STRUCTURAL INVESTIGATIONS OF VARIOUS COTTON FIBERS AND COTTON CELLULOSES

Michael Ioelovich,* and Alex Leykin

Macro- and crystalline structure, as well as chemical composition of fibers related to various types and sorts of Israeli cottons, both white and naturally colored, were investigated. The differences in structural parameters and chemical compositions of the cotton fibers were evaluated. Samples of cotton of the "Pima"-type had long, thin and strong fibers with highly ordered supermolecular structure. Fibers of middle-long and hybrid cottons had some lower-ordered structural organization in comparison to long-length cotton, while fibers of naturally colored cotton were characterized with disordered supermolecular and crystalline structure. Dependence of tensile strength on orientation of nano-fibrils towards the fiber axis was found. Conditions of cellulose isolation from the different cotton fibers were studied. Structural characteristics of isolated cotton celluloses and obtained MCC are discussed.

Keywords: Cotton fibers, White cotton, Natural colored cotton, Cotton cellulose, Microcrystalline cellulose, Structure, Chemical composition

Contact information: Polymate Ltd, P.O.Box 73, Migdal HaEmek 23100, Israel;
**Corresponding author: bd895892@zahav.net.il*

INTRODUCTION

Cotton is a vegetable fiber that comes from the seed capsules, or bolls, of an array of plants in the genus *Gossypium* of the family *Malvaceae* (Ioelovich et al. 1994). In modern times, cotton fibers remain as one of the most important types of fibers in the world, despite the high volume of wood cellulose and increasing number of synthetic fiber types available. Novel technologies of cultivation and treatment ensure widespread abundance of cotton and expand its application areas. Cotton fibers are the base material to produce a boundless range of products and commodities. These fibers historically are most popular for the textile industry due to softness, absorbency, strength and dyeability. Naturally colored cotton fibers are beyond comparison in the production of eco-textile goods, because such fiber types don't contain harmful synthetic dyes.

Currently cotton is the base raw material for a wide assortment of products, such as paper, chemicals, food additives, medical supplies, some cosmetic ingredients, tire cord, special reinforced plastics, and rubbers, etc. The major source of papermaking fibers is wood. However, also cotton fibers fill a significant place in papermaking. Cotton can be used for production high-quality and specialty paper types, such as tissue paper, technical papers, albums, drawing, and some printing papers, banknote and document papers, etc. (Cerchi and Tullio 2006). High-quality microcrystalline cellulose (MCC) produced from cotton cellulose can be used as an inactive excipient for tablets, gentle

filler cosmetic creams, and as an additive to dietary food (McGinley et al. 1993; Kleinebudde et al. 2000).

As is known, the chemical composition, macro-, and microstructure of cotton fibers have signficant influence on the technological parameters and properties of the final cellulose products. Despite the existence of a high volume of scientific information, some specific features of different sorts and types of cotton fibers have not been sufficiently clarified. To select the optimal type of cotton as a raw-material required for the certain application area, versatile investigations of its structural characteristics should be carried out.

The main purpose of this paper is to provide a detailed structural analysis of various types of cotton fibers and isolated cotton celluloses using improved investigation methods.

EXPERIMENTAL

Materials

The various sorts of white middle-length ("Acala") and long-length ("Pima") cotton fibers, their hybrids, as well as fibers of natural colored cotton ("Acala" green and brown) cultivated in Israel have been studied. Soda cooking of the natural cotton fibers was carried out at 150 ^{o}C for 3 h using a cooking solution containing 1% NaOH, 0.5% H_2O_2 and 0.5% non-ionic surfactant Tergitol NP-9 (Nonylphenol Ethoxylate, M.W. 616).

Microcrystalline cellulose (MCC) was obtained from isolated cotton celluloses by treatment with boiled 2 N HCl for 30 min; then the acidic product was washed up to neutral pH, dispersed in water by Waring-blender, and spray-dried.

Methods

The investigations were carried out by methods of optical and electron microscopy, advanced X-ray diffraction, chemical analysis, and standard methods for determination characteristics of cotton fibers. Scanning electron micrographs were obtained with a Hitachi S-430 apparatus. Diffractometer Rigaku-Ultima Plus (CuK_α – radiation, λ=0.15418 nm) was used for X-ray investigations. The degree of cellulose crystallinity (X), corrected length (L) and lateral size of nano-crystallites (H), as well as orientation parameters of nano-fibrils were calculated according to improved methods (Ioelovich 1992; Ioelovich 1999).

RESULTS AND DISCUSSION

As can be seen from the microphotography, the cotton fibers had the appearance of twisted bands (Fig. 1). The fibers had lengths of 20-40 mm, widths of 10-30 μm, and thicknesses of the cell wall of 4-6 μm. A hollow, capillary-like lumen extends the length of the fiber. The wall of the natural cotton fibers is built from an external waxy layer - cuticle, primary P, and secondary S walls (Usmanov and Razikov 1974; Ioelovich and Leykin 2006). The thin cuticle and P-wall were observed to have nano-size thickness. The S-wall has thickness of 3-5 μm and is composed of three layers S1, S2 and S3. The dominating wall's

S2-layer of 2-4 μm contains lots of thin lamellas built from nano-fibrillar bundles, having different orientation towards the fiber axis. These bundles consist of elementary fibrils having lateral size 5-8 nm and form steep spirals orientated along the fiber axis.

Cotton fibers can be subdivided on two main types, middle-length and long-length fibers. The numerous sorts of the both cotton types and also hybrid sorts are selected, improved and cultivated in Israel. Besides, naturally colored cotton sorts are created in Israel using methods of selection and genetic engineering. We studied various sorts of long-length cotton of "Pima" type and middle-length cotton of "Acala" type. Besides some hybrid sorts and naturally colored (brown and green) cotton fibers were investigated too. The "Pima" sorts had the longest and the most uniform and strength fibers, while sorts of colored cotton contained shortest and weakest fibers (Table 1).

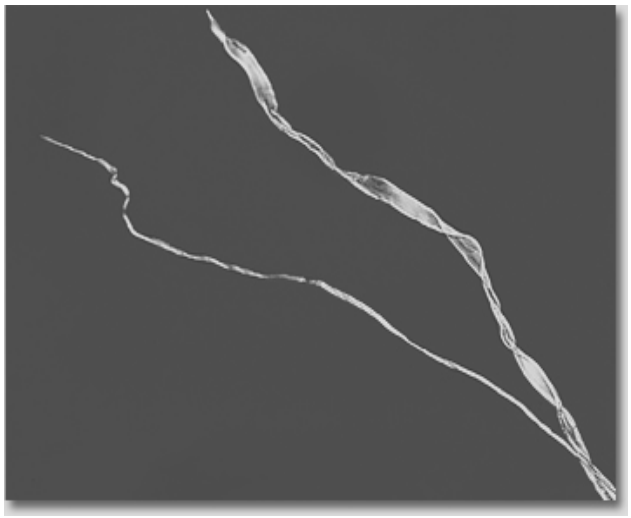

Fig. 1. Microphotograph of twisted middle-length cotton fibers of "Acala" type

Table 1. Main Characteristics of Cotton Fibers

Characteristics	Sorts "Pima"	Sorts "Acala"	Hybrid Sorts	Colored Cotton
Upper length, in	1.30-1.35	1.05-1.16	1.20-1.33	0.97-1.03
Length uniformity, %	85-87	80-82	82-86	78-80
Fineness, micronair	3.4-3.9	4.0-4.6	3.4-4.0	4.1-4.5
Tensile strength, g/tex	30-33	24-28	28-30	18-22

Fibers of white cotton of various types and sorts were found to have a high amount of α-cellulose (94-96%) and did not contain lignin. In contrast to white samples, the fibers of natural colored cotton contained lignin had decreased amount of α-cellulose and increased ash content (Table 2). Derivatives of lignin probably are responsible for the color of brown colored fibers and introduce a tint to green fibers. Green cotton is characterized by a high amount of extractive waxy component consisting mainly of suberin (Elesini et al. 2002).

Table 2. Chemical Composition of Dry Cotton Fibers

Component	Sorts "Pima"	Sorts "Acala"	Hybrid Sorts	Brown Cotton	Green Cotton
Cellulose, %	96.4	94.3	94.5	87.7	77.0
Pectin, %	0.8	2.2	1.6	2.3	2.5
Protein, %	1.2	1.4	1.5	1.3	1.4
Extractive, %	0.5	0.6	0.7	1.2	14.0
Ash, %	1.1	1.5	1.7	2.5	3.1
Lignin, %	0	0	0	5.0	2.0

Based on improved X-ray diffraction, a detailed analysis of nano-structure of cotton fibers was performed. As follows from the investigations (Table 3), fibers of "Pima" type cotton had the most ordered supermolecular structure, while fibers of natural colored cotton were characterized by decreased crystallinity, decreased crystallite sizes, and low orientated nano-fibrils.

Table 3. Structural characteristics of cotton fibers*

Characteristics	"Pima"	"Acala"	Hybrid Sorts	Brown Cotton	Green Cotton
X, %	68	66	67	65	63
H, nm	7	6	6	5	5
L, nm	120	100	110	90	83
K_{or}	0.96	0.88	0.94	0.85	0.79
a, nm	0.788	0.790	0.789	0.791	0.792
b, nm	0.818	0.819	0.818	0.820	0.820
c, nm	1.034	1.034	1.034	1.034	1.034
γ^o	96.2	96.1	96.1	96.0	96.0
ρ_{cr}, g/cm^3	1.624	1.618	1.622	1.613	1.611
ρ_o, g/cm^3	1.57	1.56	1.57	1.55	1.55

* X-crystallinity degree; L-length and H-lateral sizes of nano-crystallites; a, b, c – parameters of C1-crystalline unit cell; γ - monoclinic angle; ρ_{cr}, ρ_o - specific weight of the C1-crystallites and the fiber; K_{or} - orientation coefficient of nano-fibrils towards the fiber axis

As follows from the investigations, the orientation coefficient of nano-fibrils directly influenced the tensile strength of the cotton fibers (Fig. 2). The correlation TS $=f(K_{or})$ can be expressed by a linear equation:

$$TS\ (g/tex) = AK_{or} + B \quad (1)$$

where A = 80; B = -44.

The orientation coefficient is defined as:

$$K_{or} = 1 - 1.5 \sin^2\varphi \quad (2)$$

where φ is the average disorientation angle of crystallite's "c"-axis or nano-fibrils towards the fiber axis.

With decreasing φ-angle, the orientation coefficient increased and the greater part of the strong covalent intra-fibrillar bonds were orientated along the fiber axis that contributes to strength of the cotton fibers.

Celluloses isolated from the white cotton fibers following soda cooking had high α-cellulose content (98.5-99.2%) and better-ordered crystalline structure (Tables 4, 5). Isolation of pure cellulose from naturally colored cotton fibers is a difficult process due to presence increased amounts of lignin, waxes, and mineral impurities. As a result, a lower yield of α-cellulose can be achieved from the colored cotton after soda cooking, e.g. only 90-92%.

Table 4. Chemical Composition of Isolated Cotton Cellulose in Dry State

Component	Sorts "Pima"	Sorts "Acala"	Hybrid Sorts	Brown Cotton	Green Cotton
α-Cellulose, %	99.2	98.5	99.0	92.0	90.0
β-Cellulose, %	0.6	1.2	0.8	7.5	9.4
Ash, %	0.1	0.2	0.2	0.5	0.6

Table 5. Crystalline Structure of Isolated Cotton Cellulose

Characteristics	"Pima"	"Acala"	Hybrid Sorts	Brown Cotton	Green Cotton
X, %	72	70	71	68	66
H, nm	9	7	8	6	6
L, nm	126	110	117	96	90
a, nm	0.785	0.788	0.787	0.789	0.790
b, nm	0.818	0.818	0.818	0.819	0.819
c, nm	1.034	1.034	1.034	1.034	1.034
γ^{o}	96.3	96.2	96.2	96.0	96.0
ρ_{cr}, g/cm^3	1.631	1.625	1.627	1.620	1.618

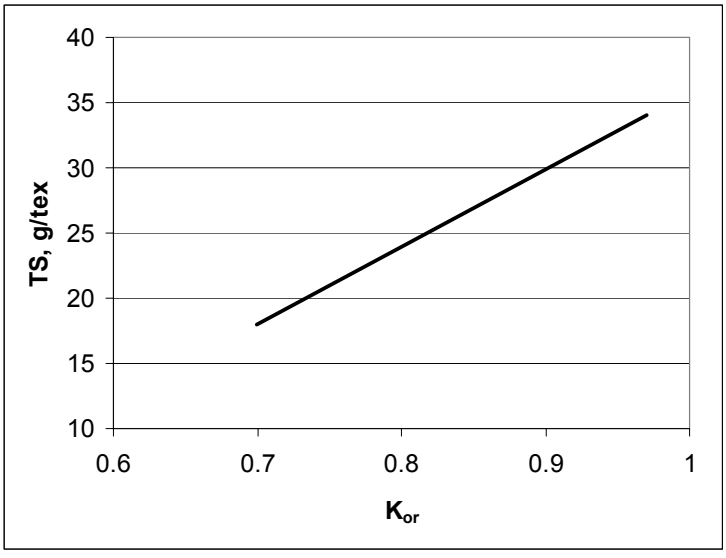

Fig. 2. Correlation between orientation coefficient (K_{or}) and tensile strength (TS) of various cotton fibers

Cotton cellulose having high degree of purity is a suitable starting material to produce cellulose derivatives and GRAS-grade microcrystalline cellulose (MCC), which are used in pharmaceuticals and/or the food industry. MCC obtained from white cotton

cellulose "Pima" and "Acala" with increased yield had a highly ordered crystalline structure and met the pharmacopeia's requirements for cellulose powders used as inactive medical excipients (Tables 6-8).

Table 6. Crystalline Structure of Cotton MCC

Characteristics	"Pima"	"Acala"	Hybrid Sorts	Brown Cotton	Green Cotton
X, %	85	80	81	76	72
H, nm	12	10	11	9	8
L, nm	126	110	117	96	90
a, nm	0.782	0.783	0.783	0.786	0.788
b, nm	0.817	0.817	0.817	0.817	0.817
c, nm	1.034	1.034	1.034	1.034	1.034
γ^o	96.3	96.3	96.3	96.2	96.2
$\rho_{cr,}$ g/cm^3	1.640	1.635	1.635	1.630	1.628

Table 7. Characteristics of MCC Samples

MCC-sample	Yield, %	DP*	Av. particle size, μm	Bulk density, g/cm^3	Tap density, g/cm^3
Pima -MCC	92	220	50	0.32	0.45
Acala-MCC	90	200	53	0.30	0.41
MCC of colored cotton	86	180	60	0.27	0.40
*DP – average degree of polymerization					

Table 8. Microcrystalline Cellulose – Specification per USP 23/NF 18

Properties	**Specification**	**MCC of Pima**	**MCC of Acala**	**MCC of colored cotton**
Appearance	A fine, white odorless, crystalline powder	Passes	Passes	**No-Passes due to a tint**
pH of aqueous extract	5.0 – 7.0	6.0	6.0	6.0
Loss on drying	7% w/w max.	2% w/w	3% w/w	5% w/w
Water soluble substances	0.24% w/w	0.1% w/w	0.2% w/w	0.3% w/w **(No-passes)**
Starch	Absent	Absent	Absent	Absent
Residue on ignition	0.05% w/w	0.03% w/w	0.04% w/w	0.07% w/w **(No-passes)**
Heavy metals	<10 ppm	5 ppm	8 ppm	12 ppm **(No-passes)**
Ether soluble	0.05%	0.01%	0.01	0.1 **(No-passes)**
MICROBIAL LIMIT				
Total aerobic microbial count	100 per g max	Passes	Passes	Passes
Total combined molds yeast count	20 per g max	Passes	Passes	Passes
Staphylococcus Aureous	Absent	Absent	Absent	Absent
Pseudomonas	Absent	Absent	Absent	Absent

The long-length cotton cellulose "Pima" had an excellent purity degree, which makes it possible to obtain high-quality MCC having the most crystalline structure. Contrary to MCC from white cotton celluloses, microcrystal-line powders can be prepared from colored cotton celluloses with lower yield and had insufficiently ordered structure. Besides, MCC of colored cotton did not meet the requirements of USP 23/NF18 due to lower purity degree.

Cooking of the cotton fibers and partial hydrolysis of cellulose in the process of preparing MCC-obtaining led to ordering of the crystallite structure, which is observed as an increase in the degree of crystallinity, lateral size, and specific weight of crystallites. This is caused by a lateral co-crystallization process of initial nano-crystallites (Ioelovich et al. 1989; Ioelovich 1991). A linear dependence of specific weight on dispersity degree (1/H) of cellulose crystallites was observed (Fig. 3). The bigger crystallites had less distortion of the lattice, which promotes increasing their specific weight (Ioelovich 1999).

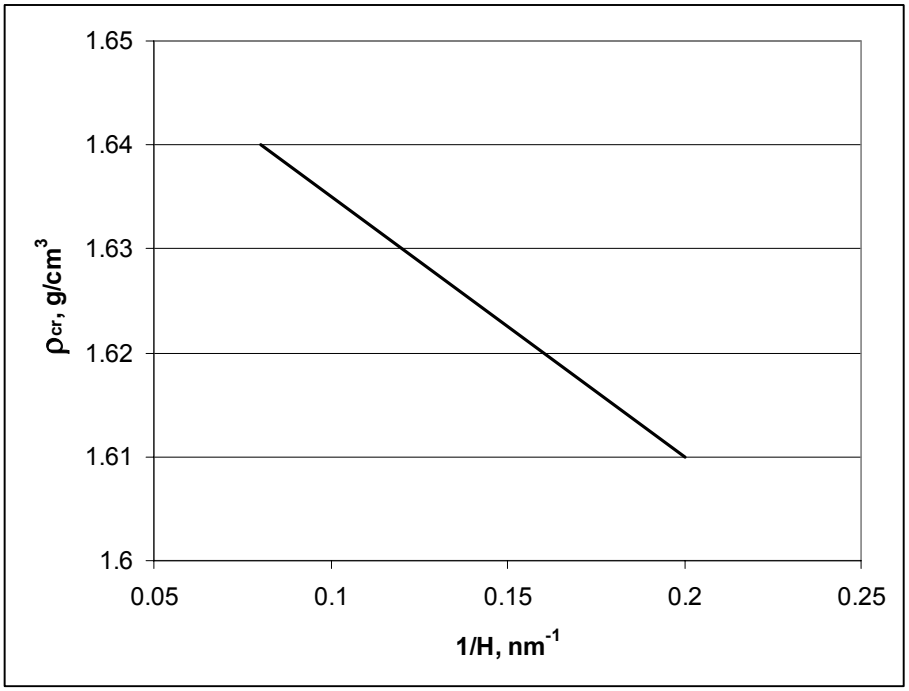

Fig. 3. Dependence of specific weight (ρ_{cr}) on lateral size (H) of cellulose crystallites

Based on ρ_{cr} and X values, the specific weight of the sample (ρ_o) can be calculated:

$$\rho_o = \rho_{am} + 0.01X\,(\rho_{cr} - \rho_{am}) \quad (3)$$

where ρ_{am} = 1.45 g/cm^3 is average specific weight of amorphous (non-crystalline) domains of the cellulose nano-fibrils.

The calculated specific weight of the cotton fibers is close to experimental value (Table 3).

CONCLUSIONS

1. The structure and chemical composition of various types of cotton fibres: "Pima", "Acala", hybrid, and naturally colored cotton, were studied.
2. Samples of white cotton "Pima" had long, thin and strong fibers with high-ordered crystalline structure, while "Acala" and hybrid cotton have some lower-ordered structural organization.
3. In contrast to white cottons, the naturally colored cotton fibers were short and weak, contain lignin and increased amounts of waxes; moreover, they were characterized with a more disordered crystalline structure.
4. To obtain pure cellulose from white cotton fibers, milder cooking conditions are required than in the case of naturally colored cotton.
5. The cellulose isolated from long-length cotton "Pima" had an excellent purity degree that permits obtaining high-quality pharmaceutical-grade MCC.
6. The tensile strength of the cotton fibers was determined by orientation degree of nano-fibrils towards fiber axis.

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