Spirality of the Crystallites of the Natural Cotton Fibers

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Synopsis

X-ray intensity analysis of the (040) profile of the natural cottons have been done. Using the Deluca and Orr mathematical procedure, the spiral angles for the different cottons have been calculated. It was found that the spiral angle varies over a wide range and it need not be constant for different genetic varieties of cotton as reported earlier.

INTRODUCTION

The cotton fibers have primary and secondary walls. The primary wall consists of a body of wax pectins and protein matter into which cellulose fibrils are interwoven in a crisscross manner.[1] The secondary wall consists of two layers of pure cellulose. The very first layer of cellulose deposited after the cell has completed its longitudinal growth is called the $S1$ layer. This layer is sometimes termed as transitory lamellae and is resistant to swelling media like the primary wall. The bulk of the secondary wall is constituted by $S2$ layers, which when swollen enables one to see the daily growth rings in the mature fiber. These layers are constituted by cellulose fibrils which appear to follow a longitudinal helical course around the lumen with frequent reversals in direction and making an acute angle with the fiber axis referred to as the spiral angle. At the center of the fiber there is a hollow space called "lumen."

Cotton fibers have a further feature due to the frequent occurrence of "twists" along the length of the fiber. These are known as convolutions. On the opening of the ripe cotton boll and on exposure to external atmospheric conditions, the unicellular cotton fiber with a tubelike hollow space lumen at the center becomes dry and collapses into an irregularly twisted ribbonlike structure. Although the exact reason for the occurrence of convolutions is not known, Balls[2] proposed that the underlying spirality of the cellulosic fibrils caused the formation of convolutions. Iyengar[3] has thrown some fresh light by examining under a low-power microscope a moist cotton fiber taken from a freshly picked ripe boll from the plant. He found that during the process of drying the fiber acquires convolutions on either side of a flat central region involving invariably a reversal in the direction of the spiraling fibrils.

Birefringence and x-ray studies of cellulosic fibers have confirmed a fairly high degree of alignment of cellulosic chains in fibrils. In cellulosic fibers, the crystallites are arranged with the crystallographic b axis more or less parallel to the axis of the fiber. Hermans and co-workers[4] (1946) have derived a mathematical expression to determine quantitatively the preferred orientation in cellulosic fibers based on the fact that the intensity distribution along an arc corresponds

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to the density distribution of the respective crystallographic planes. Herman's work was extended further to each of the different orientations about the different axes with respect to the reference direction by Stein.[5]

Clark[6] (1930) was the first to use x rays for the measurement of orientation. Segal and co-workers[7] and Creely and Conrad[8] have developed a diffractometric technique for evaluating orientation in cotton from the azimuthal width of equatorial reflections.

Balls[2] has shown that cotton has spiral structure. Rollins and Tripp[9] have reported that superposed on the spiral structure are discrete layers of cellulose, a collapsed convoluted structure, and occasional reversals in direction of the spiraling strands within the cellulose layers. Sisson[10] has shown a schematic representation of the x-ray diffraction diagram of a cotton fiber in relation to the microscopically visible spiral fibrillar structure of the fiber. Also the pitch of the spiral texture can be approximately deduced from the angular width of the arcs. However, certain refinements of the above approach have been brought about by the work of DeLuca and Orr.[11,12] They made use of the intensity profile of the (002) diffraction to determine the degree of crystallite orientation and the spiral angle in various native, decrystallized, and mercerized cottons. Using the DeLuca and Orr procedure, Kalyanaraman[13,19] has shown that the orientation factor estimated from the (002) profile would be the same as the one that would be obtained from the relatively weaker (040) reflection because the cellulose crystals are known to be uniaxial.

It has been pointed out by Meredith[15] that the spiral angle of undried cotton may be constant for all the genetic varieties. He found that the spiral angle as calculated from the birefringence measurements was affected by the convolutions of the fiber and that if suitable corrections were applied, the resulting spiral angle approached a constant value. His data for 14 samples including American upland, American Egyptian, and Indian cottons gave an average spiral angle of 21.7° ± 0.25°. The reports of Betrabet et al.[16] supported Meredith's observations by subtracting convolution angles from the optically estimated spiral angles and finding they have an approximately constant value of 24.25° ± 3.34° in their investigation of 20 cottons of different genetic varieties. Hebert[17] using Hartshorne's[18] approach, reported the spiral angle measurement of ten cottons and gave an average of 21.67° and concluded that the spiral angle made by cellulose fibrils about the fiber axis of cotton is a constant value in the range 21°–22°.

Duckett and Tripp,[14] using single fiber diffraction patterns on films and using a photometer, made an experimental determination of the spiral angle. Their procedure of locating the two resolved maximum densities on the exposed film with a photometer and measuring the half-angle between the maxima and the center of the x-ray pattern would be the experimental analog of the mathematical technique of DeLuca and Orr.[11,12] They also concluded that Meredith's[15] observation that the average spiral angle in the original unconvoluted fibers may be the same for all cotton varieties was not in complete agreement with their conclusions. They concluded that both single-fiber and optical measurements which are uncomplicated by convolutions have shown definite differences in the varieties examined. This article reports the values of the spiral angle as obtained using the DeLuca and Orr procedure[11,12] on the azimuthal scan of the meridional reflection (040) for 21 American cottons.

EXPERIMENTAL

DeLuca and Orr[11,12] separated the experimental azimuthal diffraction curve into two equal Gaussian distributions separated by twice the spiral angle ϕ. These distributions are taken against the azimuthal angle E with the origin at the position of the experimentally observed peak.

DeLuca and Orr Procedure

Assume that the maximum of the two distributions are located at $E = \pm\phi$, where ϕ is the spiral angle. The ordinates of the azimuthal intensity scan curve are the intensities in arbitrary units after subtracting the background (which is assumed to be linear for all azimuths and equal to the observed intensity at $E = 90°$). If the two Gaussian distributions are represented as I_1 and I_2, then the two Gaussians at the azimuth E are given by

$$I_1E = I_m \exp[-H^2 (E - \phi)^2] \quad (1)$$

$$I_2E = I_m \exp[-H^2 (E + \phi)^2] \quad (2)$$

where $H^2 = \log_e 2/\alpha^2$ and I_m is the net maximum intensity of the Gaussian distribution at $E = \pm\phi$, and α is the angle of the half-maximum intensity of the distributions.

The sum of the two distributions is given by

$$I_E = I_{1E} + I_{2E} \quad (3)$$

and the maximum

$$I_0 = 2\, I_m \exp(-H^2\phi^2) \quad (4)$$

Using these, the ratio of intensities at azimuth E to the one at azimuth zero is given by

$$I_E/I_0 = \cosh(2H^2\, E\phi) \exp(-H^2\, E^2) \quad (5)$$

Using the above equation and the intensities expressed as percentages of the maximum at azimuth zero, a quadratic equation could be written in the form

$$X^2 - 2\, C\, X + 1 = 0 \quad (6)$$

where $X = \exp(2H^2\, E_1\, \phi)$ and $C = I_1 \exp(H^2 \mathrm{E}_1{}^2)$ for the intensity at E_1.

The above quadratic equation is solved for X and H and the ϕ values are adjusted in such a way that those obtained for E_1 and E_2 agree very well. This is done with the help of a computer.

X-Ray Setup

The measurements are made on fiber bundles of the representative cotton. The details of the preparation of bundles are well described by Kalyanaraman[19] and Kalyanaraman and Ramakrishnan.[20] The radial scan of (040) intensity and azimuthal scan at the peak are done employing a texture goniometer, pulse height discriminator, proportional counter, and point-to-point counting technique on bundles pre-tensioned at 1 kg.

TABLE I
Spiral Angle as Calculated from DeLuca and Orr (refs. 11 and 12) Procedure using (040) Meridional Diffraction for Natural Cottons

Spiral Angle in Deg

G. Barbadense

	Pima 1	Pima 2	Pima 3	Pima 4
1	17.34	16.01	17.48	18.68
2	17.34	16.40	16.88	18.84
3	17.56	17.86	17.02	18.58
4	17.42	16.46	16.57	21.71
5	17.57	16.09	16.17	18.57
6	17.63	17.17	16.61	18.26
7	16.39	16.55	16.34	18.82
8	17.78	17.09	16.39	
9	17.05			
10	17.33		Mean	17.39

G. Hirsutum

	Florence 1	Florence 2	Florence 3	Florence 4	Florence 5
1	14.01	13.45	13.79	12.35	13.38
2	12.68	13.03	13.80	11.94	13.82
3	13.81	12.38	14.43	13.21	13.28
4	14.47	13.43	13.49	13.18	13.42
5		13.55	13.63	12.73	13.56
6		11.98	15.09	10.97	12.98
7		12.60	12.65	13.10	13.19
8		12.78	15.48	12.76	12.65
9		13.41	13.72	13.00	
10			13.43		
11			12.76		
				Mean	13.25

G. Hirsutum

	Acala 1	Acala 2	Acala 3	Acala 4	Acala 5
1	17.60	12.81	8.24	10.67	13.97
2	17.18	11.90	11.53	11.75	12.78
3	17.49	13.31	11.27	13.52	12.42
4	17.32	11.95		12.78	14.30
5	17.37	13.78		12.65	12.24
6	17.86	11.05			11.96
7	18.32	12.20			
8	17.99	13.18			
9	18.40	12.27			
				Mean	13.81

G. Hirsutum

	Deltapine 1		Deltapine 2
1	19.58		21.30
2	19.65		20.28
3	19.07		20.79
4	21.29		23.40
5	19.96		21.67
6	19.70		20.68
7	20.48		21.33
8	20.01		
		Mean	20.61

TABLE I (*Continued from previous page.*)

	Spiral Angle in Deg		
	S2690-1[a]		S2690-2[a]
1	13.55		14.48
2	12.63		14.11
3	13.61		14.00
4	13.00		14.56
5	14.32		13.19
6	13.95		14.26
7	13.84		14.27
8	13.37		14.08
		Mean	13.83
	T4852-1[a]		T4852-2[a]
1	15.38		15.47
2	14.82		15.39
3	14.79		15.87
4	15.08		15.72
5	14.79		16.01
6	14.05		15.80
7	15.17		16.69
8	13.72		14.26
9			15.44
		Mean	15.20
	T1366[a]		
1	14.58		
2	15.47		
3	15.69		
4	16.09		
5	15.69		
6	15.88		
7	14.96		
8	15.09		
Mean	15.43		

[a] Genetic name not known.

Azimuthal Scanning of Reflections

By making a radial scan with the fiber bundle, the Bragg angle of the reflection

TABLE II
Average Values of Spiral Angles Past and Present Compared

Investigator	Technique	Spiral angle (deg)	No. of observations
Meredith	Optical	21.7	14
Betrabet	Optical	24.25 ± 3.34	20
Duckett and Tripp	Optical	21.6	5
Duckett and Tripp	X ray	21.8	5
Hebert	Hartshorne's method	21.67	10
Present work	X-ray (040) profile	15.65	162

has been accurately located. Any misalignment of the fiber bundle with reference to the zero position of the texture goniometer corresponding to the center of symmetry of the intensity distribution curve is noted. In a well-aligned system, such an error never exceeds more than 1° of an arc and the corrected position is used as the zero position for the azimuthal scanning.

Evaluation of the Spiral Angle

The intensities of azimuths $E_1 = 15°$ and $E_2 = 30°$ are measured, as is the peak intensity at $E = 0$. The observations are made for a fixed counting time of 32 sec, and each observation is repeated twice on the same bundle. For each cotton, about ten bundles are taken. As mentioned earlier, those values are used to solve eq. (6) for a particular value of H. This leads one to the spiral angle ϕ for the observation at E_1. Similarly for the same value of H^2, ϕ is calculated for the azimuthal intensity at E_2. H is now incremented and the calculations are repeated until the values of ϕ by both methods agree up to the fourth decimal place. When the convergence is satisfactory, the corresponding values of ϕ are noted. These are given in Table I.

DISCUSSION

Table I gives the value of the spiral angle for the 21 American cottons as measured from the (040) meridional scan. All the values obtained here lie between 8.24° and 23.40°. The average values of spiral angles obtained by different methods by earlier workers and the average of the present investigation are given in Table II. The values obtained here are distinctly different from the range of values obtained earlier. Thus it appears that the results reported here are contrary to the earlier conclusions made by Meredith[15] and by Hebert[17] that the spiral angle of undried cotton may be constant and may have a value between 21° and 22°. From the present observations, it appears that the spiral angle can

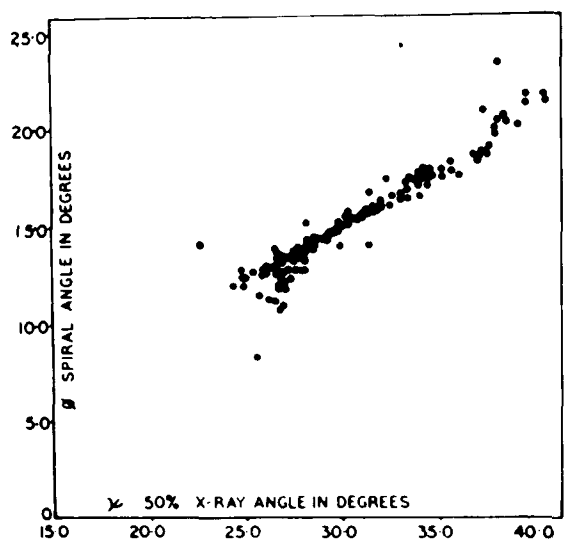

Fig. 1. Spiral angle vs. 50% x-ray angle.

have a fairly wide range of values and need not be constant for the natural cotton fibers of different genetic varieties.

However, as pointed out by Kalyanaraman,[13] the spiral angle has a close relationship with the 50% x-ray angle (Fig. 1). For the medium values of 50% x-ray angle, the spiral angle varies linearly with the 50% x-ray angle and the linearity breaks down at higher and lower values of the 50% x-ray angle.

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References

1. K. Nettelnstroch, *Text. Ind., Zurich,* **67,** 699(1965).
2. W. L. Balls, *Proc. R. Soc. London Ser. B,* **95,** 72(1923).
3. R. L. N. Iyengar, *Text. Res. J.,* **34,** 362 (1964).
4. J. J. Hermans, P. H. Hermans, D. Vermaas, and A. Weidinger, *Recl. Trav. Chim. Pays-Bas,* **65,** 427 (1946).
5. R. S. Stein, *J. Polym. Sci.,* **31,** 327 (1958).
6. G. L. Clark, *Ind. Eng. Chem.,* **22,** 474(1930).
7. L. Segal, J. J. Greely, and G. M. Conrad, *Rev. Sci. Instrum.,* **21,** 431(1950).
8. J. J. Creely and C. M. Conrad, *Text. Res. J.,* **35,** 863(1965).
9. M. L. Rollins, and V. W. Tripp, *Text. Res. J.,* **24,** 345(1954).
10. W. A. Sisson, *Ind. Eng. Chem.,* **27,** 51(1935).
11. L. B. DeLuca, and R. S. Orr, *J. Polym. Sci.,* **54,** 457(1961).
12. L. B. DeLuca and R. S. Orr, *J. Polym. Sci.,* **54,** 471(1961).
13. A. R. Kalyanaraman, *Text. Res. J.,* **48,** 582(1978).
14. K. E. Duckett and V. W. Tripp, *Text. Res. J.,* **37,** 517(1967).
15. R. Meredith, *Br. J. Appl. Phys.,* **4,** 369(1953).
16. S. M. Betrabet, K. P. R. Pillay, and R. L. N. Iyengar, *Text. Res. J.,* **33,** 720(1963).
17. J. J. Hebert, *Text. Res. J.,* **37,** 57 (1967).
18. N. H. Hartshorne, *Nature London,* **184,** 179(1959).
19. A. R. Kalyanaraman, *Text. Res. J.,* **48,** 366 (1978).
20. A. R. Kalyanaraman and R. Ramakrishnan, *J. Text. Inst.,* **69,** 351(1978).

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