

Synthesis and Study of Copper-Containing Polymers of Microcrystalline Cellulose Sulfates from Larch Wood

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Abstract—For the first time, the synthesis of water-soluble copper-containing microcrystalline cellulose sulfates (Cu-MCS) has been performed by the ion exchange method. The composition of the products has been studied by chemical methods and X-ray spectral microanalysis. The copper content in the Cu-MCS samples was 12.6–14.1%. The absence of sodium in the resulting polymer indicates the complete substitution of the sodium cations by the copper cations in the sodium salt of MCC sulfate. The structure of the copper-containing sulfates of microcrystalline cellulose has been confirmed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and electron paramagnetic resonance (EPR). According to the XRD method, Cu-MCS and Na-MCS have an amorphous structure in contrast to the original MCC samples, which have a high degree of crystallinity. The EPR data have demonstrated the formation of a pseudocrystalline structure of the copper-containing salt system in the Cu-MCS samples. As shown by atomic-force microscopy, the surface of the Cu-MCS films consists of homogeneous crystallites, which have a spherical or slightly extended form with the size of about 70 nm. The film surface is quite homogeneous in its phase composition and contains no impurities.

Keywords: cellulose sulfate, ion exchange, copper-containing polymers, microcrystalline cellulose, composition, structure

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INTRODUCTION

Polysaccharides of vegetable origin are being used as polymer carriers for targeted drug delivery [1]. Dextrans [2] and derivatives of starch [3] and cellulose [4] have found wide application for this purpose.

Polysaccharides are also widely used to produce new metal-containing polymers with unique properties [5]. Polymeric materials containing metals, such as silver, copper, iron, cobalt, and nickel are of special interest. These metals exhibit bactericidal, antimicrobial, and antifungal properties and play an important role in the regulation of many functions in the human body [6–8].

Cellulose acetate (CA) fibers were used to synthesize antibacterial nanofibers that contained silver nanoparticles on the surface [7]. CA fibers containing Ag⁺ nanoparticles with an average size of 21 nm were shown to have a high antimicrobial activity.

The preparation and properties of nanocomposites based on biodegradable carboxymethyl cellulose

(CMC) and metal cations (copper, silver, indium, and iron) are described in [8]. These nanocomposites were synthesized by the interaction of the corresponding metal salts with sodium salts of CMC in water at room temperature. The resulting nanocomposites can be used in the design of antibacterial and antifungal coatings, food packaging materials, and biomedical devices.

Water-soluble sulfates of cellulose are promising as polysaccharide templates to prepare metal-containing polymers [5]. The goal of the work is to develop a new method for the synthesis of water-soluble copper-containing polymers of microcrystalline cellulose sulfates (Cu-MCS) based on the ionic exchange and to study their structure by physicochemical methods.

EXPERIMENTAL

Microcrystalline cellulose (MCC) from Siberian larch wood (*Larix sibirica* Ledeb.) [9] was used as a raw material. The polymerization degree (PD = 134) was calculated from the viscosity of the MCC solutions in the iron-sodium tartrate complex on a VPG-3 viscometer [10]. The crystallinity degree (CD = 0.66) was evaluated

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by the ratio of the intensities of the reflexes at angles of 22° and 19° by the Segal method [11].

MCC sulfates were synthesized according to [12] by sulfation of MCC with chlorosulfonic acid in dioxane, followed by the isolation of the product (MCS) in the form of the sodium salt.

Synthesis of copper-containing polymers of MCC sulfates. Copper-containing polymers of MCC sulfates (Cu-MCS) were obtained from the sodium salt of MCS by the ionic exchange method according to the standard method [13] using a KU-2-8 ion-exchange resin in the Cu²⁺-form. The commercial Na⁺-form of this resin was preliminarily converted to the Cu²⁺-form on a column (diameter, 20–25 mm; length, 300–350 mm) with a tap at the bottom by washing the resin with 2 M CuSO₄. The solution of Na-MCS (the sulfur content, 12.4% w/w; 0.5 g in 12.5 mL of distilled water) was purified by dialysis and passed through a column with KU-2-8 in the Cu²⁺-form. The resulting copper-containing MCS was washed with distilled water (3 × 12.5 mL). The washings were collected and evaporated on a rotary evaporator to 5–10 mL at a temperature of not more than 50°C. Cu-MCS was isolated from the evaporated residue by precipitation in ethanol (100 mL). The resulting precipitate of Cu-MCS was filtered, washed with ethanol (15–25 mL), dried under vacuum, and stored before use at a temperature below 5°C in a vacuum desiccator.

The copper content in Cu-MCS was measured by the complexometric titration method using EDTA and murexide indicator [14]. The residual sodium was evaluated by X-ray analysis on a TM-1000 scanning electron microscope (Hitachi, Japan) equipped with a Swift ED-TM EDX spectrometer.

The IR spectra of MCC and its sulfation products were recorded on a Tensor-27 Fourier spectrometer (Bruker, Germany) in the range 400–4000 cm⁻¹. The spectral information was processed by the OPUS program (version 5.0). The solid samples for the analysis were prepared in the form of tablets in KBr (2 mg of the sample per 1000 mg of KBr).

The X-ray phase analysis was performed on a DRON-3 X-ray diffractometer with CuK_α monochromatic radiation (λ = 0.154 nm; voltage, 30 kV; current intensity, 25 mA; scanning step, 0.02 deg; accumulation time at a point, 1 s; the range of Bragg angles 2θ, 5.00–70.00 deg).

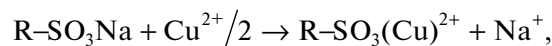
The transparent films of Cu-MCS for the AFM analysis were prepared by evaporation of 6–7% aqueous solutions on a smooth glass substrate. The resulting films were analyzed in a semicontact mode using a Solver P47 multimode scanning probe microscope (NT-MDT, Moscow) equipped with a 14-μm scanner and an SKM adjustment table. The samples were scanned at room temperature in air using silicon rectangular cantilevers (NSG30, NT-MDT, Moscow) with a typical resonance frequency of about 330 kHz

and a stiffness constant of about 40 N/m. The beam length was 125 μm; the radius of curvature of the needle was less than 10 nm. Scanning was performed at at least 3–4 points in several regions. The scanning rate was 1.5–2 Hz; resolution of the resulting image was 256 × 256 pixels. As a rule, no smoothing or other processing of images was performed except for subtraction of the second-order surface. The surface roughness was calculated from the cross-sectional profile using the Nova 026 program package according to GOST 2789–73 [15].

The EPR spectra were recorded on a BRUKER ELEXSYS E580 EPR Fourier spectrometer in the CW mode at room temperature (ultra-high frequency power, 0.2 mW; modulation value, 1 Gs).

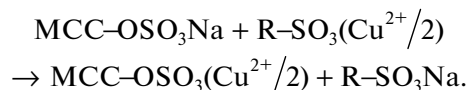
RESULTS AND DISCUSSION

The salts of cellulose sulfates with different cations of alkali and alkaline-earth metals are usually prepared by neutralization of their acidic forms with the corresponding alkali or by the exchange reactions with salts [16]. This method is not applicable to salts of weak bases. Since the sodium salt of MCS is a polyanion, which is capable of ion exchange with metal cations, we proposed this method to introduce Cu²⁺ in the MCS molecule. For this purpose, we used a KU-2-8 cation exchanger in the Cu²⁺-form, which was prepared from the commercial cation exchanger KU-2-8 in the Na⁺-form by the reaction:



where R is the matrix of KU-2-8.

The sodium ions in MCS were replaced by copper ions on the resulting resin:



The ion exchange was carried out in the dynamic mode with the molar ratio of the Cu²⁺ ions in the resin to the Na⁺ ions in MCS being (60–70) : 1.

The resulting copper-containing polymers of sulfated microcrystalline cellulose are blue-green powders or films highly soluble in water.

The completeness of the ion exchange was determined from the content of the residual sodium ions in the resulting Cu-MCS. According to the X-ray analysis, the Cu-MCS samples did not contain sodium, which indicated the complete ion exchange. The copper content in Cu-MCS assessed by the complexometric titration method was 12.6–14.1%.

The structure of initial MCC and its sulfated derivatives was studied by IR spectroscopy (Fig. 1). The IR spectra of Na-MCS and Cu-MCS contain the absorption bands at 800 cm⁻¹ (SO) and 1200 cm⁻¹ (SO₂), which confirm the presence of the sulfate groups in the

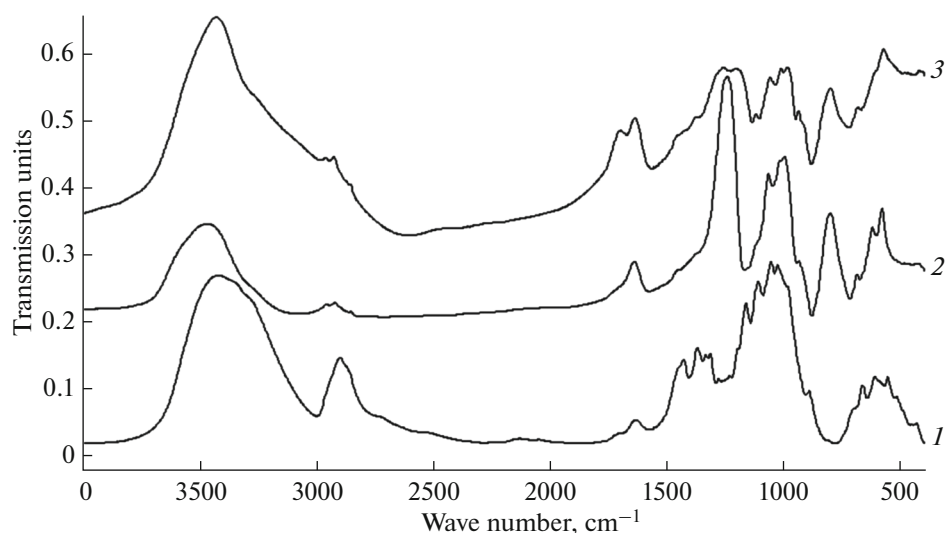


Fig. 1. IR spectra of initial MCC (1), sodium salt of MCC sulfate (2), and copper-containing MCC sulfate (13.2% of copper, w/w) (3).

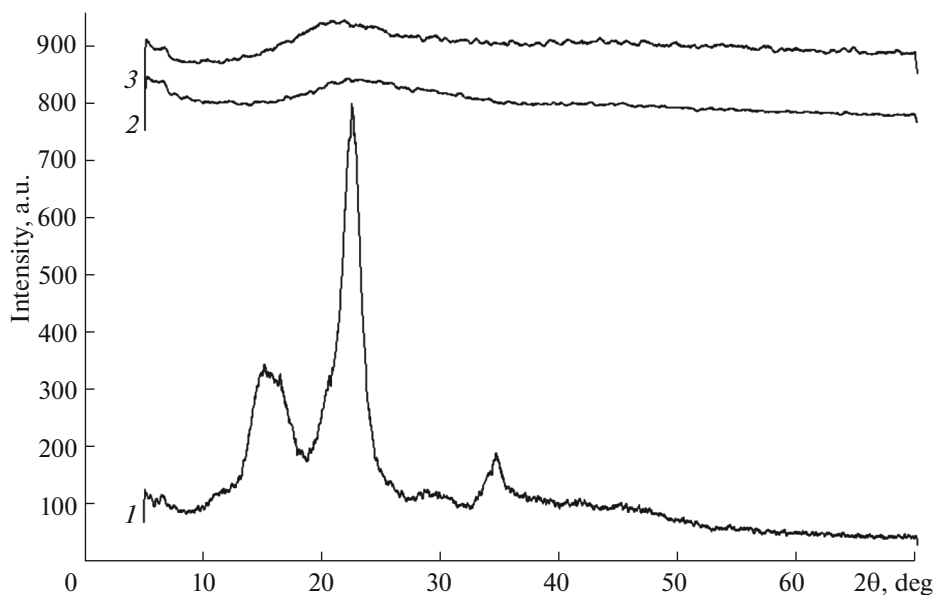


Fig. 2. X-ray diffractograms of initial MCC (1), sodium salt of MCC sulfate (2), and copper-containing MCC sulfate (13.2% of copper, w/w) (3).

cellulose structure. The band at 1200 cm^{-1} corresponds to the valence vibrations of the sulfate group $\nu_{\text{as}}(\text{O}=\text{S}=\text{O})$, which is caused, probably, by a different nature of intra- and intermolecular interaction of the copper ions with the sulfate and hydroxyl groups. We observed the broadening and splitting of this absorption band in the spectrum of Cu-MCS, in contrast to that in the spectrum of Na-MCS. Moreover, we observed an increase in the intensity of the absorption band at 1638 cm^{-1} in the spectrum of Cu-MCS, which is typical for deformation vibrations $\delta(\text{H}-\text{O}-\text{H})$ of

the molecules of adsorbed water. This is most likely related to the higher hydration degree of copper-containing MCS because of the ability of the copper(II) ions to form aqua complexes.

According to X-ray diffraction, Cu-MCS has the amorphous structure (Fig. 2). X-ray diffractograms of Na-MCS and Cu-MCS contain no distribution maximum in the region of $2\theta = 22^\circ$ typical for initial MCC [17].

A characteristic feature of the Cu^{2+} signals in the EPR spectra is a significant anisotropy in the g -tensor and hyperfine structure constants (HSC) [18]. How-

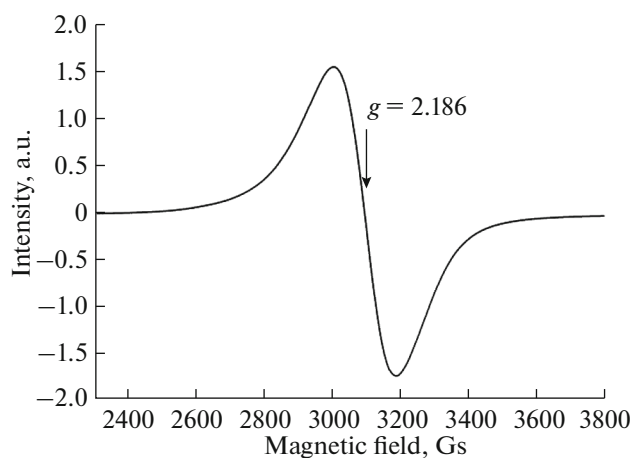


Fig. 3. EPR spectrum of copper-containing MCC sulfate (13.2% of copper, w/w).

ever, the EPR spectrum of copper-containing MCC sulfate contains the Cu^{2+} signal in the form of a slightly asymmetric line ($g_0 = 2.186$, $\Delta H = 185$ Gs) (Fig. 3), which indicates no anisotropy in the g -factor and insignificant HSC values. The absence of these constants is observed in the EPR spectra of different salts

of Cu(II) , which is explained by exchange interactions between copper ions. At the same time, the g -factor anisotropy is retained due to orientational localization ordering of paramagnetic cations in salt crystals. Therefore, the absence of anisotropy in the g -factor in the EPR spectrum of Cu-MCS (Fig. 3) is explained by the presence of the Cu^{2+} ions, which are in the exchange interactions and have a different orientation of the g -tensor axes. Thus, the Cu-MCS sample contains the copper-containing salt system with the pseudocrystalline structure. The value of $g_0 = 2.186$ is close to the average g -factor values for Cu(II) salts, which contain the oxygen atoms in the nearest coordination sphere of copper cations (e.g., for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

The Cu-MCS samples isolated as films were studied by the AFM method in semicontact mode (Fig. 4). The surface of Cu-MCS consists of sufficiently homogeneous particles of spherical or slightly extended form with a diameter of about 70 nm (Fig. 4a). The root-mean-square roughness value evaluated by the cross-sectional surface profile (Fig. 4c) was 32 nm. According to the phase contrast images, the surface of the Cu-MCS film is sufficiently homogeneous in its phase composition and does not contain any impurities (Fig. 4b).

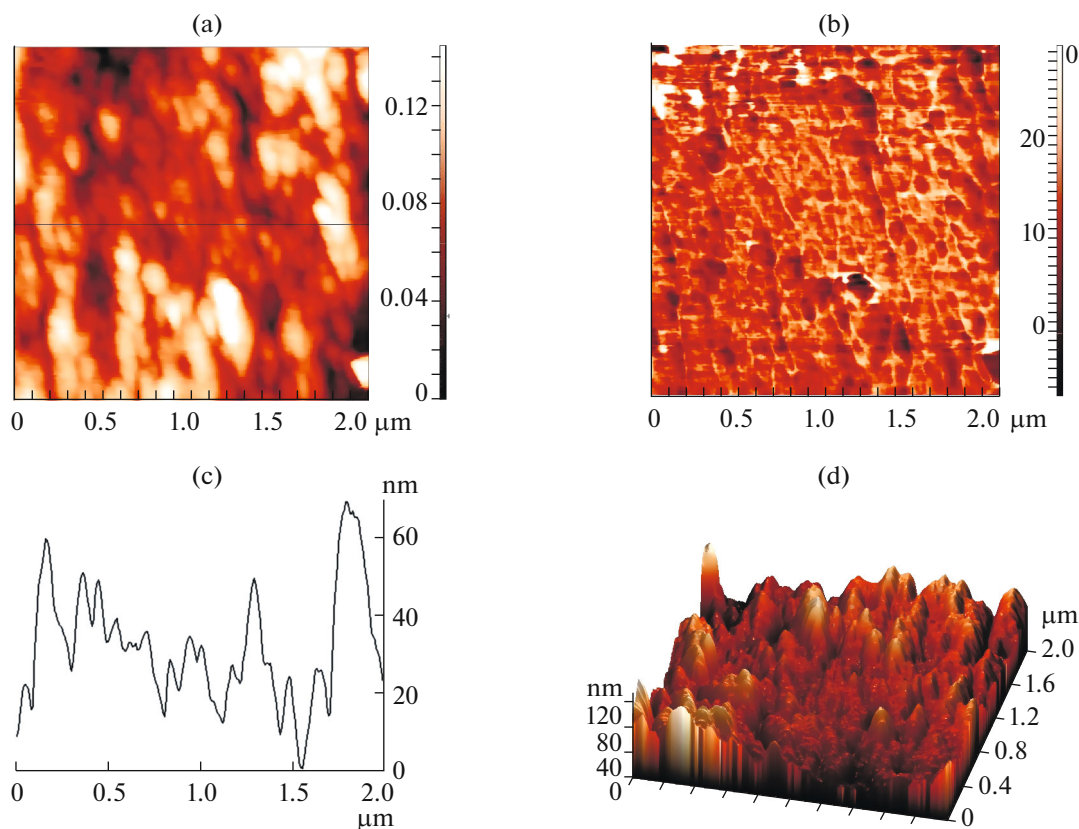


Fig. 4. AFM image of the film of copper-containing MCC sulfate (13.2% of copper, w/w). 2D image of the surface (a), phase contrast (b), cross-sectional surface profile along the line in a (c), and 3D image of the surface (d).

CONCLUSIONS

It has been shown that the ion exchange method can be used for the synthesis of copper-containing polymers based on microcrystalline cellulose sulfate. The composition and structure of the resulting Cu-MCS samples were studied. According to the chemical analysis, the copper content in the samples was 12.6–14.1%.

EPR spectroscopy showed that the Cu-MCS samples contained the pseudocrystalline structure of the copper-containing salt system.

According to the AFM data, the surface of the Cu-MCS film consists of sufficiently homogeneous particles of spherical or slightly extended form with a diameter of about 70 nm. The surface of the Cu-MCS film is sufficiently homogeneous in its phase composition and does not contain any impurities.

Water-soluble copper-containing polymers based on sulfates of microcrystalline cellulose can find application in the creation of new medicines.

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