

STUDY OF CELLULOSE PARACRYSTALLINITY

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The paracrystallinity of cellulose samples was studied with a complex of investigation methods including X-ray, NMR, sorption, calorimetry, and some others. It was found that the paracrystalline fraction of cellulose is located on the surface of crystallites as thin monomolecular layers having an average thickness of 0.4 nm. The paracrystalline surface layers have distorted and loose packing that is characterized by a high distortion parameter $\delta_p = 0.18$, increased specific volume $V_p = 0.664 \text{ cm}^3/\text{g}$, and decreased specific gravity $\rho_p = 1.51 \text{ g/cm}^3$. The paracrystalline fraction of the crystallite can be quantified by the parameter (α), which has an expressed influence on some properties of cellulose. Increasing of the α -value causes expansion of inter-plane distances in the C1 unit cell, as well as promotes mercerization and dissolution of cellulose.

Keywords: Cellulose; Paracrystallinity; Characteristics; Properties

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INTRODUCTION

Cellulose has a complicated multilevel supermolecular structure. Generally, the first structural level contains elementary nano-fibrils, and each such fibril is built from ordered crystallites and low ordered non-crystalline (amorphous) domains statistically alternated along the fibril. Cellulose chains pass through lots of crystallites and non-crystalline domains and bind them with chemical 1,4- β -glycoside bonds (Dolmetsch 1968; Hess et al. 1958; Ioelovich 1999; Krässig 1993; Usmanov et al. 1974). However many details of cellulose structure have not been elucidated yet. One of the insufficiently explored structural aspects is the problem of cellulose paracrystallinity.

According to the model of paracrystalline structure, parameters of different unit cells of the same paracrystal can be changed randomly (Hosemann 1954). Based on yearly structural investigations it was concluded that cellulose can be related to a paracrystalline polymer because its lattice has a “poor” three-dimensional order (Kitaigorodsky et al. 1959). A multiphase model of cellulose structure included an expanded paracrystalline phase that provides a gradual transition between fully amorphous and fully crystalline phases along the fibrils (Howsmon et al. 1954). Based on such a model, the contents of paracrystalline and crystalline phases were estimated (Mitra et al. 1980). The obtained paracrystallinity degree was high, while crystallinity of natural cellulose was very low - about 10% only. These modeling calculations are in disagreement with direct experimental determinations of crystallinity for natural celluloses in the range of 60-70% (Bikales et al. 1971; Hermans et al. 1949, 1951; Ioelovich et al. 2008, 2009; Jayme 1975).

The “fringed fibrils” model is built from completely crystalline elongated fibrils and a disordered amorphous “fringe” in lateral directions (Hearle 1963). Modified models of “fringed fibrils” provide arrangement in lateral directions of fibrils in both paracrystalline and amorphous domains (Newman 1999; Rånby 1969; Ruck 1978). Such models can be appropriate for interpretation of increased mechanical characteristics of cellulose fibers. However, they are not corroborated by chemical properties of cellulose. For example, it is known that destruction of amorphous domains during acid hydrolysis, alcoholysis, or acetolysis is carried out along fibrils, but not in lateral directions, and this process leads to longitudinal splitting of cellulose fibers with the formation of rod-like crystalline particles having a level-off degree of polymerization (Battista et al. 1962; Bikales et al. 1971; Ioelovich et al. 2006; Usmanov et al. 1974). These data prove that both crystallites and amorphous domains are arranged along the fibrils.

There is a significant distinction between a paracrystalline structure containing a paracrystalline phase only and an imperfect crystal having paracrystalline distortions. Diffraction of a typical paracrystal has one to two wide peaks of first Bragg’s order only, while the imperfect crystal gives lots of diffraction peaks of first and more Bragg’s orders (Lipatov et al. 1982). Natural celluloses give four to five pronounced peaks having additional diffractions of second order at the least (Bikales et al. 1971; Haase et al. 1975; Hosemann et al. 1985; Ioelovich 1992; Kulshreshtha et al. 1971). Hence, crystallites of cellulose are related to imperfect crystals having paracrystalline distortions and don’t contain an expanded paracrystalline phase both in longitudinal and lateral directions.

Structural investigations of cellulose samples have shown that only thin paracrystalline layers are present on surface of the crystallites (Ioelovich et al. 1994; Larsson et al. 1997, 2008; Wickholm et al. 1998). To estimate the content of the paracrystalline fraction by the method of solid state ^{13}C NMR, the signal from C-4 atoms between 87 and 93 ppm was separated into crystalline and paracrystalline contributions by a computerized deconvolution procedure (Larsson et al. 1997; Wickholm et al. 2001; Zuckerstätter et al. 2009). However, depending on preliminary postulated structural models and mathematical programs, various numbers of the individual constituents and their relative parts can be obtained. This makes it difficult to achieve quantitative determination of the paracrystalline fraction.

The main purpose of this paper is to study the content and characteristics of the paracrystalline fraction and its effect on some properties of cellulose using a complex of experimental methods.

EXPERIMENTAL

Materials

The following cellulose samples were investigated:

- Microcrystalline cellulose (MCC) Avicel PH-301 of FMC BioPolymer Co.
- Pure chemical grade cotton cellulose (COC) of Hercules Co.
- Bleached kraft pine chemical pulp (KCP) of Weyerhaeuser additionally refined by treatment with a cold solution of caustic soda
- Bleached high-pure sulfite spruce pulp (SFI) of Weyerhaeuser Co.

- Amorphized cellulose (AMC) obtained by treatment of cotton cellulose with liquid ammonia and following recrystallization with water and drying
- Cellulose isolated from colored cotton by soda cooking and bleaching (CCC)
- Cellulose isolated from ramie fibers by soda cooking and bleaching (RAC)

Deuteration of the Samples

Cellulose samples were treated with heavy water (D₂O) at 25°C and D₂O/cellulose ratio 10 for 24 h. After removing the excess of heavy water, the treated samples were dried in a P₂O₅ – desiccator at 25°C for 24 h and then in a dryer at 105°C up to constant weight.

X-Ray Diffraction

A Rigaku-Ultima Plus diffractometer (CuK_α – radiation, λ=0.15418 nm) was used for X-ray investigations. Diffractograms were recorded in the φ=2Θ angle range from 5 to 80°. After recording of the diffractograms, the background was separated, and selected X-ray patterns were corrected and normalized. Then diffraction intensities from crystalline and non-crystalline regions were separated by a computerized method (Vonk 1973). The procedures made it possible to calculate the degree of crystallinity (*X*) according to equation,

$$X = \int J_c d\varphi / \int J_o d\varphi \quad (1)$$

where *J_c* and *J_o* are the corrected and normalized diffraction intensities for crystalline regions and sample respectively.

The content of amorphous domains (*Y*) in a cellulose sample, as determined by the X-ray method, was calculated as:

$$Y = 1 - X \quad (2)$$

The true lateral size of crystallites (*L*) was determined by an improved method. The reflection (200) was isolated, its integral width (*B*) in radians was measured, and corrections for instrumental factor (*A*) and lattice's distortion (*δ_d*) were introduced. The *L*-value was calculated according to equation,

$$L = \lambda / [(\cos \Theta_o (B^2 - A^2)^{0.5})^2 - (2\delta_d \sin \Theta_o)^2]^{0.5} \quad (3)$$

where Θ_o is the diffraction angle of the reflection (200).

The inter-plane (200) distance (*d*) was calculated from the Bragg's equation:

$$2d \sin \Theta_o = n \lambda \quad (4)$$

where *n* is the order of reflection.

A detailed description of the X-ray diffraction method for investigation of crystalline structure of cellulose can be found in the papers of Ioelovich et al. (1992, 1994, and 1999).

Sorption of Water Vapor

The sorption of water vapor by cellulose samples was measured at 25 °C and relative vapor pressure $p/p_o = 0.7$ with the use of a vacuum *Mac-Ben* apparatus having helical spring quartz scales. The crystallinity of the cellulose was calculated from the sorption value (s , %) by the following equation,

$$X_s = 1 - (s/s_o) \quad (5)$$

where $s_o = 26\%$ is the sorption value for the amorphous cellulose at $p/p_o = 0.7$.

Wetting Enthalpy

The enthalpy of cellulose wetting with water (Q) was studied by the method of microcalorimetry at 25 °C using a TAM III calorimeter (Wadsö et al. 2001). From the enthalpy value, the crystallinity of the cellulose was calculated:

$$X_Q = 1 - (Q/Q_o) \quad (6)$$

where $Q_o = 170$ J/g is the wetting enthalpy of amorphous cellulose.

Specific Gravity

The specific gravity (ρ) of the dry samples was tested at 25 °C by the pycnometry method in hexane medium (Kalinowsky et al. 1966). The crystallinity of the cellulose was calculated by the equation,

$$X_\rho = (\rho_c/\rho) \times (\rho - \rho_a)/(\rho_c - \rho_a) \quad (7)$$

where $\rho_c = 1.62$ g/cm³ is the average specific gravity of cellulose crystallites, and $\rho_a = 1.44$ g/cm³ is the average specific gravity of amorphous cellulose.

Pulse NMR

Dry cellulose samples were tested with a proton NMR-relaxometer operating at 42 MHz, with 2.5 μ s interval of the $\pi/2$ – pulse (Ioelovich et al. 1994). The amplitude of protons induction for initial (I_o) and deuterated (I_d) cellulose samples was measured. Accessibility of cellulose samples upon deuteration was calculated using equation (8):

$$A = [1 - (I_d/I_o)]/0.3 \quad (8)$$

Alkalization

The structural changes of cellulose samples were investigated after alkalization with 12% sodium hydroxide at room temperature, liquid/solid ratio 100 for 1h. The CII content was determined by the X-ray method of inner standards (Ioelovich et al. 1983).

Solubility

Cuproxam solvent having the following composition: Cu – 13 g/l, NH₄OH – 150 g/l, and saccharose - 2 g/l, was prepared. Solubility of the cellulose samples was studied at room temperature, liquid/solid ratio 100 for 24 h.

Chemical Composition

The content of alpha-cellulose was tested after treatment of the samples with 17.5% NaOH at 20 °C for 1h. Alkali solutions were neutralized and hydrolyzed; then composition of obtained monosaccharides was analyzed by HPLC. The average degree of polymerization (DP) was measured by the viscosity method using diluted cellulose solutions in Cadoxen (Ioelovich, et al. 2004).

RESULTS AND DISCUSSION

The chemical composition and some properties of the cellulose samples are shown in Table 1. The samples contained mainly alpha-cellulose (ALC) and a lower amount of alkali-soluble fraction of cellulose (ASC).

Table 1. Characteristics of the Samples

Sample	DP	ALC, %	ASC, %	ρ , g/cm ³	s, %	Q, J/g
MCC	170	88	12	1.573	5.7	39
COC	2700	98	2	1.560	7.8	49
CCC	1400	92	7	1.554	8.7	56
RAC	1800	93	6	1.558	8.1	52
KCP	1200	97	1	1.552	9.0	61
SFI	1100	95	2	1.548	9.8	63
AMC	2100	94	6	1.532	12.2	81

X-ray diffractograms of the investigated cellulose samples were typical for C1 – crystalline polymorph (Fig. 1).

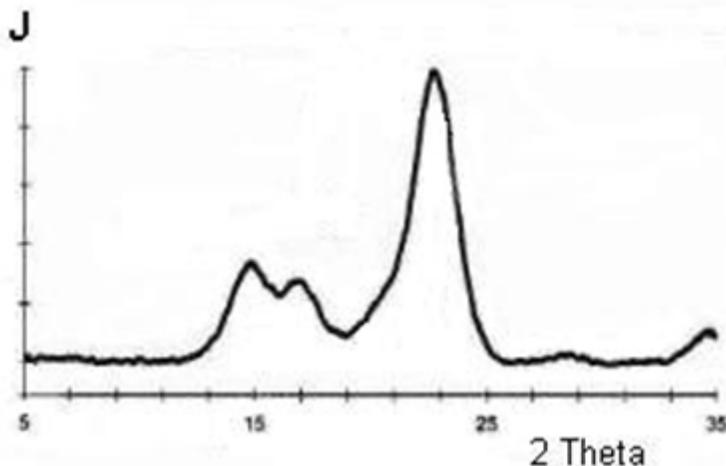


Fig.1. X-ray diffractogram of cotton cellulose

After acid hydrolysis, the crystallinity degree and lateral size of crystallites increased, and therefore the MCC sample acquired well resolved peaks (Fig. 2). Among the studied C1-samples, the amorphized cellulose (AMC) had the lowest crystallinity and size of crystallites (Table 2).

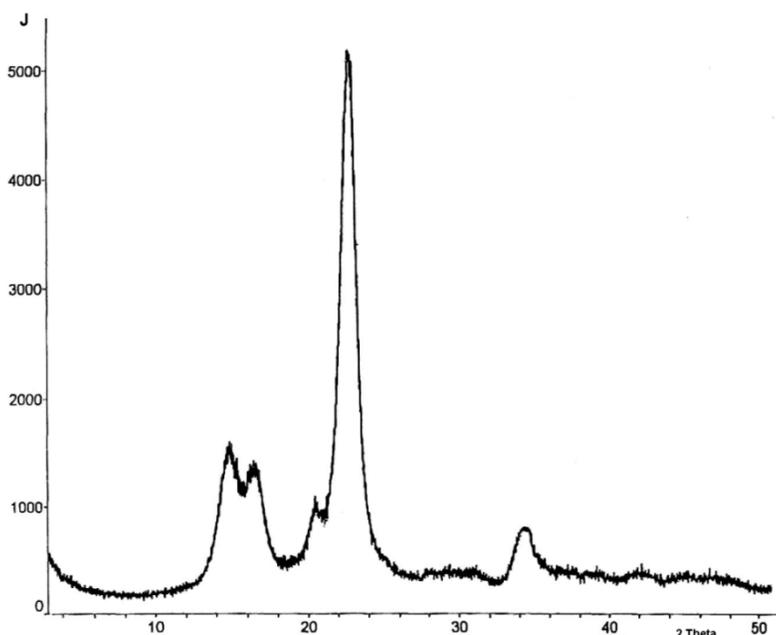


Fig. 2. X-ray diffractogram of cotton MCC (Avicel)

The crystallinity degree obtained by the X-ray method was confirmed by the following independent methods: sorption of water vapors (WV), testing of specific gravity (SG), and wetting enthalpy (Q). The average crystallinity degree of the same cellulose sample varied in the low interval: $X_{av} \pm 0.02$ (Table 2). The obtained values of crystallinity degree for some cellulose samples were confirmed by independent investigations of other researchers (Hermans et al. 1949, 1951; Jayme et al. 1964, 1975; Kleinebudde et al. 2000).

Table 2. Crystalline Structure of Cellulose Samples

Samples	d, nm	L, nm	Crystallinity degree				
			X-ray	SG	WV	Q	X_{av}
MCC	0.389	10.2	0.77	0.76	0.78	0.77	0.77
COC	0.390	8.3	0.71	0.69	0.70	0.71	0.70
CCC	0.392	6.0	0.66	0.67	0.68	0.67	0.67
RAC	0.391	7.2	0.69	0.68	0.70	0.69	0.69
KCP	0.391	6.8	0.65	0.65	0.66	0.64	0.65
SFI	0.393	5.7	0.63	0.63	0.62	0.63	0.63
AMC	0.394	4.9	0.53	0.54	0.53	0.52	0.53

Accessibility of cellulose samples upon deuteration was higher than the content of amorphous domains (Table 3) because the process of deuterium exchange affects not only amorphous but also paracrystalline regions of the cellulose (Ioelovich et al. 1994). The accessibility values obtained in this paper are in agreement with published data (Jeffries et al. 1968, 1969; Krässig 1993; Nevell et al. 1985).

Table 3. Average Content of Amorphous Domains ($Y_{av}=1-X_{av}$) and Cellulose Accessibility at Deuteration (A)

Samples	Y_{av}	A
MCC	0.23	0.35
COC	0.30	0.42
CCC	0.33	0.48
RAC	0.31	0.45
KCP	0.35	0.49
SFI	0.37	0.53
AMC	0.47	0.63

As follows from structural investigations, crystallites of cellulose contain a highly ordered crystalline core and lower-ordered surface paracrystalline layers surrounding the core (Ioelovich et al. 1994; Larsson et al. 1997, 2008; Wickholm et al. 1998). This structural agreement is schematically illustrated in Fig. 3.

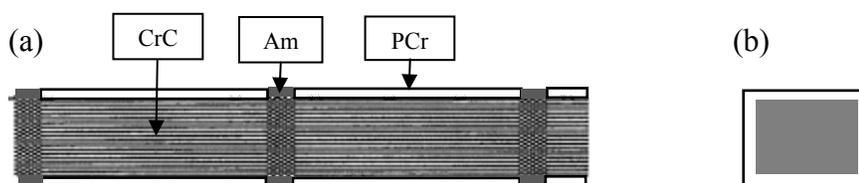


Fig. 3. Scheme of the structural arrangement of cellulose
 (a): Along the fibril; (b): Cross-section of crystallite
 CrC – Crystalline core of crystallite (Grey);
 Am – Amorphous domain (Black);
 PCr – Paracrystalline surface layers (White)

The crystallinity degree, i.e. the content of real imperfect crystallites in the sample, includes parts of the crystalline core (X_o) and the paracrystalline surface (X_p). The received results permit direct experimental determination of X_o and X_p values in the sample and part of the paracrystalline surface layers in the crystallite, α , using the following equations:

$$X_o = 1 - A \quad (9)$$

$$X_p = X - X_o \quad (10)$$

$$\alpha = X_p / X \quad (11)$$

Since the X_p -value for various cellulose samples changes in a comparatively narrow interval ($X_p = 0.14 \pm 0.02$), the part corresponding to the crystalline core, X_o , will be a linear function of crystallinity degree X (Fig. 4). By contrast, the magnitude of X_p , the fraction of paracrystalline surface layers in the crystallite, α , is a sensitive quantitative parameter of the paracrystalline regions. The highly crystalline MCC-sample had the lowest α -value (0.15), while low-crystalline cellulose sample, AMC, was characterized by a two-times higher α -value (Table 4).

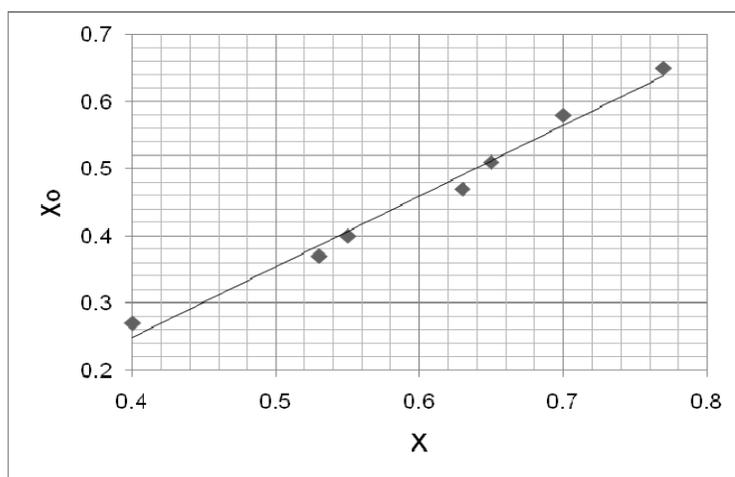


Fig. 4. Dependence of the crystalline core fraction on crystallinity degree

Table 4. Crystallinity, Fractions Corresponding to the Crystalline Core and Paracrystalline Regions in the Cellulose Samples

Samples	L , nm	X	X_o	X_p	α
MCC	10.2	0.77	0.65	0.12	0.15
COC	8.3	0.70	0.58	0.12	0.17
CCC	6.0	0.67	0.52	0.15	0.22
RAC	7.2	0.69	0.55	0.14	0.20
KCP	6.8	0.65	0.51	0.14	0.21
SFI	5.7	0.63	0.47	0.16	0.25
AMC	4.9	0.53	0.37	0.16	0.30

On the other hand, the fraction of the paracrystalline surface layers in the cellulose crystallite can be calculated from ratio of cross-section area of the paracrystalline layers (AP) to the cross-section area of the crystallite (AC),

$$\alpha = AP/AC = 4h(L-h)/L^2 \quad (12)$$

where h is the thickness of the paracrystalline surface layers, and L is the lateral size of the crystallite. Then, the thickness of the paracrystalline surface layers can be calculated as:

$$h = 0.5L(1 - \sqrt{1 - \alpha}) \quad (13)$$

As it follows from the calculations, the average thickness of the paracrystalline layers $h \approx 0.4 \text{ nm}$. This corresponds to the thickness of thin monomolecular cellulose chains located on the exterior surface of the crystallites.

X-ray crystallinity of some cellulose samples (Table 4) conforms to results of WAXS published in other papers (Hermans et al. 1949, 1951; Jayme et al. 1964, 1975; Kleinebudde et al. 2000). The crystalline structure of cellulose can be studied also by the method of solid state ^{13}C -NMR. The general crystallinity ($X = X_o + X_p$) of cotton samples estimated by this method was from 0.70 (Wickholm et al. 2001) to 0.77 (Newman 1999), while crystallinity of crystalline core (X_o) was about 0.4 (Malm et al. 2010; Wickholm et al. 2001). The lateral size of crystallites was estimated from 7 nm to 9.6 nm (Malm et al. 2010; Newman 1999). These results are comparable with crystallinity values (X and X_o) and lateral size of crystallites (L) that were obtained for samples of cotton celluloses in this paper.

The distorted structure is characterized by the distortion parameter $\delta = \Delta d/d$. The average distortion parameter in lateral directions for large and highly-ordered crystallites of algal celluloses and synthetic polymers is low: $\delta_o = 0.015 \pm 0.005$ (Hosseman et al. 1985; Fink et al. 1990), while the average distortion parameter for small nano-crystallites of various natural wood celluloses, wood pulps and cotton celluloses is higher: $\delta_c = 0.05 \pm 0.01$ (Ioelovich 1992). Based on these data, the distortion parameter of paracrystalline structure of surface layers, δ_p , can be estimated as:

$$\delta_p = [\delta_c - \delta_o (1 - \alpha)]/\alpha \quad (14)$$

The calculations showed that the average distortions parameter of paracrystalline surface layers of cellulose crystallites is high: $\delta_p = 0.18 \pm 0.03$.

Due to their distorted structure, the paracrystalline layers have looser packing than the crystalline core, which can be characterized by specific volume. To determine the specific volume of the paracrystalline layers, V_p , the following equation was used,

$$V_p = [V_c - V_o (1 - \alpha)]/\alpha \quad (15)$$

where V_c is the specific volume of crystallites of the cellulose sample, and V_o is the specific volume of the crystalline core.

On the other hand, $V_c = V_o + K/L$, and therefore:

$$V_o \alpha + K/L = V_p \alpha \quad (16)$$

$$\text{or } Z = V_p \alpha, \quad (17)$$

where function $Z = V_o \alpha + K/L$, $V_o = 0.6024 \text{ cm}^3/\text{g}$, and the coefficient $K=0.09 \text{ nm cm}^3/\text{g}$ (Ioelovich 1999).

A graph of eq. (17) based on experimental data is shown in Fig. 5. It follows from this graph that the average specific volume of the paracrystalline layers V_p is $0.664 \text{ cm}^3/\text{g}$, and their average specific gravity $\rho_p = 1/V_p$, is about 1.51 g/cm^3 . From comparative

packing analysis it follows that the specific volume, free volume, and specific gravity of the paracrystalline layers of cellulose crystallites are intermediate between the packing characteristics of highly-ordered crystalline core of crystallites and disordered amorphous domains (Table 5).

Table 5. Packing Characteristics of Crystalline Core (CC), Paracrystalline Layers (PL) of Crystallites, and Amorphous Domains (AD) of Cellulose

Characteristic	CC	PL	AD
Specific volume, cm ³ /g	0.6024	0.6640	0.6944
Specific gravity, g/cm ³	1.66	1.51	1.44
Fraction of free volume	0	0.093	0.132

Along with surface layers of crystallites, also small nuclei (1-2 nm), the centers of cellulose crystallization, have paracrystalline structure (Ioelovich 1999).

The content of the paracrystalline regions has appreciable influence on some properties of cellulose. It was found that the loosely packed structure of the paracrystalline layers of cellulose crystallites contributes to expansion of the crystalline lattice. This appears, for example, in the linear dependence of inter-plane (200) distance on the part of paracrystalline layers in cellulose crystallites (Fig. 6). The dependence $d=f(\alpha)$ can be described by the following equation:

$$d = d_o + k \alpha \quad (18)$$

where the coefficient k equals 0.034.

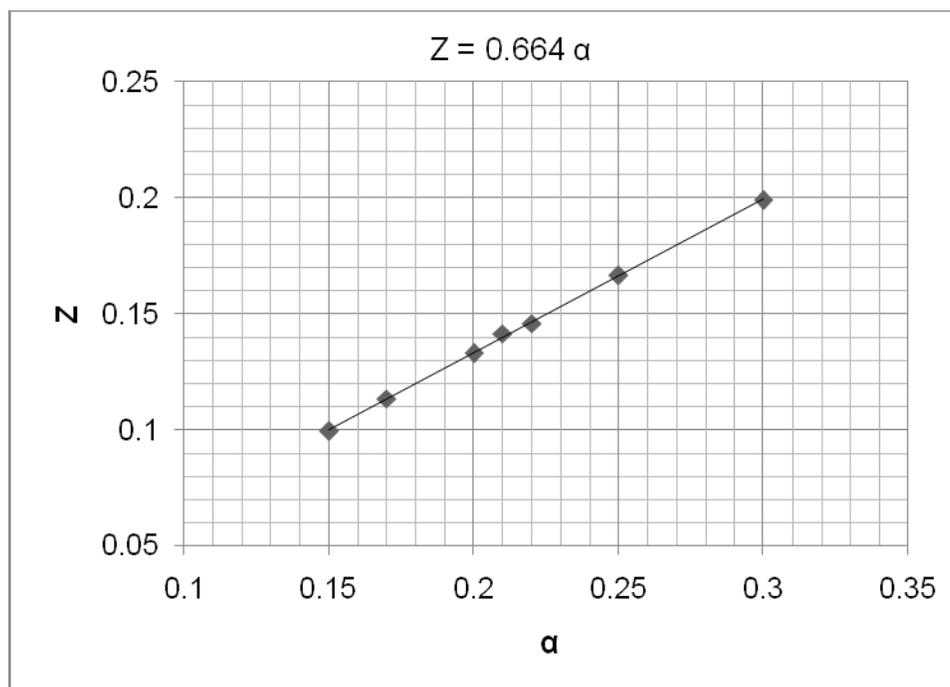


Fig. 5. Graph of the dependence $Z = F(\alpha)$

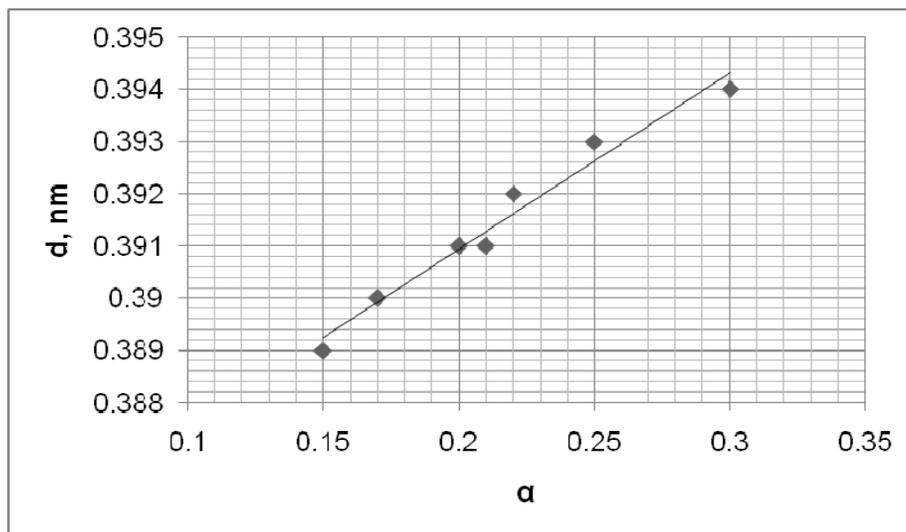


Fig. 6. Dependence of inter-plane (200) distance (d) on part of paracrystalline layers in crystallites (α)

In the case of perfect crystals, the paracrystalline layers are absent ($\alpha=0$), and the distance between (200) planes is minimal ($d_0=0.384$ nm). With increasing surface area of crystallites and part of paracrystalline layers, the inter-plane distance increases due to loosening of the crystalline structure.

Paracrystalline layers weaken the crystallites and increase their accessibility to reagents, causing intra-lattice swelling. Therefore, increasing the proportion of the paracrystalline layers promotes cellulose mercerization, i.e. transformation of C1 to CII crystalline polymorph during alkalization (Fig. 7).

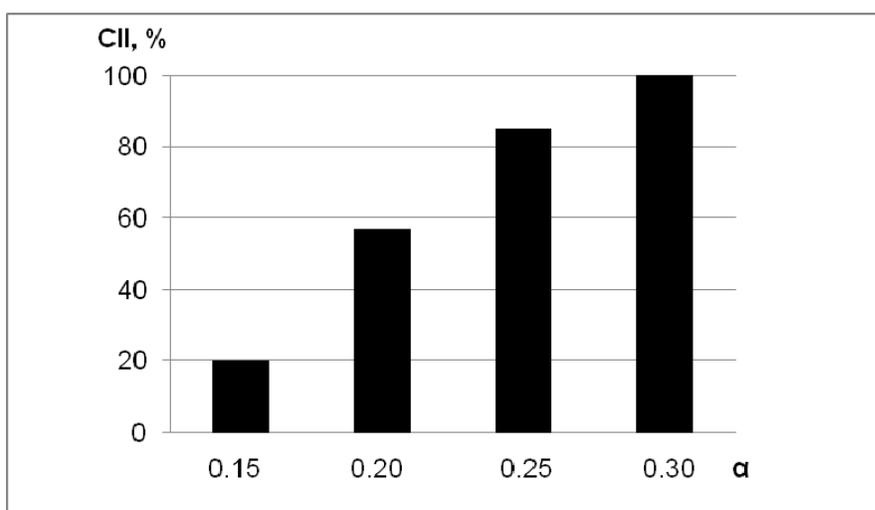


Fig. 7. Content of CII in cellulose crystallites having various part of paracrystalline layers (α) after alkalization with 12% NaOH

Moreover, developed paracrystalline layers contribute also to dissolution of cellulose samples. Dissolution experiments with samples of pure cellulose having the different fractions of paracrystalline layers showed that decreasing of α -value leads to increasing of cellulose solubility in the solvent (Fig. 8).

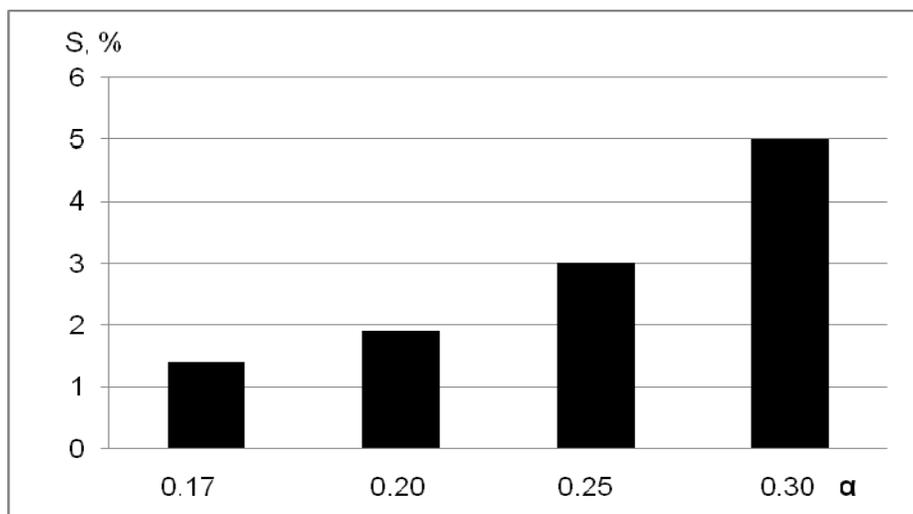


Fig. 8. Solubility in Cuproxam (S) of cellulose samples with different α - values

CONCLUSIONS

1. Characteristics of the paracrystalline fraction of cellulose and its effect on some properties of cellulose have been studied. It was shown that the paracrystalline fraction is located on the surface of crystallites as thin monomolecular layers having an average thickness of 0.4 nm.
2. The paracrystalline surface layers have distorted and loose packing, which is characterized with a high distortion parameter $\delta_p = 0.18$, increased specific volume $V_p = 0.664 \text{ cm}^3/\text{g}$, and decreased specific gravity $\rho_p = 1.51 \text{ g/cm}^3$.
3. The paracrystalline fraction in a crystallite can be quantified by the parameter α , which can be varied from 0 for perfect large crystals to 0.45 for small imperfect nanocrystallites having lateral size of 3 nm.
4. The content of the paracrystalline fraction, α , has appreciable influence on some properties of cellulose. Increasing of α -value causes expansion of inter-plane distances in the C1 unit cell, as well as promoting mercerization and dissolution of cellulose.

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