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CELLULOSE SUPRAMOLECULAR STRUCTURE CHANGES DURING ACTIVATION BY ORGANOPHOSPHORUS COMPOUNDS

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Cellulose supramolecular structure changes during activation by organophosphorus compounds were studied by electron microscopy, IR spectroscopy, and x-ray diffraction. These processes were shown to enhance interfibrillar swelling, weakening of intermolecular H-bonds between cellulose microfibrils, and loosening of the packing. As a result, the accessibility of esterification reagents to the molecules is improved.

Key words: cotton cellulose, activation, supramolecular structure.

The structure of cellulose can be regulated to increase its reactivity by selecting the appropriate conditions for its isolation and by using a sequence of physical or chemical treatments.

The structural parameters should optimally be the same so that the cellulose would react uniformly with the chemical reagents at a fast rate and form completely soluble derivatives, the solutions of which could be formed well during production of fibers, films, and other products.

We studied supramolecular structure changes of cotton cellulose after activation by certain organophosphorus compounds. The samples were cotton cellulose, cotton cellulose treated with dibutylphosphite (DBP) in alcohol (5%) at room temperature for 30 min and washed with alcohol, cotton cellulose treated with aqueous (5%) hydroxyethanediphosphonic acid (HEDP) under analogous conditions, and cotton cellulose soaked with aqueous (5%) HEDP under the influence of a DC electrical field for 30 min at room temperature and washed with water.

The measured characteristics were electron microscopy, x-ray diffraction, IR spectroscopy, and sample density.

The electron-microscope studies established that the surface of the initial cotton cellulose was wrinkled. The fibrillar structure of the primary fiber wall was not observed (Fig. 1a).

Treating cotton cellulose in alcoholic DBP leads to fiber swelling. The number of folds on its surface decreases (Fig. 1b). After treating cotton cellulose with aqueous HEDP, the folds on the fiber surface decrease more and their width increases (Fig. 1c). Combining such treatment with an electrical field leads to significant swelling of the fiber. Broad bands of shallow folds are observed on its surface (Fig. 1d).

Studies of the cross sections of cotton cellulose fibers (Fig. 1e and f) showed that a layer of the secondary wall of the initial cotton cellulose consists of densely packed microfibrils (Fig. 1e). Treatment of cotton cellulose by DBP solution causes swelling of the microfibrils of the secondary-wall layers (Fig. 1f). Swollen ends of microfibrils are noted. Treatment of cotton cellulose with HEDP solution, especially with an electrical field, enhances significantly swelling and layering of the secondary wall (Fig. 1g and h).

Studies of fragments of the secondary-wall layers that were obtained by dispersion determined that microfibrils of untreated cellulose are thin and densely packed together. Swollen fibrils of the secondary wall appear after treatment of the cotton cellulose with DBP solution. Fragmentation of secondary-wall layers of cotton cellulose activated with HEDP solution produces swollen and loosened fibrillar structures. Activation of cotton cellulose with HEDP solution and an electrical field produces more extensive lossening of the fiber secondary wall.

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TABLE 1. Effect of Activation on Degree of Crystallinity, S_{OH}, Cellulose Density, and CTA Syrup Quality

Cotton cellulose samples	DC, %	S_{OH}, cm^2	Density, g/cm^3	Transparency, %	Filterability, cm^3/70 min	Quality index (QI)
Initial	80	76	1.5515	46	130	2.7
Treated with solution						
DBP	79	68	1.5450	75	450	9.8
HEDP	79	62	1.5400	82	500	10.7
HEDP in combination with an electrical field	78	57	1.5370	86	560	12.3

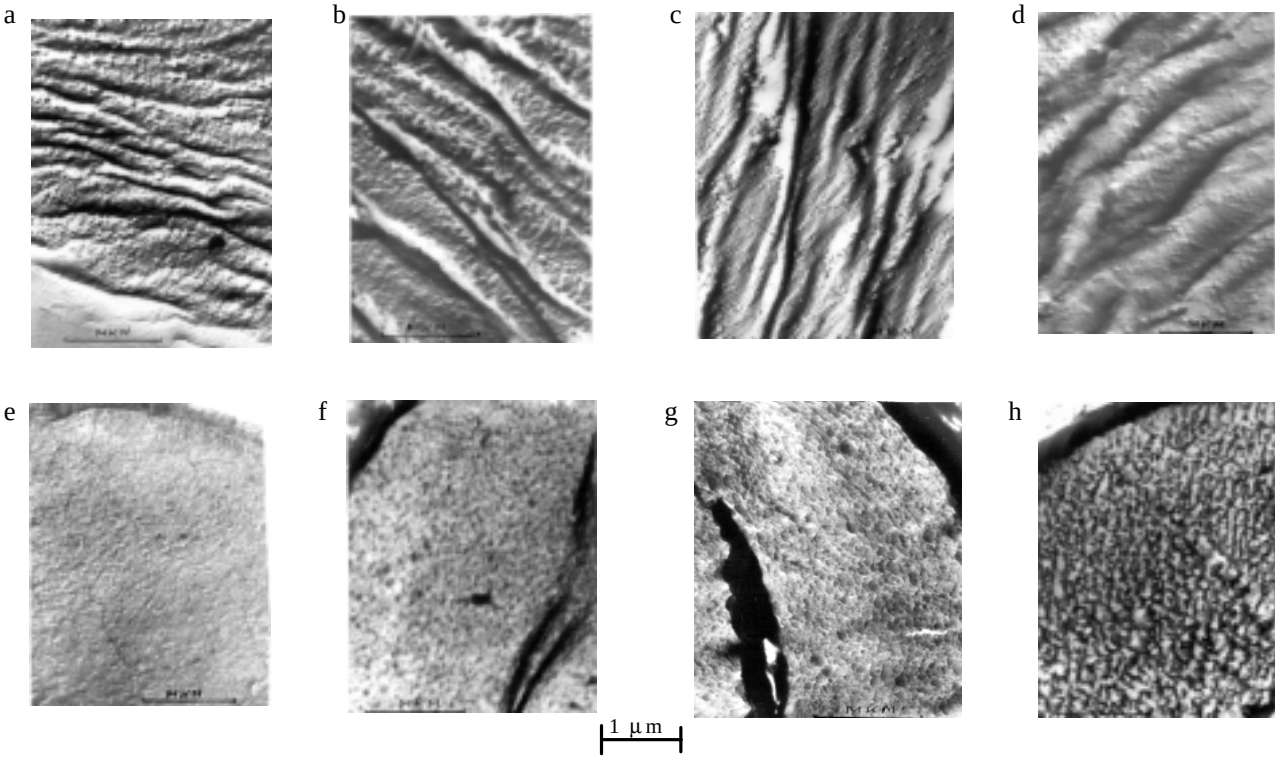

Fig. 1. Electron microscope photomicrographs of surface (a, b, c, d) and ultrathin cross sections (e, f, g, h) of cellulose: initial (a, e), treated with solutions of DBP (b, f), HEDP (c, g), HEDP and an electrical field (d, h).

X-ray patterns and IR spectra of cellulose samples were recorded in order to determine the extent of the structural changes that occur after the treatments mentioned above. The degree of crystallinity (DC) and area of hydroxyls (S_{OH}) bound by H-bonds were calculated using them (Table 1).

It can be seen that the DC of all cellulose samples is practically identical. Therefore, only interfibrillar swelling that does not affect the crystal structure occurs during these activation treatments.

The S_{OH} value of treated cellulose samples is markedly lower than for the initial untreated one. Activation weakens the H-bonds between molecules of amorphous sections and at the boundary of crystallites. As a result, the density of treated cellulose samples decreases.

The density of cellulose decreases most under the influence of an electrical field on fiber moistened with HEDP solution.

Investigation of the effect of the activation processes mentioned above on the reactivity of cellulose to acetylation indicated that activation of cellulose improves the transparency and filterability of the resulting cellulose triacetate (CTA) syrups. Although the CTA solution obtained from unactivated cellulose has QI = 2.7, the values after treatment with DBP and HEDP solutions are 9.8 and 10.7, respectively. The highest quality CTA syrup is obtained from cellulose treated with HEDP solution

and an electrical field.

Thus, it can be concluded that activation of cellulose by DBP, HEDP, and HEDP solutions combined with an electrical field leads to interfibrillar swelling and loosening of the packing. As a result, the access of esterifying reagents improves. The cellulose structure changes most during treatment with HEDP in a DC electrical field.

EXPERIMENTAL

Electron-microscope studies were performed on a TESLA-242 E electron microscope. Two-step production of polystyrene—carbon specimens from the sample surface, an ultrathin cross section of cellulose fibers, and mechanical dispersion combined with ultrasonic irradiation were used to prepare samples [1].

X-ray patterns were taken on a URS-50 IM apparatus.

IR spectra were recorded on a UR-20 spectrophotometer by the literature method [3].

Density measurements of cellulose were made using pycnometry [4].

Sample Preparation. Finely cut fibers were passed through a sieve into a special form and prepared as pellets at 0.5 t/cm^2 pressure. X-ray patterns were taken from these using monochromatized Cu Kα-radiation. The degree of crystallinity (DC) was calculated from the x-ray data using the literature method [2].

CTA Production. A suspension of cellulose (1 part) and glacial acetic acid (2.4 parts) was stirred for 1 h at 38°C and treated with glacial acetic acid and acetic anhydride (4 parts). The mixture was stirred at this temperature for another 45 min, cooled to 18°C, and treated with 98% acetic acid (2.7 parts) and conc. H_2SO_4 (6.1% of the cellulose mass). The mixture was stirred for 2-2.5 h with heating to 32-35°C. The resulting viscous and transparent syrup was treated dropwise over 1 h with a mixture of water (1 part) and acetic acid (2 parts) and filtered through two layers of calico on a special filtering apparatus.

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