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X-RAY DIFFRACTION METHOD OF DETERMINING THE DEGREE OF CRYSTALLINITY OF CELLULOSE MATERIALS OF DIFFERENT ANISOTROPY

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It is shown that the important change in the x-ray diffraction parameters in preparation of compact products from microcrystalline cellulose and ground cotton fibres by pressing is not due to the amorphous phase of cellulose. A method for determining the degree of crystallinity of cellulose in anisotropic materials using an external standard that ensures spherical scattering symmetry is substantiated. The applicability of the proposed approach for estimating the degree of crystallinity of cellulose fibres directly in fabrics, which reduces the duration of the experimental procedures by 3-4 times, is demonstrated.

Pressing is used to increase the compactness and stability of samples for x-ray diffraction analysis of cellulose materials [1-4]. A drawback of this method is the dependence of the diffraction properties on the type and conditions of formation of the samples (fibre, fabric) due to the features of the texture formed [2, 4]. The necessity and possibility of taking this factor into account are valid in solving the problem of determining the polymorphous composition of cotton materials [4]. We will examine the possibility of x-ray diffraction estimation of the degree of crystallinity of cellulose materials of different anisotropy prepared by pressing in different conditions.

Bleached cotton fabric and fibres separated from the fabric and ground into 0.2-0.5 mm fragments were investigated. Microcrystalline cellulose (MCC) obtained by hydrolysis of cotton fibres in 2.5 N solution of HCl at 100°C and powdered amylopectin of the same chemical composition as cellulose were also used. Flat samples of constant diameter were prepared by pressing in the 0 to 400 MPa pressure range in a special mold. The fabric was also used in the form of a set of disks cut with a template. In view of the effect of the moisture content of the cellulose fibres on the diffraction parameters [5, 6], the samples were dried at 105°C.

The x-ray diffraction analysis was conducted on a DRON-3 diffractometer with the "transillumination" method with simultaneous rotation of the detector and the sample (θ - 2θ scheme), which made it possible to consider the factors that affect absorption and scattering by the samples. CuKα radiation separated by balanced Ni and Co filters was used. The samples were placed in a hermetically sealed cell with polyester film windows and placed in a holder that made it possible to average the diffraction intensity by rotating the objects. The background was taken into account by separately scanning an empty cell with the sample placed in front of the detector.

The intensity of scattering by the samples I_{sam} (2θ) at diffraction angles 2θ was determined with consideration of the background and use of differential filters based on the equations from [6]. The integral value of scattering by the samples A_{sam} in the given range of angles Δ2θ was found with the equation

$$A_{sam}(\Delta 2\theta) = A_{expt}(\Delta 2\theta) - A_b(\Delta 2\theta), \quad (1)$$

where $A_{expt}(\Delta 2\theta)$ is the experimental integral value of scattering by the sample, pulses; $A_b(\Delta 2\theta)$ is the integral value of the background, pulse.

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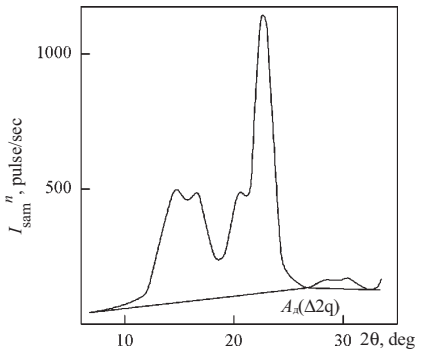

Fig.1

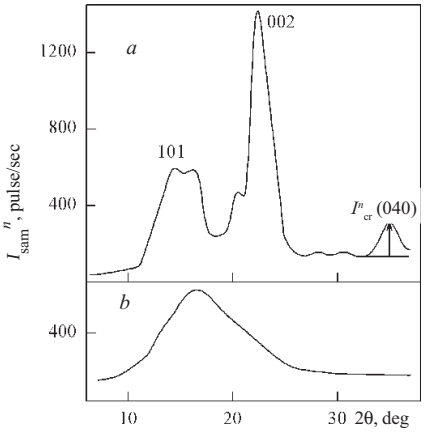

Fig.2

Fig. 1. Diagram of separation of diffuse scattering by cellulose.

Fig. 2. Diffractograms of pressed MCC (a) and amylopectin (b).

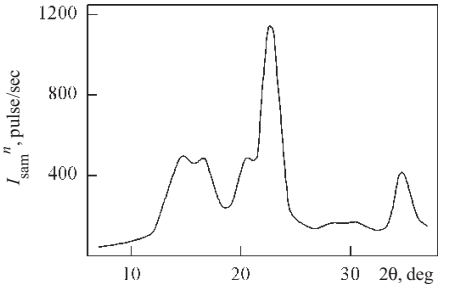

Fig. 3. Diffractogram of MCC pressed at 200 MPa.

Considering the use of differential filters, the parameters in Eq. (1) were calculated as follows:

$$A_{expt}(\Delta 2\theta) = A_{expt,Ni}(\Delta 2\theta) - A_{expt,Co}(\Delta 2\theta),$$

$$A_b(\Delta 2\theta) = A_{b,Ni}(\Delta 2\theta) - A_{b,Co}(\Delta 2\theta),$$

where the subscripts indicate the characteristics determined with the Ni and Co filters.

The use of computers in the measurements ensured that the coefficient of variation of the parameters was reduced to 1.0%.

Based on an analysis of x-ray scattering factors and the experimental values of the diffraction parameters for cellulose materials, it was previously [7] found that the degree of crystallinity P_{sam} for dry isotropic samples can be determined with the equation

$$P_{sam} = \frac{A_{sam}(\Delta 2\theta) - A_d(\Delta 2\theta)}{A_{sam} \cdot K_c(\Delta 2\theta)}, \quad (2)$$

where $A_{sam}(\Delta 2\theta)$ is the integral value of scattering in the range of $2\theta = 7.0\text{-}32.4^\circ$, pulse; $A_d(\Delta 2\theta)$ is the integral value of the diffusion halo, pulse; $K_c(\Delta 2\theta)$ is the coherent scattering fraction, 0.88 [7, 8].

To exclude the effect of overlapping of the most intense reflections for materials with different crystallite sizes and structural modifications (cellulose I, II, or III), $A_d(\Delta 2\theta)$ was calculated with the detector rotation rate and scattering intensities in minima at $2\theta = 7.0$, 26.5, and 32.4°, as demonstrated on the example of the diffractogram of ground cotton (cellulose I)

TABLE 1. Effect of Conditions of Pressing MCC and Amylopectin on Normalized Parameters

Pressure, MPa	MCC		Amylopectin
	$A_{sam}^{n}(\Delta 2\theta)$, pulse	$I_{cr}^{n}(040)$, pulse/sec	$A_{sam}^{n}(\Delta 2\theta)$, pulse
0	236500	178	236600
50	222300	213	–
100	214600	242	236200
200	211500	285	–
400	211900	283	236400

TABLE 2. Effect of Conditions of Pressing of MCC on Integral Diffuse Halo and Degree of Crystallinity of Cellulose

Pressure, MPa	$A_{d}^{n}(\Delta 2\theta)$, pulse	$P_{sam}\cdot 100$, %
0	80518	74.9
50	81100	74.7
100	80340	75.0
200	81300	74.6
400	80550	74.9

TABLE 3. Effect of Conditions of Pressing of Cotton Materials on Normalized Diffraction Parameters

Pressure, MPa	Ground fibres		Fabric	
	$A_{sam}^{n}(\Delta 2\theta)$, pulse	$Icrn(040)$, pulse/sec	$A_{sam}^{n}(\Delta 2\theta)$, pulse	$Icrn(040)$, pulse/sec
50	204500	312	213000	289
100	190000	343	204000	310
200	187000	360	195000	332
400	187100	358	195300	331

TABLE 4. Effect of Conditions of Pressing Cotton Materials on the Diffuse Halo Size and Degree of Crystallinity of Cellulose

Pressure, MPa	Ground fibres		Fabric	
	$A_{d}^{n}(\Delta 2\theta)$, pulse	$P_{sam}\cdot 100$, %	$A_{d}^{n}(\Delta 2\theta)$, pulse	$P_{sam}\cdot 100$, %
50	84802	72.9	84750	72.9
100	85200	72.7	84600	73.0
200	84600	73.0	85100	72.7
400	84700	72.9	84800	72.9

shown in Fig. 1. It should be noted that preparation of the fibres for determination of the degree of crystallinity according to Eq. (2) includes operations of preliminary grinding and formation of objects in conditions that ensure spherical scattering symmetry. This procedure is laborious, and the samples are not stable during drying and measurements. This approach, which is an "internal standard" method, also does not allow revealing and considering the appearance of anisotropy of the samples, which can affect the calculated value of the degree of crystallinity.

The quantitative comparative analysis of the scattering characteristics for textured samples requires bringing the results to a single scale of measurements. This problem can be solved by normalization of $I_{sam}(2\theta)$ and $A_{sam}(\Delta 2\theta)$ with respect to the scattering intensity of the standard and the optical density of the samples [8]. The features of the $(\theta - 2\theta)$ plotting scheme used

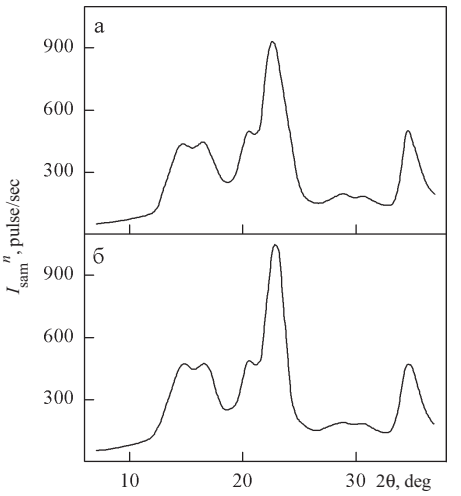

Fig. 4. Diffractograms of cotton materials pressed at 200 MPa: a) ground fibres; 6) fabric.

allow eliminating the effect of the angle factor. The obligatory identity of the overall x-ray mass attenuation coefficient μ_{sam} for the samples investigated is an important factor in normalization.

It is necessary to note that contaminants of different chemical composition capable of affecting parameter μ_{sam} are characteristic of natural cellulose fibres. As a consequence, the diffraction parameters should be normalized directly with the surface density of the flat samples directly coupled with the scattering mass.

In view of the results in [8] and the correlation of the optical D_{sam} and surface m_{sam} density of the sample ($D_{sam} = m_{sam}\mu_{sam}$), modified equations for normalization of the diffraction parameters can be represented as

$$I^n_{sam}(2\theta) = I_{sam}(2\theta) \cdot \frac{\exp D_{sam}}{D_{sam}} \cdot \frac{I_{ss}\mu_{sam}}{I_{st}\mu_{ss}},$$

$$A^n_{sam}(\Delta 2\theta) = A_{sam}(\Delta 2\theta) \cdot \frac{\exp D_{sam}}{D_{sam}} \cdot \frac{I_{ss}\mu_{sam}}{I_{st}\mu_{ss}},$$

where $I^n_{sam}(2\theta)$ is the normalized scattering intensity, pulse/sec; $A^n_{sam}(\Delta 2\theta)$ is the normalized integral value of scattering, pulse; I_{st} is the scattering intensity of the standard in the experimental conditions, pulse/sec; I_{ss} is a constant corresponding to the scattering intensity of the standard, pulse/sec; μ_{sam} is the experimental value of the x-ray mass attenuation coefficient for the sample; μ_{ss} is a constant corresponding to the mass attenuation coefficient selected for the standard.

MCC, a finely disperse powder that provides a compact sample even without pressing, is the most convenient cellulose material for quantitatively assessing the effect of anisotropy on the diffraction parameters. The curve of the normalized intensity of spherical symmetry of scattering for unpressed MCC (Fig. 2a) is characterized by reflections 101 and 002 caused by transverse organization of crystallites of cellulose I and reflection 040 related to the longitudinal structure of the polymer [4, 9]. For comparison, the diffractogram of unpressed amylopectin powder, which is a diffuse halo characteristic of amorphous polymers, is shown in Fig. 2b.

The analysis demonstrated the closeness of $A^n_{sam}(\Delta 2\theta)$ in the range of $2\theta = 7.0\text{-}32.4^\circ$ for unpressed samples (Table 1), which indicates the determining effect of the chemical composition of isotropic polymer materials on their scattering power and is in agreement with the law of "conservation of intensity" [10]. The normalized integral value of the spherical symmetry of scattering of MCC can thus be used as a standard characteristic for different cellulose materials.

It was found (Table 1) that an increase in the pressure in pressing of MCC simultaneously decreases the integral value of scattering and increases the intensity of reflection 040 at $2\theta = 34.6^\circ$ due to the periodicity of positioning of the elementary

units in cellulose along the axis of crystallite formations [4]. For this reason, $I^n_{ss}(040)$ was calculated with consideration of the intensity of the diffuse halo as shown in Fig. 2a.

The results obtain suggest perturbation of spherical symmetry of scattering as a result of pressing of MCC due to orientation of particles characterized by anisometry [11]. The quantitative data (Table 1) indicate that the maximum anisotropy of the sample of MCC is attained at a pressure ≥200 MPa. The curve of the scattering intensity for this preparation that demonstrate the change in the diffraction parameters is shown in Fig. 3. It is necessary to emphasize that the objects are in the form of strong pellets which are easy to work with.

As Table 2 shows, the conditions of pressing of MCC do not affect the integral value of the diffuse halo $A^n_d(\Delta 2\theta)$ calculated with the normalized scattering intensities at $2\theta = 7.0$, 26.5, and 32.4°. This situation indicates that "transillumination" x-ray diffraction of ground cellulose materials ensures preservation of the diffraction parameters of the amorphous phase of the polymer even when anisotropic samples are used.

The decrease in $A^n_{sam}(\Delta 2\theta)$ as a result of pressing MCC (Table 1) is thus due to a change in the number of crystallographic planes corresponding to the diffraction conditions only for crystallites, which perturbs the balance of scattering by amorphous and crystallite regions regions in the polymer. This could be the cause of scattering of the data on the crystallinity of cellulose in different versions of sample preparation and excludes the possibility of reliable quantitative analysis of P_{sam} by the "internal standard" method.

The results obtained indicate that the problem of determining the degree of crystallinity of textured cellulose preparations should be solved by using an external isotropic standard that makes it possible to consider the value of scattering. The equation for calculating the degree of crystallinity of cellulose (2) modified for materials of different anisotropy can be written as:

$$P_{sam} = \frac{A^n_{sp}(\Delta 2\theta) - A^n_d(\Delta 2\theta)}{A^n_{sp}(\Delta 2\theta) \cdot 0.88}, \quad (3)$$

where $A_{sp}{}^n(\Delta 2\theta)$ is the normalized integral value of spherical-symmetric scattering by the external standard in the range of $2\theta = 7.0$-32.4°, pulse; $A_d{}^n(\Delta 2\theta)$ is the normalized integral value of diffuse scattering by the sample, pulse.

Unpressed MCC prepared from purified fibres or amylopectin, convenient to use because of the amorphism and consequently, independence of the diffraction parameters from the pressing conditions, can be used as the external standard (Table 1).

Calculation of the degree of crystallinity of samples of MCC pressed in different conditions with Eq. (3) showed that the proposed method ensures the independence of this characteristic from the anisotropy of the preparations (Table 2).

Assessing the possibility of using this approach for determining the degree of crystallinity of cellulose for cotton materials of different anisotropy is of practical interest. The normalized diffraction parameters of ground cotton fibres and fabric pressed in different conditions are reported in Table 3. A comparison of the results obtained with the data for MCC (Table 1) reveals more important changes in the scattering characteristics of cotton materials in pressing. This phenomenon indicates the significant tendency of cotton fibres toward orientation as a result of compacting, which is due to their pronounced anisometry even after grinding. The less important texturing of the fabric samples in pressing should be due to twisting and crimping of the fibres in the material.

The results of the study indicate that the maximum possible orientation of the fibres in the materials is attained at a pressure ≥200 MPa, but the differences in the normalized diffraction parameters for the ground fibres and fabric persist (Table 3, Fig. 4). It is important to note the formation of compact stable samples as a result of pressing.

The analysis showed that the normalized integral value of the diffuse halo $A_d{}^n(\Delta 2\theta)$ of cellulose is identical for cotton materials of different anisotropy (Table 4). "Transillumination" filming with sample rotation thus preserves the diffraction parameters of the amorphous phase of cellulose not only for ground fibres but also for fabrics undergoing pressing.

The results in Table 4 show that the degree of crystallinity of cellulose calculated with Eq. (3) is identical in the analysis of cotton materials of different anisotropy. The possibility of using samples directly made of fabrics reduces the duration of the experimental procedures by 3-4 times and decreases the coefficient of variation of the data to 1.0%.

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