

X-Ray Investigations on Cellulose II and Mixtures of Cellulose I and II

2. Lateral Order in Cellulose II

JON GJØNNES and NICO NORMAN

Central Institute for Industrial Research, Oslo, Norway

The origin of broadening and displacement of the lines of cellulose II is discussed and related to the lateral order in the micelles.

In the preceding paper¹ a method is devised for characterizing samples of cellulose II and mixtures of cellulose I and II by suitable parameters measured from their X-ray diffractograms. It is the purpose of this paper to discuss the interpretation of the parameters describing the cellulose II-fraction, in particular their relation to the structure and lateral order of the micelles.

Table 1. Peak angles and half widths for samples of cellulose II. CuK α -radiation.

Specimen	(10 $\bar{1}$) reflection		(002) reflection	
	Peak angle (degree)	Half width (degree)	Peak angle (degree)	Half width (degree)
1. Mercerized cotton treated with 39 % HCl for 3 h	20.08	1.24	22.16	1.12
2. Mercerized acetate grade wood pulp	20.16	2.86	21.59	3.10

The half widths of the reflection (10 $\bar{1}$) and (002) obtained from the measurements described in the preceding article are presented in Table 1. As is well known, the X-ray line widths depend both on the size and lattice perfection of the reflecting crystallites. It is seen, however, that the data presented in Table 1 display no differences in line width of the reflections (10 $\bar{1}$) and (002)

for the same sample. This is quite remarkable, as the crystallites of cellulose II are commonly accepted to be ribbon shaped with the largest surface parallel to the (101) planes. If the particle size was the most predominant factor in determining the line widths, one would expect considerable differences in widths of the different reflections ($h0l$) from planes parallel to the chain axis, the (10 $\bar{1}$)-line being by far the narrowest. We are thus led to the conclusion that at least the width of the (10 $\bar{1}$) line to a great extent is determined by other factors, in particular lattice disorder. From the measured half widths *lower limits* for the particle size may be computed, leading to the values 30 Å for the mercerized pulp and 85 Å for the hydrolyzed sample.

There is additional evidence that the actual dimensions of the crystallites may be appreciably greater than the above mentioned values. Thus the line widths obtained for the mercerized pulp also seem to apply to mercerized samples prepared from cotton, which in the native state is reported to have lateral dimensions² of 50–80 Å. A particularly illustrative example of the alterations in line width of the cellulose II reflections resulting from chemical treatment is offered when cotton is treated with hydrochloric acid^{1,3}. At first when cellulose II is formed there is a pronounced increase in line width, whereas prolonged acid treatment results in a gradual sharpening of the lines leading to a half width still lower than for the original native sample. It seems highly improbable that these variations in line width reflect changes in the lateral dimensions of the micelles. It can therefore be concluded that transformation of native cellulose into cellulose II by mercerization or acid treatment increases lattice disorder, whereas prolonged acid treatment leads to an improvement of the lattice order. This increase in lateral order is far more pronounced than what has been found in the cellulose I fraction after chemical treatments^{3,4}.

To obtain the best possible interplanar spacings for the investigated pure cellulose II-samples, the peak positions of the (101) and (002) reflections were corrected for the effect of overlapping peaks. The correction assumed Cauchy profile for the contribution from the neighbouring peaks and was based upon the half widths given in Table 1. The resulting interplanar spacings are tabulated in Table 2 together with (101)-spacings obtained from peak angles measured above an oblique linear background in the angular region $2\theta = 10^\circ - 15^\circ$.

These results which display considerable anisotropy in the variation of cell dimensions normal to the chain axis is in conformity with other measure-

Table 2. Interplanar spacings for samples of cellulose II.

Specimen	$d_{101}(\text{Å})$	$d_{10\bar{1}}(\text{Å})$	$d_{002}(\text{Å})$
1. Mercerized cotton treated with 39 % HCl for 3 h	7.22	4.42	4.01
2. Mercerized acetate grade wood pulp	7.27	4.42	4.05

ments of interplanar spacing of cellulose II⁶⁻⁸. It is a general feature that the (10 $\bar{1}$) spacing is found to be almost constant, even when cellulose is swelled to form hydrates. The other equatorial reflections, particularly (101) show pronounced variations. According to the currently accepted structure of cellulose II the intermolecular hydrogen bonds are mainly pointing in the direction of the [101] cell diagonal, and the structure can be described as a packing of hydrogen bonded sheets of cellulose chains parallel to the (10 $\bar{1}$) planes⁹.

It is thus seen that the best ordered cellulose II-samples display a shorter interchain distance within the sheets than the less ordered one, and one may tentatively suggest these differences to reveal variations in the strength and ordering of the hydrogen bonds. Another explanation is to assume the least ordered samples to possess somewhat more inter-crystalline water than the best ordered ones, leading to a greater average interchain distance.

If the above considerations hold true, it is evident that the lateral order concept outlined by Howsmon and others^{10,11} and related to the strength and distribution of hydrogen bonds will be most intimately connected with the lattice disorder in the [101] direction. The (10 $\bar{1}$) line width will, on the other hand, depend on disorder in the packing of the hydrogen bonded sheets. The nature of this disorder can not be stated from our present knowledge. A tempting explanation may be to assume some of the sheets to be incomplete, implying edge dislocations to be contained in the micelles and taking (101) as the slip plane. Assuming cellulose II to occur in a swollen state in the strong hydrochloric acid³ this model can apparently account for the ordering resulting from acid treatment.

It should be pointed out, however, that the X-ray measurements within rather narrow limits give the same line width for all reflections from planes containing the chain axis, indicating the combined effect of disorder or distortion and possible particle size on the line width to be of the same magnitude in all directions normal to the chain axis.

REFERENCES

1. Gjønnnes, J. and Norman, N. *Acta Chem. Scand.* **14** (1960) 683.
2. Treiber, E. *Die Chemie der Pflanzenzellwand*, Springer, Berlin, 1957, p. 164.
3. Ellefsen, Ø., Gjønnnes, J. and Norman, N. *Norsk Skogind.* **13** (1959) 411.
4. Gjønnnes, J. and Norman, N. *Acta Chem. Scand.* **12** (1958) 2028.
5. Immergut, E. A. and Rånby, B. G. *Ind. Eng. Chem.* **48** (1956) 1183.
6. Wellard, H. J. *J. Polymer Sci.* **13** (1954) 471.
7. Kast, W. and Schwarz, R. *Z. Elektrochem.* **56** (1952) 220.
8. Kratky, O. and Treiber, E. *Z. Elektrochem.* **55** (1951) 716.
9. Honeyman, J. *Recent Advances in the Chemistry of Cellulose and Starch*, Heywood & Company LTD, London, 1959, p. 165.
10. Ott, E. and Spurling, M. *Cellulose and Cellulose Derivatives*, Interscience, New York, 1954, p. 251.
11. Marchessault, R. H. and Howsmon, J. A. *Textile Research J.* **27** (1957) 30.

Received November 11, 1959.