

EFFECT OF SUPRAMOLECULAR AND MORPHOLOGICAL STRUCTURE ON CELLULOSE CHARACTERISTICS

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The dependence of quality indicators of cotton cellulose obtained by an oxygen—alkaline digestion method, cellulose from the Bakai company, and wood cellulose on their supramolecular and morphological structure was studied by various physicochemical methods. The number of gel particles in cellulose solutions depends on their degree of polymerization; in solutions of their Na-CMC esters, on the content of the primary fiber wall of the starting cellulose.

Key words: cellulose, supramolecular structure, gel particles.

The degree of polymerization (DP), molecular-weight distribution (MWD), density, sorptivity, and other characteristics of cellulose are known to be related to its supramolecular and morphological structure. The presence of gel particles during production of synthetic fibers has a negative effect on the filtration of the spinning solution and the formation of fiber. Also, the number of gel particles and their shape are related to the supramolecular structure of cellulose.

Our goal was to find the quantitative dependence of DP, MWD, and the content of gel particles in solutions of certain industrial celluloses intended for chemical reprocessing on their supramolecular and morphological structure.

We investigated cotton cellulose obtained by an oxygen—alkaline digestion for acetylation, cotton cellulose from the Bakai company for viscosity modifiers, and wood cellulose (conifer) obtained by sulfate digestion and intended for production of cord fiber.

Cellulose samples were studied by electron microscopy, x-ray diffraction, viscosimetry, turbidometry, water-vapor sorption, and counting of the number of gel particles in spinning solutions.

Electron-microscope photomicrographs of the surface structure, internal fibrillar portions, and hydrolyzed preparations of the fibrillar portions differed substantially (Fig. 1). The surface of the cellulose fibers was completely cleaned of extraneous contaminants. The primary wall (P) was removed and the S₁-layer of the secondary wall was clearly visible on the surface layer of cotton cellulose fiber. Fiber parts were observed where patches of the P-layer were weakly bound to the secondary wall. The surface of Bakai cellulose fibers was devoid of the P-layer. Loose microfibrils of the S₁-layer were visible.

The primary wall of wood cellulose remains on almost all fiber surfaces. This is due to the protective action of lignin and other noncellulose substances that are present in significant quantities in the wood fibers.

Definite differences are observed in the structure of secondary wall fragments (Fig. 1). Thus, the fibrillar structure of cotton cellulose is closely packed. Dispersion of Bakai cellulose forms broad fragments of the secondary wall that have a loose structure. Fragments of the inner wall of wood cellulose are more orderly than those of cotton. The mutual orientation of the fibrillar aggregates is disrupted by shifts and breaks of the microfibrils upon removal of the lignin between them.

Crystallites of cotton cellulose that were produced by acid hydrolysis are essentially the same. However, they are slightly longer and thicker than those of wood cellulose.

Electron-microscope studies suggest that Bakai cellulose is obtained under more harsh processing conditions than those for cotton.

Data for the DP of these celluloses agree with the conclusions made above on the basis of the electron-microscope observations. For cotton cellulose, the DP is 1800; for Bakai, 1100; for wood, 800 (Table 1). Therefore, it can be concluded that the more extensive the digestion, the lower the DP of the cellulose.

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TABLE 1. Degree of Polymerization and Certain Physicochemical Parameters of Cellulose Samples and Gel-Particle Content in Cadoxen

Cellulose samples	DP	S_{sp} , M ² /g	W, cm ³ /g	r, nm	Sorption at various P/P ₀ , %			α -Cellulose, %	DC, %	Number of gel particles
					0.20	0.50	0.90			
Cotton cellulose obtained by oxygen-alkaline digestion	1800	103.69	0.19	0.36	2.6	4.5	12.2	99.8	77.0	12300
Bakai company	1100	108.26	0.20	0.37	2.8	4.8	12.7	99.9	79.0	4300
Wood cellulose	800	124.43	0.35	0.35	3.1	5.4	14.2	96.0	71.0	1100

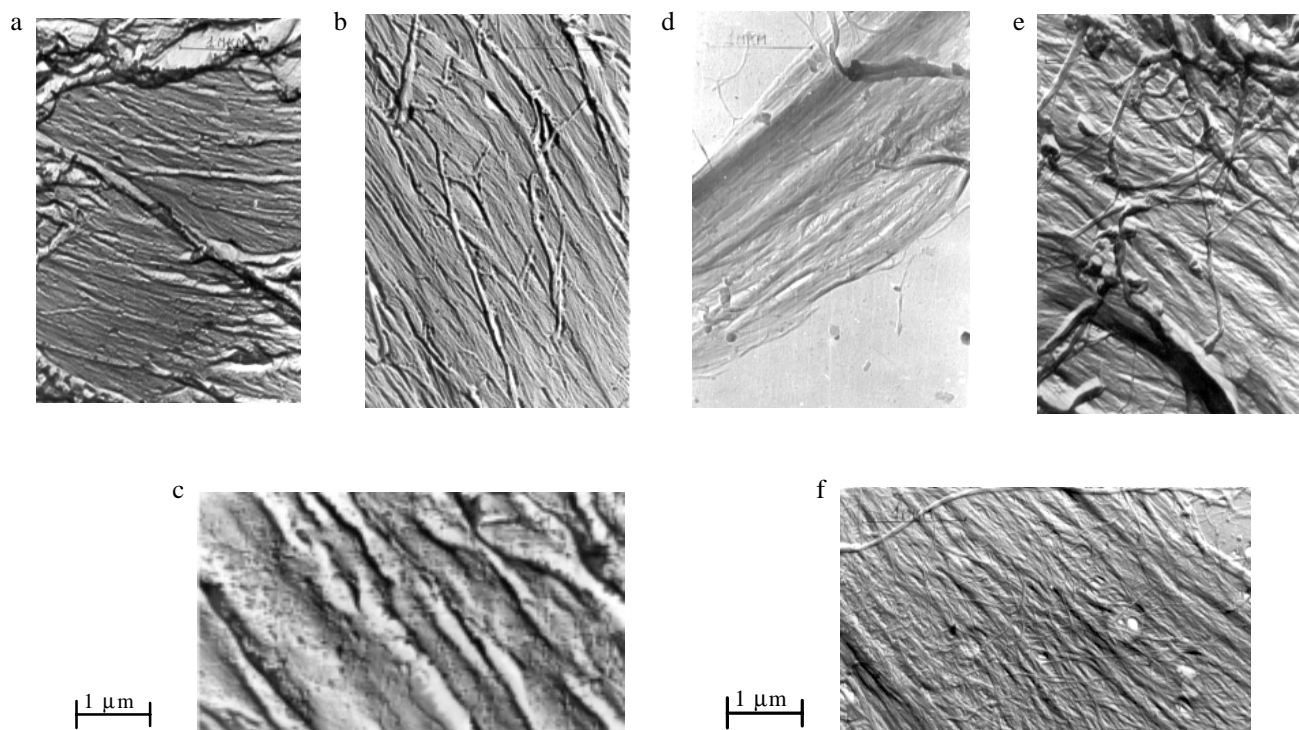


Fig. 1. Electron-microscope photomicrographs of surface (a, b, c) and internal fibrillar structure (d, e, f) of cellulose samples: cotton (a-d), Bakai company (b-e), wood (c-f).

The differential MWD curves showed that the cotton celluloses differ sharply among themselves (Fig. 2). Thus, whereas the MWD curve for cotton cellulose remains comparatively narrow in the 600-2200 DP region and contains one large maximum at 2000-2200 DP, Bakai cellulose characteristically has a broader MWD with three maxima at 600-1000, 1400-2200, and 2400-2800 DP. This means that Bakai cellulose is more polydisperse, which is obviously due to extensive digestion. Two maxima on the MWD curve at 500-1000 and 2200-2800 DP are observed for wood cellulose.

A study of water-vapor sorption by the celluloses showed that the sorption isotherms are similar in nature.

A determination of the amount of sorbed water indicated that the equilibrium content of moisture both at low relative pressure (0.05-0.03), where water vapor binds mainly to the internal cellulose surface as a monomolecular layer, and at high pressures (0.75-0.95), where mainly capillary condensation occurs, is greater in wood cellulose than in cotton celluloses. However, the hydrophilicity of Bakai cellulose is also greater than that of cotton cellulose. Based on the sorption isotherms for various cellulose samples, the specific surface area S_{sp} calculated during the initial stage using the BET equation [1], the volume W, the pore radius of submicroscopic capillaries r, and the amount of sorbed water vapor were determined (Table 1).

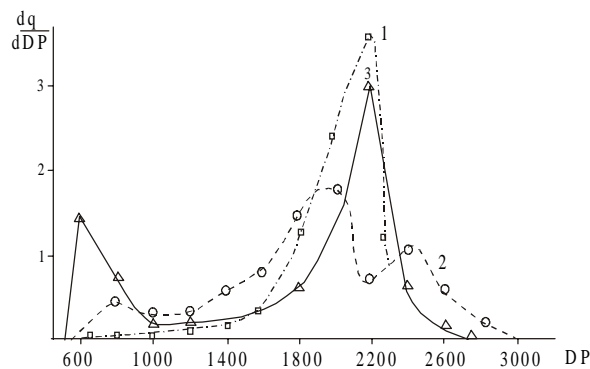


Fig. 2. Differential MWD curves of cellulose samples: cotton (1), Bakai company (2), wood (3).

The analysis showed that S_{sp} for wood cellulose is greater than that for cotton cellulose. The S_{sp} values for water represent the characteristic hydrophilicity of the cellulose preparations [2]. This is also confirmed by the DP data of the cellulose preparations. The DP will be lower and the sorptivity higher for a comparatively extensive digestion. The pore volume of wood cellulose is greater than that of cotton cellulose.

The content of gel particles in cadoxen solutions of cellulose are listed in Table 1. The greater the DP of the cellulose, the greater the content of gel particles in its solutions. Apparently this is due to a decrease of the cellulose solubility as its DP increases. Cotton cellulose typically has a comparatively large fraction of high DP. Therefore, the number of gel particles in its solution is greater. The gel particles are swollen aggregates of cellulose macromolecules with higher DP values.

It can also be seen that the degree of crystallinity (DC) of Bakai cellulose is higher than that of cotton cellulose. However, the number of gel particles in its solution is lower. Therefore, the content of gel particles in the cellulose solutions does not depend on its DC.

Cellulose-based fiber is commonly produced using its esters. Therefore, it would be interesting to determine if the relationships mentioned above between the number of gel particles and the DP of the starting cellulose persist. This issue was resolved by preparing sodium carboxymethylcellulose (Na-CMC) derivatives of these samples via a solid-state method.

A direct dependence between the DP of the starting cellulose and the content of gel particles in the CMC solution was not observed. A comparison of the number of gel particles in the CMC solutions and the morphological structure of the starting cellulose revealed that the thicker the primary wall of the fiber, the greater the number of gel particles in solutions of its esters. For cotton cellulose obtained by acid—alkaline digestion, the DP is 1800 and the content of gel particles 10,000; for Bakai cellulose, 1100 and 7200, respectively; for wood cellulose, 800 and 63,000. Cellulose macromolecules of the primary wall are packed more densely. Therefore, they are relatively unreactive. The esterification reaction occurs unevenly. The CMC solution of wood cellulose contains the greatest number of gel particles. IR spectra of Na-CMC and gel particles separated by centrifugation of its solution were taken under identical conditions on a UR-20 spectrophotometer in order to understand why the gel particles form.

The Na-CMC has a characteristic absorption band near 1600 cm^{-1} that is due to carboxylic groups [7].

The comparative analysis of the IR spectra of Na-CMC and gel particles showed that they are identical except for the strength of absorption bands near 1600 cm^{-1} and $3300\text{--}4000\text{ cm}^{-1}$. These correspond to $\text{O}=\text{C}=\text{O}$ and OH stretching vibrations. This indicates that the gel particles are slightly substituted and poorly soluble pieces of Na-CMC in a swollen gel-like state. The gel particles have a strong effect on the rheological properties of concentrated solutions. Their presence has a negative effect on filtration and fiber formation.

Thus, the number of gel particles in cellulose solutions depends directly on their DP. Gel particles in solutions of cellulose esters are slightly substituted and poorly soluble. The number of them depends on the content of primary fiber wall of the starting cellulose. Removal of the primary wall and disruption of the first layer of the secondary wall of the cellulose fiber makes the esterification reaction more uniform. As a result, the number of gel particles in the spinning solutions decreases.

EXPERIMENTAL

The DP of cellulose samples was determined by viscosimetry [3]. The solvent was cadoxen.

The molecular-weight distribution of the cellulose samples was measured by fractional precipitation from cadoxen solution using turbidometric titration by a *n*-propanol-ethylenediamine (50%) (9:1) mixture [5].

The number of gel particles was calculated using an optical instrument created for counting macrogel particles in acetylcellulose solutions [6, 7].

The extent of water-vapor sorption was measured by gravimetry on Mole—Ben scales at 25°C [1].

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