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The layer disorders defect in coir fiber under thermal and chemical treatment

D N Mahato*, B K Mathur and S Bhattacharjee

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

E-mail : dn.mahato08@yahoo.com

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Abstract : Natural coir fibers, subjected to thermal treatments in the range of 0°C to 200°C and alkali treatment with 5% to 30% concentration w/w, have been used in the present investigation to determine the interlayer variability of the cellulose planes (020), (110) and (1 $\bar{1}$ 0). Among the equatorial reflections (110), (1 $\bar{1}$ 0) and (020), the extent of variability is found to be more with the proportion of such affected planes less for (020) reflection in the native cellulose at lower temperature while at higher temperature (110) and (1 $\bar{1}$ 0) become more affected by variability defect. (110) and (1 $\bar{1}$ 0) planes are more affected also with alkali treatment.

Keywords : Variability of interlayer spacing, Proportions of plane affected, Coirfiber, Thermal and chemical treatment

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1. Introduction

Coir is a multicellular fruit fiber composed of cellulose in a polycrystalline aggregate consisting of small crystalline regions separated by amorphous boundaries and non-cellulosic materials such as hemicellulose and lignin.

In view of the escalating cost of production of the highly competitive synthetic fibers, attempts have been made to explore the possibilities of replacing these fibers by the abundantly available long hard structural fibers for application to various useful commercial purposes [1]. One such important application which has generated considerable interest over the last few years in the fabrication of the composite materials using organic matrix

* Corresponding Author : Present Address : PG Department of Physics, Tata College, Chaibasa-833 202, Jharkhand, India

resin as binders which have wide ranging applications. Already studies have been directed in these areas to utilize natural hard fibers like sisal, palm, bananas and jute [2-5]. Jute composite doors have been used for Tsunami rehabilitation in Andaman – Nicobar Island. Attempts have also been made [6-7] to fabricate composite materials based on coir and other natural fibers which are abundantly available in tropical countries like India.

The physical properties like mechanical, thermal and electrical depend on the structure of ligno – cellulosic system. Cellulose, the principal component of coir fiber, shows a distinct tendency towards crystallization, probably caused by the relative stiffness of the glycosidic chains and hydrogen bonding capacity of hydroxyl groups [8]. The flat shape of the rings and spatial distribution of the hydroxyl groups appear to favour the formation of ribbon – shaped laterally ordered sheet which exhibits a three fold anisotropy as far as bonding strength is concerned. Fibrous polymers like coir consist of long chains of thread like molecules which assume random configuration due to various factors [9]. As mentioned earlier, cellulose in solid state behaves as a laminated structure. The cellulose lattice can also be regarded as layer structure, as consisting of two dimensional layers or sheets of molecular chains held together by weak Van der Waals forces. Such layer structures which are very similar to fibrous clay minerals [10-11] are prone to develop layer disorders which are characterized by two principal types of defects : (i) Layer shift and (ii) Variability of interlayer spacing. The ab (001) projection of the monoclinic unit cell of cellulose shows that the glucopyranose units lie in the (020) (*i.e.* ac plane.) plane of the unit cell parallel to the fiber axis c . Thus, in the sheet, relatively strong hydrogen bond network occurs in ac plane whereas the weaker Van der Waals forces act perpendicular to ac – plane (*i.e.* along b) which is typical of a layer structure.

The first type of defect consists of displacement of the layers parallel to themselves by some specific fractions of the lattice spacings. The magnitude of this displacement depends on the geometry of the layer and the arrangements of the atoms in the successive layers providing the interlayer bonding. Since, in general, these displacements are favoured by the geometry of the structure as in the case of layer silicates [12] and involve no significant energy variation, the resulting structure is strain free and stable. The study of these defects requires reflections of the type $001/hkl$ with $l \neq 3n$ where the displacement in $\frac{1}{3}c$ or $\frac{2}{3}c$ similarly for displacement $\frac{1}{3}a$ or $\frac{2}{3}a$ ($\frac{1}{3}b$ or $\frac{2}{3}b$) corresponding reflections should have $h \neq 3n$ ($k \neq 3n$) as the case may be.

In general the reflections hkl with $l \neq mn$ where the displacement is $\frac{1}{m}c$ along the c -axis will be affected. These types of defect are common in clay minerals with layer structure and have been studied quantitatively by Mitra and Bhattacharjee, Loknatha and Bhattacharjee [11].

The second type of layer disorder consists of variation of interlayer spacing (d) at random intervals due to the displacements of the layers in a direction normal to the layers themselves so that the spacing is $d \pm gd$ where g is a small fraction. This type of defect generally arise due to the inclusion of water or organic molecules, whose number vary randomly, between the interlayer spaces.

These defects are of common occurrence in layer silicate clay minerals [11].

However, the possibility of existence of these defects in cellulose was first pointed by Warwicker and Wright [13] while studying the swelling reactions in cotton and ramie.

2. Theoretical basis of x-ray method

The variability defect in a crystalline material causes asymmetrical broadening of the reflections of the type 001, where interlayer spacing d_{001} normal to the plane undergoes variations.

It is well known that any hkl reflection can be converted into 001 under suitable transformation such that d_{hkl} transforms to d_{001} normal to the reflecting planes. Therefore, this single line technique first developed and applied by Mitra and Bhattacharjee [12] can be applied to any type of reflections.

If γ be the proportion of the planes affected by disorder and g be the mean fractional change in the interlayer distance d_{001} , then the defect profile from the layer structure having variability defect from the (001) planes will be given by the expression due to Wilson [14] as shown below

$$(1)$$

$$I(\omega) = \frac{2\pi F \sin 2\theta}{N \lambda} \frac{2\gamma(1 - \cos 2\pi g)}{2\pi \gamma^2 (1 - \cos 2\pi g)^2} \quad \text{where } F \text{ is the structure amplitude of a layer for the given direction and } N \text{ is the number of layers. The intensity is measured at a point in the reciprocal space corresponding to non-integral } 1 + \omega, 1 \text{ being as integer.}$$

The reciprocal lattice point corresponds to ω where ω and is a variable in reciprocal space. It follows from the eq. (1) that the shift of the peak (Δ) from the centroid of the diffraction profile and the integral width β_d will be given by

$$(2)$$

$$\beta = \frac{\gamma(1 - \cos 2\pi g)}{2} \quad (3)$$

So, that

$$g = \frac{1}{\pi d} \cot^{-1} \left(\frac{\pi \Delta}{\beta_d} \right) \quad (4)$$

Following the method described by Mitra and Bhattacharjee [12] based on the expression for variance due to Wilson [14] the variance W_d of the defect profile can be written as

$$W_d = \frac{1[\sigma\beta_d - \beta_d^2]}{\pi^2} \quad (5)$$

Taking into consideration the contribution of crystallite size the total variance of the line profile is given by

(6)

Where W_p is the variance due to crystallite size and can be written as

(7)

Where p is the true particle size of the crystallite

Using equations (5) and (6), the total variance can be written as

(8)

where $\frac{1}{p'} = \frac{1}{p} + 2\beta_d/d$

Eq. (8) shows that a plot of $W(S)$ versus $\sigma(S)$ will be a straight line. From the slope and intercept of the plot p and β_d , consequently g and γ can be calculated.

3. Experimental

Bristle retted coir fibers were obtained by the courtesy of central coir Research institute, Allepey, Kerala, India. The fibers were cut to small pieces, combed and cleaned, and then treated with different concentration of aqueous NaOH solution for two hours at each concentration 5% to 30% w/w at room temperature. A portion of this was thoroughly washed with distilled water to remove alkali to obtain mercerized fiber. Another portion was air-dried without washing to obtain soda – cellulose coir fiber which was carefully pressed to remove excess of alkali. For thermal treatment, the fibers were heated for two hours at each different temperature from 0°C to 200°C under vacuum (10^{-2} torr). The treated fibers were powdered by prolong grinding in an agate mortar and pestle and finally sieved through a screen of 200 mesh.

The X-ray diffractograms of the samples were recorded in a Philips X-ray diffractometer (PW 1710) covering the entire detectable angular range spanning between $5^\circ(2\theta)$ to $90^\circ(2\theta)$ using filtered Cu $K\alpha$ radiation at 35 kV and 30 mA.

4. Results and discussion

X-ray Diffraction (XRD) line profile analysis have been used to evaluate the layer and variability of interlayer spacing. The single line technique following Mitra and Bhattacharjee

has been used [12]. The XRD pattern is overlapped one and the three important planes (020), (110) and (110) were separated assuming Gaussian distribution of intensity.

Figures (1) and (2) show the fractional change in interlayer spacing (g) and the proportion of planes affected (τ) under thermal and chemical treatment respectively. The effect of thermal treatment on the proportion of a planes affected by disorder (τ) appears to be quite large (Figure 1) along (110) and (1 0) directions compared to (020) direction, which is not affected by thermal treatment and maintains a constant value of 0.03. For (110) and (1 0) directions, there is a gradual decrease in τ value with rise in the temperature of thermal treatment. The mean fractional change in interlayer spacing (g) for (020) plane is greater than that of (110) and (1 0) planes indicating that the sheets of planes are loosely held by weak Van der Waals forces [8]. Mean fractional change in interlayer spacing (g) appears to decrease marginally up to 120°C, and beyond 120°C increases appreciably corresponding to (110) and (1 0) directions. This indicates that upto 120°C not many planes are severely affected and only water molecules and volatile materials are removed from interchain spacings of the cellulose molecules of the coir fiber which are responsible for the marginal changes. Beyond 200°C g tends to increase while τ appears to decrease corresponding to all directions. This behaviour suggests that thermal break down starts around 200°C. Perhaps the time of heating was not enough to affect sufficient number of planes. If the time of heating is increased, probably more number of planes will be affected and the process continues till the collapse is complete like latent heat of transformation as suggested by Mitra and Bhattacharjee [12].

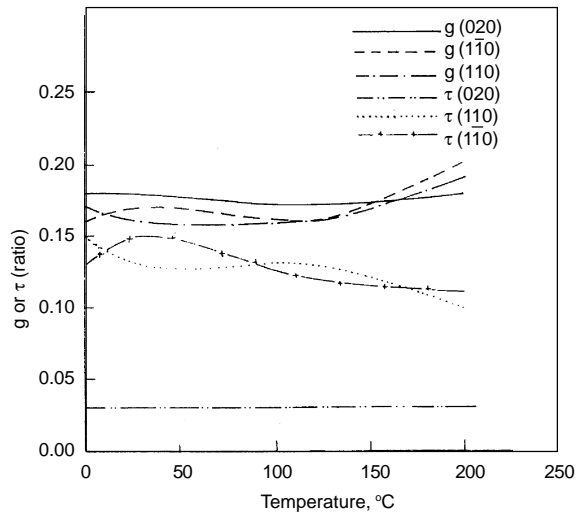


Figure 1. Variation of interlayer variability defect (g) and fraction of affected plane (τ) with temperature

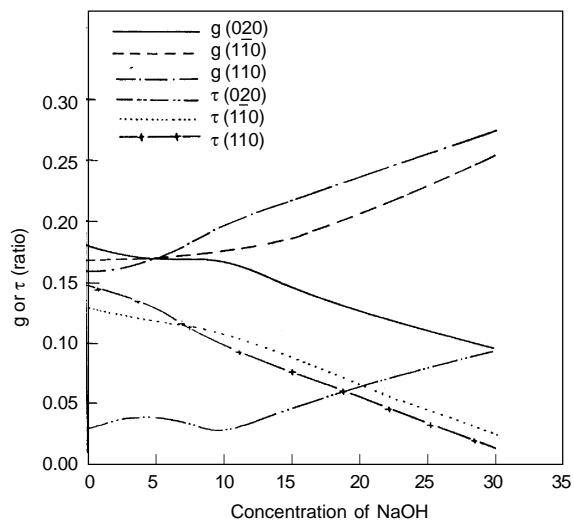


Figure 2. Variation of interlayer variability (g) and fraction of affected plane (τ) with concentration of NaOH solution.

It is seen (Figure 2) that on mercerization and at lower concentration g and γ values change quite appreciably but anisotropically. While at higher concentration, the extent of variability along (110) and (1 0) directions shows a steady rise, the values of proportion of planes affected surprisingly exhibit a regular decline. It indicates that swelling in (110) direction is more, which is due to diffusion of lower molecular weight molecules in the coir fiber. As has been observed by crystallinity study [15], a major fraction of the sample is amorphous and each step of mercerization adds further to this region. Hence goes on decreasing with higher concentration accompanied by conversion into amorphous cellulose phase, conversion of the residual crystalline part to amorphous results in lower value of

Thus the results show that in the coir – cellulose crystallites, the extent of variability seems to be more marked with alkali treatment than with thermal treatment. This is more pronounced along (110) and (1 0) directions compared to (020) direction. Those marked changes of variability parameter along (110) and (1 0) compared to (020) are in conformity with the results of thermal variations of domain size and distortion [16]. Since the (020) plane coincides with the plane of anhydroglucose rings as pointed out earlier, possibly they are affected less due to dehydration and thermal degradation in the temperature range studied compared to (110) and (1 0) planes, which are densely populated in hydrogen bonding groups. Perhaps, an increase either in the duration or in the concentration of the alkali or both may affect more number of planes which converted into amorphous phase with increase of concentration.

On soda-cellulose treatment, the variability defect (g values) corresponding to most of the reflections are observed to be more although γ values are quite small compared to the raw and mercerized sample. Thus it may be concluded that soda-cellulose treatment increases the variability because of penetration of excess of soda-solution in the interchain space.

5. Conclusion

The variation of variability defect parameters g and γ in alkali treated coir quantitatively support the concept of Warwicker and Wright [13] that the fundamental unit involved in swelling reaction of cellulose is a sheet of molecular chains. Among the equatorial reflections (110), (1 0) and (020) the extent of variability (g) is found to be more with the proportion of such affected planes (γ) less for (020) reflection in the native cellulose at lower temperature while at higher temperature (110) and (1 0) become more affected by variability defect, with alkali treatment also (110) and (1 0) planes are more affected. Planes (110) and (1 0) are the two faces which according to the traditional view, laterally bound the crystallite.

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