha et al.,[5] studying the axial order in ramie, reported evidence of paracrystallinity in the fiber.

The optical constants of native and mercerized ramie were determined by several workers[6-12] by measuring birefringence under polarized light. Hermans[1,11] discussed the effect of porosity and optical orientation in relation to the observed birefringence. He obtained fair agreement between the orientation factor derived from the optical and that derived from the x-ray data. Iyer et al.[12] also correlated crystallite orientation with the optical orientation of the fiber.

Varieties of ramie in the decorticated state contain gum that may vary from 19% to 30%[13] of the weight of the dry fiber. The physical properties of the fiber at various stages of degumming were studied by Chakravarty et al.[14] Earlier studies, both x-ray and optical, were confined on ramie fibers that were degummed, in which state ramie might be considered a purely cellulosic fiber.

The present article is a report on the effect of gum on the fine structure of ramie as revealed by x-ray and optical methods.

EXPERIMENTAL

Fiber Sample. Ramie fibers having average residual gum contents of 24%, 14%, 7%, and 2% of the dry fiber weights were taken for study. Decorticated ramie had the maximum amount of gum. A method for removal of gum to various residual gum contents has been described elsewhere.[15]

X-Ray Study. Ni-filtered CuK_α radiation at 20 kV and 15 mA from a sealed tube was used for x-ray study. For the determination of crystallite orientation and interplanar spacing, x-ray photographs of bundles of parallel fibers were taken. Crystallite orientation and crystallinity were computed following the methods of Hermans[16] and Hermans and Weidinger,[7] respectively. A thin film of paste made from aluminum hydroxide and pure gypsum was used as a standard sample inside a Goppel camera. The method for the determination of the interplanar spacings and Bragg angles for various planes was that of Banerjee et al.[18] Other details were same as described earlier.[19]

Optical Study. For measuring refractive indices for light vibrations along and at right angles to the axis of the fiber, the well-known Becke line method[20] was followed. Individual fibers, made free from twist, were mounted on microscope slides. Each group of ten fibers, mounted on a slide and under a cover glass, was then flooded with the immersion liquids. Observations were made under polarizing microscope, at a magnification 100×, using plane-polarized light from a sodium vapor lamp. Extinction directions for each of the fibers were obtained, as usual, with both the nicols crossed.

The immersion liquids were α-monobromonaphthalene ($n_D^{20} = 1.659$), diluted to different extents while on microscope slide by adding liquid paraffin ($n_D^{20} = 1.481$). This practice was found more suitable and time-saving compared to the use of stock liquid mixtures. The refractive index of the liquid mixture satisfying the Becke line criterion was then measured by an Abbe-type refractometer.

The density of the fibers at different stages of degumming was determined in a density gradient column following Chakravarty's method.[21]

RESULTS AND DISCUSSION

Values for the angles of diffraction and the interplanar spacings are given in Table I. Other results from x-ray studies are given in Table II. Typical x-ray photographs of raw and degummed (2% gum content) fibers are shown in Figures 1a & 1b. The refractive indices in extinction directions along and perpendicular to the fiber axis are given in Table III.

It has been established that the main portion of the gum removed from ramie fiber is of the nature of glucan,[22] a polysaccharide, and the association of the gum with the crystalline structure would be expected to change the dimensions of the crystalline repeating unit. But it is observed from Table I that the interplanar spacings corresponding to the (101), (10$\bar{1}$), (002), and (021) reflections do not change appreciably with the gradual removal of the gum. It is proposed, therefore, that the removable gum resides in the amorphous region and does not take part in the formation of the crystalline regions. This behavior of the gum may be compared to that of hemicelluloses in jute.[22] It is also observed, from Table II, that the crystalline area, computed from x-ray intensity curves, goes on increasing with gradual removal of the gum. This might be due to the fact that the gum by its presence in the amorphous region restricts the alignment of the chain
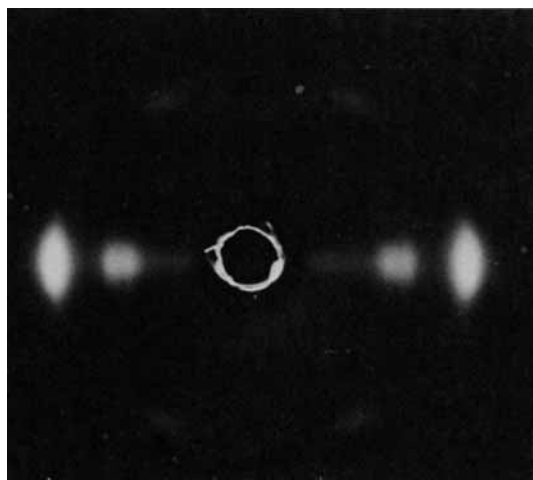
(a)
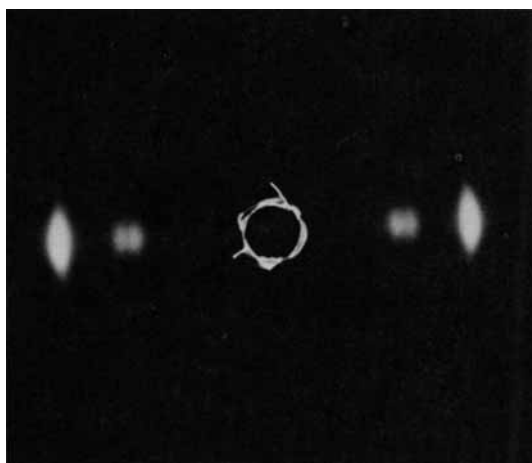
(b)

Fig. 1. (a) X-Ray photograph of raw ramie fiber. (b) X-Ray photograph of degummed (2% gum content) ramie fiber.

molecules and thus gives rise to strains in the crystalline regions. On removal of the gum, the restrictive force being withdrawn, the molecular chains are free to rearrange. In the process, the crystallites are apt to increase their lateral size. The increased sharpness of the (002) spot on removal of gum, as the half-width values indicate, lends support to this view.

However, Chowdhury and Sen,[23] working with jute from which hemicelluloses were removed, remarked that the slight increase in the degree of prefection would not influence the very small width of the crystallites. But in a recent work, Preston[24] has shown, from low-angle x-ray scattering and electron microscope studies, that the width of the scattering particles in natural cellulosic fibers is as high as 230 Å. This value is much higher than 35 Å as was observed by Frey-Wyssling,[25] Muhletheler,[26,27] and Manley.[28] Thus, our observation made above seems to be not without basis.

TABLE I

Angle of Diffraction (2θ) and Interplanar Spacing (d) of
Ramie Fiber of Different Gum Content

| Gum content, % | Indices of crystallographic planes | | | | | | | |
| | 101 | | 101 | | 002 | | 021 | |
	2θ	d, Å	2θ	d, Å	2θ	d, Å	2θ	d, Å
24	15°06′	5.86	16°54′	5.23	22°55′	3.87	21°43′	4.08
14	15°39′	5.64	16°59′	5.20	23°39′	3.75	21°19′	4.15
7	15°06′	5.86	16°43′	5.31	22°55′	3.87	21°42′	4.08
2	14°50′	5.96	16°59′	5.20	23°09′	3.83	21°15′	4.17

TABLE II

Crystalline Area (C), Crystalline Area Corrected to 2% Gum Content ($\bar{C}$), Amorphous Height (A), Half-Width of (002) Spot (W), Peak Height (H), Hermans' Average Angle of Orientation (α_m), and X-Ray Orientation Factor (fx)[a]

Gum content, %	C	$\bar{C}$	A	W	H	α_m	fx
24	204	262	10.75	6.75	16.75	8°24′	0.968
14	249	283	9.00	6.00	17.75	9°05′	0.962
7	273	287	9.00	5.00	27.50	8°55′	0.964
2	315	315	7.50	4.00	32.00	8°49′	0.964

[a] The data represent the mean of two sets of samples.   All (except α_m) in arbitrary units.

TABLE III

Birefringence and Optical Orientation of Ramie Fiber of Different Gum Content: Refractive Index Parallel to Fiber Axis (n_{11}), Refractive Index Perpendicular to Fiber Axis (n_1), Birefringence of Actual Fiber (Δn), True Density (d), Birefringence at Ideal Orientation Reduced to Observed Density ($\Delta n'$), and Optical Orientation Factor (f_0)

Gum content, %	n_{11}	n_1	$\Delta n = n_{11} - n_1$	d	$\Delta n'$	f_0
24	1.5843	1.5160	0.0683	1.540	0.07196	0.949
14	1.5885	1.5218	0.0667	1.544	0.07216	0.924
7	1.5915	1.5263	0.0652	1.552	0.07244	0.900
2	1.5953	1.5310	0.0643	1.552	0.07253	0.886

Results given in Table II, on the other hand, indicate a general deterioration in the crystallite orientation with the removal of gum.   We thus assume that at least a part of the gum helps in cementing the microfibrils of cellulose as lignin does in jute.[18]   With the removal of this part of the gum, the microfibrils get disoriented and are more or less set at that state.

The birefringence, as shown in Table III, decreases with the gradual removal of the gum.   But the values of the two refractive indices increase with decreasing gum content.   Since the Becke line effect is regarded as diffraction pattern caused by the edge of the fiber, gradual increase of the indices indicates that some of the gum also stays on the surface of the fiber.   The optical orientation factor, calculated according to Hermans[11] is the ratio of the birefringence of the fiber to that of an ideally oriented fiber taken at equal density.   The birefringence of the

ideally oriented fiber has been taken as 0.0744[1,11] at a density of 1.592. It may be seen from Table III that with the gradual removal of gum, the optical orientation factor decreases. This indicates a gradual disorientation in the molecular chains as the gum is removed, a conclusion already obtained from x-ray data.

A comparison of Tables II and III shows that the orientation factors calculated from x-ray data and optical data agree fairly well in the decorticated state (maximum gum). As the gum is removed, the crystallite orientation (x-ray) changes slowly, whereas the change in optical orientation is much more rapid. Also the optical orientation is always less than the corresponding x-ray crystallite orientation. Iyer et al.[12] reported results contrary to those of ours. They suggested a revision of data for refractive indices as given by Hermans[1,11] for fiber of ideal orientation.

The necessity for such a revision arose from the fact that though the value of the optical orientation obtained by them was comparable to ours as well as to Hermans' data, the value of x-ray orientation fell as low as 0.89 in ramie. The corresponding angle of orientation of ramie becomes 16°, which seems very unlikely. Moreover, the x-ray orientation factors measured by them seem to be lower for all the fibers.

We have seen that with removal of gum, the drop in average orientation of the molecular chains (optical) is greater than the corresponding drop in crystallite orientation (x-ray). This may be interpreted as follows. The optical orientation arises from the entire fibrous matter; since gum resides mainly in the amorphous regions as revealed by x-ray studies, the imperfect orientation of the molecules in the amorphous region is very sensitive to degumming. So, the disorientation of the molecular chains in the amorphous regions, with gradual removal of the gum, would be more than that of the crystallites of the crystalline region. This may explain the lower value of the average optical orientation as compared to the x-ray orientation at different stages of degumming of ramie fiber.

CONCLUSIONS

The above observations lead us to conclude that (1) the gum in decorticated ramie resides mostly in the fibrous matter but does not take part in the crystalline structure of the cellulose in ramie, (2) removal of the gum enables the fiber to take a more crystalline form, and (3) as the gum is removed, the crystallites increase in width (or there is a higher degree of perfection of the crystalline order) but deteriorate as regards their alignments along the fiber axis.

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