Cellulose Crystallite Sizes in Diploid and Tetraploid Native Cotton

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ABSTRACT: Cellulose crystallite sizes in directions perpendicular to (101), (10$\bar{1}$), and (002) planes, have been estimated from X-ray powder diffraction patterns. The diffraction peaks were resolved using the FIT X-ray diffraction data analysis program (written by SOCABIM, Siemens DIFFRAC AT Software System, Siemens, Germany). The complete data for all the three equatorial planes was analyzed for 2θ, d values, full width at half-maximum (FWHM), and the normalized area under the three diffraction peaks, for seven cotton cultivars grown at four different locations in India in different crop years. The mean crystallite sizes were determined using the Scherrer equation. The reference standard included degummed and purified ramie fibers for relative crystallinity estimation in cotton cultivars. It has been observed that, though the computed crystallite sizes corresponding to (101), (10$\bar{1}$), and (002) planes vary within individual varieties with location and year of growth, the combined average crystallite size corresponding to (101) and (10$\bar{1}$) planes taken together for individual varieties from all locations and crop years is close to the combined average crystallite size corresponding to the (002) planes, irrespective of the species of cotton. The values of the average relative crystallinity with respect to highly oriented degummed and purified ramie fibers of individual varieties from all locations and crop years do not significantly vary between varieties and species of cotton. It is visualized that variations in crystallite sizes arise as a result of the differences in the amount of cellulose synthesized within fibers of individual varieties and their disposition within the matrix of their developing fibers. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 2107–2112, 1998

Key words: native cotton; cellulose X-ray; crystallite sizes

INTRODUCTION

Native cotton fibers are composed mainly of pure crystalline cellulose.[1–3] This cellulose is deposited as long microfibrils that spiral around the axis of fiber in diurnal secondary growth layers of developing cotton fibers.[1–7] Knowledge of relative variations in degree of polymerization, crystallite size, crystallinity, and orientation of crystallites to the fiber axis is helpful in understanding intercotton differences, fiber properties, and chemical reactivity.[1,2,8,9] The measurements of crystallinity in native cellulosic materials have received much attention in the last few decades[1,2,10] for reasons of commercial applications and the importance of cellulose as industrial raw material. Although it is generally agreed that native cotton exhibits variation in the value of crystallinity between cotton varieties,[11–24] a very narrow spread (67–72%) in crystallinity values by itself is insufficient to pinpoint intercotton differences.[21,24,25] However, it is now generally accepted that the estimates of

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Table I Data on Crystallite Sizes and Relative Crystallinity in Respect of the Same Cotton Cultivars Grown at Different Locations and in Different Crop Years

Serial No.	Cotton Variety and Species [1][a]	Years of Growth [2]	Location of Growth [3]	Crystallite Sizes (Å) 101 [4(a)]	$10\bar{1}$ [4(b)]	Average of $101 + 10\bar{1}$ [4(c)]	002 [4(d)]	Average of $101 + 10\bar{1} + 002$ [4(e)]	Relative Crystallinity–Orientation WRT Ramie [5]
Gossypium arboreum									
1	Y-1	1994	Sirsa	27.1	73.1	50.1	49.9	50.0	0.365
2.	Y-1	1994	New Delhi	25.8 (L)	80.4	53.1	54.6 (H)	53.6	0.270 (L)
3.	Y-1	1994	Nagpur	34.7	86.0 (H)	60.3 (H)	51.0	57.2 (H)	0.413 (H)
4.	Y-1	1995	Nagpur	44.2 (H)	43.4 (L)	43.8 (L)	49.0 (L)	45.6 (L)	0.294
5.	Average within			32.9	70.7	51.8	51.2	51.6	0.335
	the variety: range (H–L)[b]			18.4	42.6	8.5	3.6	11.6	0.143
6.	Maljari	1992	Nagpur	27.6 (L)	49.9	38.7	50.8	42.8	0.346
7.	Maljari	1992	Coimbatore	39.0	66.2	52.6 (H)	53.8 (H)	53.0 (H)	0.396
8.	Maljari	1994	Sirsa	35.5	70.7	53.1	51.5	52.6	0.318 (L)
9.	Maljari	1994	Nagpur	33.6	69.1	51.3	52.2	51.6	0.397
10.	Maljari	1995	New Delhi	27.4	47.7 (L)	37.5 (L)	50.5	41.8 (L)	0.347
11.	Maljari	1995	Nagpur	32.6	72.1 (H)	52.3	51.6	52.1	0.437 (H)
12.	Maljari	1995	Coimbatore	43.9 (H)	52.0	47.9	49.4 (L)	48.4	0.418
13.	Average within			34.2	61.1	47.6	51.4	48.9	0.379
	the variety: range (H–L)			16.3	24.4	15.1	4.4	11.2	0.119
14.	AKH-4	1992	Nagpur	27.1	72.9	50.0	54.2	51.4	0.245 (L)
15.	AKH-4	1992	Coimbatore	23.0 (L)	140.7 (H)	81.8 (H)	56.1	73.3 (H)	0.319
16.	AKH-4	1994	Sirsa	36.8	75.7	56.2	56.2 (H)	56.2 (L)	0.309
17.	AKH-4	1994	Nagpur	36.2	61.2	48.7	50.1	49.2	0.400 (H)
18.	AKH-4	1995	New Delhi	26.4	58.3	42.3 (L)	51.5	45.4	0.301
19.	AKH-4	1995	Nagpur	45.6 (H)	44.9 (L)	45.2	49.0 (L)	46.5	0.330
20.	Average within			32.5	75.6	54.0	52.9	53.7	0.317
	the variety: range (H–L)			22.6	95.8	39.5	7.2	17.1	0.155
21.	AKA-5	1992	Nagpur	26.7 (L)	75.0	50.8	53.5 (H)	51.7	0.292
22.	AKA-5	1992	Coimbatore	27.4	112.9 (H)	70.1 (H)	51.5	63.9 (H)	0.348
23.	AKA-5	1994	Sirsa	33.7	69.6	51.6	53.4	52.2	0.273 (L)
24.	AKA-5	1994	Nagpur	33.8	85.6	59.7	51.0	56.8	0.323
25.	AKA-5	1995	New Delhi	29.7	43.3 (L)	36.5 (L)	49.2 (L)	40.7 (L)	0.409 (H)
26.	AKA-5	1995	Nagpur	36.4 (H)	63.0	49.7	50.7	49.8	0.347
27.	Average within the variety:			31.3	74.9	50.3	51.5	52.5	0.332
	range (H–L)			9.7	69.6	34.6	4.3	23.2	0.136

Gossypium hirsutum									
28.	BN	1992	Nagpur	27.7	89.2	58.4	53.2	56.7	0.339
29.	BN	1992	Coimbatore	40.0	63.2	50.6	52.5	51.9	0.393
30.	BN	1994	Sirsa	24.2 (L)	93.1	58.6	56.9 (H)	58.1	0.323 (L)
31.	BN	1994	New Delhi	25.6	103.6 (H)	64.6 (H)	52.0	60.4 (H)	0.374
32.	BN	1994	Nagpur	34.1	65.3	49.7	51.8	50.4	0.403 (H)
33.	BN	1995	New Delhi	48.1 (H)	62.4	55.2	55.7	55.4	0.339
34.	BN	1995	Nagpur	39.4	54.1 (L)	46.7 (L)	48.7 (L)	47.4 (L)	0.382
35.	Average within the variety:			34.2	75.8	54.8	53.0	54.3	0.364
	range (H−L)			13.9	49.5	18.9	12.2	13.0	0.080
36.	LH-900	1992	Nagpur	43.8	62.5	53.1	54.6 (H)	53.6	0.327
37.	LH-900	1992	Coimbatore	28.1 (L)	83.1	55.6	51.8 (L)	54.3	0.389
38.	LH-900	1994	Sirsa	28.9	94.9 (H)	61.9 (H)	54.4	59.4 (H)	0.472 (H)
39.	LH-900	1994	Nagpur	29.5	72.7	51.1 (L)	53.6	51.9 (L)	0.368
40.	LH-900	1995	New Delhi	44.5 (H)	60.8 (L)	52.6	52.4	52.6	0.313 (L)
41.	Average within			35.3	74.8	54.8	53.3	54.3	0.373
	the variety: range (H−L)			16.4	34.1	10.8	2.8	7.5	0.159
42.	LRA-5166	1992	Nagpur	41.8	54.0 (L)	47.9	49.7	48.8	0.323
43.	LRA-5166	1992	Coimbatore	44.9 (H)	57.4	51.1	52.1	51.6	0.362
44.	LRA-5166	1994	Sirsa	27.8	67.0	47.4	54.4 (H)	50.9	0.313
45.	LRA-5166	1994	New Delhi	28.3	58.7	43.5 (L)	44.6 (L)	44.0 (L)	0.281
46.	LRA-5166	1994	Nagpur	33.3	80.7	57.0	52.8	54.9	0.274 (L)
47.	LRA-5166	1994	Coimbatore	25.6 (L)	105.9 (H)	65.7 (H)	53.3	61.6 (H)	0.291
48.	LRA-5166	1995	New Delhi	37.6	58.1	47.8	48.3	48.0	0.449 (H)
49.	LRA-5166	1995	Nagpur	43.4	58.0	50.7	47.5	49.1	0.398
50.	Average within			34.0	67.4	51.3	50.3	51.1	0.336
	the variety: range (H−L)			19.3	51.9	22.2	9.8	17.6	0.175
51.	Combined average of all varieties taken together			33.5	71.6	52.0	51.9	52.3	0.348

[a] Column numbers are given in brackets.
[b] H represents the highest value within the variety; L, the lowest value within the variety; H−L, the range of variation within the individual variety.

crystallinity based on a simplified crystalline–amorphous system is not very meaningful.[26–28] The literature on the crystallite size of cellulose is again conflicting on account of various techniques used such as small- and wide-angle X-ray diffraction (WAXD), scanning and transmission electron microscopy, and electron diffraction, in addition to chemical methods.[1–3,29–31] It has been complicated further as a result of direct and indirect comparisons of data on cellulosic materials of different origins.[1–3,32] In recent communications,[31,33,34] it has been concluded that the mass density of cellulose in never-dried cotton, the degree of polymerization, the nature and size of crystallographic units, or the supramolecular crystalline aggregates between cotton varieties and their orientation to the fiber axis remain practically invariant, irrespective of species and varieties. The observed differences in mechanical properties of fibers are believed to be the result of the arrangement of orientation or differences at higher levels of structural organization.[31] Sundaram et al.,[30] based on their X-ray orientation studies, observed differences in fiber strength and structure resulting from change of place of growth of cotton. Crystalline character of cotton fiber is therefore real and indispensable for technological performance and, therefore, the necessity for determination of crystallite sizes.[22–24]

In this article, data on crystallite sizes in raw cotton fibers of seven cultivars belonging to diploid *Gossypium arboreum* and tetraploid *Gossypium hirsutum* species grown at different places during different years and crop seasons, are presented and discussed. To the best of our knowledge, it is the first comprehensive study of this kind exclusively on same cotton cultivars grown at different locations and in different crop years.

MATERIALS AND METHODS

Seven cotton cultivars, belonging to diploid *Gossypium arboreum* and tetraploid *Gossypium hirsutum* were grown at 4 locations, namely, Sirsa and New Delhi (in North India), Nagpur (Central India), and Coimbatore (South India) during the 1992, 1994, and 1995 crop years under standard agronomic and fertilization practices specific to these locations. Mature seed cotton was harvested from the first picking from all locations and ginned on CTRL-model laboratory gin. The ginned fibers were collected and purified for removal of waxes, pectic materials, and protoplasmic residues by soaking for 6 h each in carbon tetrachloride and methanol and subsequent boiling for 3 h in 2% sodium hydroxide solution. The fibers were neutralized for 1 h with 0.1*N* HCl, washed with distilled water, and dried at room temperature.[35] Well-parallelized bundles of purified cotton fibers were mounted on poly(methyl methacrylate) sample holders, and their X-ray diffractograms were recorded on Siemens D-500 X-ray diffractometer using copper K_α radiation in conjunction with scintillation counter as detector and graphite monochromator in the diffracted beam direction. The experimental conditions for recording X-ray diffractograms from all cotton cultivars were uniformly kept constant as follows.

Rating:	35 kV, 14 mA
Scanning speed:	0.02°/s
Slit system:	1°, 1°, 1°, 0.15°, 0.15°
Range (2θ):	10-40°

The 3 broad diffraction peaks in the X-ray diffraction (XRD) patterns, corresponding to *d* values of 5.89, 5.31, and 3.85 Å, representing (101), ($10\bar{1}$), and (002) reflections, were resolved by the XRD-FIT data analysis program (Written by SOCABIM, Siemens DIFFRAC AT Software System, Siemens, Germany) for full width at half-maximum (FWHM) and normalized area under the peaks for all samples. Degummed and purified ramie fibers were used as the reference standard, and a normalized area under the (002) peak was measured. Considering this to be 100% crystalline, the normalized area enclosed by the (002) peaks of individual cotton varieties were compared. The relative crystallinity index with respect to ramie were thus computed, and the data are presented in Table I, along with the data on average crystallite sizes corresponding to (101), ($10\bar{1}$), and (002) individual planes, within individual varieties and combined average of all varieties taken together.

RESULTS AND DISCUSSION

It is observed from Table I, columns 4(a) and 4(b), that the crystallite sizes perpendicular to (101) and ($10\bar{1}$) planes, as measured, show maximum variation within individual cotton varieties grown at different locations and in different crop years. This variation in crystallite sizes perpen-

Table II Latitude and Longitude of the Locations of Growth of Cotton in India

Name of the Location	Latitude	Longitude
Sirsa (North India)	29°10′N	75°44′E
New Delhi (North India)	28°39′N	77°13′E
Nagpur (Central India)	21°10′N	79°12′E
Coimbatore (South India)	11°00′N	76°58′E

dicular to (002) plane is, however, the least within individual varieties, as seen from column 4(d). It is known that (101), $(10\bar{1})$, and (002) planes contribute to the intense equatorial diffraction of X-ray intensity, although interferences from (200), (201), (102), $(\bar{2}01)$, and $(\bar{1}02)$ planes, which also diffract in the region, are generally attributed to (002).[32] In columns 4(c) and 4(e) of Table I are given the average crystallite sizes corresponding to (101) and $(10\bar{1})$ planes taken together and (101), $(10\bar{1})$, and (002) planes taken together, respectively. Whereas both these average values of crystallite sizes still vary within the same cultivars grown at different locations in different crop years, in a narrow range, their combined averages, as given at serial numbers 5, 13, 20, 27, 35, 41, and 51, columns 4(c) and 4(e), correspond almost exactly with the average crystallite sizes of (002) planes given in column 4(d) at the same serial numbers as above, irrespective of the species, crop year, and location of growth of cotton. This result and observation is parallel to the observation of Dobb et al.[31] that there are no basic differences in the size of supramolecular crystalline aggregates or crystallographic units of cellulose within different varieties and species of cotton. Crystallite sizes have been measured by several workers in cotton of different varieties and species,[22–24] but the present study is perhaps the first to report variations in the same cotton cultivars grown at different locations and crop years. In Table II are given the latitude and longitude positions of the locations of growth of cotton cultivars. And it may be clearly observed from Tables I and II that differences in the latitudinal positions of the place of cultivation of same cotton varieties do not result in the changes in the average cellulose crystallographic units synthesized in them.

The relative orientation/crystallinity with respect to ramie fibers in cotton varieties are given in Table I, column 5. It may again be observed that values of this relative crystallinity vary within individual varieties when grown in different crop years and at different locations. The average values of relative crystallinity, of individual varieties from all locations and crop years, as given in column 5 of Table I, serial numbers 5, 13, 20, 27, 35, and 41, do not appreciably differ from the combined average values of relative crystallinity of all varieties of both species of cotton grown at different locations and in different crop years, given in column 5, Table I, serial number 51. Perhaps this may be the reason why the small spread of values of crystallinity within cotton varieties reported earlier[22–24] has not led to any meaningful conclusions and for the proposition of the concept of paracrystallinity and disorder function by Hosemann and others.[26–28]

In conclusion, it may be stated that the same cotton varieties, grown at different locations and in different crop years, show variations in their crystallite sizes corresponding to (101), $(10\bar{1})$, and (002) planes, but the combined average crystallite size corresponding to (101) and $(10\bar{1})$ planes taken together is always equal to the average crystallite size of (002) plane.

It is visualized that minor variations observed in individual varieties from different locations and crop years might be arising as a result of the variations in rate of cellulose synthesis observed within the same cotton variety[36,37] with location of growth. Since cellulose synthesis, its deposition, and aggregation into crystalline units is a complex of genotype, environment, and metabolic interactions, the reason for differences between varieties of cotton must be seen in the differences in the rates of cellulose synthesis with location of growth of cotton.[37] This also holds a clue to the explanation of the evident specificity of some cotton cultivars to specific locations of their growth.[38]

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