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SUPERMOLECULAR STRUCTURE OF COTTON CELLULOSE ISOLATED BY THE SODA-OXYGEN METHOD

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The supermolecular and fine structures of celluloses obtained on the soda-oxygen digestion of cotton lint under various conditions have been investigated by electron microscopy, IR spectroscopy, and x-radiography. It has been shown that under these conditions there is a weakening of intermolecular hydrogen bonds between the cellulose microfibrils and a loosening of their packing.

The use of a comparatively new, effective, and ecologically harmless method of isolating cellulose from low-quality cotton lint – the soda-oxygen cook – enables the content of harmful substances in the waste waters to be decreased considerably, the temperature to be lowered, the duration of the cook to be shortened, the bleaching process to be simplified, and the stability of the bleached cellulose to be improved [1].

It has been established that the presence of a small amount of copper sulfate in the cooking liquor enables the whiteness of the cellulose to be raised by 4-5% and the time of a cook to be shortened by 30-40 min. In order to prevent degradation of the cellulose it has been proposed to add a very small amount of hexamethylenetetramine to the cooking liquor in combination with copper sulfate, and for comparison a soda cook of lint has been conducted under the same conditions [2], whereupon, in addition to an improvement to the cellulose, structural transformations took place in it.

We have investigated the structural changes of cotton cellulose fibers during the above-mentioned processes by electron microscopy, IR spectroscopy, and x-radiography. The conditions for isolating the cellulose from cotton lint are given in Table 1.

The surface structure of the lint was characterized by the presence of wrinkles arranged at an acute angle to the axis of the fiber, while no fibrillar structure of the surface layer appeared, and it was coated with a layer of fatty-waxy and pectin substances (Fig. 1*a*). After a cook with sodium carbonate, fairly large fissures appeared in the surface of the fiber and products of the breakdown of the noncellulosic mass were seen in the form of small granular particles (Fig. 1*b*).

In the case of a soda-oxygen cook, there was considerable destruction of the layer of fatty-waxy substances on the surface of the fiber and of the noncellulosic impurities, as was shown by the presence of a large number of spherical particles (Fig. 1*c*). The presence of copper ions and hexamethylenetetramine led to a more powerful swelling of the fiber, as a result of which its surface became smooth, although the fibrillar structure of the primary wall did not appear (Fig. 1*d*).

The changes in the internal fibrillar structure that took place during the above-mentioned processes were studied on fragments of the secondary wall obtained by mechanical dispersion, followed by ultrasonic treatment. The layers of the secondary wall of cotton lint consisted of highly ordered and strictly oriented fibrillar aggregates (Fig. 2*a*). Because of the dirtiness of the lint, the fragments of the fibrillar structure were veiled by a layer of mechanical mixtures. After a soda cook, thanks to a considerable elimination of noncellulosic substances, a swollen partially loosened fibrillar structure of fragments of the secondary wall was observed (Fig. 2*b*). In the case of soda-oxygen digestion of the lint, this effect was seen even more clearly (Fig. 2*c*).

The addition of copper sulfate in a soda-oxygen cook led to a stronger swelling of the fiber and to the destruction of the cellulose macromolecules. Therefore, in the dispersion of the secondary wall, swollen and more oriented fragments were formed. The presence of a small amount of hexamethylenetetramine in the cooking liquor slowed down the degradation of the cellulose macromolecules and preserved the ordered and interpacked structure of the swollen fibers (Fig. 2*d*).

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Fig. 1

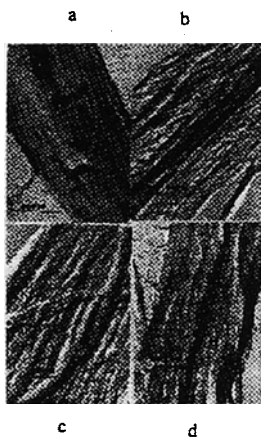

Fig. 2

Fig. 1. Electron micrographs of replicas of the surfaces of cellulosic materials: *a*) initial lint; *b*) after a soda cook; *c*) after a soda-oxygen cook; *d*) after a soda-oxygen cook in the presence of copper ions and hexamethylenetetramine.

Fig. 2. Electron micrographs of fragments of the fibrillar structures of cellulosic materials. For the arbitrary symbols, see Fig. 1.

The results of the electron microscope investigations indicated that, in the isolation of cellulose from cotton lint, simultaneously with the dissolution of the noncellulosic components, changes took place in both the surface structure and the internal structure of the cellulose fiber. In order to investigate the changes taking place in the fine structure of cellulose – i.e., in the degree of packing of the macromolecules and the bond between them – IR spectroscopic and x-radiographic analyses were made of the samples obtained (Fig. 3*). The results of the calculations are given in Table 1.

The absorption bands at 1430 and 900 cm^{-1} in the IR spectra are interpreted as characterizing crystallinity and amorphousness, respectively [3]. The ratio of the optical densities D_{1430}/D_{900} rose both on crystallization and on a rise in the cellulose content. We therefore call this ratio the index of secondary orderedness.

The highest values of the optical densities were observed in samples of cellulose after a soda cook of the lint, while in a soda-oxygen cook in the presence of copper ions and hexamethylenetetramine this ratio diminished (see Table 1). Consequently, these processes were accompanied by a disruption of intermolecular hydrogen bonds.

The increase in the area of the IR absorption band of hydroxy groups bound by hydrogen bonds after a soda cook of the lint can be explained by a considerable elimination of noncellulosic substances. In the IR spectra of the cellulose after soda-oxygen cooks without and with the addition of copper ions and hexamethylenetetramine there was a decrease in the area of the absorption band of hydroxy groups bound by hydrogen bonds. There was also a shift of the band of hydroxy groups in the low-frequency direction. These changes are possible because of a weakening of the intermolecular hydrogen bonds under the conditions of the above-mentioned treatments.

It can be seen from Table 1 that the DCs of the samples of cellulose obtained by the different methods of digestion were higher than the DC of the initial lint, which can be explained by an appreciable elimination of the amorphous noncellulosic fraction.

The results of the IR-spectroscopic and x-radiographic investigations showed that in the isolation of cellulose from cotton lint by various methods of digestion, inconsiderable changes take place in its fine structure.

Thus, it may be concluded that in the lint cooking process a weakening of the hydrogen bonds and a loosening of the supermolecular structure of the cellulose take place and that these changes are most pronounced in the case of a soda-oxygen cook with the addition of copper ions and hexamethylenetetramine.

*There is no Fig. 3 in the Russian original – Translator.

TABLE 1. Changes in the Area of the Absorption Band of Hydroxy Groups Bound by Hydrogen Bonds (S_{OH}) and in the Degree of Crystallinity (DC) of Celluloses Obtained by Various Methods

Experiment No.	Characteristics of the samples	S_{OH}, cm^2	D_{1430}/D_{900}	DC, %
1	Initial lint	48	0.84	66
2	After a soda cook	76	0.95	74
3	After a soda-oxygen cook	68	0.89	72
4	After a soda-oxygen cook in the presence of copper ions and hexamethylenetetramine	63	0.92	70

EXPERIMENTAL

The electron microscope investigations were conducted on a Tesla BS-242E electron microscope. Preparation involved the two-stage production of polystyrene-carbon replicas from the surfaces of the samples and mechanical dispersion in combination with ultrasonic treatment [4].

The IR-spectroscopic investigations were conducted on a UR-20 spectrophotometer as described in [5], and the x-radiographic studies on a URS-50 IM apparatus. Fine-cut fibers were passed through a sieve into a special mold, and tablets were made under a pressure of 500 kg/cm^2. The x-radiograms were obtained with monochromatized CuK_α radiation. Degrees of crystallinity were calculated by means of a formula in [6].

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