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Small-Angle X-Ray Scattering of Cellulose. I. Shape and Extent of Scattering in Some Vegetable Fibers

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Synopsis

It was shown that the shape of the scattering pattern is not only related to the shape but also to the face-orientation of the lamellar scattering units, and an actual observation of its characteristic shape depends on the amount and dispersion of their spiral angle. The following results were obtained: (*1*) For observing a cross-pattern, the critical spiral angles corresponding to minimum and maximum dispersions are 7.5° and 30° respectively, whereas in an actual fiber, coir, the critical angle is about 16.75°. (*2*) The jute pattern changes from a uniformly narrow to a triangular shape on disorientation and reverts to the former on reorientation. The corresponding changes in ramie are from a triangular to a uniformly wide and then to a uniformly narrow shape. Both native and disoriented cottons give weak, fan-shaped scattering superimposed on a more intense elliptical pattern. The pattern given by reoriented cotton is roughly a narrow streak. Delignified jute gives a somewhat shaving-brush-shaped pattern which changes to a uniformly wide streak on alkali treatment. (*3*) The extent of scattering decreases on swelling and increases on stretching in jute, ramie, and cotton, but decreases in stretched coir.

INTRODUCTION

When examined by a point-beam technique, vegetable fibers generally show two types of small-angle x-ray scattering patterns, one of which may be described as single-banded and the other double-banded or cross-shaped.[1-6] Heyn attempted to explain the single-banded patterns in accordance with Kratky's idea of variable micelle diffraction, and, in this respect, his emphasis was on the effect of swelling on the area or extent of scattering.[5,7] In accounting for the cross pattern, Heyn observed that the micelles at the side of the spiral which were parallel to the fiber axis, as seen from the direction of the x-ray beam, did not play a great part in the small-angle scattering. While he suggested that an explanation of the cross-shaped wide-angle diffraction pattern might be possible on the hypothesis of lamellar micelles, he did not seem to have envisaged a similar lamellar form for the small-angle scattering units, which, according to him, are also micelles.[5] That the cross-shaped small-angle pattern could be explained by assuming the scattering elements as lamellar in shape was indicated by Guinier, who further pointed out that if the elements were cylindrical the pattern would be fan-shaped.[8] These ideas are shown

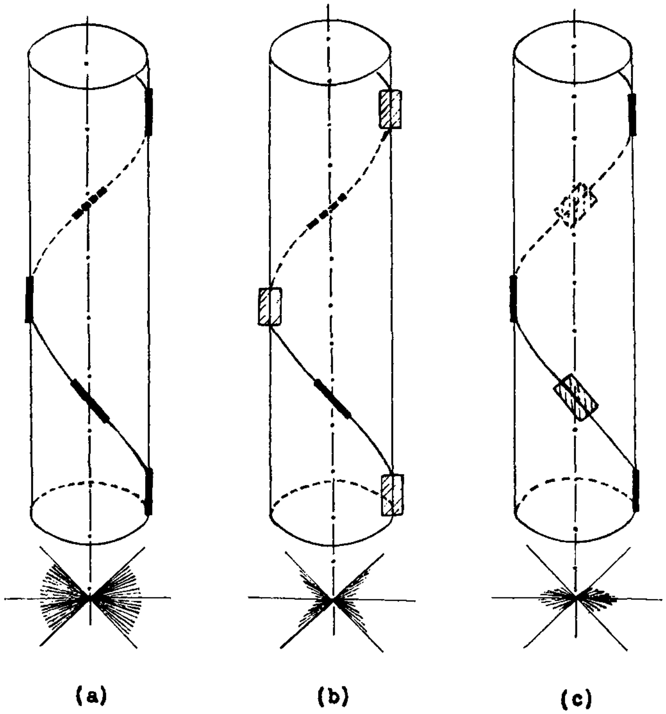

Fig. 1. Schematic small-angle scattering by (*a*) cylindrical units; (*b*) perpendicular face-oriented lamellar units; (*c*) parallel face-oriented lamellar units.

schematically in Figure 1, from which it is evident that for the appearance of the cross shape the scattering units must not only be lamellar in form but also selectively face-oriented, with their faces (widths) radially disposed with respect to the cylindrical cell-wall surface; and if the faces are tangential to the surface, the corresponding small-angle pattern will be tapering or triangular in shape. Thus, apart from the shape, the selective face orientation of the scattering elements will control the shape of the small-angle scattering patterns. It is to be noted that the theory of "particle" or "form factor" scattering[8,9] is tacitly assumed in this discussion, and although Guinier has used the term micelle, the lamellar hypothesis is not bound up with the concept of micellar origin of the scattering units.

The above analysis indicates how the shape of the small-angle scattering pattern is related to the shape and face orientation of the scattering units. An actual observation of the characteristic pattern will, however, depend on the magnitude and dispersion of the spiral angle of these units with the fiber axis. When the spiral angle is small, the scattering pattern will be more or less uniformly wide streak or rod-shaped, irrespective of the cross-sectional shape or face orientation of the elements, and the effect of the latter will be evident when the spiral angle exceeds a certain limiting minimum value depending on its dispersion. It will thus be worthwhile to study changes in the pattern shape following changes in the spiral orientation, and one way of effecting the latter is to treat the fiber in alkali, e.g., to freely swell in alkali to produce disorientation, and to stretch, while swollen in alkali, to produce reorientation.[10,11] Moreover, as these treatments involve certain changes in the lateral dimensions of the fiber, it will be of interest to observe the corresponding changes in the extent of scattering. In this regard, we shall also study the relative influence of the magnitude and dispersion of the spiral angle[12] in some model samples.

EXPERIMENTAL

The materials were jute, ramie, cotton, and coir. Dewaxed jute, 2% NaOH-boiled degummed ramie, 2% NaOH-boiled dewaxed cotton, and water-retted coir are referred to as either native or untreated samples. The fibers treated with 17.5% NaOH solution for 1 hr. at room temperature (23°C. approximately) are described as mercerized or disoriented, and those freely swollen in 17.5% NaOH, stretched while swollen in alkali and washed and air-dried under tension are referred to as stretched or reoriented samples. (Note: Jute could be stretched to a maximum of 96%, while ramie to about 104%, cotton to 115%, and coir to 125% of the original length.) The fibers exposed to x-rays while saturated with alkali (5–17.5%) are termed alkali-swollen samples.

In view of their high orientation,[11,13,14] a parallel bundle of jute fibers twisted at a given angle ϕ ($\phi = 20°, 25°, 30°, 35°$, etc.) at the periphery was taken to represent a system of elongated scatterers whose long axes lay between the angles $0°–\phi°$ with reference to the specimen axis[12] and thus corresponded to a case of maximum dispersion of the spiral angle. Two ribbons or bundles of parallel jute fibers placed upon each other at a given inclination 2ϕ ($2\phi = 10°, 15°, 20°$, etc.) were regarded as corresponding to a case of definite spiral angle at minimum dispersion.

The x-rays were Ni-filtered CuKα radiation from a Raymax tube collimated down a distance of 5–8 cm. through a pinhole or a lead glass capillary slit 0.25–0.5 mm. in diameter. The specimens were about 0.5–1.0 mm. thick and the photographs were taken with a flat camera with the fiber bundles exposed to a beam perpendicular to the fiber axis. The alkali-swollen specimens were sealed in a cell of polystyrene film during exposure. The nominal specimen-to-film distance was 10 cm., the exact distance being determined by referring to either 020 or any other known equatorial line.

RESULTS AND DISCUSSION

Figures 2–25 represent some of the small-angle x-ray photographs of untreated and treated fibers. The name of the sample and the size of the collimator bore corresponding to each photograph are given in Table I. Tables II and III contain a brief description of the shape, size, and other characteristics of the scattering patterns.

TABLE I

Samples and Collimator Bores for Different X-Ray Figures

Figure	Sample	Collimator bore, mm.
2	Native coir	0.4
3	115% stretched coir	0.4
4	125% " "	0.4
5	Twisted bundle of jute ($\phi = 30°$)	0.4
6	Crossed bundle of jute ($\phi = 7.5°$)	0.4
7	Crossed bundle of jute ($\phi = 10°$)	0.4
8	Native jute	0.4
9	" ramie	0.4
10	" cotton	0.4
11	" jute	0.25
12	" ramie	0.25
13	" cotton	0.25
14	Disoriented jute	0.4
15	" ramie	0.4
16	" jute	0.25
17	" ramie	0.25
18	" cotton	0.25
19	Reoriented jute	0.4
20	" ramie	0.4
21	" cotton	0.4
22	" "	0.25
23	9.5% NaOH treated, stretched cotton	0.25
24	Delignified jute	0.25
25	Delignified, 9.5% NaOH-treated jute	0.25

TABLE II

Characteristics of the Small-Angle X-Ray Patterns of Coir and Twisted and Crossed Bundles of Jute

Sample	Actual or equivalent spiral angle, ϕ	Shape of scattering	Extent of scattering	
			2θ	A.
Untreated coir	45°	Crossed, double band	2.07°	42.6
Reoriented coir (stretched to 115% of the original length)	24°	" " "	1.60°	55.2
Reoriented coir (stretched to 125% of the original length)	16.75°	Single band	1.43°	61.6
Twisted bundle of jute	0–30°	Crossed, double band just discernible	3.41	25.9
" " " "	0.35°	Crossed, double band	3.41°	25.9
Crossed bundles of jute	5°	Single band	3.41°	25.9
" " " "	7.5°	Crossed, double band just discernible	3.41°	25.9
" " " "	10°	Crossed, double band	3.41°	25.9

TABLE III
Characteristics of the Small-Angle X-Ray Patterns of Jute, Ramie, and Cotton

Sample	Shape of scattering	Extent of scattering	
		2θ	A.
Untreated jute	Uniformly narrow streak	3.41°	25.9
" ramie	Slightly triangular streak	2.52°	35.0
" cotton	Triangular or elliptical streak[a]	1.26°	70.0
	Brush-shaped streak[b]	1.80°	49.0
17.5% NaOH-swollen jute	Triangular streak	1.50°	59.0
" " ramie	" "	1.43°	61.6
Disoriented jute	" "	1.85°	47.6
" ramie	Uniformly wide streak	1.78°	49.5
" cotton	Brush-shaped streak[b]	1.65°	53.5
Reoriented jute	Uniformly narrow streak	2.98°	29.6
" ramie	" " "	2.98°	29.6
" cotton	" " "	2.45°	36.0
9.5% NaOH-treated and stretched cotton	Slightly triangular streak	1.63°	54.2
Delignified jute	Slightly brush-shaped streak	3.16°	27.9
Delignified and alkali-treated jute	Uniformly wide streak	2.52°	35.1

[a] Refers to Figure 10.

[b] Refers to outer zones of Figures 13 and 18.

Coir and Model Samples

The small-angle scattering of untreated coir exposed to a beam perpendicular to the fiber axis consists of a cross, and the two arms of the cross are at about 90°.[5] This angle is reduced on stretching the fiber in

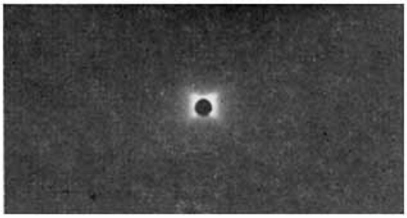

Figure 2.

Figure 3.

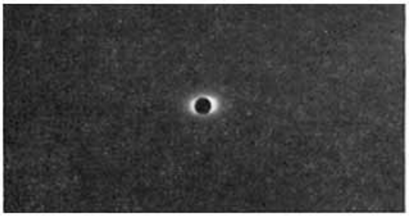

Figure 4.

Figure 5.

Figure 6.

Figure 7.

alkali. When the fiber is stretched to 115% of its original length, the spiral angle is reduced from 45° to 24°, the two arms of the cross coming closer together. On stretching the fiber to 125%, it is rather difficult to discern the cross shape, as the two arms of the small-angle cross are not clearly resolved; but the discontinuous character of the diffraction arcs is still visible, and the spiral angle can be measured as being 16.75°. An interesting feature of the results is that the extent of scattering is noticeably reduced in stretched coir, whereas an opposite effect is observed in stretched jute, ramie, or cotton.

The small-angle pattern of the model sample made of a twisted bundle of jute fibers just shows the cross when the maximum angle of twist, i.e., the angle at the periphery, is about 30°, and the cross shape becomes more pronounced as the angle of twist exceeds this limit. On the other hand, a clearly resolved cross pattern is still observed in the other model sample when the angle between the two bundles of jute constituting the sample, is about 15°, i.e., when the equivalent spiral angle is about 7.5°.

The above results give an idea about the influence of dispersion on the visibility of the cross-shaped small-angle pattern. The results on the model samples further show that associated with the two limits of dispersion (i.e., maximum and minimum), there are two minimum limits of the spiral angle for observing this shape, which are 7.5° and 30° respectively, but which could conceivably be still less under ideal experimental conditions, e.g., when the finite width and divergence of the beam and the angular deviation and dispersion of the scattering units relative to individual jute filaments constituting the model specimen were obviated.

The observed decrease in the extent of scattering shown by the samples of stretched coir apparently indicates a corresponding increase in the thickness of the lamellar scattering units,[8] but since under similar conditions of treatment an opposite effect is observed in jute, ramie, cotton, etc., it is rather difficult to elucidate it further except by drawing attention to a possible difference in the face-orientation of the scattering elements in the two groups of fibers (Introduction).

Jute, Ramie, and Cotton Fibers

Shape of Scattering. The small-angle scattering of native jute consists of a long, intense, sharp, and uniformly narrow equatorial streak. Com-

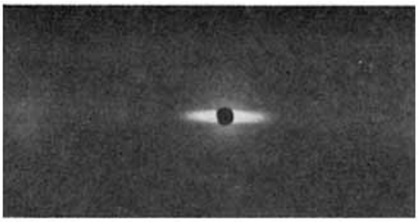

Figure 8.

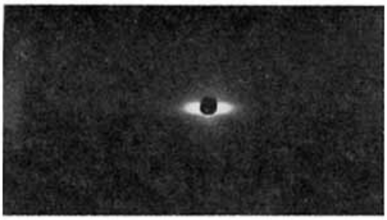

Figure 9.

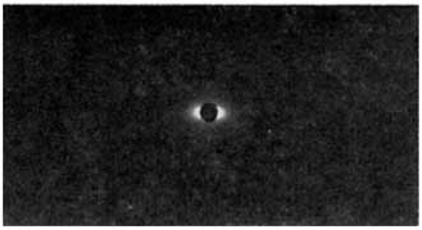

Figure 10.

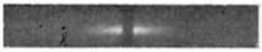

Figure 11.

Figure 12.

Figure 13.

Figure 14.

Figure 15.

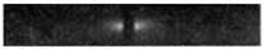

Figure 16.

Figure 17.

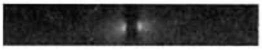

Figure 18.

pared to jute, the scattering streak of native ramie is a little shorter, less intense, less sharp, and slightly triangular or tapering in shape. The scattering pattern of native cotton appears to consist of two zones: the inner zone is very short, broad at the base, and triangular or elliptical in shape, while the outer zone is longer, less intense, and shaped like a shaving brush or fan. The latter was observed when the incident beam was very fine.

Figure 19.

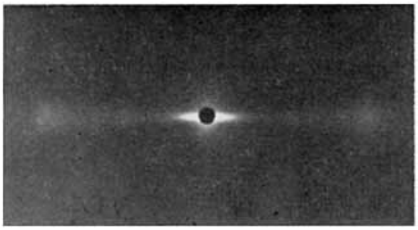

Figure 20.

Figure 21.

Figure 22.

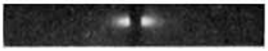

Figure 23.

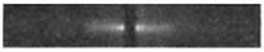

Figure 24.

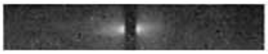

Figure 25.

The scattering streak of mercerized or disoriented jute is triangular in shape, but the scattering streak of disoriented ramie is rather more uniformly wide than that of the untreated fiber. The pattern due to mercerized cotton is similar to that of native cotton in shape but a little shorter in size, and this seems to hold for the outer as well as the inner zone. The scattering patterns of the reoriented samples of the three fibers (jute, ramie, and cotton) are all long and more or less uniformly narrow streaks.

The small-angle pattern of delignified jute is also an intense, long, and narrow streak and very similar to that of untreated jute except at the tip, which has the appearance of a shaving brush. When the delignified sample is treated with alkali, the scattering streak becomes more or less uniformly wide but broader, shorter, and less intense than before and roughly resembling that of mercerized ramie.

Some of these results are very similar to those reported by earlier workers,[4–6] who, however, did not specifically deal with the shape of the scattering pattern and its change with orientation and other treatments, which is the object of the present investigation. Assuming that the angular orientation of the scattering elements in these fibers is similar to that of the crystallites, and that for any change in the crystallite orientation there is a corresponding change in the angular orientation of these elements, the small-angle patterns of a series of fibers will be more and more triangular, if these fibers are characterized by parallel face-oriented lamellae of greater and greater spiral angle; for the same reason, the scattering streak of a given fiber will be more triangular with disorientation and less so with reorientation treatment (Introduction). It will be seen that the results for the three fibers, jute, ramie, and cotton, which are in the decreasing order of spiral orientation[11] are broadly in accord with these conclusions, although there are certain deviations in this respect. First, in view of a very small difference between the orientations of the two fibers,[11,13,14] the tapering shape of the scattering pattern of native ramie would appear to be in marked contrast with the uniformly narrow shape of the jute pattern, particularly when it is remembered that, allowing some divergence of the incident x-ray beam, the scattering streak should so tend to broaden at the tip that the observed taper cannot be an artifact. Secondly, while the disorientation on alkali treatment, as judged by crystalline alignment, is very pronounced in ramie,[11] the shape of the corresponding small-angle scattering streak is rather more uniformly wide than more tapering, as one would expect from the change in orientation. This can be explained if it is assumed that either the shape of the elements has tended to change from lamellar to cylindrical, or their face orientation has tended to change from selective to random upon treatment (Introduction). A change of this type can conceivably be associated with a reduction in the rigidity of ramie following the treatment, which is, to some extent, suggested by the results on delignified jute; for, when relieved of its higher rigidity[15–17] by the combined action of delignification and alkali treatment, this fiber seems to behave more or less similarly as ramie.

Extent of Scattering. Besides shape, the extent of scattering was also noted for the above samples, as recorded in Table III. It will be seen that the extent of scattering decreases in the three untreated fibers in the order: jute, ramie, and cotton. When a particular fiber such as jute or ramie is swollen in NaOH, the scattering length decreases with increasing concentration of the alkali within the range 5–17.5%, reaching a minimum at 17.5%. When the fiber is washed clean of optimum (17.5%) concentration of alkali and air-dried, there is a small increase in the extent of scattering, while the stretched sample again shows a considerable increase of length. An appreciable increase of length also occurs for the sample of cotton which has been stretched while in premercerizing alkali. Further, a comparison of the wide-angle pellet diagrams of native, mercerized, and stretched cottons shows that there is little difference in the breadth of the 002 diffraction arcs in the three samples.

Most of these results are in essential agreement with those obtained by Heyn, using a similar point-beam technique.[5] But we could not confirm his finding of increased extent of scattering for mercerized cotton;[6] our results rather show that the length decreases in cotton, as in jute or ramie, on free mercerization; this is true for both the inner and outer zones of scattering. One would thus hesitate to accept Heyn's postulate of a longitudinal splitting of the micelles of this fiber during the process of lattice transformation,[5] more so as this fiber, when stretched in premercerizing alkali, which should involve no lattice transformation and consequently no micellar splitting, also gives an increased extent of scattering, and there is no indication of an increase in the width of the diffraction line in either mercerized or stretched cotton. Based on the particle or form-factor theory, an alternative explanation would be to assume the scattering units as susceptible to lateral changes observed on swelling and stretching. In fact, if it is accepted that the micelles or crystallites are randomly disposed with respect to the cell-wall surface of the fiber as concluded by Sisson,[12] whereas the small-angle units are selectively face-oriented as indicated in this work, the hypothesis of micellar or crystallite origin of small-angle scattering will not seem acceptable. Further, as judged by the extent of scattering, the lateral dimensions of the small-angle elements increase in the order: jute, ramie, and cotton,[5] whereas, as reported by Woods,[18] the lateral dimensions of the crystalline particles are larger in ramie than in cotton.

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References

1. Herzog, R. O., *J. Phys. Chem.*, **30**, 457 (1926).
2. Hengstenberg, J., and H. Mark, *Z. Krystallog.*, **69**, 271 (1928).
3. Kratky, O., and F. Schoszberger, *Z. Physik. Chem.*, **B39**, 145 (1938).
4. Clark, C. L., and E. A. Parker, *Science*, **85**, 203 (1937).
5. Heyn, A. N. J., *Textile Res. J.*, **19**, 163 (1949).
6. Heyn, A. N. J., *J. Am. Chem. Soc.*, **70**, 3138 (1948); *ibid.*, **71**, 1873 (1949); *ibid.*, **72**, 2284, 5768 (1950).
7. Kratky, O., *Naturwiss.*, **26**, 94 (1938); *ibid.*, **30**, 542 (1942).
8. Guinier, A., and G. Fournet, *Small-Angle Scattering of X-Rays*, Wiley, New York, 1955, pp. 3, 30, 178.
9. Heyn, A. N. J., *J. Appl. Phys.*, **26**, 519 (1955).
10. Hermans, P. H., *Physics and Chemistry of Cellulose Fibres*, Elsevier, New York, 1949, p. 257.
11. Roy, S. C., *J. Appl. Polymer Sci.*, **6**, 541 (1962).
12. Sisson, W. A., *Ind. Eng. Chem.*, **27**, 51 (1935).
13. Hock, C. W., *Am. Dyestuff. Reptr.*, **31**, 334 (1942).
14. Sen, M. K., and H. J. Woods, *Proc. Leeds. Phil. Soc. Sci. Sec.*, **5**, Pt. 2, 155 (1949).
15. Sen, M. K., and M. Ramaswamy, *J. Textile Inst.*, **48**, T75 (1957).
16. Roy, S. C., and M. K. Sen, *J. Textile Inst.*, **50**, T640 (1959).
17. Roy, S. C., *Textile Res. J.*, **30**, 451 (1960).
18. Woods, H. J., *Physics of Fibres*, Institute of Physics, London, 1955, p. 83.

Résumé

La forme du diagramme de diffusion n'est pas seulement liéé à la forme mais aussi à l'orientation faciale des unités lamellaires diffusantes, et une observation actuelle de la forme caractéristique dépend de leur quantité et de la dispersion de leurs angles d'enroulement On a obtenu les résultats suivants: (*1*) pour observer des diagrammes transversaux les angles critiques correspondant aux dispersions minimum et maximum sont de 7.5 et 30° respectivement, alors que dans la fibre de caire l'angle critique est environ de 16.75°. (*2*) le diagramme du jute change d'une forme étroite uniforme à une forme triangulaire par suite de la désorientation, et retourne à la première par réorientation. Les changements correspondants pour la ramie vont d'une forme triangulaire à une forme uniformément large, et de celle-ci à une forme uniformément étroite. Le coton à l'état natif aussi bien que désorienté, présente une diffusion faible ressemblant à un éventail, et qui se superpose à un diagramme elliptique plus intense. Le diagramme fourni par du coton réorienté est grossièrement une raie étroite. Le jute délignifié donne un diagramme ressemblant quelque peu à un blaireau qui change en une raie uniformément large par traitements aux alcalins. (*3*) l'importance de la diffusion décroît par gonflement, et croît par étirement du jute, de la ramie, et du coton, mais decroît dans du caire étiré.

Zusammenfassung

Es wurde gezeigt, dass die Gestalt des Streudiagramms nicht nur zur Gestalt, sondern auch zur Flächenorientierung der lamellaren Streueinheiten in Beziehung steht und eine tatsächliche Beobachtung ihrer charakteristischen Gestalt von Betrag und Dispersion ihres Schraubenwinkels abhängt. Folgende Ergebnisse wurden erhalten: (*1*) Für die Beobachtung eines Kreuzdiagramms betragen die kritischen, der minimalen und maximalen Dispersion entsprechenden Schraubenwinkel 7,5 bzw. 30°, während in einer wirklichen Faser, Kokosfaser, der kritische Winkel etwa 16,75° ist. (*2*) Das Jutediagramm geht bei der Desorientierung von einer einheitlich engen zu einer dreieckigen Gestalt über und kehrt bei der Reorientierung zur ersteren zurück. Die entsprechenden Änderungen bei Ramie bestehen in einem Übergang von einer dreieckigen zu einer einheitlich breiten und von dieser zu einer einheitlich engen Gestalt. Sowohl native als auch desorientierte Baumwolle liefert eine schwache fächerartige Streuung, welche einem intensiveren elliptischen Diagramm überlagert ist. Das Diagramm der reorientierten Baumwolle ist angenähert ein enger Streifen. Von Lignin befreite Jute liefert ein etwa rasierpinselartiges Diagramm, welches sich bei Alkalibehandlung in einen einheitlich breiten Streifen umwandelt. (*3*) Das Ausmass der Streuung nimmt beim Quellen ab und bei Jute, Ramie, und Baumwolle bei Dehnung zu, jedoch in gestreckten Kokosfasern ab.

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