

NOTE

X-ray Line Profile Analysis in Alkali-Treated Ramie Fiber

INTRODUCTION

The crystalline structure of cellulose can be better characterized by size and distortion that contribute to the broadening of the X-ray line profile. The cellulose lattice has been shown^{1,2} to be paracrystalline in nature with distortions of the second kind (type II). Such distortions where the long-range order is lost in the lattice can be thought to be generated due to the packing disorder of near-neighbor chain molecules in the structure. Fourier analysis by the Warren-Averbach method^{3,4} can be applied for a reliable separation of size and distortion broadenings of the line profile in the polymeric diffraction pattern.⁵ However, this requires several orders of a reflection that are generally difficult to observe in the diffraction pattern of cellulose. In such a case single line techniques of profile analysis may prove useful for the separation of size and distortion effects.² But these methods must take into account the practical problem of background and truncation errors that severely affect the results.^{6,7} In this regard a method described by Zocchi⁷ was shown to be useful in cellulose.² Using this method, this article reports on a systematic study of lateral crystallite size and paracrystalline distortion parameter in ramie fibers treated with various concentrations of alkali at room temperature ($\sim 30^\circ\text{C}$) and at 0°C , respectively. The conversion mechanism from cellulose I to cellulose II lattice in the light of the changes in both size and distortion of the crystallites is also discussed. It may be mentioned here that although the transitions in cellulose accompanying the well-known mercerization process have been investigated using various techniques,⁸⁻¹⁵ the mechanism is yet to be fully understood. The present work forms a part of the effort for further in-depth investigation by improved experimental techniques duly supported by appropriate theory.

BRIEF THEORETICAL BACKGROUND

The normalized cosine part of the t th order Fourier coefficient of an X-ray line profile in the presence of paracrystalline distortion is given by²

$$A_t(l) = A_t^S A_t^D(l) = \left(1 - \frac{t}{\bar{M}}\right) \exp(-2\pi^2 l^2 g_p^2 t/d) \quad (1)$$

where A_t^S and A_t^D are cosine parts of size and distortion coefficients; l is the order of the reflection considering it of the type $00l$ by proper change of axes; $t = nd$ 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. $\bar{M} = \bar{N}d$ where \bar{N} is the number-average crystallite size. g_p is the paracrystalline distortion parameter defined as²

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

The main problem in using eq. (1) for the determination of size and distortion parameter is that the results are severely affected by background and truncation errors. Fourier coefficients of lower orders are affected more than those of higher orders for which the error in Fourier coefficient versus background error curve is oscillatory.⁶ Zocchi⁷ showed that the truncation error also changed the functional behavior of A_t . In other words the experimentally determined coefficients do not oscillate about A_t but about a different function of t . Thus any procedure based on least square fitting of eq. (1) may give erroneous values of microstructural parameters. However, the first derivative of eq. (1) can be approximated as^{2,7}

$$A'_t = \left(D^2 + \frac{2D}{\bar{M}}\right) \cdot t - \left(D + \frac{1}{\bar{M}}\right) \quad (3)$$

where

$$D = \frac{2\pi^2 l^2 g_p^2}{d} \quad (4)$$

The first derivatives of experimentally determined coefficients were shown⁷ to oscillate about the theoretical curve A'_t in a damped fashion, and a least square fitting based on the function A'_t can give meaningful microstructural parameters even in the presence of large truncation error.

EXPERIMENTAL

The ramie fiber sample and the methods of aqueous NaOH treatments at room temperature ($\sim 30^\circ\text{C}$) and at 0°C ,

respectively, were the same as described in detail earlier.^{2,15} The equatorial X-ray line profiles of finely powdered and randomized samples were recorded by a Phillips X-ray diffractometer PW 1710 at 40 kV and 20 mA. The corrections for background and the separation of partially overlapped peaks were carried out following the procedures described elsewhere.² Because the profiles were quite broad in nature, the correction for instrumental broadening was considered negligible compared to the intrinsic broadening of the fiber sample. The crystallite size and paracrystalline distortion parameters were determined using eq. (3) as described in detail earlier.²

RESULTS AND DISCUSSION

A typical plot of A'_n versus n for the $(1\bar{1}0)$ profile of raw ramie (c axis is taken as the fiber axis) is shown in Figure 1. Table I gives the results of Fourier analysis for crystallite size and paracrystalline distortion parameters of alkali-treated ramie with concentration and temperature as variables. It is seen from Table I that at lower concentration of alkali (e.g., below 12% NaOH at room temperature or 6% NaOH at 0°C), there is no appreciable change in crystalline cellulose I lattice to cellulose II and the paracrystalline distortion in general decreases significantly with an increase in crystallite size. This indicates that the lower concentrations of alkali probably affect the amorphous and also highly distorted smaller paracrystalline regions,¹⁵ thereby reducing the distortion. The increase in crystallite size can be explained² by assuming a distribution of lateral crystallite size where the smaller and highly distorted crystallites are first affected by alkali at lower concentration, thereby aiding the resultant crystallite size. These highly distorted paracrystalline domains may lie on the fringe of crystallites so that at higher concentrations, say above 12% at room temperature or above 6% at 0°C, alkali penetrates the more perfect crystalline regions converting cellulose I lattice to cellulose II.

It is further seen from Table I that in the mercerized cellulose II lattice the lateral crystallite size corresponding to the $(1\bar{1}0)$ reflection is less while the paracrystalline distortion is more compared to that of the native cellulose I

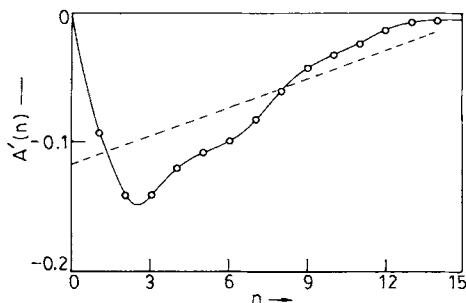


Figure 1 A typical plot of the first derivative of Fourier coefficients (A'_n) versus harmonic number (n).

Table I Lateral Crystallite Size (\bar{M}) and Paracrystalline Distortion (g_p) in Alkali-Treated Ramie

Treatments	Reflection and Lattice Type								
	$(1\bar{1}0)_{II}$		$(110)_I$		$(020)_{I&II}$				
	\bar{N} (No. Av.)	\bar{M} (Å)	g_p (%)	\bar{N} (No. Av.)	\bar{M} (Å)	g_p (%)	\bar{N} (No. Av.)	\bar{M} (Å)	g_p (%)
Untreated	—	—	—	—	—	—	16.2	64	4.0
8% NaOH (RT)	—	—	—	—	—	—	21.5	84	3.5
12% NaOH (RT)	—	—	—	—	—	—	22.4	88	3.6
15% NaOH (RT)	8.5	63	5.5	8.7	46	5.8	15.1	60	3.7
18% NaOH (RT)	8.5	63	5.7	8.3	44	5.6	15.9	64	4.0
30% NaOH (RT)	8.5	63	5.9	7.9	47	5.1	14.7	61	4.2
6% NaOH (0°C)	—	—	—	13.4	72	—	19.6	77	3.6
9% NaOH (0°C)	8.1	60	5.7	9.8	53	5.8	17.2	67	3.8
12% NaOH (0°C)	8.1	60	5.9	7.9	43	6.0	12.8	53	4.4

crystallites. However, no appreciable change in this size of cellulose II crystallites is seen with increasing concentration of alkali above the mercerizing strength, although the distortion appears to increase slowly with concentration. Similar effects are observed at the 0°C treatment but at a much lower concentration of alkali compared to that of the room temperature treatment. The size of the cellulose II crystallites corresponding to the (110) reflection is smaller with higher value of distortion parameter compared to that of the native cellulose I crystallites. With increasing concentration of alkali above mercerizing strength, this size of cellulose II crystallites appears to increase, indicating an aggregating tendency with a corresponding decrease in the distortion parameter. The higher distortion parameter observed in 15% NaOH at room temperature and in 9% NaOH at 0°C might be due to the highly disturbed state owing to the incomplete transformation to cellulose II. Due to the close proximity of the (020) reflections of cellulose I and cellulose II, no attempt was made to separate the composite peak from the observed pattern of the mixed lattice. However, the results in general show a decrease in crystallite size value corresponding to this reflection on mercerization treatments at room temperature as well as at 0°C. It is further seen from Table I that at room temperature (RT) and at 0°C treatments, the size of the cellulose I crystallite decreases while the distortion parameter increases with increasing concentration of alkali above mercerizing strength.

It may be worthwhile to mention here that there are two different points of view regarding the conversion of cellulose I crystallites to cellulose II. One considers the peeling off mechanism^{10,16} where the cellulose I crystallite size should decrease with more and more conversion to cellulose II; the other view holds that at a given NaOH concentration of mercerizing strength, either a cellulose I crystallite is completely transformed to cellulose II or not at all.⁹ These two apparently opposite views can be reconciled if the measured lateral dimensions of the crystallites can be identified either with the elementary fibril^{17,18} or the microfibril that may be a disordered aggregate of elementary fibrils.^{19,20} It is seen from Table I that the value of size obtained does not seem to fit the dimension of elementary fibril¹⁷ and is much higher. However, in the conversion of cellulose I to cellulose II, the most important basic problem is the transformation of parallel chain structure to antiparallel chain structure. As pointed out by Blackwell et al.,²¹ the conversion to cellulose II must be viewed as a thermodynamically more stable rearrangement of chains and a large lateral shift of chains is hard to rationalize. Nishimura and Sarko¹⁰ assumed the presence of oriented amorphous regions containing chains of both polarity where the formation of cellulose II starts.

To better understand the results of our experiments, a model of ramie fiber structure consisting of crystalline, oriented amorphous, highly distorted crystalline, and amorphous regions respectively [shown in a simplified way in Fig. 2(a)] may be considered. The amorphous and highly distorted crystalline regions lie on the fringe of the crys-

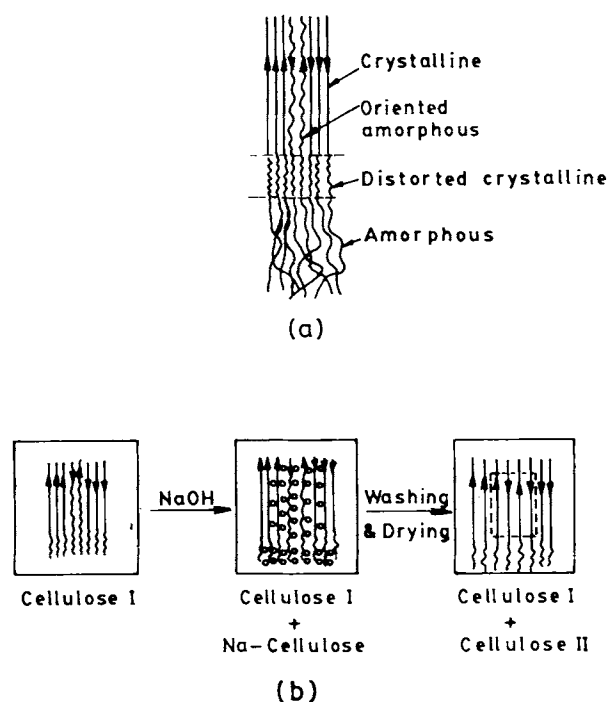


Figure 2 (a) Model of ramie fiber structure. (b) Mechanism of transformation of cellulose I to cellulose II where arrow indicates chain direction.

tallites that may be coupled to the adjacent crystallites through the oriented amorphous zones containing cellulose chains of both polarities. The alkali of concentration lower than the mercerizing strength affects, respectively, the amorphous and the highly distorted smaller crystalline regions, thereby reducing the distortion and aiding the resultant crystallite size. At concentrations of mercerizing strength, the alkali affects the oriented amorphous regions and finally the crystalline regions. Thus cellulose I crystallite with parallel chain structure decreases in lateral size on conversion to cellulose II lattice with antiparallel chain structure as shown in Figure 2(b). The above mechanism of mercerization, depending largely on the availability of oriented amorphous coupling regions between the cellulose I crystallites, seems to well explain why it is difficult to completely disrupt the cellulose I lattice in a single mercerization treatment and also the high resistance to mercerization of highly crystalline valonia cellulose and microcrystalline cellulose.²² However, the model offered for explanation is not beyond dispute and more light needs to be focused on the nature of these oriented amorphous zones and disordered amorphous regions.

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