

Variance-range function analysis of X-ray line profile broadening in ramie cellulose

K P Sao*, B K Samantaray and S Bhattacharjee

Department of Physics & Meteorology, Indian Institute of Technology,
Kharagpur-721 302, West Bengal, India

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Abstract : Cellulose lattice can be characterized as a paracrystalline with distortions of second kind and also as a layered structure consisting of two dimensional layers or sheets of chain molecules. The paracrystalline distortion and the variability of interlayer spacing in ramie fibre have been studied respectively using a single peak X-ray diffraction method based on the analysis of variance-range function of line profile. The results show the anisotropic behaviour of raw (Cellulose I) and mercerized (Cellulose II) ramie crystallites with respect to lateral dimensions, paracrystalline distortions and variability of interlayer spacing defects. In general, there is a broad agreement between the analysis of paracrystalline distortion and variability defect parameters in ramie on mercerization treatment.

Keywords : Cellulose, paracrystalline distortion, variability of interlayer spacing

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1. Introduction

The structure of cellulose has been the subject of sustained study largely because of its complexity of structural features and multiplicity of applications and uses [1,2]. The crystalline structure of cellulose due to the lateral packing of glucosidic chains and the hydrogen bonding capacity of its hydroxyl groups, is generally characterized by distortions and defects to a greater or lesser degree. Cellulose lattice has been considered to be paracrystalline in nature with distortions of second kind (type II). Such distortions in which long range order is lost in the lattice, can be thought to be generated due to the packing disorder of near-neighbour chain molecules in the structure [3,4]. Based on the paracrystalline model, several studies [3–7] have been reported on the structural characterization of cellulose. However, cellulose in solid state behaves as a layered structure [2, 8–10]. The cellulose lattice can be regarded as consisting of two dimensional

* Present address : Physics Division, JTRL (ICAR), 12, Regent Park, Calcutta-700 040, India

layers or sheets of chain molecules held together by weak van der Waals forces. In such a layered structure, the variability in the interlayer spacing constitutes an important defect [9,10]. This defect consists of the variation of interlayer spacing (d) at random intervals due to the displacements of the layers in a direction normal to the layer themselves so that the spacing is $d \pm gd$ where g is a fraction of interlayer spacing. It is well known [4, 9–14] that the mathematical analysis of the variance-range function of X-ray line profile broadening provides a reliable method for the quantitative analysis of the different types of defects in the crystallite. However in cellulose, not much attention has been paid in this direction. In our earlier communication [10], a single line X-ray technique based on the analysis of variance-range function, has been described for the quantitative analysis of variability defects in cellulose. In the present work, both the paracrystalline and layered structure models of cellulose have been considered and the disorder parameters have been studied. Such studies are of considerable interest not only for a better understanding of the complex behaviour of cellulose but also for examining the reliability of new methods in structural analysis.

2. Theoretical considerations

For scattering of X-rays from an aggregate of distorted crystallites, the t -th order Fourier coefficient of the line profile due to distribution of intensity around a reciprocal lattice point can be written as [3,4]

$$A(t) = A_s(t)A_d(t), \quad (1)$$

where $A_s(t)$ and $A_d(t)$ refers to the terms due to crystallite size and due to defects other than crystallite size respectively. $t = nd$ is a distance in real space normal to the given set of reflecting planes. d is the interlayer spacing and n is the harmonic number. The general expression for variance as given by Wilson [11] is

$$W(s) = -\frac{1}{4\pi^2} \left[2\alpha(s) \frac{J'(0)}{J(0)} + \frac{J''(0)}{J(0)} + \left(\frac{K'(0)}{J(0)} \right)^2 \right], \quad (2)$$

where $s = 2 \sin \theta / \lambda$ is the diffraction space variable. $J(t)$ and $K(t)$ refers respectively to the real and imaginary parts of equation (1) such that

$$A(t) = J(t) - iK(t), \quad (3)$$

$\alpha(s)$ being the total range given by

$$\alpha(s) = \left(\frac{\cos \theta}{\lambda} \right) \cdot \Delta 2\theta, \quad (4)$$

where $\Delta 2\theta = 2\theta_1 - 2\theta_2$ is the angular range over which the variance $W_{2\theta}$ is evaluated and

$$W(s) = W_{2\theta} \frac{\cos^2 \theta}{\lambda^2}. \quad (5)$$

From eqs. (1) and (2), the general expression for the variance-range function of defect profile can be written as

$$W(s) = K_{0,s}\sigma(s) - W_{0,s}, \quad (6)$$

which shows that the plot of $W(s)$ versus $\sigma(s)$ is linear with slope and intercept given by $K_{0,s}$ and $W_{0,s}$, respectively.

2.1. Paracrystalline distortion :

The paracrystalline distortion parameter g_p is defined by the relation [3,4]

$$g_p^2 = \frac{\langle d^2 \rangle - \langle d \rangle^2}{\langle d \rangle^2} \quad (7)$$

The quantity g_p^2 is the reduced variance of the interplanar spacing vector. The normalised cosine part of Fourier coefficients for size and paracrystalline distortion broadening can be written as [3-6]

$$AJ(t) = \left(1 - \frac{t}{M}\right) \exp\left(-2\pi^2 m^2 g_p^2 \cdot \frac{t}{d}\right), \quad (8)$$

where \bar{M} is the average crystallite size and m is the order of reflection. The variance-range function from eqs. (2) and (8), has been worked out in cellulose by several workers [4,5,13]. The slope and intercept of eq. (6) are given by

$$K_{0,s} = \frac{1}{2\pi^2} \left(D + \frac{1}{M}\right) \quad (9)$$

and
$$W_{0,s} = \frac{1}{4\pi^2} \left(D^2 + \frac{2D}{M}\right). \quad (10)$$

where $D = 2\pi^2 m^2 g_p^2 / d$. Thus \bar{M} and D and hence g_p can be determined from the above equations.

2.2. Variability defects in layered structure :

Variability defect is best identified by asymmetrical broadening of reflections of type (001). By suitable transformation any hkl reflection can be converted into a (001) reflection and d_{hkl} to d_{001} normal to the reflecting planes. If γ be the transition probability and g be the mean fractional change of spacing in the d_{001} direction, then the defect profile from a layer structure is given by [9-11]

$$I(\omega) = NF^2 \frac{2\gamma(1 - \cos 2\pi l g)}{\gamma^2(1 - \cos 2\pi l g)^2 + (2\pi\omega + \gamma \sin 2\pi l g)} \quad (11)$$

where N is the number of layers and F is the structure amplitude of a layer for a given direction. The intensity being measured in the reciprocal space corresponding to a non-integral index $l + \omega$, l being an integer and $\omega = 0$ corresponds to the reciprocal lattice point.

If Δ be the shift of the peak from the centroid of the diffraction profile and β_d the integral width, then it can be shown that

$$\Delta = \frac{\gamma}{2\pi} \sin 2\pi l g \quad (12)$$

and
$$\beta_d = \frac{\gamma}{2} (1 - \cos 2\pi l g), \quad (13)$$

so that
$$g = \frac{1}{\pi l} \cdot \cot^{-1} \left(\frac{\pi \Delta}{\beta_d} \right). \quad (14)$$

The Fourier transform of the defect profile can be written as [9–11]

$$A(t) = NF^2 \exp(-2\beta_d t) \exp(-ibt), \quad (15)$$

where $b = \gamma \sin 2\pi l g$. From eqs. (2), (3) and (15) we obtain

$$W_d(s) = \frac{1}{\pi^2} [\sigma(s)\beta_d - \beta_d^2]. \quad (16)$$

The variance due to particle size is given by [9–12]

$$W_p(s) = \frac{1}{2\pi^2 p} \cdot \sigma(s), \quad (17)$$

where p is the true particle size. Thus the total variance can be written as

$$W(s) = \frac{1}{2\pi^2 p'} \sigma(s) - \frac{\beta_d^2}{\pi^2}, \quad (18)$$

where $1/p' = 1/p + 2\beta_d$. Eq. (18) shows that a plot of $W(s)$ versus $\sigma(s)$ will be linear. From the slope and intercept of the linear plot p and β_d and hence g and γ can be determined using eqs. (12) and (13).

3. Experimental

Ramie fibres degummed to 2–3 % gum content and mildly bleached were taken for present study. The fibres were mercerized by treatment with strong aqueous NaOH solutions of concentration 18% and 30% (w/w) respectively at room temperature (~ 30°C) and 12% (w/w) at 0°C following the procedures described elsewhere [3,4]. The X-ray line profiles of finely powdered and randomised fibre samples were recorded by a Phillips PW 1710 X-ray diffractometer at 40 KV and 20 mA using Ni filtered CuK_α radiation. The methods for the various corrections and the separation of partially overlapped peaks were the same as described earlier [3,4]. Due to close proximity of the (020) reflections (*c*-axis is taken as the fibre axis) of cellulose I and cellulose II, no attempt was made to separate the composite peak in the observed pattern of mixed lattice. Since the profiles were quite broad in nature, the correction for instrumental broadening was considered to be negligible compared to the

intrinsic broadening of the fibre sample. For calculation of variance-range function, a computer program in FORTRAN was written and run in a Cyber 180 computer. From the slope and intercept of the variance-range function plot, lateral crystallite size (\bar{M}), paracrystalline distortion (g_p) and variability defect parameters (g and γ) were determined as described above.

4. Results and discussion

The variance-range plots for (1 $\bar{1}$ 0), (110) and (020) profiles of raw (cellulose I) and mercerized (cellulose II) ramie crystallites are shown in Figures 1 and 2. Table 1 gives the

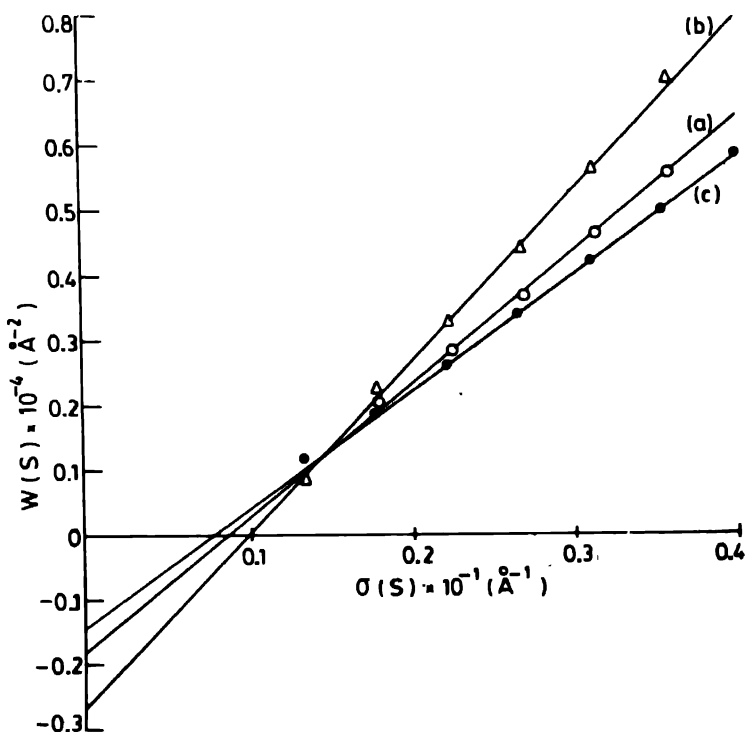


Figure 1. Variance-range function of raw ramie (a) (1 $\bar{1}$ 0), (b) (110) and (c) (020) reflections.

results of analysis for lateral crystallite size and paracrystalline distortion parameter. The variability defect parameters g and γ are given in Table 2.

Table 1 shows the anisotropic nature of the crystallites in ramie fibre in terms of lateral size and paracrystalline distortion parameter. It may be mentioned here that there have developed over the years two different points of view regarding the nature and size of basic structural entity beyond unit cell of the crystalline structure of cellulose. The first one considers [15,16] the so called microfibrils (100–200 Å wide) as the ultimate building blocks of cellulose while the second view considers [17–19] the elementary or protofibrils (~ 35 Å wide) as the building blocks. Moreover, the crystallization habits of cellulose are not

yet completely understood. The traditionally held view is that they are bound laterally by $(1\bar{1}0)$ and (110) faces parallel to the fibre axis [20]. According to this view, the cross

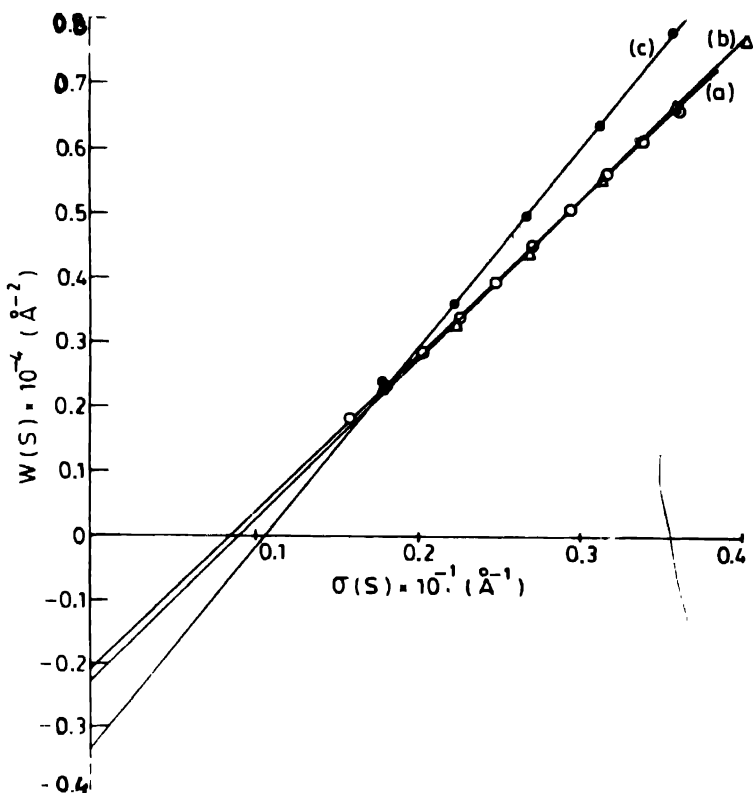


Figure 2. Variance-range function of mercerized (18 % NaOH at RT) ramie cellulose II reflections (a) $(1\bar{1}0)$, (b) (110) and (c) (020) .

section $31 \text{ \AA} \times 23 \text{ \AA}$ of the crystallites in ramie (Table 1), agrees well with that of elementary fibrils [21]. Table 1 also shows that the paracrystalline distortion parameter (g_p) values are more for the (110) and $(1\bar{1}0)$ planes compared to that corresponding to (020) planes. In the native cellulose I lattice (020) plane coincides with the plane of chain rings while the hydroxyl rich (110) and $(1\bar{1}0)$ planes may be more vulnerable to structural distortion [2,5]. In the mercerized cellulose II lattice, it is observed from Table 1 that the g_p value is higher for the $(1\bar{1}0)$ planes compared to those of (110) and (020) planes. This may be due to the change in the molecular chain conformation on transition to cellulose II lattice. Due to the breaking of the hydrogen bonds and rotation of the plane of anhydroglucose unit during swelling reaction, the hydroxyl groups lie in the $(1\bar{1}0)$ planes of the mercerized cellulose [2]. This might contribute to the increase in distortion for the $(1\bar{1}0)$ reflection as observed above. It is interesting to see from the Table 1 that the cross sectional shape of cellulose II crystallite in the mercerized sample, is more or less square. This result is in

accordance with the electron microscopic observation by Hindeleh and Johnson [22] in Fortisan sample.

Table 1. Lateral crystallite size and paracrystalline distortion parameter in ramie by variance-range function analysis.

Sample	Cellulose lattice type	Reflection					
		(1 $\bar{1}$ 0)		(110)		(020)	
		\bar{M} (Å)	g_p (%)	\bar{M} (Å)	g_p (%)	\bar{M} (Å)	g_p (%)
Untreated ramie	I	31	5.2	23	5.5	32	4.2
Mercerized ramie		II					
i) 18% NaOH at R. T.		26	5.9	26	4.8	21	4.8
ii) 30% NaOH at R. T.		24	6.2	25	4.8	20	4.9
iii) 12% NaOH at 0°C		26	6.2	23	4.9	18	4.9

Table 2. Variability defect parameters (g and γ) in ramie.

Sample	Cellulose lattice type	Reflection								
		(1 $\bar{1}$ 0)			(110)			(020)		
		d (Å)	g	γ	d (Å)	g	γ	d (Å)	g	γ
Untreated ramie	I	5.99	0.19	0.04	5.40	0.20	0.05	3.90	0.23	0.01
Mercerized ramie		II								
i) 18% NaOH at R. T.		7.38	0.31	0.02	4.42	0.26	0.03	4.04	0.12	0.04
ii) 30% NaOH at R. T.		7.38	0.38	0.02	4.42	0.28	0.03	4.11	0.10	0.05
iii) 12% NaOH at 0°C		7.38	0.41	0.02	4.40	0.17	0.07	4.11	0.09	0.07

Table 2 shows the anisotropic nature of variability defect parameters (g and γ) in ramie. It is seen that in ramie cellulose I crystallites, the extent of variability (g) is more while the proportion of such affected planes (γ) is less corresponding to (020) planes compared to those corresponding to (1 $\bar{1}$ 0) and (110) planes. It is further seen that by mercerization treatments both at room temperature and at 0°C, g and γ values change appreciably in all directions. In the cellulose II lattice in general, g value is more and γ is less for the (1 $\bar{1}$ 0) planes compared to those for (110) and (020) planes. The principal physical process responsible for swelling is diffusion of swelling reagent molecules of low molecular weight in the polymer. It is generally argued that swelling causes an expansion in the direction perpendicular to (1 $\bar{1}$ 0) plane [2]. The decrease in γ with increase in g can be explained [9,10] considering that the existence of variability defect in a layer may induce other layers to follow suit in a cooperative way as van der Waals interaction exists among them. With the increase in g value, the weaker van der Waals forces between the layers reduce decreasing γ . The reverse effect namely decrease of g value accompanied by corresponding increase in γ values as observed in case of (020) reflection, can be explained

in the same way by considering the increase in the van der Waals forces with decrease of g . This indicates a possible relatively strong interlayer bonding between molecular sheets along these directions. The change in g and γ on conversion from cellulose I to cellulose II crystallite, indicates that the layer or sheet of chains plays an important role in swelling reaction. It is also evident that there is in general, a broad agreement between the results of analysis of paracrystalline distortion and variability defects in ramie on mercerization treatment.

5. Conclusions

The results show that ramie cellulose crystallites are anisotropic with respect to lateral dimensions, paracrystalline distortions and variability of interlayer spacing defects. The lateral size of crystallites in raw ramie, supports the elementary fibrillar model of cellulose and the values of paracrystalline distortion parameters (g_p) corresponding to the (110) and ($1\bar{1}0$) reflections are more compared to that corresponding to (020) reflection. The transverse cross sectional shape of the cellulose II crystallite appears to be more or less square. The mercerized cellulose II crystallite shows higher value of paracrystalline distortion parameter corresponding to the ($1\bar{1}0$) reflection compared to those corresponding to (110) and (020) reflections. The variability defect parameters namely, the mean fractional change in the interlayer spacing (g) and the proportion of such affected planes (γ), are observed to change appreciably on mercerization. The mercerized cellulose II lattice shows a higher value of g and corresponding lower value of γ for the ($1\bar{1}0$) planes compared to those for the (110) and (020) planes. The results show that there is in general, a broad agreement between the analysis of paracrystalline distortion and variability defects in ramie on mercerization treatment.

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