

X-ray Diffraction Analysis of Yemeni Cotton Fibers

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Abstract: The lowland and coastal regions are the areas where cotton is cultivated in Yemen. The land used for this purpose exceeds 120 acres and expandable in the upcoming seasons. We have selected the earlier two varieties of cotton fibers cultivated in two different areas Abyan and Zabid. Wide Angle X-ray Scattering (WAXS) data from these fibers have been recorded and analysed to obtain the micro-structural parameters with the application of Line Profile Analysis (LPA). Linked Atom Least Squares (LALS) program has been used to obtain molecular structure and packing in these fibers. For the first time micro-structural parameters of these cotton fibers cultivated in Yemen are computed and reported. This study will be of help to understand the structure-property relation in these cotton fibers.

Keywords: Cotton fibers, Crystal structure, Disorder, Microstructure, WAXS

Introduction

Cotton cultivation played a dominant role to upturn the economical level of Yemen during 1989 [1]. There are four different varieties of cotton cultivated in Yemen and these belong to long staple fibers (*Gossypium herbaceum*- cotton) [2]. There is a continued interest in the study of cotton fibers to understand molecular and crystal structure of these fibers [3-5]. Recently, it is reported structure- property relation in Indian cotton fibers [6,7]. In this paper, we have used X-ray data of these cotton fibers along with an in-house built mathematical model to simulate the experimental intensities profiles. Further, we have utilized Linked Atom Least Squares (LALS), program implemented in our PC (Linux OS), to construct a molecular model and hence to compute crystal structure parameters of these fibers. Based on these structure parameters, we have computed elastic constant-matrix for these two fibers. X-ray diffraction technique is adequate to refine for the crystalline structures starting from known parameters and relate these aspects to properties of polymers or fibers. In recent years high-intensity X-ray beams and area detectors with increased computing power have emerged and are quite used. There are several earlier papers on polymer fibers wherein refinements of structure, not structure studying, have been carried out with LALS program employing X-ray powder like data [7-14].

Experimental

Materials

Raw cotton of Abyan and Zabid varieties is plucked manually after ripening. This cotton is freed from the buds and taken for ginning. Ginning is a process where raw cotton

is separated from seed. After removing the seed, it is taken for baling till it becomes lint. The lint raw cotton sample is used for our study here, without any additional treatment.

Recording of X-ray Diffraction Pattern

The small bundles of sample are clamped into a sample holder. Sample holder is mounted on a goniometer (radius 240 mm) such that the rotational axis of the goniometer is parallel to fibers axis and perpendicular to X-ray beam. X-ray diffraction facility (X'pert PRO) at Central Electrochemical Research Institute, Karaikudi 630 006, Tamil Nadu, India has been used to record X-ray pattern. The scanning range is 8-45 ° with a step size (0.02 °). Wavelength of X-ray radiation is $\lambda=1.5406 \text{ \AA}$ using Cu K_{α} . The exposure time of X-ray radiation was 20 min. The X-ray generator is operated at 40 kV and 30 mA. The recorded X-ray diffraction patterns are given in Figures 1 and 2.

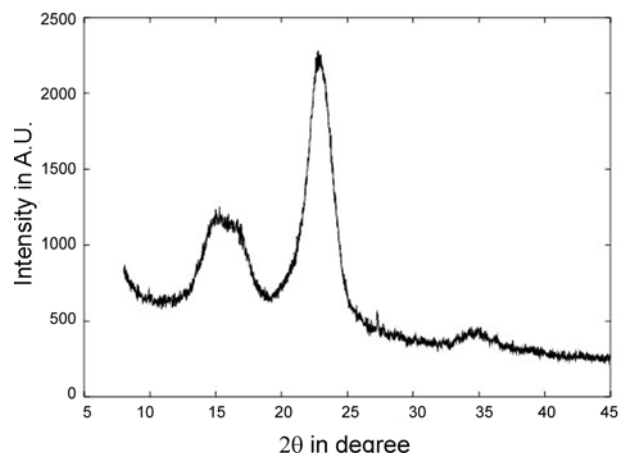


Figure 1. The X-ray diffraction pattern of Abyan cotton fibers.

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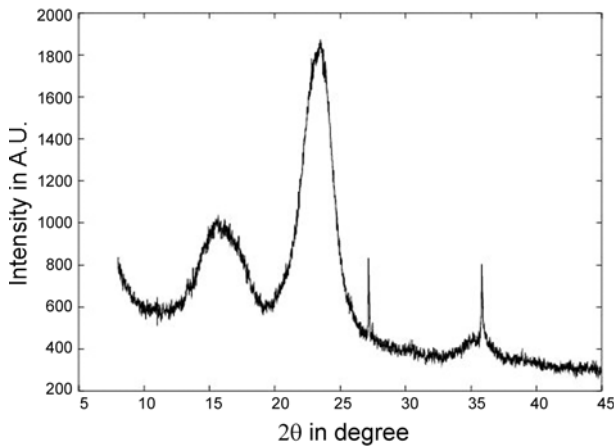


Figure 2. The X-ray diffraction pattern of Zabid cotton fibers.

Analysis

We have analysed the X-ray data in two parts. In part I, we have carried out Line Profile Analysis (LPA) [15] of all the observed Bragg reflections in two different samples Abyan and Zabid, to compute the micro-structural parameters. In part II, we have analysed the X-ray intensity data of Bragg reflections by constructing a molecular model and have accounted for the observed Bragg intensities using (LALS) method. We have not included corrections for thermal disorder in this paper.

Part I: Line Profile Analysis

Intensity profile, in a direction along the line joining the origin to the center of the reflection, can be expanded using Fourier cosine series, that is normally referred to as Fourier method (Warren and Averbach) [16-18].

$$I_{cal}(s) = \sum_{n=-\infty}^{\infty} A(n) \cos\{2\pi nd(s-s_o)\} \quad (1)$$

where $A(n)$ are the harmonic coefficients. $A(n)$ is a function of crystal size and lattice distortion. Here, d is the interplanar spacing, s is the value of $(\sin\theta)/\lambda$, s_o is the value of s at peak position of the reflection, θ is Bragg's angle, λ is the wavelength of the radiation and n is the harmonic number. The Fourier coefficients $A(n)$ of the profile are convolution of crystal size $A_s(n)$ and lattice strain $A_d(n)$ coefficients and are given by

$$A(n) = A_s(n) \cdot A_d(n) \quad (2)$$

The lattice disorder component of the Fourier coefficient is:

$$A_d(n) = \exp(-2\pi^2 m^2 n g^2) \quad (3)$$

Here m is the order of reflection and $g(=\Delta d/d)$ is the lattice strain.

In order to interpret some symbols, which are essential for

the analysis, we have considered the crystalline region in a polymer to be made up of columns of unit cells, along the direction of the scattering vector. Let i be the number of unit cells in a column. The number of cells N_n having n neighbours is,

$$N_n = i - n \quad (4)$$

If $P(i)$ is the probability distribution function of column lengths, then the average number of cells having n neighbours is,

$$N_n = \int_{i=n}^{+\infty} (i-n)P(i)di \quad (5)$$

Simplifying this we have,

$$N_n = \int_0^{\infty} [iP(i)di - nP(i)]di - \left[\int_0^n iP(i)di - n \int_0^n P(i)di \right] \quad (6)$$

$$\text{Defining } \langle N \rangle = \int_0^n iP(i)di,$$

we have,

$$\frac{\langle N_n \rangle}{\langle N \rangle} = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n iP(i)di - n \int_0^n P(i)di \right] \quad (7)$$

For a probability distribution of column lengths $P(i)$, the crystal contribution to the Fourier coefficient is $\langle N \rangle = D/d$.

where, D is the crystallite size. The second derivative of the Fourier coefficient $A_s(n)$ is proportional to the surface-weighted column-length distribution $P_s(L)$, and is given by

$$P_s(L) \propto \left(\frac{d^2 A_s(L)}{dL^2} \right); \quad L = nd \quad (9)$$

The volume-weighted column-length distribution function $P_v(L)$ is,

$$P_v(L) \propto L \left(\frac{d^2 A_s(L)}{dL^2} \right); \quad L = nd \quad (10)$$

In cotton fibers, it is very rare to find multiple reflections and hence we cannot use Warren and Averbach multiple order method [19]. In order to get over this difficulty, we have developed a single order method wherein it is assumed that an exponential function is the probability function $P(i)$ [19]. In fact, various other types of symmetric and asymmetric functions have been examined by us and it has been suggested that a symmetric exponential function gives good results [20]. This distribution depends on the fact that there are no columns containing fewer than p unit cells and those with more than p will decay exponentially. Hence $P(i)$ can be expressed as,

$$P(i) = \begin{cases} 0 & \text{if } p < i \\ \alpha \exp\{-\alpha(n-p)\} & \text{if } p \geq i \end{cases} \quad (11)$$

where $\alpha = 1/(N-p)$ is the width of the distribution. Then the simplified expression for size Fourier coefficient is given by,

$$A_s(n) = \begin{cases} A(0)\left(1 - \frac{n}{N}\right) & \text{if } n \leq p \\ A(0)\exp\{-\alpha(n-p)\}/(\alpha N) & \text{if } n > p \end{cases} \quad (12)$$

The surface- and volume-weighted values are computed using equations (9) and (10).

The reliability of this approach is verified by Round Robin method [21,22]. The experimental profiles between s_o the scattering vector at the peak and $s_o + s_o/2$ is matched with the simulated profiles using equations (1), (2), (3), (4), and (6) for various values of $\langle N \rangle$, g , α and a background correction parameter (BG) to minimize the difference between the observed and the simulated data. For this purpose we have used a multidimensional minimization program SIMPLEX [23]. The goodness of the fit between experimental and simulated intensity profiles is less than 10 % of the mean value. Essential, we have minimised the standard deviation Δ , where Δ is given by

$$\Delta^2 = [I_{cal} - (I_{exp} + BG)]^2 / NPT \quad (13)$$

with NPT giving the number of experimental points in a profile. Here I_{cal} , I_{exp} , and BG represent calculated intensity, experimental intensity and background correction factor. The background level is assumed to be constant over the range of the profile and this value is estimated as the intensity at the limits of s at which the intrusion of neighbouring peaks is likely to be insignificant. Within the limits of the peak, the background value is subtracted from the intensity at all points of the profile. Outside the profile, the intensity is assumed to be zero. Here I_{cal} is given by equation (1) along with equations (2), (3), and (12). The observed X-ray diffraction patterns of cotton fibers were resolved into fifteen individual reflections and for this purpose, we have used the residual-peak fitting software [24]. This program helps to detect, separate, and quantify hidden peaks that standard instrumentation misses. PeakFit also includes 18 different nonlinear spectral application line shapes. There are three AutoFit Peaks options offered by PeakFit. We have selected one of these options. In this option, the hidden peaks are detected by the “sharpening” achieved by deconvolving a Gaussian instrument response with the raw data. Baseline is also fitted with a Gaussian deconvolution procedure. Fitting procedure also ensures a good convergence factor. Figure 3 shows the snapshot of several individual reflections identified by peak fit procedure. We have used the standard cell parameters for cellulose-I [25] as starting values for “CHEKCELL” program to identify the Bragg reflections [26]. CHEKCELL program is a powder Indexing software.

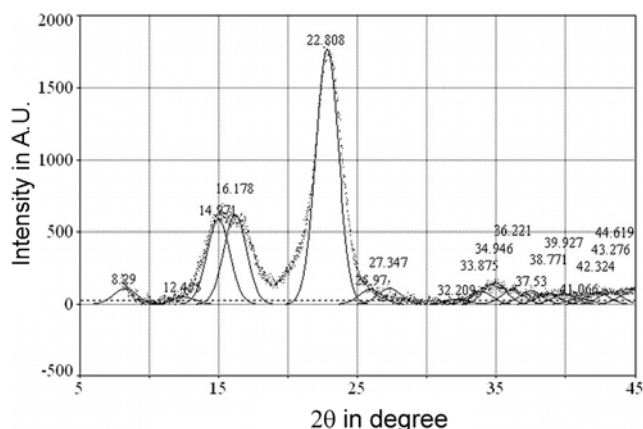


Figure 3. The snapshot of PEAKFIT program of Abyan cotton fibers.

Part II: Linked Atom Least Squares (LALS) Method

Cellulose is a polymer of D-glucopyranose in which pyranose rings are linked by $\beta(1-4)$ glucosidic linkage and the pyranose ring takes the chair conformation which is the most probable conformation in solid state. Molecular models, having the 2/1-helical symmetry and the fiber repeating period of 10.45 Å together with the pyranose ring with the standard bond lengths and bond angles [8], were constructed and used in LALS program [11]. There are two dihedral angles (ϕ , ψ) between two adjacent pyranose rings which are called glycosidic linkage angles. There is also a dihedral angle (χ) to define the orientation of O6 oxygen atom. The molecular model, which is constructed with standard bond lengths, bond angles, and torsion angles, is used along with cell parameters, space group, and the appropriate space group positional coordinates. To begin with, we do start with two/four molecular units in a unit cell and compute fractional coordinates of atoms in a molecular chain. Along with this model, appropriate standard atomic structure factors are used to compute a Bragg reflection spot. The input file into LALS program includes:

- The fractional coordinates of the atom (root atom) chosen as the origin of the Cartesian coordinate system fixed on the molecule.
- The helical structure parameters of the molecular model.
- Eulerian angles of root atom which is related to the Cartesian coordinate system fixed on the molecule.
- The internal coordinates of the molecular chain.
- The overall and/or individual temperature factors and the scale factors.
- Constraint parameters such as bond lengths, bond angles and torsion angles.

In the first step of refinement, the fractional coordinates (u , v , Ω) of the origin atom (C_1) are determined by step wise refinement. The weight of the reflection (w) was fixed at 1.0 for observed reflections. The normal residual factor and

weighted residual factor, R and R_w , are computed such that, after convergence, there is best agreement between observed and calculated structure amplitudes (F_{ob} , F_{cal}), and appropriate equations are:

$$R = \sum_1^q \frac{\|F_{ob}\| - |F_{cal}|}{\sum_1^q \|F_{ob}\|},$$

$$R_w = \sum_1^q \frac{w(|F_{ob}| - |F_{cal}|)^2}{\sum_1^q w|F_{ob}|^2}$$

Here q is the number of reflections, w is the weight factor for each reflection. The observed structure amplitude F_{ob} is calculated using: $F_{ob} = \sqrt{I_{ob}/LP}$, where I_{ob} is the observed intensity, L and P are Lorentz and polarization correction factors, respectively. The refined crystal structure shows the monoclinic crystal for these fibers with space group $P2_1$. The number of chemical repeating unit is one which is called cellobiose, with two pyranose rings in every monomer and there are two parallel chains in this monoclinic crystal [27]. Here, we emphasize that we have carried out structural refinement and not structure solution, as we are constrained with a limited number of X-ray reflections.

Elastic Constant Calculation

The elastic constants of the fibers depend on factors such as the molecular conformation, inter-chain bonds and intra-chain bonds [28]. To compute elastic tensor components, we have used Treloar's mathematical simplified model [29]. For monoclinic crystal, the elastic constant-matrix is given by Perelomova and Tagieva [30]

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & C_{15} & 0 \\ C_{21} & C_{22} & C_{23} & 0 & C_{25} & 0 \\ C_{31} & C_{32} & C_{33} & 0 & C_{35} & 0 \\ 0 & 0 & 0 & C_{44} & 0 & C_{46} \\ C_{51} & C_{52} & C_{53} & 0 & C_{55} & 0 \\ 0 & 0 & 0 & C_{64} & 0 & C_{66} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{13} & 0 & S_{15} & 0 \\ S_{21} & S_{22} & S_{23} & 0 & S_{25} & 0 \\ S_{31} & S_{32} & S_{33} & 0 & S_{35} & 0 \\ 0 & 0 & 0 & S_{44} & 0 & S_{46} \\ S_{51} & S_{52} & S_{53} & 0 & S_{55} & 0 \\ 0 & 0 & 0 & S_{64} & 0 & S_{66} \end{bmatrix}^{-1}$$

where C_{ij} are stiffness constants and S_{ij} are compliance constants. Treloar [29] assumed that $C_{15}=C_{25}=C_{35}=C_{46}=S_{15}=S_{25}=S_{35}=S_{46}=0$, since they are very small. The C_{11} , C_{22} , and C_{33} are the stiffness constants along [100], [010], and [001] respectively; and C_{44} , C_{55} , and C_{66} are the shear constants referring [010], [001]; [001], [100]; [100], [010] respectively. Remaining C_{12} , C_{23} , and C_{31} constants are the Poisson ratios. These elastic constants can be computed using Treloar's equations [29] along with crystal structure parameters. We reproduce here the necessary equations used for computation purpose. For the description of the symbols, see reference [29].

C_{22} is the important elastic constant along the chain and hence it is influenced by primary, inter-, and intra-chain bonds.

Results and Discussion

Micro-structural Parameters

Using the micro-structural parameters given in Tables 1 and 2 and the equations mentioned in the text, we have simulated the intensity profile and compared it with experimental profile in Figures 4(a), (b), (c), and (d). For the

Table 1. Microstructure parameters of Yemeni cotton fiber Abyan, using exponential distribution function

hkl	2θ in deg.	d_{hkl} in nm	$\langle N \rangle$	g in %	α	D_s in nm	Δ
0 0 1	8.29	1.07	4.05±0.16	0.1±0.004	1.69	4.33±0.17	0.04
1 0 1	14.97	0.60	6.14±0.25	0.1±0.004	1.21	3.68±0.15	0.04
2 0 0	22.81	0.39	10.55±0.53	0.1±0.01	0.57	4.12±0.21	0.05
0 0 3	25.97	0.34	11.28±0.34	0.1±0.003	0.42	3.84±0.12	0.03
-1 0 3	27.35	0.33	11.91±0.36	0.1±0.003	0.39	3.93±0.12	0.03
-2 2 1	32.21	0.28	13.18±0.53	0.1±0.004	0.36	3.69±0.15	0.04
0 3 1	33.88	0.26	14.56±0.44	0.1±0.003	0.31	3.79±0.11	0.03
0 0 4	34.95	0.26	15.70±0.47	0.1±0.003	0.29	4.08±0.12	0.03
-3 1 0	36.22	0.25	15.69±0.47	0.1±0.003	0.29	3.92±0.12	0.03
2 2 2	37.53	0.24	16.61±0.50	0.5±0.003	0.29	3.99±0.12	0.03
-3 1 2	38.77	0.23	16.65±0.50	0.1±0.003	0.28	3.83±0.12	0.03
-2 0 4	39.93	0.23	18.26±0.91	1.5±0.08	7.85	4.19±0.21	0.05
-3 2 0	41.07	0.22	18.61±0.93	1.5±0.08	4.49	4.09±0.21	0.05
0 3 3	42.32	0.21	19.27±0.96	1.5±0.08	5.76	4.05±0.20	0.05
-3 2 2	43.28	0.21	19.98±0.99	1±0.05	5.14	4.19±0.21	0.05

(hkl) Bragg's plane, 2θ is scattering angle, $\langle N \rangle$ is the average number of cells, g is lattice strain, d_{hkl} is the interplanar spacing, α is the width of the distribution, D_s is surface-weighted of crystallite size, Δ is the standard deviation.

Table 2. Microstructure parameters of Yemeni cotton fiber Zabid, using exponential distribution function

$h\ k\ l$	2θ in deg.	d_{hkl} in nm	$\langle N \rangle$	g in %	α	D_s in nm	Δ
0 0 1	8.34	1.06	4.61 ± 0.18	0.5 ± 0.02	1.05	4.88 ± 0.19	0.04
-1 0 1	13.31	0.665	7.36 ± 0.29	0.1 ± 0.01	0.67	4.89 ± 0.19	0.04
-1 1 0	15.60	0.57	9.20 ± 0.37	0.5 ± 0.02	0.42	5.22 ± 0.26	0.05
1 1 1	18.95	0.47	10.23 ± 0.41	0.1 ± 0.004	0.51	4.79 ± 0.19	0.04
0 1 2	20.38	0.44	11.23 ± 0.45	0.1 ± 0.004	0.45	4.89 ± 0.19	0.04
0 2 1	23.54	0.38	12.92 ± 0.52	0.1 ± 0.01	0.49	4.88 ± 0.24	0.05
0 0 3	25.85	0.34	14.05 ± 0.56	0.1 ± 0.004	0.38	4.84 ± 0.19	0.04
-1 0 3	27.23	0.33	15.11 ± 0.60	0.1 ± 0.004	0.34	4.95 ± 0.20	0.04
2 1 2	32.14	0.28	16.21 ± 0.65	0.1 ± 0.004	0.34	4.51 ± 0.18	0.04
-2 1 3	34.62	0.26	17.71 ± 0.71	0.1 ± 0.004	0.31	4.59 ± 0.18	0.04
-1 3 1	35.89	0.25	20.42 ± 0.82	0.1 ± 0.004	0.25	5.10 ± 0.20	0.04
-1 1 4	37.24	0.24	20.17 ± 0.81	0.1 ± 0.004	8.31	4.87 ± 0.19	0.04
1 1 4	39.55	0.23	21.17 ± 0.85	1 ± 0.04	4.50	4.82 ± 0.19	0.04

(hkl) Bragg's plane, 2θ is scattering angle, $\langle N \rangle$ is the average number of cells, g is lattice strain, d_{hkl} is the interplanar spacing, α is the width of the distribution, D_s is surface-weighted crystallite size, Δ is the standard deviation.

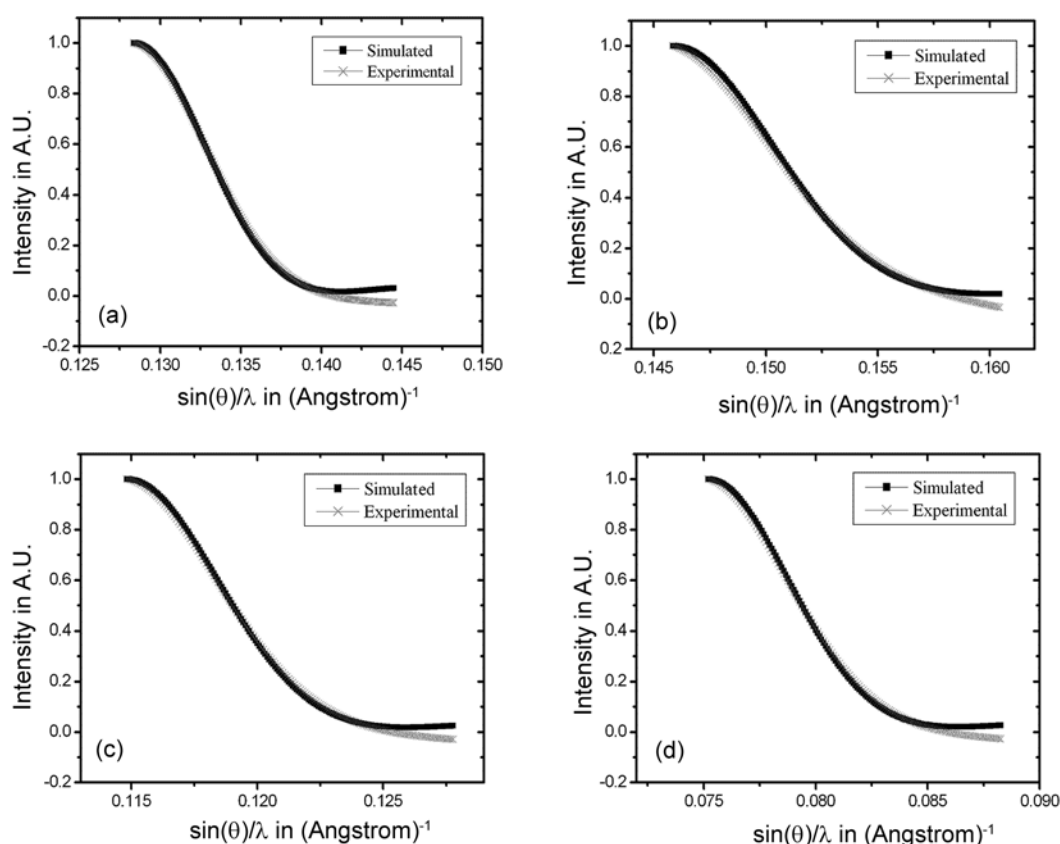


Figure 4. (a),(b) The experimental and simulated intensity profiles of Abyan cotton fiber at [2 0 0] and [0 0 3] Bragg reflections, respectively, (c),(d) The experimental and simulated intensity profiles of Zabid cotton fiber at [0 2 1] and [-1 0 1] Bragg reflections, respectively.

discrepancy at larger $\sin(\theta)/\lambda$ in Figures 4(a), (b), (c), and (d), a study of the second coefficients, crystallite size, will have to wait on improved functions for measuring the size

and size-distribution of the crystalline areas. This is needed for more accuracy, specially, at the tail of the simulated intensity profiles.

From Tables 1 and 2, the results show isotropically intrinsic strains, which are small but different along different directions for these cotton fibers. For a better perspective of the results obtained in these fibers and given in Tables 1 and 2, we have projected the crystallite shape into a plane so that a comparison could be made between the crystallite shapes of Abyan and Zabid cotton fibers, using the equation

$$\left(\frac{2}{D_{hkl}}\right)^2 = \left(\frac{\cos\phi}{Y}\right)^2 + \left(\frac{\sin\phi}{X}\right)^2 \quad (15)$$

Here ϕ is the angle between (hkl) planes. This ϕ can be determined using the cell parameters. The resulting crystallite shape is given in Figure 5. It is evident from this Figure that the volume of the crystallite shape ellipsoid in Zabid cotton fiber is comparatively more than that of Abyan cotton fiber.

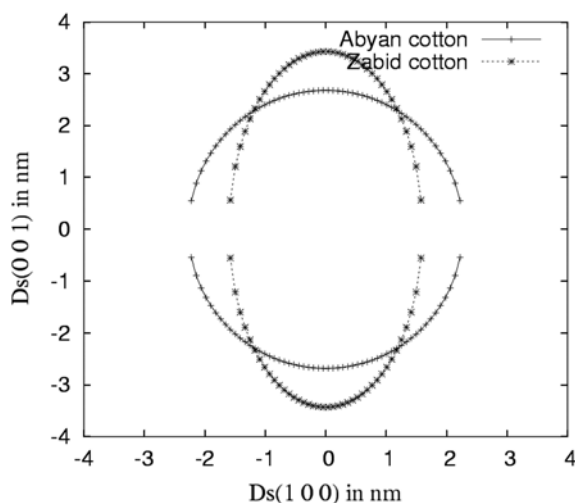


Figure 5. The ellipsoid crystallite shape of both cotton fibers Abyan and Zabid.

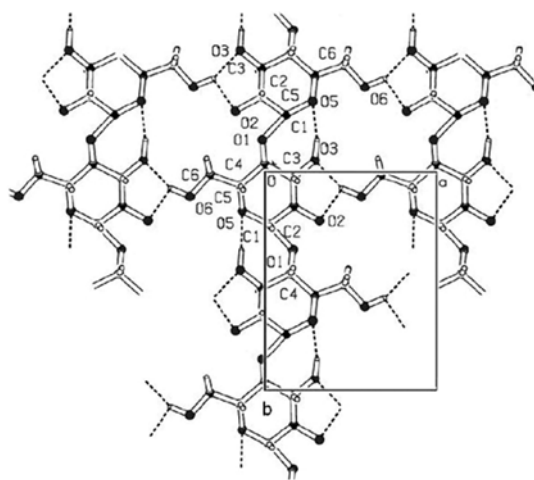


Figure 6. The molecular and crystal structure of Abyan cotton fibers.

Molecular Structure

The molecular structure for cellulose is a typical structure for $\beta(1-4)$ linked polysaccharides as of chitosan and chitin [9]. The main-chain conformation angles, $\phi(C2-C1-O1-C4)$ and $\psi(C1-O1-C4-C3)$, are $(148.17^\circ, 58.41^\circ)$, and $(147.74^\circ,$

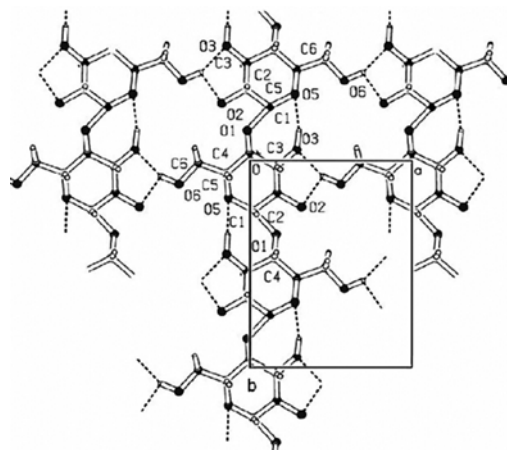


Figure 7. The molecular and crystal structure of Zabid cotton fibers.

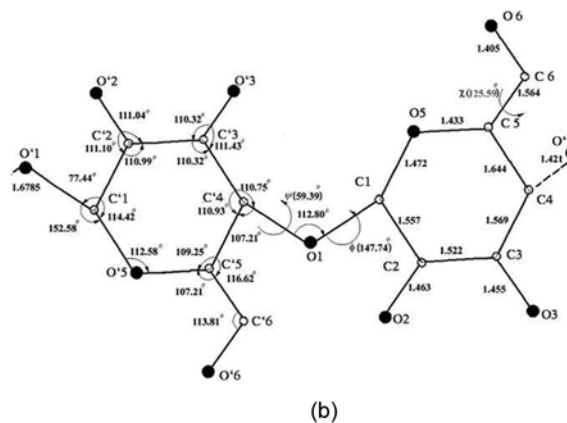
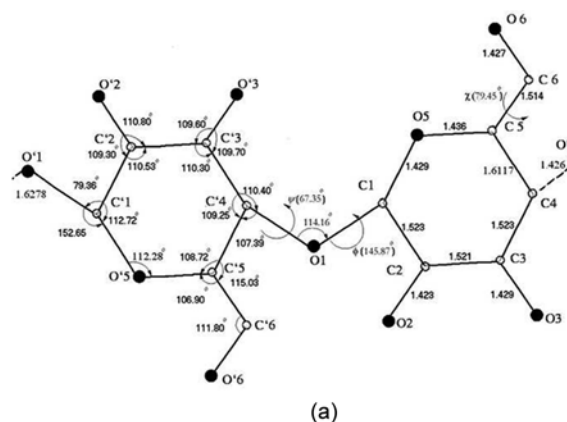


Figure 8. (a), (b) The standard and calculated molecular models of cellulose-I for Zabid cotton fibers.

59.39 °) respectively for the Abyan and the Zabid cotton fibers. The value of $\chi(\text{O5-C5-C6-O6})$, which defines the orientation of O6, is (122.77 and 125.59 °) respectively for Abyan and Zabid. This orientation of O6 is gauche-trans (*gt*) and this conformation is the second most common conformation in the single crystal structures of oligosaccharides and also in polysaccharides including cellulose [4]. With regard to certain discrepancies observed between F_{ob} and F_{cal} , for certain reflections, we submit that within the available intensity data and starting parameters for the molecular model, the refinement converged to a minimum defined by the R factors, and whatever be the variation of parameters within the limits of constraints and restraints, we could not get a better convergence. We have plotted the map of molecular and crystal structure of cellulose-I, by using "PLATON" software [31], and is given in Figures 6 and 7. Figure 8 shows the standard and calculated molecular models for cellulose-I in the case of Zabid cotton fibers. Tables 3 and 4 show the final parameters of cotton fibers studied here.

Table 3. Final parameters, amplitude structure factors (observed F_{ob} and calculated F_{cal}), M multiplicity and reflection planes of Yemeni cotton fibers Abyan

$h\ k\ l$	M	F_{cal}	F_{ob}
0 0 1	2	0.00	2.36
1 0 1	2	12.41	12.98
2 0 0	2	39.26	39.06
0 0 3	2	0.00	2.33
-1 0 3	2	2.10	2.44
0 3 1	4	0.10	2.03
0 0 4	2	3.62	3.28
-3 1 0	4	0.16	2.16
2 2 2	4	0.12	2.06
0 3 3	4	0.17	1.80
-3 2 2	4	0.02	2.33
R		21.88	
R_w		13.35	
Scale		0.022	
Atten.		138.79	
μ_1 in deg.		171.78 °	
Ω_1		0.408	
μ_2 in deg.		88.26 °	
Ω_2		-0.066	

ⁱ R and R_w are the normal and weighted residual factors, ⁱⁱfactor by which the calculated intensities should be multiplied with this value in Table 2 to give the observed intensities, which is used initially to bring the magnitude within the range of experimental data, ⁱⁱⁱthe amount of absorption of the radiation by the atoms, ^{iv} μ_1 and μ_2 are the azimuth angles for two separated chains around their molecular axes, and ^v Ω_1 and Ω_2 are the heights of the origin atoms for the separated chains along c-axis.

Crystal Structure

The cell parameters for Abyan cotton fiber are $a=0.783$ nm, $b=0.821$ nm, $c(\text{fiber axis})=1.032$ nm, $\alpha=90^\circ$, $\beta=96.03^\circ$, and $\gamma=90^\circ$ and for Zabid cotton fiber are $a=0.789$ nm, $b=0.812$ nm, $c(\text{fiber axis})=1.035$ nm, $\alpha=90^\circ$, $\beta=96.24^\circ$, and $\gamma=90^\circ$. The crystal system is monoclinic unit cell with space group $P2_1$ for both cotton fibers Abyan and Zabid. Figures 6 and 7 show the projection of molecular structure along b- axis for both fibers. The two pyranose rings along c-axis represent the repeating monomer of this polymer chain, and the two adjacent polymer chains along c-axis are independent. These are arranged in parallel fashion. These two polymer chains have translational difference along the c-axis of approximately one of the fiber repeating unit. They are linked to each other by inter-chain bonds (O6-H....O3) and (O6-H....O2) and intra-chain bonds (O3-H.....O5) through hydrogen bonds along b-axis and c-axis respectively [32]. These aspects make the sheet structure parallel to ac-plane. These sheets are accumulated along the b- direction, such that neighboring sheets are related by crystallographic

Table 4. Final parameters, amplitude structure factors (observed F_{ob} and calculated F_{cal}), M multiplicity and reflection planes of Yemeni cotton fibers Zabid

$h\ k\ l$	M	F_{cal}	F_{ob}
0 0 1	2	0.00	8.23
-1 0 1	2	15.34	10.48
-1 1 0	4	19.92	24.63
0 1 2	4	11.84	10.22
0 2 1	4	70.66	70.55
0 0 3	2	0.00	7.50
-1 0 3	2	10.04	10.73
-2 1 3	4	7.64	2.89
-1 3 1	4	9.48	13.04
-1 1 4	4	1.31	2.63
1 1 4	4	2.62	1.61
R		23.61	
R_w		18.41	
Scale		0.050	
Atten.		64.24	
μ_1 in deg.		174.49 °	
Ω_1		0.77	
μ_2 in deg.		85.37 °	
Ω_2		0.315	

ⁱ R and R_w are the normal and weighted residual factors, ⁱⁱfactor by which the calculated intensities should be multiplied with this value in Table 2 to give the observed intensities, which is used initially to bring the magnitude within the range of experimental data, ⁱⁱⁱthe amount of absorption of the radiation by the atoms, ^{iv} μ_1 and μ_2 are the azimuth angles for two separated chains around their molecular axes, and ^v Ω_1 and Ω_2 are the heights of the origin atoms for the separated chains along c-axis.

Table 5. Atomic fractional coordinates of one molecule of cellulose of the Abyan cotton fibers

Atom	X	Y	Z
C1	0.022	0.263	-0.255
O5	-0.139	0.222	-0.317
C5	-0.153	0.312	-0.436
C6	-0.335	0.270	-0.484
O6	-0.421	0.413	-0.504
C2	0.173	0.224	-0.339
O2	0.329	0.274	-0.273
C3	0.169	0.310	-0.470
O3	0.300	0.259	-0.551
C4	-0.005	0.269	-0.534
O1	-0.019	0.368	-0.646

ⁱFor any atom with position (X_n, Y_n, Z_n) from the other independent chain can be generated by using (X_o, Y_o, Z_o) the position of the same atom in the above chain and the following equation [25] X_n=(X_o-0.25)cosξ+Y_o sinξ+0.75, Y_n=(X_o-0.25) sinξ+Y_o cosξ, Z_n=Z_o-Ω₁+Ω₂, where ξ=μ₁-μ₂.

Table 6. Atomic fractional coordinates of one molecule of cellulose of the Zabid cotton fibers

Atom	X	Y	Z
C1	0.023	0.262	0.123
O5	-0.137	0.221	0.0611
C5	-0.152	0.312	-0.056
C6	-0.332	0.268	-0.105
O6	-0.415	0.413	-0.129
C2	0.173	0.224	0.039
O2	0.328	0.274	0.105
C3	0.168	0.310	-0.090
O3	0.299	0.259	-0.171
C4	-0.004	0.268	-0.154
O1	-0.018	0.368	-0.266

ⁱFor any atom with position (X_n, Y_n, Z_n) from the other independent chain can be generated by using (X_o, Y_o, Z_o) the position of the same atom in the above chain and the following equation [25] X_n=(X_o-0.25)cosξ+Y_o sinξ+0.75, Y_n=(X_o-0.25) sinξ+Y_o cosξ, Z_n=Z_o-Ω₁+Ω₂, where ξ=μ₁-μ₂.

2₁-symmetry. Tables 5 and 6 show the fractional atomic coordinates for the chain of cellulose-I polymer.

Computation of Crystal Modulus

The numerical calculation of elastic constant-matrix requires suitable structural parameters in the formulae, for primary bonds and hydrogen bonds. We have used bond angles and bond lengths for both primary bonds and hydrogen bonds and also auxiliary angles to calculate the elastic constants. The stiffness matrix of Abyan cotton fiber turns out to be:

in N/m²

$$\begin{bmatrix} 3.49 \times 10^{10} & 0.91 \times 10^{10} & - & - & - & - \\ 0.91 \times 10^{10} & 3.33 \times 10^{11} & 1.35 \times 10^{10} & - & - & - \\ - & 1.35 \times 10^{10} & 7.81 \times 10^{10} & - & - & - \\ - & - & - & 1.85 \times 10^9 & - & - \\ - & - & - & - & 1.95 \times 10^{10} & - \\ - & - & - & - & - & 0.83 \times 10^{10} \end{bmatrix}$$

$$E_{11}=3.47 \times 10^{10} \text{ N/m}^2$$

$$G_{12}=1.85 \times 10^{10} \text{ N/m}^2$$

$$E_{22}=3.28 \times 10^{11} \text{ N/m}^2$$

$$G_{23}=1.95 \times 10^{10} \text{ N/m}^2$$

$$E_{33}=7.75 \times 10^9 \text{ N/m}^2$$

$$G_{31}=0.83 \times 10^{10} \text{ N/m}^2$$

$$\mu_{12}=0.028$$

$$\mu_{21}=0.260$$

$$\mu_{23}=0.172$$

$$\mu_{32}=0.041$$

$$\mu_{31}=-0.011$$

$$\mu_{13}=-0.047$$

The elastic constant-matrix for Zabid cotton fiber turns out to be:

in N/m²

$$\begin{bmatrix} 3.36 \times 10^{10} & 0.93 \times 10^{10} & - & - & - & - \\ 0.93 \times 10^{10} & 3.43 \times 10^{11} & 1.37 \times 10^{10} & - & - & - \\ - & 1.37 \times 10^{10} & 7.78 \times 10^{10} & - & - & - \\ - & - & - & 1.88 \times 10^{10} & - & - \\ - & - & - & - & 1.89 \times 10^{10} & - \\ - & - & - & - & - & 0.84 \times 10^{10} \end{bmatrix}$$

$$E_{11}=3.33 \times 10^{10} \text{ N/m}^2$$

$$G_{12}=1.88 \times 10^{10} \text{ N/m}^2$$

$$E_{22}=3.38 \times 10^{11} \text{ N/m}^2$$

$$G_{23}=1.88 \times 10^{10} \text{ N/m}^2$$

$$E_{33}=7.72 \times 10^{10} \text{ N/m}^2$$

$$G_{31}=0.84 \times 10^{10} \text{ N/m}^2$$

$$\mu_{12}=0.027$$

$$\mu_{21}=0.278$$

$$\mu_{23}=0.176$$

$$\mu_{32}=0.040$$

$$\mu_{31}=-0.011$$

$$\mu_{13}=-0.004$$

Here E_{ii} ($=1/S_{ij}$, for $i=1, 2, 3$) are the Young modulus along different axis, G_{ij} are the shear modulus along different directions and μ_{ij} ($=-S_{ij}/S_{ii}$) are the Poisson ratios along different directions. We find from above results that E_{22} value of Zabid cotton fibers is ($3.38 \times 10^{11} \text{ N/m}^2$) which is greater than E_{22} value of Abyan cotton fibers ($3.28 \times 10^{11} \text{ N/m}^2$) and the reported value for (dch32) Indian cotton fiber is ($0.155 \times 10^{10} \text{ N/m}^2$) [7]. The negative values of some Poisson ratio along some directions denote that while stretching there is a transverse expansion instead of a contraction. This has been observed for some materials, usually referred to as auxetic materials [33].

Conclusion

We have carried out Wide Angle X-ray Scattering profile analysis of Abyan and Zabid cotton fibers and have computed the unit cell and micro-structural parameters of these fibers. These computations indicate that the strains are small and these cotton fibers have different values of

crystallite size components in different directions. The reason is that the binding forces between molecules/atoms of cellulose arise due to inter- and intra- hydrogen bonds and also covalent bonds. With the available number of Bragg reflections, we could achieve good convergence using LALS program for both the cotton fibers. We observe fractional changes in molecular and crystal structure between the Abyan and the Zabid cotton fibers. These include bond lengths, bond angles and cell parameters. Broadening of X-ray diffraction in cotton fibers is due to the presence of small crystallites of the order of 4.5 nm, and not due to the intrinsic strain, which is a misconception that exists. We have also computed the elastic constants from crystal structure parameters, and the longitudinal Young modulus (3.28×10^{10} N/m² and 3.38×10^{10} N/m²) for both cotton fibers are in broad agreement with Jaswon's value (5.65×10^{10} N/m²) [34].

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