Crystal structure and elastic constants of Dharwar cotton fibre using WAXS data

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Abstract. Wide-angle X-ray scattering (WAXS) recordings were carried out on raw Dharwar cotton fibres available in Karnataka. Using this data and employing linked atom least squares (LALS) method, we report here the molecular and crystal structure of these cotton fibres. Employing structural data, we have computed elastic moduli tensor components of these fibres. From these investigations, it turns out that the intrinsic strains present in the fibre arise due to hydrogen bonds and not covalent bonds, which is a significant result.

Keywords. WAXS; cotton fibres; LALS; elastic constants.

1. Introduction

Cotton fibre belongs to a family of '*Gossypium*' (Brubaker *et al* 1999). It has been used for more than 3000 years because of its versatility and costless to produce finished products. Cotton is essentially pure cellulose. The structure–property relation of cotton is considered as an important factor in textile industry. The elastic constants of cellulose were computed by assuming molecular models of Jaswan (Jaswan *et al* 1968). In this model, the strains present along the chain depend on the deformation of primary (covalent) bonds and hydrogen bonds. A comparison of this model has been carried out by Eichhorn and Davies (2006). Northolt and Vries (1985) reexamined tensile deformation of well-oriented cellulose fibres and the results show the prospect for improving the mechanical properties of cellulose fibres. Here, by using two different sets of hydrogen bond force constants of 24.6 and 31.9×10^{10} N/m², the Young's modulus has been estimated along the chain direction (Gillis 1969). Tashiro and Kobayashi (1991) concluded that Young's modulus along chain axis is not affected by inter-chain interaction but by intra-chain hydrogen bonds. Mann and Roldan-Gonzalez (1962) reported elastic moduli at different stages of relative humidity and the average value of elastic moduli was around $7\text{--}9 \times 10^{10}$ N/m². Here, we have employed wide angle X-ray scattering (WAXS) data to estimate the intrinsic strain and crystal size of Dharwar (cellulose I) cotton fibres. For this purpose, we have used line profile analysis (LPA) developed by us. We have also investigated the crystal structural features of these fibres using linked atom least squares (LALS) technique. The elastic tensor components of these fibres were determined using

Treloar's (1960) equations and structural data, which were determined by LALS technique here.

2. Materials and methods

2.1 Preparation of sample

Raw cotton (Dharwar) 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, seed hulls and other small objects. This process must be done before cotton fibres can be used for studying. Depending on the varieties of cotton, ginning machine is employed. After removing the seed, it is taken for baling till it became as lint. The lint raw cotton sample is used for our study, without any additional treatment.

2.2 X-ray diffraction measurement

The sample is taken as small bundles and clamped into a sample holder. Then this sample holder is mounted on a goniometer such that the rotational axis is parallel to fibres axis and perpendicular to X-ray beam. Here, we have used an imaging plate system (Dip-3200) with dimensions (440/240) mm², which is moved parallel to the axis of rotation. The wavelength of X-ray radiation is $\lambda = 0.71073$ Å (Mo target). The X-ray generator (RIGAKU) settings were 50 kV and 32 mA. The time of exposure was kept at 400 s and X-ray diffraction pattern of cotton fibre (Dharwar) recorded using Weissenberg geometry is given in figure 1. Equatorial scan of intensity vs 2θ was carried out using the 'MOSFLM' software supplied with the instrument. This data was analysed using Peak-Fit software (Chen *et al* 2004). Background intensity was subtracted during peak fitting

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procedures. For peak fitting purpose, a Gaussian deconvolution was selected as peak profile of X-ray diffraction line of cotton fibres. The position of each diffraction line was calculated by resolving the symmetric peak position and was identified from residual peak-fitting procedure of Peak-Fit. The 2θ positions were computed by calculating the mean and standard deviation of each diffraction profile. Cell parameters and space group of crystal system of Dharwar cotton fibre were determined by using a 'CHEKCELL' freely available program. This program was developed for Windows by Jean Laugier and Bernard Bochu, which is a user-friendly procedure and was quite useful for identifying appropriate cell parameters with estimated STD and space group of the system. 'CHEKCELL' program was executed until a set minimum standard deviation was achieved. We could identify 11 reflections. Observed reflections were indexed by a unit cell with dimensions, $a = 4.49 \text{ \AA}$; $b = 6.19 \text{ \AA}$; $c = 5.36 \text{ \AA}$ and the space group was $P2_1$.

2.3 X-ray diffraction data analysis

To find the microstructural parameters of Dharwar cotton fibre, we have made simulation for intensity profiles using line profile analysis (LPA) method. This method is based on Fourier cosine series of Warren and Averbach (Warren and Averbach 1952; Warren 1955, 1969) and Hosemann's one-dimensional paracrystal model (Hosemann 1982). The broadening of intensity profile is due to both crystal size and distortion of the lattice. Intensity profile in a direction joining the origin to the centre of the reflection is

Figure 1. X-ray diffraction pattern recorded from Dharwar cotton fibre.

$$I(s) = \sum_{n=-\infty}^{\infty} (A_s(n) \cdot A_d(n)) \cos\{2\pi n d(s - s_0)\}, \quad (1)$$

where $A_s(n)$ are size coefficients, $A_d(n)$ are lattice strain coefficients, d the interplanar spacing, s the value of $\{\sin(\theta)/\lambda\}$, s_0 the value of s at peak of the reflection, θ the Bragg's angle, λ the wavelength of radiation and n the harmonic number. The disorder component contribution is

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

Here m is the order of reflection and $g (= \Delta d/d)$ the lattice disorder. For a probability distribution of column length, $P(i)$, the crystal size contribution will be

$$A_s(n) = 1 - \frac{nd}{D} - \frac{d}{D} \left[\int_0^n i P(i) di - n \int_0^n P(i) di \right]. \quad (3)$$

In cotton fibres, it is rare to obtain multiple reflections and hence we cannot use Warren and Averbach multiple order method. We have used single order method (Hall and Somashekar 1991; Pope and Balzar 2002; Balzar 2004) to obtain crystal size and lattice strain, using an analytical function for the probability distribution, $P(i)$. For this reason, we have chosen an asymmetric function (exponential distribution) to find out the finer details of the microstructural parameters of Dharwar cotton fibres (Somashekar and Somashekarappa 1997). This distribution depends on the fact that there are no columns containing less than an assumed number of unit cells and those with more than the assumed number of cells will decay exponentially. There are four unknown parameters and to determine these, we have used a multidimensional minimization program SIMPLEX (Press *et al* 1986). The goodness of fit between experimental and simulated intensity profiles have been computed by

$$\Delta^2 = [I_{\text{cal}} - (I_{\text{exp}} + BG)]^2 / \text{number of points}. \quad (4)$$

Here I_{cal} , I_{exp} and BG represent calculated intensity, experimental intensity and a background correction term.

2.4 Molecular model

It is well known that cellulose is a linear polymer of $\beta(1-4)$ -D-glucopyranose units in 4C_1 conformation (Fried 2002). There are two types of cellulose I which are cellulose, I_α and cellulose I_β , but for higher plants such as cotton fibre the dominant one is cellulose, I_β (Atalla 1999). The chair conformation of β -linked glucopyranose residues stabilizes the structure. The flexibility of polysaccharide chains depends on the ease of rotation around this glycosidic linkage. To find molecular structure of cotton fibres, we have considered molecular models having the 2/1-helical symmetry and the fibre-repeating period of 10.38 $\text{\AA}$ together with the pyranose ring in the standard with all bond lengths and angles. There are two dihedral angles (ϕ , ψ)

between two adjacent pyranose rings, which are called glycosidic linkage angles, and there is a dihedral angle (χ) to define the orientation of O₆ oxygen atom (French and Johnson 2004). There are three possible values of O₆, depending on the orientation of this atom related to pyranose ring, *gauche-gauche*, *gauche-trans* and *trans-gauche*. The molecular model of cotton fibres with standard bond lengths, bond angles and dihedral angles is shown in figure 2.

2.5 Crystal structure packing

There are two molecular chains with 2/1 helical symmetry in a unit cell with space group, $P2_1$ (French and Johnson 2004). These two independent polymer chains are taken in parallel positions and pointing in the same direction in the unit cell. To obtain appropriate packing models, the fractional coordinates (u , w , v) of the origin atom (C₁) were refined with stepwise procedures and the one which gives minimum standard deviation was used (Okuyama *et al* 1997). Here, u and v are the positional parameters of polymer chain in the ac -plane; w is the height of the origin along the b -direction and the azimuth angle (μ) around the molecular axis. The Eulerian angles (ε_x , ε_y , ε_z), the three angular parameters that specify the orientation of a molecule with respect to reference axes, were also determined using stepwise method. Other required packing parameters were also determined.

2.6 Linked atom least squares (LALS) program

With the development of computer-based physical modeling, it is now possible to create accurate molecular model

Figure 2. The molecular model of cellulose, (1) carbon atom is black ball and oxygen atom is grey ball, (2) torsion angles [ϕ (C2–C1–O1–C4), ψ (C1–O1–C4–C3) and χ (O5–C5–C6–O6)] and (3) glycosidic angle [τ (C1–O1–C4)].

in a unit cell by inputting the required parameters of this molecular structure into the program. This molecular and crystal structure was generated by using LALS method (Smith and Arnott 1978) and the computations were carried out using a Linux based PC. We have compiled the software, LALS, for execution using LINUX operating system. Actually there is a method to pack the two polymer chains with 2/1-helical symmetry in a unit cell with space group, $P2_1$, i.e. by locating the polymer chains at special positions on the crystallographic axes at ($u = 0.25$, $v = 0.0$) and ($u = 0.75$, $v = 0.0$). The azimuthal angles, μ_1 and μ_2 , are searched within the asymmetric unit by calculating R -values for the equatorial reflections (Okuyama *et al* 1997). The two independent polymer chains are in the same direction. In the next step, we have searched the positional parameter, w , of the polymer chain along the c -direction. Then, this model was refined against all reflections, including unobserved ones. We have observed 15 reflections, of which 13 reflections have been identified conclusively in LALS program. The weight of reflection (w) was fixed at 1.0 for observed reflections. R and R_w were used to evaluate the agreement between observed and calculated structure amplitudes. We have carried out refinement of molecular and crystal structure parameters to minimize the difference in structure amplitudes of experimental F_{obs} and simulated F_{cal} in terms of R and R_w factors given as

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|,$$

$$R_w = \sum w(|F_o| - |F_c|)^2 / \sum wF_o^2. \quad (5)$$

Atomic scattering factors for calculating structure factors were obtained by using the method and values given in the literature (Ibers and Hamilton 1974). Final values of refined parameters are listed in table 2 and fractional coordinates are given in table 3. Observed and calculated structure amplitudes are given in table 4. The X-ray agreement factors, R and R_w , are 17.43% and 21.06%, respectively, for reflection data. The packing structure is

Table 1. Microstructural parameters of Dharwar cotton fibre using exponential distribution function.

($h k l$)	d_{hkl} (Å)	$\langle N \rangle$	g (%)	D_s (Å)	Δ
(0 1 0)	8.25	4.45	0.10	36.71	0.035
(0 1 1)	6.44	6.30	0.50	40.57	0.042
(1 1 0)	5.38	7.79	0.10	41.91	0.051
(0 1 2)	4.37	9.08	1.00	39.68	0.062
(0 0 2)	4.13	10.19	0.10	42.09	0.051
(0 2 1)	3.83	10.13	0.60	38.80	0.035
(-2 1 1)	3.47	11.92	0.10	41.36	0.055
(2 1 2)	2.83	14.80	0.50	41.88	0.061
(2 2 0)	2.69	15.01	0.50	40.38	0.036
(-1 2 3)	2.56	16.11	0.10	41.24	0.052
(2 1 3)	2.41	16.89	0.10	40.71	0.054
(-3 1 2)	2.29	17.60	0.50	40.30	0.068
(3 1 2)	2.18	18.54	0.60	40.42	0.058

shown in figure 4 in which hydrogen bonds are denoted by dashed lines.

Table 2. Final model parameters of cellulose for Dharwar cotton fibre after several refinements using experimental intensities.

Torsion angles at glycosidic linkage (deg.)	
$\phi(\text{C2-C1-O1-C4})$	147.09°
$\psi(\text{C1-O1-C4-C3})$	62.19°
Glycosidic angle (deg)	
$\tau(\text{C1-O1-C4})$	112.52°
Eulerian angles (deg)	
ε_x	103.38°
ε_y	58.39°
ε_z	-118.87°
Orientation of O6 (deg)	
$\chi(\text{O5-C5-C6-O6})$	126.15°
Packing parameters of polymer chains	
μ_1	105.69°
w_1	0.49
μ_2	106.25°
w_2	0.67
Scale factor	0.28
Attenuation factor	19.86
Stereo-chemical energy	4.79E + 06 Cal/mol
R	0.174
R_w	0.211

μ_1 and μ_2 , the azimuth angles for two separated chains around their molecular axes; w_1 and w_2 , the heights of the origin atoms for the separated chains along c -axis; scale factor (factor 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); attenuation factor, the amount of absorption of the radiation by the atoms; stereo-chemical energy is related to the spatial arrangement of atoms within a molecule; R and R_w (the normal and weighted residual factors).

Table 3. Fractional atomic coordinates for one molecule of cellulose (chain-a) model from LALS program after several refinements against X-ray intensities.

Atom	X	Y	Z
C1	0.023	0.269	0.163
O1	-0.019	0.377	-0.226
C2	0.173	0.216	0.079
O2	0.328	0.248	0.146
C3	0.169	0.300	-0.050
O3	0.299	0.237	-0.131
C4	-0.005	0.278	-0.114
C5	-0.152	0.336	-0.016
O5	-0.138	0.245	0.101
C6	-0.333	0.313	-0.065
O6	-0.416	0.463	-0.088

For any atom with position (Xn, Yn, Zn) from the other independent chain can be generated by using (Xo, Yo, Zo) , the position of the same atom in the above chain and the following equation: $Xn = (Xo - 0.25)\cos\theta + Yo\sin\theta + 0.75$, $Yn = (Xo - 0.25)\sin\theta + Yoc\cos\theta$, $Zn = Zo - w_1 + w_2$, where $\theta = \mu_1 - \mu_2$.

2.7 Calculation of stiffness constants

Modulus of elasticity of Dharwar cotton fibre depends mainly on molecular structure and morphology (Ravve 2000). For monoclinic crystal, the elastic constants are given by Perelomova and Tagieva (1983).

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

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

where C_{11} , C_{22} , C_{33} are stiffness constants, C_{44} , C_{55} and C_{66} are the shear constants and C_{12} , C_{23} and C_{13} are Poisson's ratios. For simplifying the calculation, Treloar assumed the additional constants in monoclinic matrix to be equivalent to the orthorhombic matrix (Treloar 1960). The main and most important elastic constant is C_{22} , which gives the elastic constant along chain direction (Treloar 1960; Jaswon *et al* 1968), and is influenced by three forces: primary bonds (covalent bonds), inter-chain bonds (hydrogen bonds which exist between chains) and intra-chain bonds (hydrogen bonds which exist between two atoms within a chain). The C_{22} can be expressed as follows

$$C_{22} = C'_{22} + C''_{22} + C'''_{22}. \quad (6)$$

Table 4. Observed F_o and calculated F_{cal} structure amplitudes for Dharwar cotton fibre, (hkl) Bragg reflections and multiplicity (M).

hkl	M	F_{cal}	F_o
0 1 0	2	135.65	55.95
0 1 1	4	101.37	106.45
1 1 0	4	201.46	191.29
0 1 2	4	132.28	121.61
0 0 2	2	142.78	151.72
0 2 1	4	320.57	382.93
-2 1 1	4	121.76	106.05
2 1 2	4	67.32	77.41
2 2 0	2	87.69	72.53
-1 2 3	4	92.91	93.36
2 1 3	4	105.62	73.50
-3 1 2	4	72.09	66.28
3 1 2	4	75.68	60.17

Figure 3. Experimental and simulated intensity profiles for different (*hkl*) reflections: (a) (0 1 0), (b) (0 1 1), (c) (1 1 0), and (d) (0 2 1).

According to Treloar's (1960), C'_{22} is given by

$$C'_{22} = CL^2/V. \quad (7)$$

Here L is repeat distance in chain direction axis, V the volume of unit cell of cellulose (monoclinic) and C a gross constant, which can be computed by using bond angles, bond lengths, linear force constants and angular force constants of primary bonds. C''_2 is computed (Treloar 1960) using

$$C''_{22} = (2D_2^2/V)[C_{h2} \sin^2 \Phi_2 + (K_{h2}/h_2^2) \cos^2 \Phi_2], \quad (8)$$

where Φ_2 is the angle formed by (O5-H...O3) in the chain. Treloar (1960) has shown that

$$C_{11} = (2D_1^2/V)(C_{h1} \cos^2 \Phi_1 + (K_{h1}/h_1^2) \sin^2 \Phi_1) \cos^2 \Omega, \quad (9)$$

$$C''_{22} = (2/V)(C_{h1} h_1^2 \sin^4 \Phi_1 + C_{h3} h_3^2 \sin^4 \Phi_3 + K_{h1} \sin^2 \Phi_1 \cos^2 \Phi_1 + K_{h3} \sin^2 \Phi_3 \cos^2 \Phi_3), \quad (10)$$

$$C_{33} = (2D_3^2/V)[C_{h3} \cos^2 \Phi_3 + (K_{h3}/h_3^2) \sin^2 \Phi_3] \cos^2 \Omega_3, \quad (11)$$

$$C_{12} = (2D_1 h_1/V)[C_{h1} - (K_{h1}/h_1^2)] \sin^2 \Phi_1 \cos \Phi_1 \cos \Omega_1, \quad (12)$$

$$C_{23} = (2D_3 h_3/V)[C_{h3} - (K_{h3}/h_3^2)] \sin^2 \Phi_3 \cos \Phi_3 \cos \Omega_3. \quad (13)$$

Figure 4. The molecular and crystal structure of Dharwar cotton fibres along the three projections: (a) *a*-axis, (b) *b*-axis, and (c) *c*-axis, respectively. Dashed lines indicate the hydrogen bonds.

For explanations of angles and various symbols, we refer to the reference by Treloar (1960). Utilizing all these equations, we have written a source code in FORTRAN language to calculate the elastic constants for Dharwar cotton fibres.

3. Results and discussion

3.1 Microstructural parameters

Using (1)–(4) and X-ray data, the computed microstructural parameters are given in table 1. Figure 3 has been plotted to show the goodness of fit between experimental and simulated intensity profiles. The computed intrinsic strain components (*g*) are small and have different values

in different Bragg planes, indicating the anisotropic nature of the intrinsic strains that are present during fibre formation.

3.2 Molecular structure

The molecular structure for cellulose is a typical structure with $\beta(1-4)$ linked polysaccharides as observed in chitosan and chitin (Okuyama *et al* 1997). The main-chain conformation angles, $\phi(C2-C1-O1-C4)$ and $\psi(C1-O1-C4-C3)$, are 62.19° and 147.09° , respectively. The value of $\chi(O5-C5-C6-O6)$, which defines the orientation of O6, is 126.15° . This orientation of O6 is *gauche-trans* (*gt*) and this conformation being the second most common conformation in the single crystal structures of oligosa-

ccharides and also in polysaccharides including cellulose (Allen *et al* 1979). Table 2 shows the final parameters of cellulose-I using LALS program obtained after several refinements. The Eulerian angles (ε_x , ε_y , ε_z) were also given in table 2.

3.3 Crystal structure

The unit cell parameters of cotton fibre studied here are $a = 7.84 \text{ \AA}$, b (fibre axis) $= 10.38 \text{ \AA}$, $c = 8.30 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 89.80^\circ$, and $\gamma = 90^\circ$ with monoclinic and space group, $P2_1$. The two pyrasone rings along the b -axis represent the repeating monomer of this polymer chain, and the two adjacent polymer chains along b -axis are independent. These are arranged in parallel fashion. These two polymer chains have translational difference along the b -axis of approximately 1 fibre repeat unit and are linked to each other by inter-chain bonds (O6–H...O3) and intra-chain bonds (O3–H...O5) along the c - and b -axes, respectively (Langan *et al* 1999). These features make the sheet structure parallel to a.c.-plane. The sheets are accumulated along the c -direction, such that each neighbouring sheets are related by crystallographic 2_1 -symmetry.

3.4 Evaluation of crystal modulus

The numerical calculation of elastic stiffness matrix $|C_{ij}|$ requires suitable values for substitution into the formulas. We have used the values by Treloar for force constants (linear and angular) for primary bonds and hydrogen bonds and they are:

$$C_1 = 4.54 \times 10^4 \text{ N/m}^2, C_2 = 4.54 \times 10^4 \text{ N/m}^2,$$

$$C_3 = 4.54 \times 10^4 \text{ N/m}^2, K_1 = 1.105 \times 10^{-18} \text{ N.m/rad},$$

$$K_2 = 0.912 \times 10^{-18} \text{ N.m/rad}, K_3 = 1.027 \times 10^{-18} \text{ N.m/rad},$$

$$K_4 = 0.883 \times 10^{-18} \text{ N.m/rad}, C_{hl} = 0.30 \times 10^4 \text{ N/m}^2,$$

$$C_{h3} = 0.30 \times 10^4 \text{ N/m}^2, K_{hl} = K_{h3} = 1.027 \times 10^{-18} \text{ N.m/rad}.$$

We have used bond angles and bond lengths for both primary bonds and hydrogen bonds and also auxiliary angles to calculate the elastic constants. We have adopted Treloar assumptions even though that the chains of cellulose take parallel position to each other, which is contrary to Treloar assumption. Further, hydrogen bonds of the type O–H...O are dominant within a sheet and it takes perpendicular projection with the chain axes, whereas hydrogen bonds of the type C–H...O connect between every chains in different sheets. Treloar has mentioned that only O–H...O type are available for calculations and this may have an effect on the assumed values.

The stiffness matrix of Dharwar cotton fibres so computed is (in GPa):

$$\begin{bmatrix} 4.21 \times 10^{10} & 1.6 \times 10^9 & - & - & - & - \\ 1.6 \times 10^9 & 3.706 \times 10^{11} & 1.51 \times 10^{10} & - & - & - \\ - & 1.51 \times 10^{10} & 3.38 \times 10^{10} & - & - & - \\ - & - & - & 2.5 \times 10^9 & - & - \\ - & - & - & - & 1.85 \times 10^{10} & - \\ - & - & - & - & - & 2.83 \times 10^{10} \end{bmatrix}$$

$$\begin{aligned} E_{11} &= 4.14 \times 10^9 \text{ N/m}^2, G_{12} = 0.708 \times 10^9 \text{ N/m}^2, \\ E_{22} &= 3.58 \times 10^{10} \text{ N/m}^2, G_{23} = 0.625 \times 10^{10} \text{ N/m}^2, \\ E_{33} &= 3.32 \times 10^9 \text{ N/m}^2, G_{31} = 0.463 \times 10^{10} \text{ N/m}^2, \\ \mu_{12} &= 0.045, \mu_{21} = 0.382, \\ \mu_{23} &= 0.446, \mu_{32} = 0.042, \\ \mu_{31} &= -0.016, \mu_{13} = 0.0199. \end{aligned}$$

We find from the above results that E_{22} value is 35.8 GPa which is higher than that reported in our paper for (*dch32*) cotton fibre which is 1.55 GPa, which has been calculated using intrinsic strain tensor components (Samir and Somashekar 2007). The negative values of some Poisson's ratio in some directions denote that while stretching a chain there is a transverse expansion with stretching instead of a contraction and this is relative to longitudinal extension. This has been observed for some materials (auxetic materials such as cellular solid foams) and materials with chiral microstructure with non-central force interaction or non-affine deformation (Lakes 1987). We have examined and quantified the disorder present in the cotton fibres using line profile analysis and a well established single order method. The observed broadening of reflection in cotton fibre is due to crystallite size of the order, 40–50 $\text{\AA}$, and intrinsic strain present in the cotton fibres. These intrinsic strain tensor components affect slightly the hydrogen bonds only and not the primary bonds. By using this assumption and neglecting the deformation of primary bonds (3), we have also recalculated the elastic constants (in GPa), and we find

$$\begin{bmatrix} 4.27 \times 10^{10} & 1.63 \times 10^{10} & - & - & - & - \\ 1.63 \times 10^{10} & 5.13 \times 10^{10} & 1.47 \times 10^{10} & - & - & - \\ - & 1.47 \times 10^{10} & 3.48 \times 10^{10} & - & - & - \\ - & - & - & 2.44 \times 10^{10} & - & - \\ - & - & - & - & 1.89 \times 10^{10} & - \\ - & - & - & - & - & 2.9 \times 10^{10} \end{bmatrix}$$

$$E_{11} = 3.68 \times 10^9 \text{ N/m}^2, G_{12} = 0.72 \times 10^{10} \text{ N/m}^2,$$

$$E_{22} = 3.88 \times 10^9 \text{ N/m}^2, G_{23} = 0.61 \times 10^{10} \text{ N/m}^2,$$

$$E_{33} = 3.00 \times 10^9 \text{ N/m}^2, G_{31} = 0.47 \times 10^{10} \text{ N/m}^2,$$

$$\mu_{12} = 0.36, \mu_{21} = 0.38,$$

$$\mu_{23} = 0.42, \mu_{32} = 0.33,$$

$$\mu_{31} = -0.15, \mu_{13} = -0.12.$$

The value of E_{22} (Young's modulus) is in agreement with the reported range of values of Young's modulus (5.5–12.5 GPa) (Eichhorn *et al* 2001). The shear modulus has a high value in the [100] and [010] directions and are of same magnitude. The Poisson's ratios agree with the previous reported value (Roberts *et al* 1994), which is 0.30 for microcrystalline cellulose.

4. Conclusions

In this paper, first, we have recorded wide angle X-ray scattering data from Dharwar cotton fibre. This WAXS data has been used to obtain the unit cell parameters and microstructural parameters of these fibres. For this purpose, we have analysed the data using line profile analysis, developed by us. The results show that the intrinsic strain components of cotton fibre are very small and have different values in different Bragg's planes. This indicates the anisotropy nature of intrinsic strains present during fibre formation. We have also constructed molecular and crystal structures of this cotton fibre by using LALS and PLATON programs (Spek 2003). This is based on a model wherein two chains in a unit cell are parallel with the same conformations. We have also computed the elastic constants from microstructure data. There is an agreement between our result of longitudinal Young's modulus ($3.58 \times 10^{10} \text{ N/m}^2$) and that of Jaswon *et al*'s (1968) value ($5.65 \times 10^{10} \text{ N/m}^2$). In the absence of primary bonds, the recalculated elastic constants give a significant value of Young's modulus ($3.88 \times 10^9 \text{ N/m}^2$).

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