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Determination of Distortions and Sizes of Cellulose Nanocrystallites

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ABSTRACT

The wide angle X-ray scattering (WAXS) is widely used method to evaluate sizes of cellulose nanocrystallites by means of the Scherrer's equation. However, the Scherrer's methodology has a limitation, since a width of X-ray diffraction peaks depends not only on the size of crystallites but also on other factors, such as instrumental effect, second-order distortion degree of crystalline lattice, δ, and factor $\Delta=4\delta tg\Theta$. Since these factors are ignored this leads to understated sizes of nanocrystallites. In this research a simple procedure was proposed to determine δ and Δ factors, as well as actual sizes of CIβ nanocrystallites. Values of δ were calculated using average deviation of interplanar spacing in the distorted lattice from its value in undistorted crystalline lattice. It was also shown that δ and Δ factors are linear functions of interplanar spacings (d) of crystalline lattice. After finding the δ and Δ factors, the correction for broadening of diffraction peaks was calculated, which allows determining the actual width (D_a) and actual length (L_a) of nanocrystallites. Study of various samples of CIβ showed that tunicate cellulose has the largest crystallites: D_a=13 nm and L_a = 400 nm. Actual sizes of nanocrystallites in isolated celluloses of other origin (herbaceous plants, wood, bast fibers, cotton fibers, etc.) were smaller: D_a was in the range of 4.2 to 10 nm, whereas L_a in the range of 48 to 116 nm.

Keywords: *WAXS, Peaks broadening, Instrumental factor, Lattice distortions, Cellulose, Nanocrystallites, Approximate sizes, Actual sizes*

INTRODUCTION

As is known, natural cellulose of various origin is a semi-crystalline polysaccharide, which contains 50-80% of crystalline phase in a form of rod-like nanocrystallites of different sizes [1]. Knowledge of sizes of nanocrystallites is very important because it allows clarify the supra molecular organization of cellulose fibers and structure of cellulosic products such as nano crystalline particles, nanofibrils, etc. There are several methods for measuring the size of the nanocrystallites: electron microscopy (EM), atomic force microscopy (AFM), wide-angle X-ray scattering (WAXS), etc. Besides the average length of crystallites can be estimated from level-off degree of polymerization (P) of the hydrolyzed cellulose samples [2, 3]. The results of EM, AFM, P and other methods showed that nanocrystallites of natural cellulose have rod-like shape, 3-15 nm in transverse direction and 100-500 nm in longitudinal direction [4-6].

However, the EM, AFM and P methods require prior isolation of the free nanocrystallites, for example by acid hydrolysis. On the other hand, WAXS is considered as a non-destructive method that is widely used to estimate the sizes of crystallites by means of the Scherrer equation. This equation was proposed as early as the beginning of the 20th century [7], and it continues to be widely used at present, despite significant limitation, and namely: width of the X-ray diffraction peaks depends not only on the size of crystallites but also on other factors, such as instrumental effect and second-order distortions of crystalline lattice caused by paracrystallinity, dislocations, twinning, internal stresses, boundaries of crystallites, etc. [8].

This limitation of the Scherrer equation is often ignored, which leads to unreliable results. For example, study of pulp, bast fibers and cotton cellulose by approximate WAXS - Scherrer method gave low Scherrer's length of nano crystallites, 20-35 nm [9-11], instead of their actual length of 100-200 nm [4-6]. This discrepancy may be due to neglect of such factors as lattice distortions, instrumental factor, incorrect orientation of the sample during recording, overlapping of reflection (004) by other reflexes, etc. When measuring the transverse sizes of cellulose nanocrystallites, the difference between the results obtained by WAXS-Scherrer method and independent methods is smaller than in the case of determination the length of crystallites.

The method of measuring the correction for the instrumental factor is well known [12]. However, the methodology for determining the contribution of lattice distortions to the width of diffraction peaks is complex, and therefore it was used in a minor extent. For instance, the correction in the broadening of peaks due to effect of lattice distortions in transverse directions of crystallites was estimated at 0.02-0.03 radians [13, 14].

The purpose of this research was elaboration of simple algorithm for determining the contribution of lattice distortions to broadening of diffraction peaks, which allows to find the actual sizes of cellulose nanocrystallites by means of non-destructive WAXS method.

EXPERIMENTAL

Raw-Materials

The following natural sources were used for isolation of cellulose:

- Wheat straw (WS)
- Bagasse of sugar cane (BG)
- Chips of soft (spruce) wood (SW)
- Chips of hard (poplar) wood (HW)
- Bast fibers of flax (FL)
- Cotton fibers *Acala* (CT)
- Tunicate *Halocynthia roretzi* (TN)

Pure cellulose samples having CIβ crystalline allomorph were isolation from raw-materials by methods described in [15]. Besides, two additional cellulose samples were studied, and namely microcrystalline celluloses prepared from isolated cotton cellulose (CM) and cellulose of softwood (WM) by hydrolysis with boiling 2.5 N HCl for 60 min.

Acid Hydrolysis

Hydrolysis of the cellulose samples up to level-off degree of polymerization (P) was carried out by boiling 2.5 N HCl for 60 min followed by washing and drying. The P value was measured by Cuen-viscosity method [16]. Determination of P enables to estimate the average length of cellulose crystallites (L, nm) [3]:

$$L_p = 0.517P \quad (1)$$

METHOD OF X-RAY DIFFRACTION

X-ray measurements have been carried out by a diffractometer in the 2Θ angle range from 5 to 80°. CuKα radiation had wavelength λ = 0.15418 nm. Collimation included a system consisting of vertical slits and Soller slits. Procedure of 0.02^o step-by-step scanning was used to determine the exact position of the peaks. The weak peaks were identified by a step-by-step scanning method with accumulation of impulses at the each step.

A few of diffractograms of the same sample were recorded in order to obtain more reliable results. The incoherent background and scattering from non-crystalline (amorphous) domains were subtracted from diffractograms. Then profiles of the isolated crystalline peaks were improved using corrections on absorption, combined PL factor and *Rietveld refinement*. The angular positions of the peaks were checked using a narrow line of NaF standard at 2Θ of 38.83^o. Overlapped peaks were separated using a least-square program. Interplanar spacing in transverse direction (d_t) perpendicularly to [200] planes and interplanar spacing in longitudinal direction (d_L) perpendicularly to [004] planes of crystalline unit cell were calculated by the Bragg equation

$$d_i = 0.5\,\lambda\,(\sin\Theta_i)^{-1} \quad (2)$$

Approximate sizes of nanocrystallites ($S_{sh,i}$) in the directions perpendicularly to planes of [200] (width) and [004] (length) were estimated by the equation of Scherrer:

$$S_{sh,i} = K\lambda[(\cos\Theta_i)^2 (B_i^2 - b_i^2)]^{-0.5} \quad (3)$$

Where λ is wavelength of X-ray radiation; B_i is experimental width of the peak; b_i is instrumental factor; Θ_i is angle of the peak maximum; and K is coefficient depending on the shape of crystallites that in the case of cellulose is close to unity.

The degree of crystallinity (X) of the samples was determined by the WAXS method described in [1, 14].

RESULTS AND DISCUSSION

According to data of chemical analysis, all isolated cellulose samples have a high content of alpha-cellulose, 97-99%, indicating their chemical purity.

Table1. *Structural characteristics of isolated celluloses of various origin*

Origin	X	*D_{sh}, nm	*L_{sh}, nm	d_t, nm	d_L, nm
TN	0.82	11.5	77	0.387	0.25957
CM	0.75	8.8	28	0.388	0.25883
WM	0.73	6.7	20	0.390	0.25836
CT	0.70	6.2	20	0.391	0.25835
FL	0.67	5.6	19	0.392	0.25827
SW	0.63	5.1	16	0.392	0.25794
HW	0.62	4.6	16	0.393	0.25794
BG	0.54	3.9	12	0.394	0.25727
WS	0.53	3.6	11	0.395	0.25702

**D_{sh} and L_{sh} are approximate Scherrer's width and length of nanocrystallites*

Study of structural parameters of the samples showed (Table 1) that tunicate cellulose has the most ordered supramolecular structure among all studied CIβ celluloses. X-ray diffractogram of this cellulose type contains sharp, narrow and separated peaks (Fig. 1). As it follows from the obtained results, cellulose isolated from tunicate is highly crystalline (X=0.82) and has large crystallites with the Scherrer's width D_{sh}=11.5 nm and length L_{sh} = 77 nm.

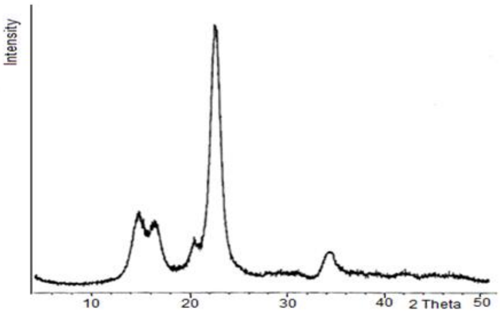

Figure1. *X-ray diffractogram of isolated tunicate cellulose*

Others isolated CIβ celluloses of various origins were less ordered than tunicate cellulose; diffractograms of these samples had badly separated peaks and lesser Scherrer's sizes of crystallites (see e.g. Fig. 2, Table 1).

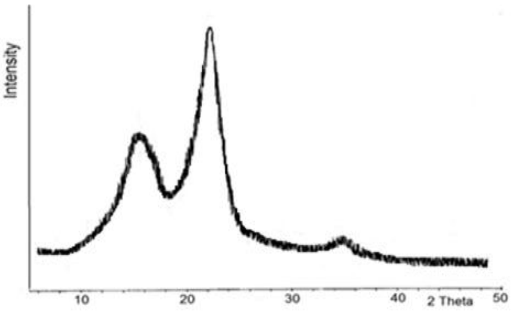

Figure2. *X-ray diffractogram of isolated wheat straw cellulose*

As known [14], to calculate the actual sizes of crystallites (S_a) from X-ray diffractograms the improved equation should be used, as follows:

$$S_{a,i} = \lambda [(\cos \Theta_i)^2 (B_i^2 - b_i^2 - \Delta_i^2)]^{-0.5} \quad (4)$$

Where B_i is experimental width of the peak; b_i is instrumental factor, which was found by the peak width of D-cellobiose crystals using as a crystalline standard; and Δ_i is contribution of lattice distortions to broadening of the peak.

On the other hand, the $\boldsymbol{\Delta_i}$ –factor can be calculated using the theoretical equation [14, 17]:

$$\Delta_i = 4\delta_i \mathrm{tg}\Theta_i \quad (5)$$

Where $\boldsymbol{\delta_i}$ is distortion parameter, i.e.average deviation of interplanar spacing (**d_i**) in distorted lattice from its value in undistorted crystalline lattice, $d_{i,o}$:

$$\boldsymbol{\delta_{i.}} = \left|(d_i - d_{i,o})\right| d_{i,o}^{-1} \quad (6)$$

The experiments showed that the interplanar spacing of crystalline lattice in the transverse direction (d_t) perpendicularly to [200] planes and the spacing in the longitudinal direction (d_L) perpendicularly to [004] planes were inversely proportional to Scherrer's width (D_{sh}) and length ($L_{sh)}$ of crystallites, respectively (Fig. 3 and 4). Extrapolation of linear dependencies $d_t = f(D_{sh}^{-1})$ and $d_L = f(L_{sh}^{-1})$ to $D_{sh}^{-1} = 0$ and $L_{sh}^{-1} = 0$ gives the values $d_{t,o}$ = 0.384 nm and $d_{L,o}$ = 0.260 nm for undistorted crystalline lattice of CI. This allows to calculate the distortion parameters by the equation (6) and the delta-factors by the equations (5).

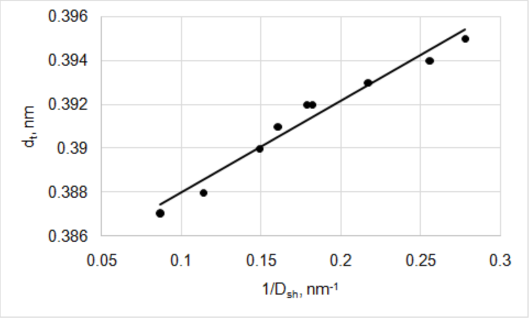

Figure3. *Dependence of interplanar spacing of crystalline lattice in the transverse direction on the Scherrer's width of cellulose nanocrystallites*

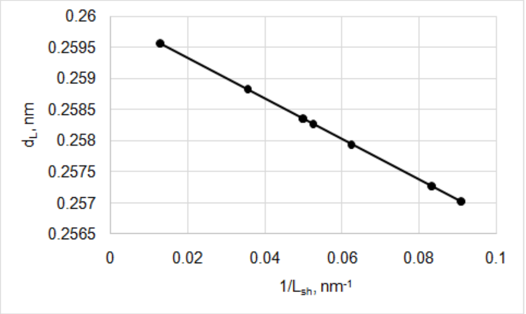

Figure4. *Dependence of interplanar spacing of crystalline lattice in the longitudinal direction on the Scherrer's length of cellulose nanocrystallites*

The calculated distortion parameters and delta-factors of crystalline lattice were given in Table 2.

Table2. *Distortion parameters in transverse (δ_t) and longitudinal (δ_L) directions of crystallites, as well as Δ_t -and Δ_L- factors*

Origin	δ_t	Δ_t	δ_L	Δ_L
TN	0.0078	0.00624	0.00165	0.00206
CM	0.0104	0.0083	0.00449	0.0056
WM	0.0156	0.0125	0.00629	0.00785
CT	0.0182	0.0146	0.00633	0.0079
FL	0.0208	0.0167	0.00665	0.0083
SW	0.0208	0.0167	0.00793	0.0099
HW	0.0230	0.0187	0.00793	0.0099
BG	0.0260	0.0208	0.0105	0.0131
WS	0.0290	0.0229	0.01146	0.0143

Since in the longitudinal direction there are strong chemical bonds, the lattice distortions in this direction are smaller than in the transverse direction, where the weaker physical bonds are present.

It was also found that both δ_i-parameter and $\mathbf{\Delta_i}$ – factor are linear functions of interplanar spacing, d_i (Fig. 5, 6). These dependences can be expressed as follows:

$$\delta_t = 2.608\mathbf{d_t} - 1.0015 \qquad (7)$$

$$\Delta_t = 2.083\mathbf{d_t} - 0.7997 \qquad (8)$$

$$\delta_L = 1.0004 - 3.8478\mathbf{d_L} \qquad (9)$$

$$\Delta_L = 1.2484 - 4.8016\mathbf{d_L} \qquad (10)$$

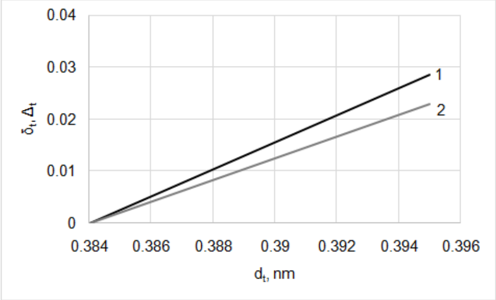

Figure5. *Dependence of δ_t - parameter (1) and Δ_t-factor (2) on interplanar spacing (d_t) in transverse direction of cellulose nanocrystallites*

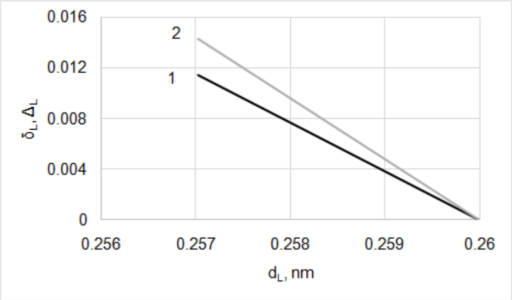

Figure6. *Dependence of δ_L - parameter (1) and Δ_L-factor (2) on interplanar spacing (d_L) in longitudinal direction of cellulose nanocrystallites*

Substituting Δ_t- factor from eq. (8) and (10) in eq. (4), the actual width (D_a) and the actual length (L_a) of crystallites can be calculated:

$$\mathbf{D_a} = \lambda\{(\cos\Theta_t)^2[(B_t^2 - b_t^2 - (2.083\mathbf{d_t} - 0.7997)^2]\}^{-0.5} \qquad (11)$$

$$\mathbf{L_a} = \lambda\{(\cos\Theta_L)^2\,[B_L^2 - b_L^2 - (1.2484 - 4.8016\mathbf{d_L})^2]\}^{-0.5} \qquad (12)$$

Where Θ_t and Θ_L is angle at maximum of (200) and (004) peaks, respectively;

B_t and B_L is experimental width of (200) and (004) peaks, respectively;

b_t and b_L is contribution of instrumental factor to width of (200) and (004) peaks, respectively.

Table3. *Approximate (D_{sh}, L_{sh}) and actual (D_a, L_a) sizes of nanocrystallites*

Origin	D_{sh}, nm	D_a,nm	L_{sh}, nm	L_a, nm	L_p, nm
TN	11.5	12.9	77	400	-
CM	8.8	10.0	28	116	100
WM	6.7	7.9	20	85	90
CT	6.2	7.6	20	96	100
FL	5.6	7.0	19	88	90
SW	5.1	6.1	16	82	76
HW	4.6	5.5	16	82	75
BG	3.9	4.6	12	52	57
WS	3.6	4.2	11	48	50

The results showed that width (D_a) of nanocrystallites is higher than approximate Scherrer's size (D_{sh}) by 10-20% (Table 3). However, the difference between the actual and approximate length of nanocrystallites is much larger. As was found, the actual length (L_a) of nanocrystallites exceeds the approximate Scherrer's length (L_{sh}) by 4-5 times (Table 3). Thus, the actual length of cellulose nano crystallites can be estimated using the simplified equation:

$$\mathbf{L_a} = 4.5\lambda\,[(\cos\Theta_L)^2(B_L^2 - b_L^2)]^{-0.5} \qquad (13)$$

The actual length of nanocrystallites determined by improved WAXS method (L_a) is close the length obtained by determination of level-off degree of polymerization (L_p) or found by EM and AFM methods [4-6].

CONCLUSION

In this paper WAXS method was used to determine distortion degrees of crystalline lattice, **δ**, and factors **Δ**=4δtgΘ, as well as actual sizes of CIβ nanocrystallites. Values of **δ** were calculated using average deviation of interplanar spacing in the distorted lattice from its value in undistorted crystalline lattice. It was also shown that **δ** and **Δ** factors are linear functions of interplanar spacings ($\mathbf{d}_t$ and $\mathbf{d}_L$) of crystalline lattice. After finding the **δ** and **Δ** factors, the correction for broadening of diffraction peaks was calculated, which allows to determine the actual width ($\mathbf{D}_a$) and actual length ($\mathbf{L}_a$) of nanocrystallites by the equations:

$$\mathbf{D}_a = \lambda\{(\cos \Theta_t)^2 [(B_t^2 - b_t^2 - (k_t\mathbf{d}_t + C_t)^2]\}^{-0.5}$$

$$\mathbf{L}_a = \lambda\{(\cos \Theta_L)^2 [B_L^2 - b_L^2 - (k_L\mathbf{d}_L + C_L)^2]\}^{-0.5}$$

Study of various samples of CIβ showed that tunicate cellulose has the largest crystallites: D_a=13 nm; L_a = 400 nm. Actual sizes of nanocrystallites in isolated celluloses of other origin (herbaceous plants, wood, bast fibers, cotton fibers, etc.) were smaller: D_a was in the range of 4.2 to 10 nm, whereas L_a in the range of 48 to 116 nm.

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