

RESEARCH METHODS

IR SPECTRAL STUDY AND X-RAY STRUCTURAL ANALYSIS OF THE SUPRAMOLECULAR STRUCTURE OF CELLULOSE POWDER

E. G. Kazakova*, **L. A. Aleshina****,
L. A. Lugovskaya**, **V. A. Demin*****,
E. U. Ipatova*, and **E. V. Udoratina***

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IR spectroscopy and x-ray structural analysis were used to study the supramolecular structure of cellulose powders obtained by the hydrolytic decomposition of bleached coniferous cellulose using mineral acids and its mercerized form. IR spectroscopy was used to establish the nature of the intermolecular bonds in the cellulose powder macromolecules. The Rietveld refinement was used to determine crystallinity and size of coherent scattering regions as well as to calculate the lattice periods of the crystalline component of these materials.

Most of the physicochemical, biological, and mechanical properties of cellulose are a function of its supramolecular structure dictated by the arrangement of the macromolecular chains and existence of bonding forces [1].

IR spectroscopy and x-ray structural analysis prove most useful for solving complex questions related to the morphology, fine structure, and conformation of polymer chains. These two methods may provide conclusive information on the three-dimensional structure of polymers. X-ray diffraction studies permit us to determine the identity periods of fibres and select the most probable conformation of the chains in a crystalline polymer. IR spectroscopy is used to elucidate the nature of the intermolecular hydrogen bonds in crystalline polysaccharides [2].

Many studies have now appeared on the properties and structure of cellulose derivatives, in particular, cellulose powder (CP) and microcrystalline cellulose (MCC) [1, 3-7]. CP and MCC may be obtained from various raw materials such cotton cellulose [7, 8], wood cellulose [9, 10], rye straw [7, 11], and flax fibre by the action of hydrolytic and oxidizing reagents along with hydrolysis, thermolysis, oxidative-hydrolytic treatment, and oxidative--thermal treatment. Many publications have appeared describing methods for the preparation of CP and MCC: by decomposition using ozone [12], nitric acid [13], sulfuric acid [6, 10], peroxymonosulfuric acid [11], and Lewis acids [14, 15].

The interest in the properties of CP and MCC is related to the search for new methods for the preparation and use of these materials [16], which are highly reactive in alkylation, esterification [17], acetylation [18], and sulfate preparation [19], CP and MCC are used in the pharmaceutical, cosmetic, and food industries. Various powder forms may be obtained depending on the type of chemical action on cellulose fibre differing in morphological structure crystallinity, and granulometric composition. These properties determine the possible applications of the powders.

Mercerized cellulose (MC) obtained by alkaline treatment of the raw material is no less interesting. This treatment leads to swelling of the cellulose crystallites and subsequent recrystallization, altering the cellulose structural modification I to give modification II [20]. The mercerization process is commonly used in industry to improve the functional properties of the fibres by imparting softness, sheen, strength, and hygroscopicity [3]. This process is also used in polymer chemistry to enhance the reactivity of such materials upon their modification.

*Institute of Chemistry, Komi Science Center, Urals Branch of the Russian Academy of Science, **Petrozavodsk State University, ***Syktyvkar Forest Institute. E-mail: egkazakov@mail.ru. Translated from *Khimisheskie Volokna*, Vol. 48, No. 4, pp. 85-92, July-August, 2016.

Table 1. Classification of Cellulose Samples

Sample no.	Type of cellulose	Treatment
1	Starting	–
2	Mercedized (MC)	Mercedization with 18% aq. NaOH
	Powder forms of starting bleached coniferous cellulose (CP)	
3	CP - H ₂ SO ₄	Treatment with 10% aq. H ₂ SO ₄
4	CP - HNO ₃	Treatment with 5% aq. HNO ₃
5	CP - HCl	Treatment with 9% aq. HCl
	Powder forms of MC (PC-MC)	
6	CP - MC - H ₂ SO ₄	Treatment with 10% aq. H ₂ SO ₄
7	CP - MC - HNO ₃	Treatment with 5% aq. HNO ₃
8	CP - MC - HCl	Treatment with 9% aq. HCl

Analysis of the literature showed that the parameters of the supramolecular structure of cellulose derivatives depend both on the origin of the cellulose materials and their method of preparation.

In the present work, we studied the supramolecular structure of cellulose powders obtained by the action of mineral acids on bleached coniferous cellulose and its mercedized form.

The raw material was a sample of bleached coniferous cellulose from the Mondi Corporation factory in Syktyvkar with degree of polymerization 1000 and 95.7% α -cellulose content. Mercedization of the bleached coniferous cellulose was carried out using 18% aq. NaOH by the method recommended by Obolenskaya [21].

The powder form was obtained by treating the starting and mercedized cellulose samples with 10% aq. H₂SO₄, 9% aq. HCl, or 5% aq. HNO₃. The treatment with hydrochloric acid was carried out for 60 min, while the treatments with sulfuric and nitric acids were carried out over 120 min at the boiling point. After hydrolytic treatment, the product was washed with hot distilled water on a vacuum filter until the wash water was neutral. The sample was subjected to inclusion using acetone and dried in the air [9].

The type, mineral acid concentration, and treatment conditions were selected in light of our previous results and literature data on the hydrolysis of cellulose. The sample numbers, type of cellulose, and treatment method are given in Table 1.

The IR absorption spectra were taken on a Shimadzu Prestige 21 FTIR spectrometer with 4 cm⁻¹ resolution at 400-4000 cm⁻¹ with a DLATGS detector. Spectra were taken for samples pressed into KBr pellets.

The diffractograms were taken on a DRON-6 diffractometer with Fe-K _{α} radiation monochromatized using a pyrolytic graphite crystal in the scattering angle range from 3° to 145°. The samples were pressed into tablets without binder. The refinement of the crystal lattice periods and selection of an atomic structure model were carried out by the full-matrix Rietveld method for analyzing diffractograms of polycrystals using the Burevestnik PDWin-4.0 program package [23]. The error was 5%.

The crystallinity (CR) of the cellulose samples was determined using the modified Ruland method according to the following formula

$$CR = (I - I_{am})/I,$$

where I is the total integral crystalline and amorphous phase scattering intensity and I_{am} is the integral amorphous phase scattering intensity of the sample [4, 24].

The crystallite dimensions D_{hkl} , termed coherent scattering regions (CSR), were calculated using the Scherrer formula and the widths of the Bragg reflections β_{hkl} in the cellulose crystalline lattice: $\beta_{hkl} = \lambda/D_{hkl} \cos \theta$. This method was described in detail by Melekh [4]. We should note that the diffractograms of all the samples were obtained in reflection and transmission geometries. In the reflection geometry, the fine crystals, whose planes are parallel to the fibril axis, most strongly scatter the incident radiation. This permits us to determine the thickness of the unit fibril. In the transmission geometry, the fine crystals, whose planes are perpendicular to the fibril axis, most strongly scatter the incident radiation. This explains why the intensity of the (004) line in the diffractogram increases and the width of this line decreases, which permits us to determine the length of the unit fibril.

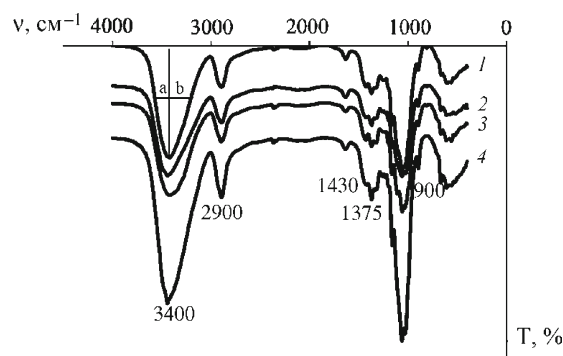


Fig. 1. IR spectra: 1) starting cellulose (sample 1), 2) MC (sample 2), 3) CP-H₂SO₄ (sample 3), 4) CP-MC-HCl (sample 8).

Table 2. IR Spectral Characteristics of the Supramolecular Structure of Cellulose

Sample no.	Characteristic of OH groups		Relative band optical density	
	ν_{OH} (max), cm ⁻¹	$a/b(\nu_{\text{OH}})$	D_{1375}/D_{2900}	D_{1430}/D_{900}
1	3421	0.67	1.13	1.68
2	3439	0.53	1.06	1.46

Figure 1 gives the spectra of the starting, mercerized, and, as an example, two powder samples. The shapes of the other CP spectra are similar. The spectrum of the starting cellulose (sample 1) has major absorption bands at ~3400 cm⁻¹ (stretching vibrations of hydrogen-bonded OH groups) ~2900 cm⁻¹ (stretching vibrations for CH and CH₂ groups), 1420-1430 cm⁻¹ (internal deformation vibrations of the CH₂ group), 1200--1300 cm⁻¹ (external deformation vibrations of the CH₂ group), 1000-1200 cm⁻¹ (stretching vibrations of pyranose ring C-O-C and C-O bonds), and 900 cm⁻¹ (CH group deformation vibrations).

The region of the OH group stretching vibrations provides information on the extent of substitution of these groups in modified cellulose. The shape of this band provides information on the extent of homogeneity of these derivatives [20]. The following absorption spectra characteristics are usually employed in studying the structure of cellulose: position of the OH group stretching band (ν_{OH}), symmetry index of the band for hydrogen-bonded OH groups ($a/b(\nu_{\text{OH}})$), absorption band intensity ratio (D_{1375}/D_{2900}) used for calculating the supramolecular order (the structural order of the sample is greater when this value increases), optical density ratio D_{1430}/D_{900} characterizing the cellulose crystallinity according to the O'Connor method [26] (a high value of this index indicates greater fraction of the crystalline phase, i.e., formation of a more ordered structure).

Mercerization and hydrolytic decomposition lead to a shift of the major absorption bands in the spectra.

Tables 2-4 give the IR spectral data for treatment of bleached coniferous cellulose, mercerized cellulose, and their powder forms.

Mercerization of bleached coniferous cellulose shows a shift in the ν_{OH} band toward higher frequencies to 3439 cm⁻¹ (Table 2), which characterizes predominance of OH groups in weaker hydrogen bonds. In addition to the general decrease in strength of the hydrogen bonds upon mercerization, the absorption band becomes more asymmetric (the symmetry index $a/b(\nu_{\text{OH}})$ is reduced by a factor of 2), indicating the existence of OH groups in strong hydrogen bonds, which are not affected in the reaction. This finding indicates a heterogeneous distribution of free OH groups in the macromolecule chains. The absorption band intensity ratios D_{1375}/D_{2900} and D_{1430}/D_{900} , which characterize the structural order and crystallinity, respectively, are lower in the MC spectrum than in the starting cellulose, which suggests a loss of orderedness of the structure upon mercerization.

The position of the ν_{OH} absorption band maximum is shifted from 3421 to 3414 cm⁻¹ with increasing hydrolytic decomposition of cellulose by various weak acids in order to obtain the powdered forms (Table 3). This finding indicates that the removal of weakly hydrogen-bonded cellulose fragments upon hydrolysis and that the remaining cellulose hydroxyl groups are in stronger hydrogen bonds. Sample 3 (CP-H₂SO₄) has a looser hydrogen bond network since the

Table 3. Characteristics of the Supramolecular Structure Powder Forms of original cellulose

Sample no.	Characteristic of OH groups		Relative band optical density	
	ν_{OH} (max), cm^{-1}	a/b (ν_{OH})	D_{1375}/D_{2900}	D_{1430}/D_{900}
1	3421	0.67	1.13	1.68
3	3415	0.75	1.11	1.53
4	3414	0.65	1.08	1.67
5	3414	0.62	1.09	1.67

Table 4. Characteristics of the Supramolecular Structure of CP-MC

Sample no.	Characteristic of OH groups		Relative band optical density	
	ν_{OH} (max), cm^{-1}	a/b (ν_{OH})	D_{1375}/D_{2900}	D_{1430}/D_{900}
2	3439	0.53	1.06	1.46
6	3442	0.57	1.01	1.45
7	3442	0.48	1.01	1.48
8	3443	0.50	1.07	1.49

maximum symmetry index $a/b(\nu_{\text{OH}}) = 0.75$. A denser hydrogen bond network is found for sample 5 (obtained using 9% aq. HCl), which has the lowest such index, $a/b(\nu_{\text{OH}}) = 0.62$.

Hydrolytic decomposition of cellulose leads to only slight disordering of its structure as seen in the somewhat reduced band intensity index D_{1375}/D_{2900} in the powder form in comparison with the starting sample. The oscillations of the supramolecular order index (D_{1375}/D_{2900}) for the various cellulose powders are slight (1.08-1.11); the greatest value is found for sample 3. The crystallinity indices of samples 4 and 5 and the same as for the starting cellulose but this value is much lower for sample 3. Thus, the cellulose powder obtained upon sulfuric acid hydrolysis has the least ordered structure.

The position of the OH group absorption band (ν_{OH}) remains virtually the same after treatment of MC with mineral acids but there is a change in the asymmetry (Table 4). The greater absorption band symmetry index in the spectrum of sample 6 indicates greater homogeneity for CP obtained by sulfuric acid treatment than in the case of the two other hydrolytic treatments. The most ordered structure is found for sample 8 ($D_{1375}/D_{2900} = 1.07$ and $D_{1430}/D_{900} = 1.49$), which was obtained using hydrochloric acid.

According to Petropavlovskii [20], cellulose should be considered a mixture of fibres differing in their access to reaction. In the heterogeneous reaction of cellulose fibres, the most available hydroxyl groups participating in the weakest hydrogen bonds react initially. In the case of an overall decrease in the amount of these hydroxyl groups due to reaction, the relative amount of hydroxyl groups with strong hydrogen bonding increases. The symmetry index decreases in this case, as seen in our work for the mercerized sample. Subsequent hydrolytic action leads to a decrease in the strength of the hydrogen bonding between the remaining hydroxyl groups. In the general case, the fraction of strongly hydrogen-bonded hydroxyl groups decreases upon hydrolysis of the starting cellulose using mineral acids, which leads to a weakening of the structure. However, our results are not unequivocal and exceptions from these conclusions are seen in some cases.

Since analysis of the absorption spectra of the cellulose samples studied revealed the most pronounced changes in the supramolecular structure of samples 1, 2, 3, and 8, the structure of these samples was further studied by x-ray diffraction.

Starting cellulose (sample 1) and its powder form (sample 3) have similar diffractograms characteristic for cellulose modification I β (Fig. 2). The position of the strongest diffraction maximum with index (200) and observed at $2\theta_{\text{Fe}} = 28.2^\circ$ remains unchanged in the powder form but its intensity is enhanced.

Mercerization is seen to lead to change in the cellulose structure. The diffractograms show reflections at $2\theta_{\text{Fe}} = 15.0$, 25.2 , and 27.4° , i.e., lines with indices (1 $\bar{1}$ 0), (110), and (002) characteristic for cellulose II (Fig. 2c,d). The reflections in the diffractogram of CP-MC are narrower (Fig. 2d).

The Scherrer equation postulates that the width of the x-ray diffraction lines depends on the crystallite (CSR) size. The x-ray diffraction lines are narrower with increasing size of the coherent scattering regions. Thus, analysis of the width of the Bragg reflections may provide information on the fine structure of the object studied [27]. The results of

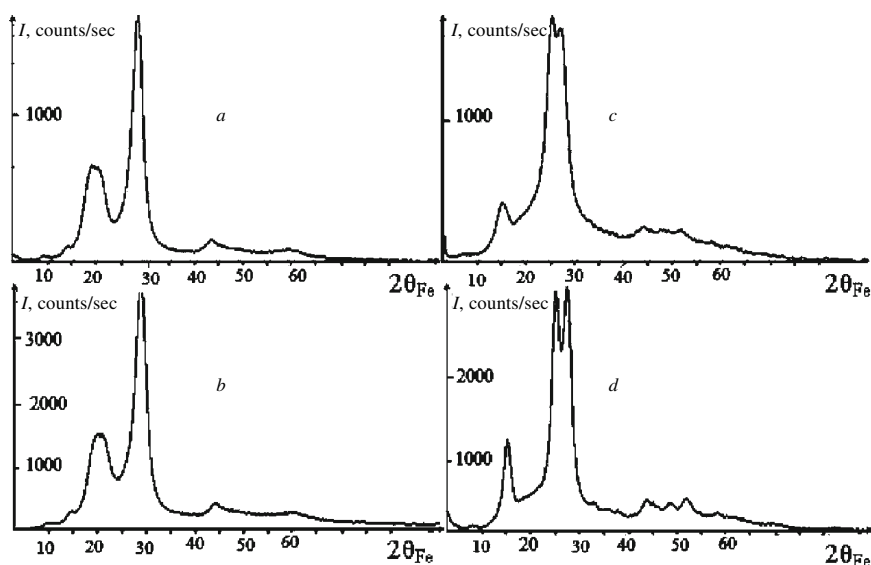


Fig. 2. Diffractograms of samples of original cellulose (*a*, sample 1), mercerized cellulose (*c*, sample 2), and powder forms (*b*, sample 3 and *d*, sample 8)

Table 5. Characteristics of the Crystal Structure of Original and Mercerized Cellulose and Their Powder Forms

Structural state characteristics	Sample and type of cellulose						
	sample 1	sample 3	sample 2	sample 8	ramie [28]	regenerated monocrystal line [29]	mercerized ramie [30]
CR, ±5%	72	78	52	74			
[<i>hkl</i>] – direction indices	Dimensions of crystallinity regions D_{hkl} , Å; $D_{hkl} = \pm 5$ Å						
1 $\bar{1}$ 0	36	36	30	54			
110	40	44	43	54			
102	47	37	–	–			
100	44	44	–	–			
010	–	–	55	55			
average	42	40	43	54			
Unit cell periods (<i>a, b, c</i>), angle (γ), volume (<i>V</i>)							
<i>a</i> , Å	7.91(2)	7.95(3)	8.12(2)	8.04(2)	7.85	8.01	8.10
<i>b</i> , Å	7.99(9)	8.02(5)	9.30(3)	9.10(3)	8.17	9.04	9.03
<i>c</i> , Å	10.35(2)	10.35(3)	10.32(3)	10.34(2)	10.34	10.36	10.31
γ , Å	96.1(2)	96.0(2)	117.9(3)	117.4(3)	96.4	117.1	117.1
<i>V</i> , Å ³	651(2)	655(2)	689(3)	672(3)	659	670	

Note: The error in the final digit of the number is indicated in parentheses.

refinement of the unit cell periods, calculated crystallinity (CR), and size of the CSR (D_{hkl}) for cellulose samples 1, 2, 3, and 8 are given in Table 5.

Mercerization of starting cellulose I β (CR 72%) leads to the formation of cellulose II with low crystallinity (52%) due to the structure becoming looser and more amorphous. Hydrolytic decomposition of the cellulose fibre samples leads to a greater fraction of the crystalline phase, i.e., CP is formed with a more ordered structure. In particular, the crystallinity of CP-MC is 22% higher.

The dimensions of the CSR calculated from the width of reflections (110), (1 $\bar{1}$ 0), and (200) (lattice directions [110], [1 $\bar{1}$ 0], and [100], respectively) almost do not change upon going from the starting coniferous cellulose to the powder form in directions [1 $\bar{1}$ 0] and [100] but increase by 4 Å in direction [110]. The CSR dimensions of mercerized

Table 6. CR and SCR of Starting and Powdered Cellulose; $[hkl]$ are indices of the direction, in which the SCR dimension is determined, (hkl) are indices of reflections, from which the SCR dimension is

Exposure geometry	Sample 1		Powdered cellulose from sample 1					
			sample 3		sample 4		sample 5	
	reflection	transmission	reflection	transmission	reflection	transmission	reflection	transmission
CR, $\pm 5\%$	72	75	78	77	77	77	75	80
$[hkl]$ (hkl)	Gaussian approximation $D_{hkl}^g, \text{Å}; \Delta D_{hkl} = \pm 5 \text{Å}$							
1 $\bar{1}$ 0 1 $\bar{1}$ 0	36	37	36	37	36	36	32	31
110 110	40	50	44	37	43	46	36	46
102 102	47	53	37	70	44	58	44	56
100 200	44	47	44	52	44	44	44	44
001 004	43	126	39	126	39	130	43	80
Unit cell periods (a, b, c), angle (γ), volume (V)								
$a, \text{Å}$	7.91(1)		7.95(1)		7.96(1)		7.96(3)	
$b, \text{Å}$	7.99(2)		8.02(3)		8.02(3)		8.03(2)	
$c, \text{Å}$	10.35(3)		10.35(2)		10.35(1)		10.34(3)	
$\gamma, ^\circ$	96.1(2)		96.0(1)		96.0(1)		96.0(1)	
$V, \text{Å}^3$	651(3)		655(3)		655(3)		657(3)	

Note: The error in the final digit of the number is given in parentheses.

cellulose II increase in going to the powder form by 24 Å in direction $[1\bar{1}0]$ and by 11 Å in direction $[110]$ but remain unchanged in direction $[010]$. The dimension of the crystallinity regions averaged over all directions is about 42 Å for starting cellulose and 40 Å for CP, while this value increases significantly for the powder form of MC (by 11 Å).

The CSR dimensions calculated from the width of the (110) , $(1\bar{1}0)$, and (200) reflections characterize the shape of the unit fibrils in the direction perpendicular to the fibrils, i.e., the thickness. These data showed that the thickness of the microfibrils of the starting bleached coniferous cellulose is not altered upon hydrolysis but is larger for CP obtained from mercerized cellulose.

The results of previous workers [28-30] served as starting data for refinement of the unit cell periods using the Rietveld method for all the samples.

Bleached coniferous cellulose and its powder form have cellulose structures with antiparallel chain packing, which is characterized by period ratio $a < b$ (for the starting cellulose, $a = 7.91$, $b = 7.99$ and for CP, $a = 7.95$, $b = 8.02$ Å). These values are in accord with the data French and Howley [28]. The crystal lattice periods calculated by the Rietveld method change such that the volume of the unit cell ($V, \text{Å}^3$) increases in going to the powdered form. However, in going from MC to its powder form, the unit cell volume decreases. The unit cell periods a and b for the powder form are 0.1--0.2 Å less than for MC, which is in accord with the literature data given in Table 5. In all likelihood, this finding is related both to lower crystallinity and smaller size of the MC SCR. The bond angle of the glucose residues is virtually invariant because the period c is the same for each pair of cellulose sample and its powder form.

We then compared the crystallographic characteristics of CP obtained by hydrolytic decomposition of the starting sample with the various mineral acids used (Table 6). The thickness of the unit fibril was calculated from the width of the (110) , $(1\bar{1}0)$, and (200) reflections, while the length was calculated from the width of the (004) reflections. The direction $[001]$ coincides with the fibril axis [4].

The thickness of the unit fibril in going from the starting cellulose to the powder form in the case of sulfuric acid decomposition (sample 3) does not change in the $[1\bar{1}0]$ direction, decreases significantly in the $[110]$ direction (by 13 Å), and increases by 5 Å in the $[100]$ direction, while its length does not change ($[001]$ direction). A similar tendency for change in the thickness of the unit fibril was observed for CP obtained by treatment with hydrochloric acid but the length of the fibril increases in this case. A sharp drop of the length of the unit fibril by a factor of 1.5 was found for the CP sample obtained by treatment with nitric acid (sample 5). The volume of the unit cell (v) of the powder samples increases slightly due to an increase in periods a and b .

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