On the Discrete Diffraction of Small Angle X-ray Scattering of Bamboo (*Phyllostachs mitis*)*

Takaya NOMURA** and Tadashi YAMADA**

Abstract——Discrete diffraction depending on a periodically recurring elements, that is, interparticle interference, is recognized in both the equatorial and meridional direction of bamboo using a fixed time counting technique of small angle x-ray analysis. From the position of the discrete diffraction about 110 Å long along fiber length and about 48 Å wide laterally were obtained.

Introduction

For the interpretation of small angle x-ray scattering, we must consider both dilute and condensed systems. In general, the two cases cannot be experimentally distinguished from each other as both may give rise to similar intensity curves of an ordinary exponentially decending type. If, however, intensity curves with inflection points or maxima are observed, this would be unmistakable evidence of interparticle interferences. It is generally said that small angle x-ray scattering of natural cellulosic materials almost always shows an exponentially decending curve, that is, diffuse scattering. But the fiber diagram of wide angle x-ray diffraction of these materials, such as cotton, ramie, jute, wood and bamboo, shows clearly the existence of the crystallites substance. The width and the length of these crystallite were measured by an x-ray line broadening method. They have widths varying from 30 to 60 A[9]. For their length it was originally deduced by Hengstenberg and MARK[1] that the crystallite of cellulose at least 600 Å long along chain length. In the studies of electron microscopy, it is now well established that the cellulose is deposited in an fibrillar form in a plant cell wall and the microfibrils were shown by many authors to have widths ranging from 35 to 380 Å, averagewise 50 Å with normal wood[9]. On the other hand, concerning crystallite length, RANBY[2] showed 310～500 for cotton and partially hydrolysed pulp, 250～400 for mercerized pulp and 100～170 A for viscose rayon.

It may be assumed from those facts that those materials have a structurally regular system in which interparticle interference occurs in small angle x-ray

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** Division of Wood Physics.

scattering. From these view points it will be deduced that bamboo must exhibits a discrete diffraction based on the structure of the microfibril, that is, interparticle interference.

Most of the studies of discrete diffraction of small angle x-ray scattering have been done on oriented fibers. Hess and Kiessig observed that the small-angle diagram of synthetic fibers showed discrete diffraction on the meridian. This means that some structural features in the direction of the fiber axes had a long-period repitition. Statton[4,5] showed that the long-period appeared on the meridian in many viscose rayons: The values are 220 Å for Fiber G, 178 Å for Tire Cord and 178 to 221 Å for many commercial rayons.

In this paper, we have found discrete diffraction in both equatorial and meridional directions by using a small angle x-ray scattering method.

Materials and Methods

Materials

The samples are prepared from the 12th internode Moso Bamboo (*Phyllostachs mitis*, 6 years old) and the bamboo shoot which was in a growing stage, 854 cm high. The size of sample is 20 (longitudinal) $\times$ 10 (tangential) $\times$ 1 (radial) mm. The powder sample is prepared for matured bamboo as follows: The powder which passed through a 200 mesh screen is dried at room temperature. 300 mg powder is compressed in a desc, 20 mm in diameter and about 0.85 mm in thickness.

Small angle x-ray scattering

The collimation employed is shown in Fig. 1. The diffraction profile is recorded in steps of 0.1 degree to 7.0 degree, (2θ) using a fixed time counting technique (200 seconds). Cu-Kα radiation with Ni-filter, using a Rotarflex, RU-3L x-ray diffractometer (Rigaku Denki Co., Ltd) is used (50 kV, 80 mA).

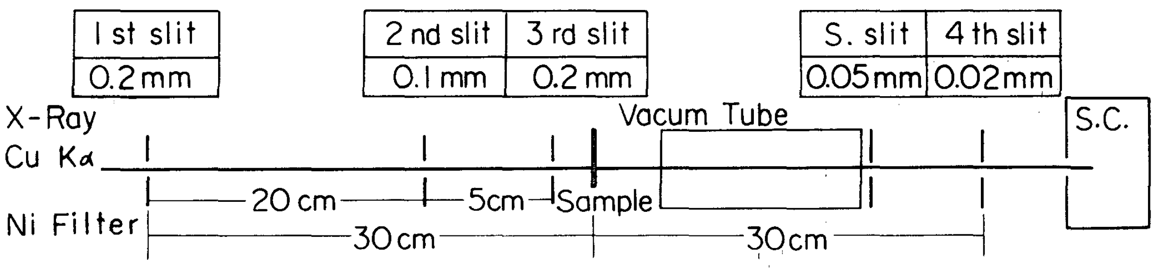

Fig. 1. Slit collimation of small angle x-ray.

Wide angle x-ray diffraction

Ni-filtered Cu-Kα radiation (45 kV, 60 mA) is employed and 1/2 divergent and receiving slits are used in the goniometer. The diffraction profile was recorded with a scanning speed 1/4 degree/min and chart speed 10 mm/min for (040), 5 mm/min for (002) reflextion. Crystallinity was measured by area method. Crystallite length and crystallite width were obtained from the line profile for the resolved (040) and (002) reflections by applying the following Sherrer's equation:

$D=K\lambda/\beta \cos\theta$, where D=average crystallte size normal to diffracting planes. K=constant (0.9), λ=x-ray wave length (0.1518 Å) θ=Bragg's angle, β=the pure breadth for the (040) and (002) at half-peak intensity(in radian). The observed line breadth at half-peak intensity(B) for the (040) and (002) reflection is affected by the average crystallite strain and instrumental broadening. Accordinly, in order to apply Sherrer's equation, it was assumed that no strain were present, and the observed line breadth was corrected for instrumental line broadening. Hexamethylenetetramine $(CH_2)_6N_4$ was used as a standard for assessing the instrumental line broadening under the same experimental conditions. For $(CH_2)_6N_4$ crystals, the instrumental line broadening (b) amounted to 0.085 degree (2θ). Warren's correction was applied in the calculation by using Sherrer's equaiton whereby $\beta=(B^2-b^2)^{1/2}$.

The technique of decrystallization employed was the same as that described by SHIRAISHI, et al.[6] The block of bamboo were treated with a strong cellulose solvent, dimethylsulfoxide solution of sulfer dioxide-diethylamine complex, under a condition suitable for dissolving pure cellulose, the decrease in the weight of bamboo was fairly small, indicating that the cellulose component of the bamboo cell wall was not dissolved out.

Results and Discussion

Figs. 2a and 2b show small angle x-ray scattering in the equatorial and the meridional direction of Moso bamboo under the air dry condition. It is clear that discrete diffraction depending on periodically recurring elements, that is, interparticle interference, is recognized in the parallel and perpendicular directions of fiber. For comparison the intensity of the equatorial scattering with the meridional one, it is normalized at 0.1 degree and the result is shown in Fig. 3. In Fig. 3, m is the distance from the center of direct x-rya beam. It shows that (1) interparticle interference in the equatorial direction is stronger than in the meridional. (2) discrete diffraction in the meridional direction appears at a lower angle than the equatorial one. The 2nd result shows, considering Bragg's law, the former has a larger dimension of the interparticle than the latter. Fig. 4 shows the small angle scattering of powder sample of matured Moso bamboo. The broadning of discrete diffraction is recognized. This broadning may be caused by the random orientation of the fiber. Fig. 5 shows the small angle scattering in the equatorial direction

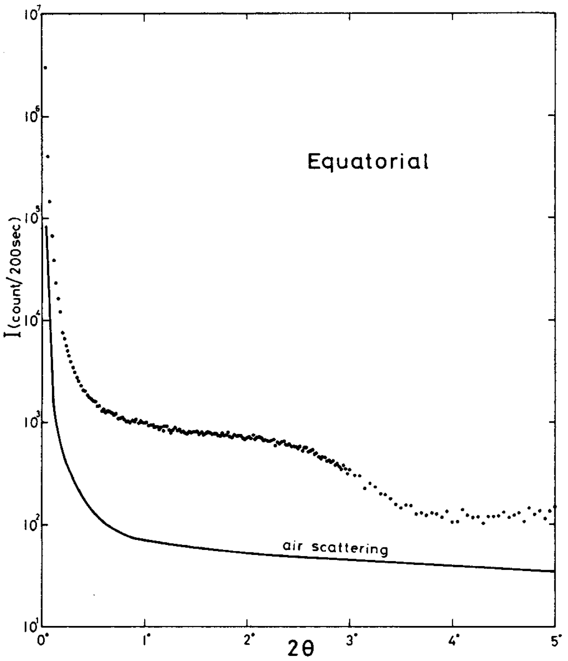

Fig. 2a. Small angle x-ray scattering of Moso bamboo. Equatorial scattering (dotted line) and air scattering (smooth line).

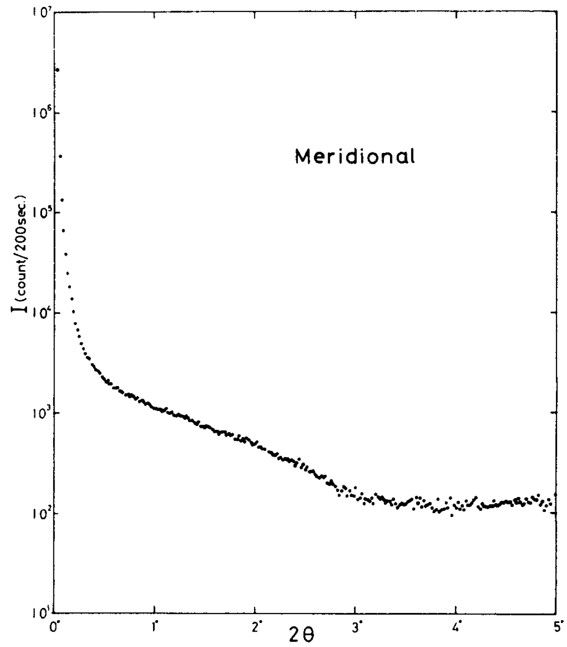

Fig. 2b. Small angle x-ray scattering of Moso bamboo. Meridional scattering.

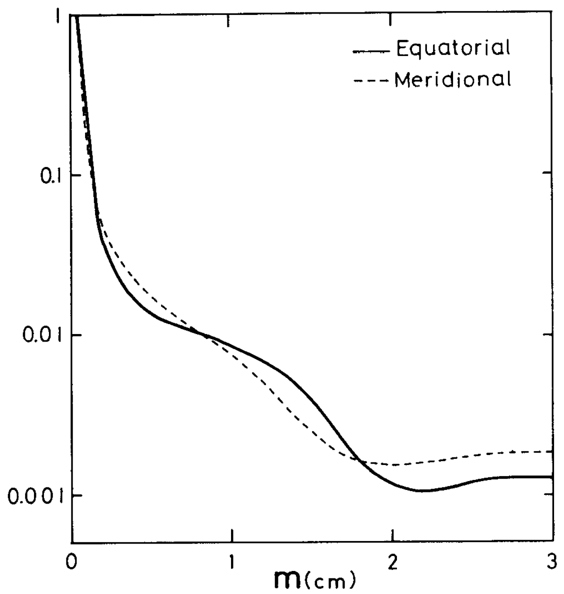

Fig. 3. Small angle x-ray scattering curves of Moso bamboo normalized at 0.1 degree.

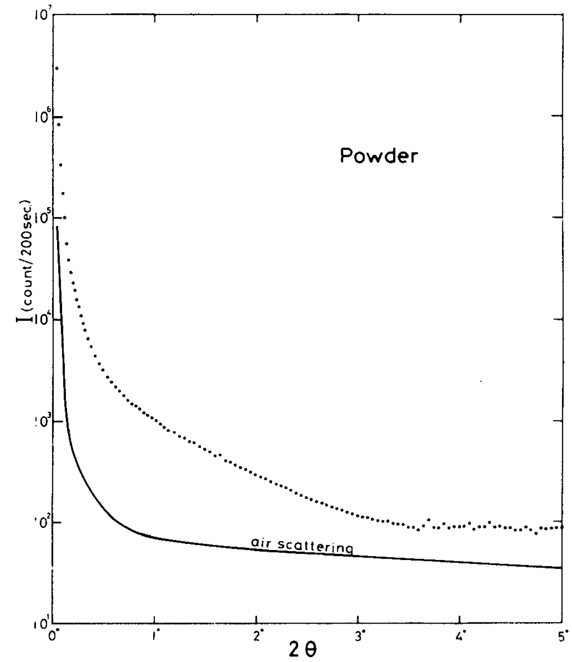

Fig. 4. Small angle x-ray scattering of powder sample (Moso bamboo).

of a decrystallized sample treated with DMSO. The weight loss of sample after decrystallization is 0.3%. The degree of decrystallization is measured by the x-ray pattern which is shown in Fig. 6. It is about 30%. For comparison with the

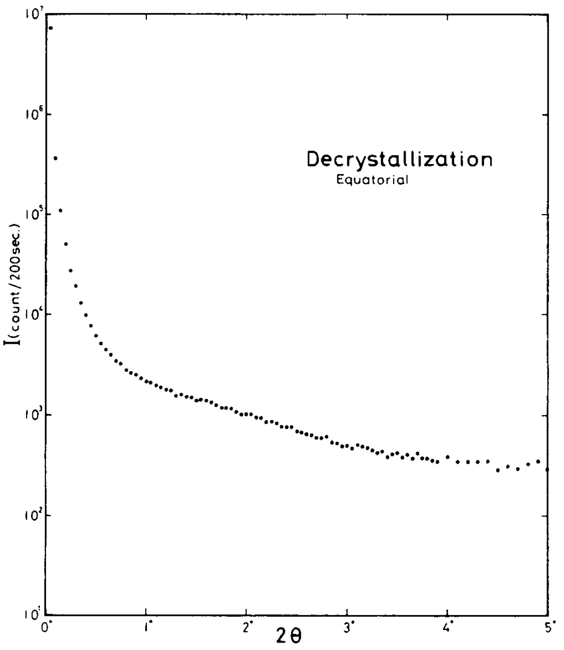

Fig. 5. Small angle x-ray scattering curves of the equatorial direction of decrystallized sample treated with DMSO.

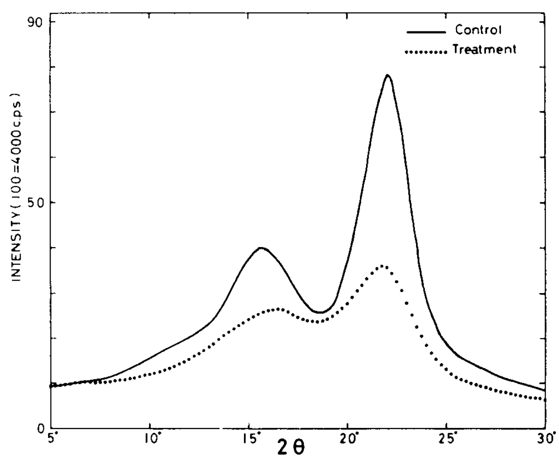

Fig. 6. Wide angle x-ray diffraction patterns of treated and untreated samples with DMSO.

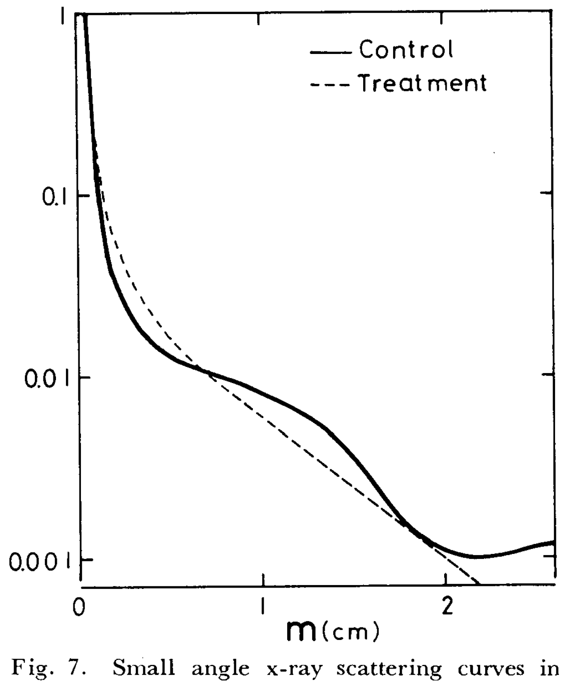

Fig. 7. Small angle x-ray scattering curves in the equatorial direction of decrystallized sample and untreated sample normalized at 0.1 degree.

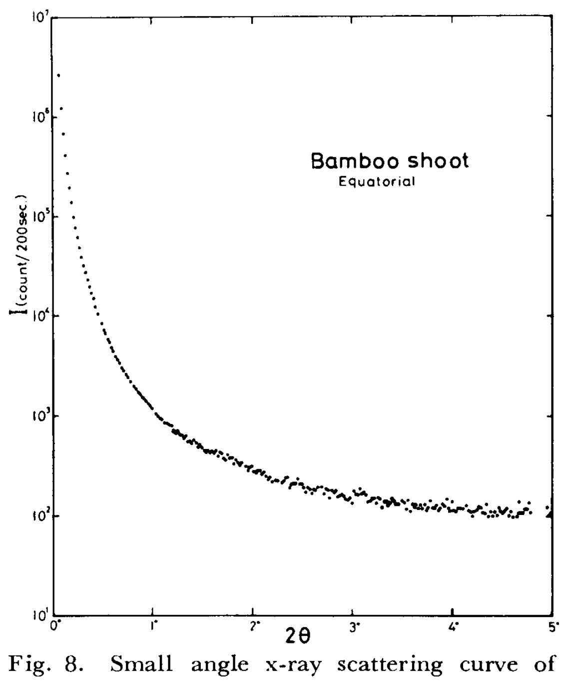

Fig. 8. Small angle x-ray scattering curve of Moso bamboo shoot (854 cm height, 14th internode).

samples before and after treatment, intensity of Fig. 2a and Fig. 5 is normalized at 0.1 degree and the result is shown in Fig. 7. In this case, discrete diffraction is clearly degraded in the equatorial direction. On the growing stage, discrete diffraction is not recognized in the edible part of bamboo shoot Fig. 8. The degree of crystallinity in this stage from wide angle x-ray is only a little, too. From the facts described above, we may conclude that discrete diffraction of small angle x-ray scattering of Moso bamboo is influenced by the orientation of microfibril and cellulose crystallite.

An interpretation of small angle x-ray scattering curves of bamboo in terms of its structure seems to be impossible at the present time on a rigorous theoretical basis. In dilute systems of identical particles the scattering curve could be translated in terms of particle size only if the shape of the particles is known. But in denser systems the conditions become to be so complicated as to make theoretical predictions on the scattering curves.

The occurrence of discrete diffraction in the scattering curves of either dense or diluted systems is undoubtedly an indication of the presence of approximately uniform particles packed in an almost regular manner. The deflection angle at which the maximum appears will correspond to a period approximately given by the Bragg relation. In dense systems KRATKY[7)] and POROD[8)] assumed the existence of lamellae, the thickness of which varies according to some distribution function that determines the small angle x-ray scattering. (The other dimensions of the lamellae are assumed to be considerably larger.) According to these authors, the experimental intensity curves (I versus m, where m is the distance from the center of direct x-ray beam.) should be transformed into Im-m curves in order to eliminate the Lorentz factor of lamellae, if the system is statistically inhomogeneous. Curves thus transformed would, in the first approximation at least, represent distribution curves of the statistically varying "spacing" in the lamellae clusters. Hence, if such a curve exhibits a maximum, the Bragg spacing corresponding to it will give the most frequently occuring period. Fig. 9 shows Im-m curves of Fig. 2a and 2b. From the position of the maximum we obtained the interparticle distance of 110 Å for fiber length and 48 A for lateral direction. Discrete maximum on the meridian are interpreted in temrs of a regularity of placement of the crystallites in the structure, such that each crystallite acts as a diffracting Center. The long period calculated from such a maximum will give the separation of crystalline centers; the long period therefore would include one crystallite length and one adjacent amorphous region. Discrete maximum on the equatorial is interpreted, too, as a width of a diffracting cylinder or lamella. The crystallite length can be measured in the wide-angle pattern; when this length is subtracted from the long period, the amorphous length can be deduced. In the same manner, we may deducethe state of the crystallite and paracrystallni

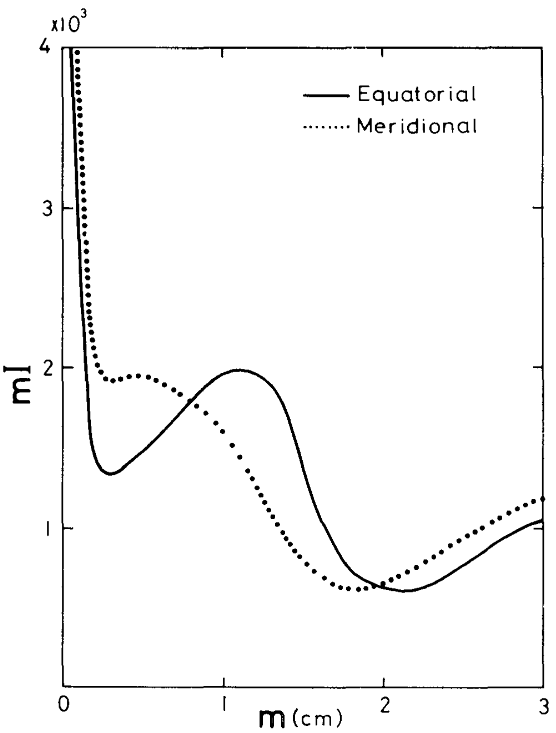

Fig. 9. Im plotted against m.

to lateral direction from the crystallite width and the lateral order by using small angle x-ray. Wide angle crystallite size was measured from the x-ray line broadening by Sherrer's equation and we obtained both crystallite length and width; the former was 103 Å and the latter was 30 Å. When we compare the results from small angle x-ray with those from wide angle, the value of the long period is about the same of crystallite length. In the lateral direction the value from small angle x-ray is larger than the one from wide angle x-ray. The results of small angle x-ray analysis and wide angle x-ray experimental on bamboo fiber were summed up as follows.

1) The fact that the dimension of long period and crystallite length are almost the same indicates that there is not a little amorphous region along the longitudinal direction of bamboo fiber.

2) If we assume the existene of lamellae to the lateral direction, "spacing" in the lamella clusters is calculated to 48 Å and the width of lamella is calculated to be 30 Å from wide angle x-ray analysis; when the width of lamella is subtracted from "spacing" obtained from small angle x-ray, the interval of lamella is 18 Å from the assumption of Kratky and POROD[7,8].

In order to interpret the results completely, however, more experimental data may be necessary.

Acknowledgment

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References

1) J. Hengstenberg and H. Mark, Zeit. Kristallogr., **69**, 271 (1928).
2) Ranby, Tappi, **35**, 53 (1952).
3) K. Hess and H. Kiessig, Z. Physik. Chem., **193**, 196 (1944).
4) W. O. Statton and G. M. Godard, J. Appl. Phys., **28**, 1111 (1957).
5) W. O. Statton, J. Polymer Sci., **41**, 143 (1959).
6) N. Shiraishi, S. Sato and T. Yokota Mokuzaigakkaishi, **21**, No. 5, 297 (1975).
7) O. Kratky and G. Porod, J. Colloid Sci., **4**, 35 (1949).
8) G. Porod, Kollod-Z., **124**, 83 (1951), **125**, 51 (1952).
9) Cited from "Cellular Ultrastructure of Woody Plants". pp. 191～197. Syracuse Univ. Press, 1965.