COMPARATIVE STUDY OF SUPRAMOLECULAR STRUCTURE OF CELLULOSE IN COTTON FIBERS OF *GOSSYPIUM HIRSUTUM* AND *GOSSYPIUM BARBADENSE*

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In this article, fifteen varieties of cotton fibers belonging to *G. hirsutum* and ten varieties of cotton fibers belonging to *G. barbadense* species of different origin have been studied by WAXS and several other methods. Various characteristics of supramolecular structure of these fibers were obtained, such as crystallinity, size and paracrystallinity degree of crystallites, parameters of the crystalline unit cell, microfibrilar angle (MFA) and coefficient of orientation (K_o). From the results, it follows that cotton fibers of *G. barbadense* have a noticeably more ordered structure than *G. hirsutum* fibers. In particular, cotton fibers of *G. barbadense* were more crystalline, while the cellulose crystallites of *G. barbadense* were longer, wider, denser and less disordered than those of *G. hirsutum*. The measurements also showed that cotton microfibrils of *G. barbadense* were better oriented. The revealed structural features of *G. barbadense* cotton fibers explain their higher density, strength and elasticity, compared to *G. hirsutum* fibers.

Keywords: cotton fibers, *G. hirsutum*, *G. barbadense*, textile characteristics, structural features, structure and properties relationship

INTRODUCTION

Cotton fibers are an important source of natural cellulose. World production of cotton fibers reaches 25 million tons per year.[1] Currently, the largest producers of cotton are India, USA and China. The main part of cotton fibers is intended for the textile industry, while short fibers and residues (*e.g.* fuzz) are used for manufacturing microcrystalline cellulose, nanocellulose, cellulose derivatives, special papers, as well as fillers, reinforcing agents, food additives, medical products, cosmetic ingredients, chemicals, explosives and other products.

Among the *Gossypium* genus, the species *G. hirsutum*, *G. barbadense*, *G. arboreum* and *G. herbaceum* are best known.[2] *G. hirsutum*, also known as upland cotton or Acala cotton (in the USA), is the most widespread species of cotton in the world. This kind of cotton contains medium-quality fibers; nevertheless, they can be produced in a high yield due to the plant's good environmental adaptability.

G. barbadense cotton has fibers of superior quality – long, fine, silky and strong, which are used to produce luxury quality fabrics.[3] In the USA, this cotton type is called Pima, because Pima Indians helped to grow this long-fiber cotton on experimental farms in Arizona in the early 20th century. However, *G. barbadense* cotton is a tropical plant, and therefore, for its growth, special cultivation conditions are required – full sun and high humidity. Due to this limitation, *G. barbadense* fibers are rare and expensive.

G. arboreum cotton, also called tree cotton, is a cotton type growing in India and Pakistan. This cotton is relatively cheap and has a high yield of fibers. Although these fibers are short and thick, they are strong enough for use in the textile industry.

G. herbaceum cotton is native to the semi-arid regions of Africa, Saudi Arabia and some other Asian regions. Despite their very high cellulose content, these cotton fibers are considered short

and coarse, and are used mainly in medicine for the production of cotton wool and pads.

In the USA and the countries of Central Asia, cotton varieties of *G. hirsutum* are mainly cultivated, as well as small amounts (5-10%) of *G. barbadense*. Egypt specializes in the cultivation of *G. barbadense* cotton. India is the only country in the world, where all four species of cotton are grown commercially.

Despite numerous data on the morphology and textile characteristics of cotton fibers of different species and varieties, the internal supramolecular structure of these fibers is poorly studied. In some publications, the species, varieties and/or origin of cotton samples are not indicated at all. For example, in the study by Y. Li *et al*.,[4] an undefined cotton sample was used to obtain nanocellulose.

In many cases, the supramolecular structure of the most common *G. hirsutum* cotton species has been studied.[5] In the paper reported by X.P. Su *et al*.,[6] the crystallinity of several cotton varieties was evaluated, and the results were compared with previous data published on the crystallinity of cotton fibers belonging to *G. hirsutum* and *G. barbadense* species. However, the obtained results were contradictory, since the crystallinity index depended not only on the cotton species and varieties, but also on the method and conditions for determining this structural parameter.

Previous research[7] discussed the structure of cellulose in mature cotton fibers belonging to three different species – *G. hirsutum*, *G. barbadense* and *G. arboretum*. Using a core-shell model, it was shown that microfibrils can consist of a ca. 2 nm crystalline core with a partially hydrated amorphous and paracrystalline shell surrounding this core, with a total cross section of 3.6-4.7 nm. However, the proposed model was not original as it repeated the outdated Hearle model of fringed fibrils.[8] Moreover, the core (fibril) – shell (fringe) Hearle model does not apply to cotton fibers; in particular, it cannot explain a sharp decrease in the degree of polymerization up to the level-off degree of polymerization (LODP) and longitudinal splitting of the fibers into micro- and nano-scale crystalline particles during acid hydrolysis. In addition, the study[7] does not explain whether there were noticeable structural differences between the chosen cotton species, or not. Thus, despite the study of three different cotton species, the obtained results are not reliable enough.

As follows from the introduction, the cited papers are not sufficiently informative. Thereby, the main purpose of this research was a detailed study of the supramolecular structure of cotton fibers of various varieties belonging to two different species of cotton, *G. hirsutum* and *G. barbadense*, using improved research methods.

EXPERIMENTAL

Samples

Mature cotton fibers of various varieties and various origins, belonging to *G. hirsutum* and *G. barbadense* species, have been studied. As known, breeders and geneticists are continuously working to develop new varieties of cotton in order to increase the resistance to diseases, pests and enhance the productivity and yield of fibers. There is a huge number of experimental and commercial varieties. They get different names (brands) depending on the company, year and country, where these varieties were developed and grown. For example, the following Central Asian cotton varieties were known in the 20th century: F-108, Tashkent-6, Samarkand-3, Ashgabat-25, Regar-37, C-4727, 8386-B, 9732-I, *etc*. In recent years, new cotton varieties have been created, such as Andizhon-37, Buhoro-127, Namangan-102, Chorezm-150, Genetik-1, Gulbahor-2, Porlok-3, C-8294, *etc*. Other cotton producing regions and countries also have their own names for cotton varieties.

Such obscure names or brands do not characterize the species, quality, structure and/or properties of cotton fibers. Therefore, instead of them, we used the following marking: COh-N and COb-N, where CO is the abbreviation of the country producing the cotton; h stands for *G. hirsutum*, b for *G. barbadense*, and N is the serial number of the variety.

Methods

Characteristics of cotton fibers

Textile characteristics of cotton fibers were obtained using a high-volume testing instrument (HVI), and a Zeiss Axio Lab 5 optical microscope.

X-ray scattering

Wide-angle X-ray scattering (WAXS) studies were carried out using a Rigaku Ultima Plus diffractometer, in the 2θ angle range from 5 to 80°. CuKα radiation had the wavelength λ = 0.15418 nm. Collimation included a system consisting of vertical slits and Soller slits. The procedure of 0.02^{o} step-by-step scanning was used to determine the exact position of the peaks. The weak peaks were identified by the step-by-step scanning method, with the accumulation of impulses at the each step. A few diffractograms of the same sample were recorded in order to obtain reliable results. The incoherent background and scattering from non-crystalline (amorphous) domains were subtracted from diffractograms. Then, the profiles of the isolated

crystalline peaks were improved using corrections on absorption, combined PL factor and Rietveld refinement. The angular positions of the peaks were checked using a narrow line of NaF standard at 2θ of 38.83°. Overlapping peaks were separated using a least-square program.

The degree of crystallinity (X) of the samples was determined by the WAXS method described in:[9]

$$X = \int J_c \, d\theta / \int J_o \, d\theta \quad (1)$$

where J_c and J_o are the corrected and normalized intensities of X-ray diffraction from crystalline regions only and the whole sample, respectively.

The actual lateral dimension (size) of crystallites (D) in the direction perpendicular to [200]-planes was calculated by the following equation:[9]

$$D = \lambda/[(\cos\theta)^2 (B^2 - b^2 - \Delta^2)]^{0.5} \quad (2)$$

where B is the experimental width of the peak, b is the instrumental factor, which can be obtained from the peak width of D-cellobiose crystals using as a crystalline standard; and Δ is the contribution of lattice distortions to broadening of the peak. For cotton samples $\Delta \approx 0.015$.

In addition, the paracrystallinity degree (P, %) of crystallites can be calculated, as follows:[10]

$$P = 400h (D - h)/D^2 \quad (3)$$

where $h \approx 0.4$ nm is the thickness of the paracrystalline layer on the surface of crystallites.

Interplanar spacings (d_i) in crystallites were calculated by the Bragg equation:

$$d_i = \lambda /(2 \sin\theta_i) \quad (4)$$

The indexation of the reflections was made using the results of classic research.[11,12] The parameters of the crystalline unit cell were calculated by standard equations comprising interplanar spacings and Miller indices of reflections.[13]

The microfibril angle (MFA) was estimated from the azimuthal distribution of intensity of the (200) peak at 2θ (200) = const. The parallel bundle of fibers is oriented so that the intensity of diffraction reaches a maximum. Then, an azimuthal angle φ is changed in the step-by-step mode until the intensity of diffraction attains its minimum value. Using the azimuthal intensity distribution, the angular width at half height Δφ is determined. After that, the average MFA angle was calculated, as follows:[9]

$$MFA \approx k \, \Delta\varphi \quad (5)$$

where k is a coefficient close to 1.

Using Herman's equation (6), the coefficient of orientation (K_o) was also calculated:

$$K_o = 1 - 1.5 \sin^2(MFA) \quad (6)$$

Determination of LODP and length of crystallites

Hydrolysis of the cellulose samples up to the level-off degree of polymerization (LODP) was carried out by boiling the samples in 2.5 N HCl for 60 min, followed by washing and drying. The LODP value was measured by the Cuen-viscosity method.[14] The determination of LODP enables to estimate the average length of cellulose crystallites (L, nm):[10]

$$L = 0.517 \, LODP \quad (7)$$

Determination of specific gravity

The specific gravity (ρ) of the dry samples was tested at 25 °C by the pycnometry method in hexane medium.

Determination of α-cellulose

The content of α-cellulose in cotton samples was found using the standard method T-203 of TAPPI.

Statistics

A standard sample of 225 g of each cotton variety was taken to test the textile characteristics of cotton fibers in the HVI. The statistical processing of the results was carried out automatically.

For structural studies and chemical analysis, about 10 samples of each cotton variety were tested to calculate the arithmetic mean and standard deviation.

RESULTS AND DISCUSSION

Some textile characteristics of cotton fibers are shown in Tables 1 and 2. A comparison of the textile characteristics of the cotton fibers confirms that the varieties of *G. barbadense* are longer, thinner, stronger, elastic and contain fewer short fibers than the varieties of *G. hirsutum*.

Chemical analysis showed that all the studied cotton samples had high cellulose content: of 93-96%. Therefore, it is not surprising that the X-ray diffractograms of the two cotton species, *G. hirsutum* and *G. barbadense*, contained the peaks ($1\bar{1}0$), (110), (200), (004) and others that are characteristic of the C1β crystalline allomorph of cellulose (Fig. 1).

The results of the investigation of the supramolecular structure of the cotton fibers are presented in Tables 3 and 4. From these results, it follows that cotton fibers from the varieties of *G. barbadense* have a noticeably more ordered structure than the cotton fibers from the varieties of *G. hirsutum*. In particular, the fibers of *G. barbadense* are denser and crystalline, while the crystallites of these fibers are longer and wider. In addition, the measurements of MFA and K_o showed that the microfibrils in the cotton fibers of *G. barbadense* are better oriented than those in the cotton fibers of *G. hirsutum* (Table 5).

Table 1
Textile characteristics of *G. hirsutum* cotton varieties

Country	Marking of variety	SF, %	l, mm	w, µm	TS, cN/tex	e, %
Uzbekistan	UZh-1	7	27.9	22	26	5
	UZh-2	5	27.2	20	23	3
	UZh-3	6	28.4	21	24	4
	UZh-4	6	28.2	23	25	4
Tajikistan	TAh-1	7	27.4	20	23	4
	TAh-2	7	26.9	24	25	3
	TAh-3	6	27.9	22	24	5
USA	USh-1	5	29.5	19	27	4
	USh-2	5	29.7	19	28	5
	USh-3	6	28.9	21	26	5
Israel	ISh-1	6	29.2	20	27	4
	ISh-2	5	28.7	20	25	4
Mexico	MEh-1	6	28.2	22	25	3
Turkey	TUh-1	7	27.9	24	24	3
Australia	AUh-1	6	28.7	21	26	5
Mean		6.0 ± 0.7	28.3 ± 0.8	21.3 ± 1.6	25.2 ± 1.5	4.1 ± 0.8

Note: SF – content of short fibers, l – staple length, w – average width, TS – tensile strength, e – elongation at break

Table 2
Textile characteristics of *G. barbadense* cotton varieties

Country	Marking of variety	SF, %	l, mm	w, µm	TS, cN/tex	e, %
Uzbekistan	UZb-1	2	35.5	16	31	6
	UZb-2	1	34.5	17	30	5
Tajikistan	TAb-1	2	34.8	16	29	6
	TAb-2	2	34.5	18	31	6
USA	USb-1	1	40.9	15	34	7
	USb-2	1	38.1	16	33	6
Israel	ISb-1	1	40.6	16	33	7
Egypt	EGb-2	1	39.1	15	34	6
Sudan	SUb-2	2	36.0	17	32	5
China	CHb-2	2	38.1	16	32	6
Mean		1.5 ± 0.5	37.2 ± 2.3	16.2 ± 0.8	32.0 ± 1.6	6.0 ± 0.6

Note: SF – content of short fibers, l – staple length, w – average width, TS – tensile strength, e – elongation at break

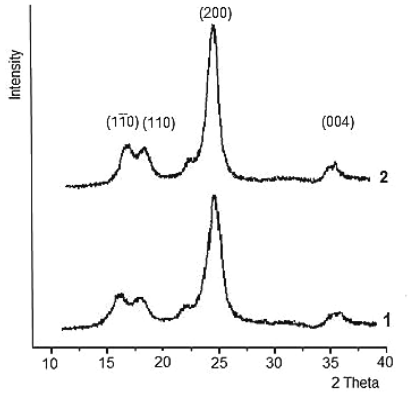

Figure 1: X-ray diffractograms of mixed cotton varieties of *G. hirsutum* (1) and *G. barbadense* (2)

Table 3
Characteristics of supramolecular structure of *G. hirsutum* cotton varieties

Country	Marking of variety	X, %	D, nm	LODP	L, nm	MFA°	ρ, g/cm³
Uzbekistan	UZh-1	67.2	5.6	188	97	24	1.55
	UZh-2	66.5	6.0	193	100	25	1.54
	UZh-3	68.0	5.5	190	98	24	1.56
	UZh-4	67.6	5.7	186	96	23	1.55
Tajikistan	TAh-1	67.4	5.5	190	98	25	1.54
	TAh-2	66.8	6.3	189	98	23	1.56
	TAh-3	68.1	5.5	190	98	24	1.53
USA	USh-1	67.3	6.1	193	100	23	1.54
	USh-2	69.0	5.8	188	97	22	1.56
	USh-3	68.4	6.0	190	98	21	1.56
Israel	ISh-1	67.7	5.8	186	96	23	1.55
	ISh-2	68.3	6.1	191	99	22	1.54
Mexico	MEh-1	67.5	5.2	184	95	23	1.56
Turkey	TUh-1	68.1	5.6	190	98	24	1.53
Australia	AUh-1	68.3	5.8	188	97	22	1.55
Mean		67.7 ± 0.6	5.8 ± 0.3	189 ± 3	98 ± 1	23 ± 1	1.55 ± 0.01

Table 4
Characteristics of supramolecular structure of *G. barbadense* cotton varieties

Country	Marking of variety	X, %	D, nm	LODP	L, nm	MFA°	ρ, g/cm³
Uzbekistan	UZb-1	69.4	6.4	232	120	18	1.57
	UZb-2	70.2	6.2	213	110	16	1.56
Tajikistan	TAb-1	70.0	6.6	207	107	17	1.55
	TAb-2	69.7	6.7	213	110	18	1.57
USA	USb-1	69.5	6.8	201	104	17	1.55
	USb-2	71.3	6.5	212	110	17	1.58
Israel	ISb-1	70.3	6.7	232	120	18	1.57
Egypt	EGb-2	71.0	6.5	222	115	16	1.56
Sudan	SUb-2	70.1	6.2	207	107	17	1.57
China	CHb-2	70.6	6.6	213	110	17	1.58
Mean		70.2 ± 0.6	6.5 ± 0.2	215 ± 9	111 ± 5	17 ± 1	1.57 ± 0.01

These structural features allow explaining why the strength of *G. barbadense* cotton fibers is approximately 30% higher than that of *G. hirsutum* fibers.

To determine the parameters of the crystalline unit cell, mixed cotton varieties of *G. hirsutum* and mixed cotton varieties *G. barbadense* were used. For these two samples, X-ray peaks in the step-by-step scanning mode were obtained, and the interplanar spacings in cellulose crystallites were measured. Some interplanar spacings in crystallites are shown, for example, in Tables 6 and 7.

Knowing the numerical values of interplanar spacings, the parameters of the crystalline unit cell were calculated by the standard procedure.[13]

Table 5
Orientation parameters and tensile strength of cotton fibers

Cotton species	MFA°	K_o	TS, cN/tex
G. hirsutum	23.2	0.77	25.2
G. barbadense	17.1	0.87	32.0

Table 6
Interplanar spacings (d) in crystallites of cotton fibers of *G. hirsutum*

Miller's index	2θ°	d, nm
$1\bar{1}0$	14.81 ± 0.01	0.598 ± 0.001
110	16.58 ± 0.01	0.535 ± 0.001
012	20.33 ± 0.01	0.437 ± 0.001
102	20.62 ± 0.01	0.431 ± 0.001
200	22.63 ± 0.01	0.393 ± 0.001
021	23.46 ± 0.01	0.380 ± 0.001
210	26.51 ± 0.01	0.337 ± 0.001
211	27.90 ± 0.01	0.321 ± 0.001
013	28.00 ± 0.01	0.319 ± 0.001
122	31.12 ± 0.01	0.288 ± 0.001
004	34.70 ± 0.01	0.2585 ± 0.0005
040	44.41 ± 0.01	0.2040 ± 0.0001

Table 7
Interplanar spacings (d) in crystallites of cotton fibers of *G. barbadense*

Miller's index	2θ°	d, nm
$1\bar{1}0$	14.84 ± 0.01	0.597 ± 0.001
110	16.60 ± 0.01	0.534 ± 0.001
012	20.33 ± 0.01	0.437 ± 0.001
102	20.65 ± 0.01	0.430 ± 0.001
200	22.73 ± 0.01	0.391 ± 0.001
021	23.47 ± 0.01	0.379 ± 0.001
210	26.52 ± 0.01	0.336 ± 0.001
211	27.88 ± 0.01	0.320 ± 0.001
013	28. 06 ± 0.01	0.318 ± 0.001
122	31.16 ± 0.01	0.287 ± 0.001
004	34.70 ± 0.01	0.2585 ± 0.0005
040	44.45 ± 0.01	0.2038 ± 0.0001

Table 8
Comparative characteristics of *G. hirsutum* and *G. barbadense* species

Characteristics	*G. hirsutum*	*G. barbadense*
X (%)	67.7	70.2
L/D	16.8	17.1
P (%)	2.6	2.3
ρ_c (g/cm^3)	1.613	1.621
K_o	0.77	0.87
l/w	1330	2300
SF (%)	6.0	1.5
TS (cN/tex)	25.2	32.0
e (%)	4.1	6.0
ρ (g/cm^3)	1.55	1.57

The results obtained for the cotton fibers of *G. hirsutum* were as follows: a = 0.791 nm, b = 0.822 nm, c = 1.034 nm, γ = 96.6°. The specific volume of crystallites was V_c = 0.620 cm^3/g, specific gravity ρ_c = 1.613 g/cm^3 and paracrystallinity degree P = 2.6%.

As regards the cotton fibers of *G. barbadense*, the following values were obtained: a = 0.788 nm, b = 0.821 nm, c = 1.034 nm, γ = 96.6°. The specific volume of crystallites was V_c = 0.617 cm^3/g, specific gravity ρ_c = 1.621 g/cm^3 and paracrystallinity degree P = 2.3%.

The obtained parameters are in the range of values found for the crystalline domains of various natural celluloses, having predominantly CIβ allomorph.[15,16]

A comparison of the various characteristics of two cotton species, namely, *G. hirsutum* and *G. barbadense*, reveals that the crystalline structure of cellulose in *G. barbadense* fibers is denser, more ordered and less distorted than of that of cellulose in *G. hirsutum* fibers (Table 8). Due to these structural features, the cotton fibers belonging to *G. barbadense* species are denser, stronger and more elastic than the cotton fibers belonging to *G. hirsutum* species.

CONCLUSION

Different varieties of cotton fibers belonging to two different species, *G. hirsutum* and *G. barbadense*, were studied using WAXS and several other methods. The obtained results showed that cotton fibers of *G. barbadense* have a noticeably more ordered structure than cotton fibers of *G.* hirsutum. In particular, the fibers of *G. barbadense* were more crystalline, while the crystallites in the cellulose of *G. barbadense* fibers were longer, wider, denser and less disordered than those in the cellulose of *G. hirsutum* fibers. Furthermore, the measurements showed that the microfibrils in the cotton fibers of *G. barbadense* were better oriented. The revealed structural features of cotton fibers belonging to *G. barbadense* species explain their higher density, strength and elasticity, compared to cotton fibers belonging to *G. hirsutum* species.

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