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# REACTION OF MICROCRYSTALLINE CELLULOSE WITH WATER

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*The properties of microcrystalline cellulose prepared by classical (thermohydrolytic) and nonclassical (UHF) treatment of cotton cellulose are compared. The mechanisms of its reaction with water were studied to obtain stable gelatinous suspensions.*

**Key words:** microcrystalline and cotton cellulose, swelling, water retention, classical and nonclassical methods.

Two forms of powdered cellulose that differ in morphological structure, degree of crystallinity (DC) and polymerization (DP), granulometric composition, and other properties are recognized. These characteristics define their properties and areas of application [1-3].

The first form consists of amorphotized powdered cellulose that partially retains the fibrous structure. It is produced by mechanical, thermomechanical grinding, or precipitation from its solutions.

The second form is powdered cellulose with a high degree of ordering, so-called microcrystalline cellulose (MCC). This is produced via hydrolysis by acids, acid salts, or alkaline-oxidative destruction [4].

The study of the composition, structure, and physicochemical properties of MCC produced by various methods can explain the fine structure of the starting cellulose and determine possible applications of it.

Depending on the nature of the starting material (wood of higher plants, cotton, flax, hemp, jute, ramie, alga, etc.) and the production method, properties such as the DP, DC, granulometic composition, sorption characteristics, etc., can greatly vary [5, 6].

Results of investigations of the reaction of MCC with water are presented here.

MCC samples were produced from cotton cellulose by classical (MCC-1) and nonclassical (MCC-2) methods.

The range of particle sizes in the MCC samples was compared by dispersing them in a laboratory mill and passing them through sieves of 100, 71, and 25 μm in succession (Fig. 1).

It can be seen that the particle-size distribution of MCC-1 and MCC-2 decreases identically. The yield of particles (<25 μm) is 63.5 and 61.8%, respectively.

The results showed that the degree of thermohydrolytic cleavage of the cellulose macromolecules achieved in acidic medium after 3.5 h is reached in 30 min if the process is carried out using UHF. The yield and particle-size distribution of the MCC samples remain practically identical.

The DP of MCC-1 and MCC-2 were determined from the viscosity in copper-ammonium solution. It has been found that the DP for MCC-1 of particle size <25 μm is 161.7; for MCC-2, 166.7. For particle size >100 μm, the values are 171.8 and 173.8, respectively.

Therefore, the DP of MCC samples prepared by different methods are approximately equal. This can be explained by the decreased rate of cleavage of cellulose macromolecules upon attaining MCC of the limiting DP regardless of the destruction method.

Then we compared the reactions of MCC-1 and MCC-2 with water. MCC gels are known to have a high capacity to retain water [7]. MCC-1 and MCC-2 at concentrations of 10-15% in water have the same limiting water-retention values, 300-320%.

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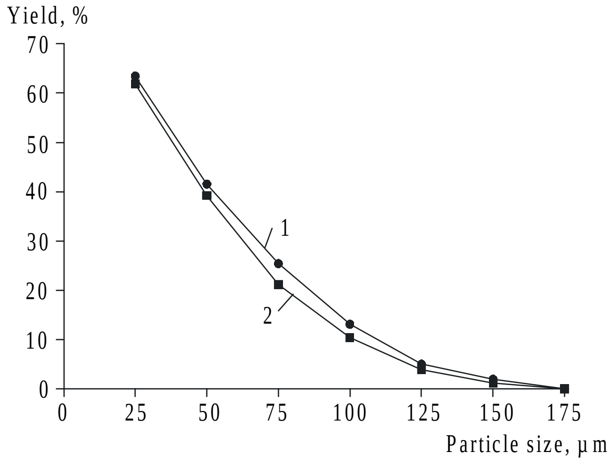

Fig. 1

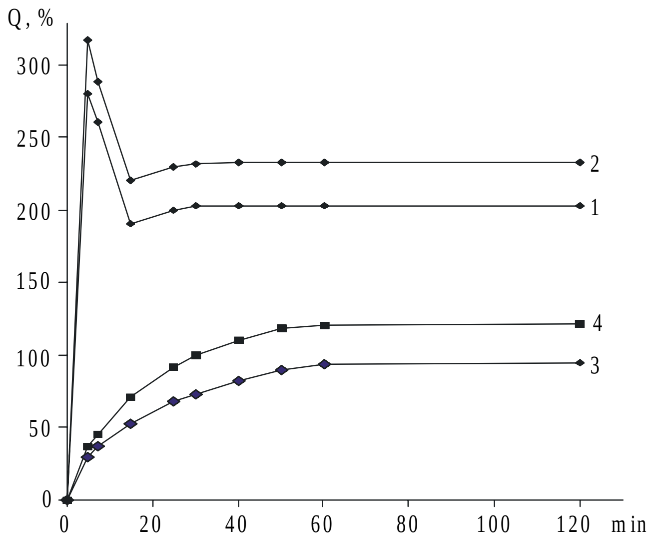

Fig. 2

Fig. 1. Yield of MCC-1 (1) and MCC-2 (2) after dispersion as a function of particle size.

Fig. 2. Kinetics of swelling in water: MCC-1 (1, 3) and MCC-2 (2, 4).

In order to separate the water-retention and swelling of MCC-1 and MCC-2, we investigated the kinetics of the limiting swelling in water and alkaline and copper-ammonium solutions. We observed that the swelling of these samples in these solutions is significantly greater than in water.

Swelling of MCC-1 and MCC-2 in water was monitored both visually (from the change of overall MCC volume) and using an optical microscope (from the change of particle size).

Figure 2 shows the kinetics of swelling of MCC-1 and MCC-2 in water that are determined from the change of overall volume in water (1, 2) and particle sizes determined using an optical microscope (3, 4).

It can be seen that swelling of MCC-1 and MCC-2 occurs in the first minutes according to overall volume. Then, the MCC volume decreases for 10-15 min. This is explained by the partial desorption of interfacial water.

The desorption of interfacial water is complete for MCC-1 after 15-17 min; for MCC-2, 13-15 min. Then, the volume of the samples increases due to particle swelling. This is consistent with the kinetics of MCC-1 and MCC-2 swelling determined by microscopic methods (3, 4). The differences in the nature of the swelling kinetics found by the different methods are explained by the fact that both the actual MCC particle swelling and interfacial water retention (1, 2) are included in determining the overall swelling volume. The actual degree of MCC particle swelling is determined if the degree of swelling is estimated by the microscopic method (3, 4). MCC-1 has a relatively slow rate and time of limiting swelling and water retention compared with MCC-2. This is due to its structural features.

It has been noted during a study of the mechanism of reaction of MCC-1 and MCC-2 with water that the crystallites of both samples are bonded to each other by bonds weaker than chemical ones. The bonds between structural elements of hydrolyzed cellulose are easily broken by mechanical and ultrasonic action in hydroxyl-containing media (water). The smaller particles are freed with a narrower size distribution. However, they retain the initial crystallinity. It has been found experimentally that ultrasonic dispersion of MCC-1 and MCC-2 in water for 20 min produces fractions with particle sizes <25 μm of 63.8% for MCC-1 and 93.6% for MCC-2. The fraction of size <10 μm is 23% for MCC-1 and 61.4% for MCC-2. The degree of crystallinity of dispersed MCC-1 and MCC-2 samples remained at the level of the initial MCC samples and varied in the range 0.78-0.83.

Thus, the experimental results have shown that rapid swelling of MCC (first maximum) in the first minutes involves mainly interfacial water retention (Fig. 2). Two competing processes begin when the maximum interfacial water retention is achieved. These are partial desorption of interfacial water and swelling of elemental MCC particles.

A second maximum appears on the curves when equilibrium is established between sorption and desorption of interfacial water. This is characteristic of swelling of elemental MCC particles.

The actual MCC particle swelling and their interfacial water retention were found by comparing the swelling curves determined visually and by microscopic methods.

It has been shown that MCC-2 obtained by the nonclassical method has high values of both interfacial water retention and swelling.

Further investigation of the mechanism of formation of stable gelatinous MCC suspensions upon reaction with water is required.

## EXPERIMENTAL

**Classical Method of MCC Production.** Cotton cellulose was hydrolyzed by aqueous $HNO_3$ (5%) using a 1:16 ratio for 3-5 h at 95-98°C.

**Nonclassical Method of MCC Production.** Cotton cellulose in aqueous $HNO_3$ (5%) was treated at a 1:16 ratio for 25-30 min with UHF irradiation in an MS 283 TD/MS-282 TD apparatus at 2450 MHz and 1300 W.

Samples of MCC-1 and MCC-2 were dispersed in a KM-1 laboratory mill at 25°C for 1-3 min. The DP was determined by measuring the viscosity of MCC solutions (0.1-0.3%) in copper-ammonium solution [8].

The degree of swelling of MCC samples was found visually from the overall volume change of MCC in a graduated glass cylinder 25 mm in diameter and 250 mm high and by microscopy from the swelling of elemental MCC particles with time on a MBI-6 microscope.

Hydrogels of MCC-1 and MCC-2 were prepared by dispersing aqueous dispersions (5-15%) in an UZDN-2 T apparatus for 10-20 min.

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