HYDROGELS PRODUCED FROM COTTON CELLULOSE

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Hydrogels with high water retention can be produced from cotton cellulose. Treating aqueous suspensions of microcrystalline cellulose, lint, and powdered cellulose with mechanical pulses of various frequencies, amplitudes, and shear stresses turns them into gels.

Key words: cotton cellulose, hydrolysis, cellulose hydrogels.

Cellulose is a high-molecular-weight linear polysaccharide. Intramolecular bonds in it form a rigid structure that imparts rather high mechanical strength to the plant material. One macromolecule incorporates several crystalline portions [1].

Cellulose raw material was treated chemically to prepare mainly low-molecular-weight products (glucose, ethanol, xylite, etc.) in addition to cellulose ethers and esters [2]. Hydrolysis of cellulose occurs in two steps. In the first step, amorphous parts of the cellulose are mainly hydrolyzed. Dense cellulose with 100-200 degree of polymerization and up to 80% crystallinity is isolated. In the second step, these portions are hydrolyzed under harder conditions. In the 1950s and 1960s, reports appeared in which these cellulose portions, i.e., microcrystalline cellulose (MCC), was viewed as the final product. A series of studies was published on the application of powdered MCC in various areas [3]. An interesting feature of MCC is that gels can be prepared from it.

Methods of preparing cellulose hydrogels have been reported. Thus, a gel of depolymerized cellulose was prepared by soaking fibrous cellulose with 3-10 portions (by vol.) of 18-40% base at 20°C, pressing to 35-45% mass increase, and heating at 40-70°C under 5-6 atm for 8 h [4]. Cotton lint that was depolymerized by 2.5 N base was washed with water until the washings were neutral [5]. The final rinse was 1% ammonia. The washed sample was dried under vacuum for 16 h at 60°C. A thixotropic gel was prepared by treating a 5% cellulose sample with water in a Waring Blender for 1 h. Cellulose was rendered into a gel via microfibrillation from an aqueous suspension in a homogenizer [6-8]. The suspension stream was passed through a narrow opening and subjected to high pressure (35-55 mPa) and shearing from impact of the high-speed stream against the hard surface of a barrier situated vertical to the stream. The water retention of such cellulose is >280% of its mass. One method for preparing cellulose hydrogels is the treatment of aqueous MCC suspensions with ultrasound [9]. A stable gel is obtained by treatment of a 15% MCC suspension in a UZDN-1 apparatus with 15 kHz ultrasound.

The above methods for preparing cellulose hydrogels include many steps, are time-consuming, or are preparative in nature. The present study involves new methods for preparing and using cotton-cellulose hydrogels.

The raw materials for preparing MCC and cellulose powder were wastes from the cotton industry: lint, cyclone lint, etc. MCC and finely dispersed cotton cellulose were prepared by hydrolytic decomposition and radiative-mechanical destruction of native cellulose macromolecules.

It is known [10] that MCC in water is affected by high shear stresses to form gelatinous dispersions. We studied the possibility of preparing hydrogels by treating an aqueous MCC suspension containing 3-40% solids by pulses in the frequency range 1,800-10,600 Hz with an amplitude of 0.1-1.0 mm in combination with transverse shear stresses of 500-1000 N/m. Such treatment ensures that the suspension turns into a gel. The MCC gel does not form layers on standing. It has good water retention and specific surface area (Table 1).

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TABLE 1. Properties of MCC-Gel and Preparation Conditions

MCC conc. in suspension, mass %	Field parameters			Water retention	Specific surface area, m^2/g
	frequency, $\times 10^3$, Hz	amplitude, mm	shear stress, N/m		
6.0	1.8	0.1	500	122	10.0
10.0	1.8	0.1	500	235	14.5
15.0	7.2	0.2	700	278	18.5
20.0	10.6	1.0	1000	380	22.0
25.0	7.0	0.2	700	226	12.0

Table 1 shows that treatment of 20 mass % MCC at 1.0 mm amplitude, 10.6×10^3 Hz, and 1000 N/m produces a gel with the best quality parameters. Under these conditions MCC (1 g) retains water (380 g) in a bound state without separation from the solid particles. The MCC-gel is a gelatinous mass with the consistency and color of sour cream and a pH value of 7.2.

We also studied the effect of MCC concentration on the water retention of the resulting gel. The data show that the water retention of the gels depends on the cellulose concentration. For a concentration >20%, the water retention begins to decrease:

MCC concentration of suspension, mass %	Water retention, g/g
3.0	120
5.0	150
10.0	250
15.0	270
20.0	380
30.0	360
40.0	250

The results suggest that MCC-gel with a concentration of 20 mass % should be used.

The gel from lint, like that from MCC, was prepared by dispersing an aqueous suspension of powdered lint using mechanical vibrations of amplitude 0.1-1.0 mm. However, more time is required to disperse the lint. The gel particles of lint are larger. The water retention is lower compared with MCC. It was proposed, like for powdered MCC, to grind the lint by adding mineral particles to the starting suspension for subsequent mutual wet grinding in order to reduce the energy requirements for the dispersion. This method of preparing a hydrogel was used to formulate a clay for the preparation of porcelain.

The particle size of MCC prepared by hydrolytic cleavage under various conditions is known to vary depending on the type of starting cellulose over a wide range [11]. We studied the effect of dose during preliminary treatment with ionizing radiation on the grinding of commercial cotton cellulose in a ball grinder in order to prepare powdered cellulose with various particle sizes. It should be mentioned that cotton cellulose is fibrous and does not form powder without treatment with at least 200 kGy of ionizing radiation during grinding in a ball grinder. Table 2 shows that increasing the integrated dose from 400 to 700 kGy increases the yield of powdered cellulose from 44 to 100%. This also produced finely dispersed powdered cellulose with average particle size from 40 to 250 μm.

EXPERIMENTAL

MCC was prepared by hydrolysis of cotton cellulose with HCl-acid (18% of the cellulose mass). The hydrolysis was performed at 80-120°C for 6 h at a 1:10 ratio. The product was filtered, washed free of acid traces, and dried.

Powdered cellulose was prepared from cotton cellulose and purified lint by γ-irradiation (^{60}Co) at 30-35°C in a "well" irradiator at the Institute of Nuclear Physics of the Academy of Sciences of the Republic of Uzbekistan. The radiation dose varied from 400 to 1500 kGy. The irradiated cotton cellulose and lint were ground in a laboratory porcelain ball grinder

TABLE 2. Effect of Preparation Conditions on Cellulose Powder Particle Size*

Irradiation dose, kGy	Yield of powdered cellulose, %	Particle size, μm		
		max.	aver.	min.
0.0	0.0	3000	600-1300	210
400	44	900	250	120
500	80	600	150	30
700	100	320	120	7
800	100	180	100	5
1000	100	120	70	5
1500	100	70	40	5

*Grinding time 2 h.

(2 L volume). The yield of powdered cellulose was determined by passing the ground mass through a 1000-μm sieve. The particle size was determined on a MBI-6 microscope.

The specific surface area of MCC and the water retention of the hydrogels were determined by the literature methods [12, 13].

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