Vol. 5, No. 4, 2011 Chemical Technology

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COPPER NANOPARTICAL COMPOSITES BASED ON CELLULOSE DERIVATIVES

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Received: August 19, 2010 / Revised: October 26, 2010 / Accepted: January 25, 2011

Abstract. Polymer hydroxyethylcellulose matrix modification was made by mechanochemical method using copper containing nanoparticles, obtained by electrochemical reduction from copper sulphate solutions in water- ethanol medium. Interactions of copper containing nanoparticles with hydroxyethylcellulose were studies. Antimicrobial effect of the nanocomposites obtained was found.

Keywords: cellulose, metal nanoparticles, electrolysis, nanocomposites, antimicrobial properties.

1. Introduction

Synthesis of nanocomposite materials and studies of their properties are the most dynamically developing directions of modern technologies [1-3]. Materials containing metal nanoparticles are extensively studied due to possible applications of their physicochemical properties unobserved for the corresponding bulk solids [4, 5].

Ultradispersed metal and metal oxide powders are often used for preparation of new polymer composites. This is because small size and high surface energy of the nanoparticles results in unique properties of immobilized materials such as magnetic, nonlinear optical, catalytic, *etc*. Use of copper containing powders for preparation of medical material biocidic to many kinds of bacteria is very promising [6, 7].

However, synthesis of metal nanoparticles is connected with certain difficulties due to thermodynamic instability of the particles. The copper containing powders were prepared by cathode reduction method from electrolyte solutions in water-organic solvents [8, 9]. It should be noted that a high degree of dispersivity of electrodeposited particles can be reached in the presence of surfactants at limiting current densities [10]. The limiting current density provides the uniform delivery of metal cations to all points on the cathodic surface to compensate their loss at their discharge. Organic solvents allow to exclude the interaction between the particles and to keep their optimum size characteristics and thermodynamic stability.

Methods of immobilization of nanoparticles in polymer matrix are classified as physical, physicochemical, and chemical [11]. The physical method consists in mixing of dispersed particles and dispersing polymer medium. The advantage of this method in comparison with others is the possibility of synthesis of the nanoparticles of a given size which are stable during long time. As stabilizers, water-soluble cellulose derivatives can be used. These polymers immobilized by metal nanoparticles are antimicrobial and can be applied for development of various medical materials [12].

The aim of this work is the synthesis of the ultrafine copper containing powders by cathode deposition, their immobilization into cellulose matrix, and the study of physicochemical and antimicrobial properties of the obtained nanocomposites.

2. Experimental

Synthesis of the ultrafine copper containing powders was carried out in glass electrochemical cell equipped with a steel cathode and two ruthenium-titanium oxide anodes (Fig. 1). Aqueous solution of copper sulphate with additions of ethyl alcohol was used as electrolyte.

A metal spongy deposit is formed on the cathode. After finishing of the process the spongy deposit was isolated from the cathode and was washed with distilled water up to constant electroconductivity of the mother solution. Then the deposit was dried at room temperature up to a constant mass. The obtained powder was brown.

To determine the working electrolyte concentration and the current density corresponding to the limiting mass

transfer mode, the first step was conducting the polarization measurements (Fig. 1). For a linear potential scanning (scanning rate 5 mV/s, $E = E_o + a\tau$) due to the slowly changing conditions, a mode close to the steady state measurements was maintained. A copper disk was used as the working electrode. A platinum electrode served as the counter electrode.

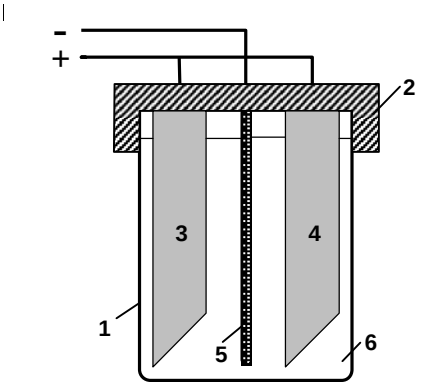

Fig. 1. Schematic representation of the experimental setup: electrochemical cell (1); vinyl lid (2); anodes (3, 4); cathode (5) and electrolyte solution (6)

Hydroxyethylcellulose ($\{C_6H_7O_2(OH)_{3-x}[(OCH_2CH_2)_yOH]_x\}_n$) (HEC, brand «Hercules» U.S. with a molecular mass of ~ 300000) was chosen as polymer matrix for immobilization of the copper nanoparticles. The nanocomposite films were obtained by mechanochemical dispersion of the copper containing particles in HEC matrix. The aqueous solution of HEC (3 wt %) was prepared and remained for swelling. Then, copper powder (0.035 wt % of the polymer mass) was added. The film was prepared on glass support and was dried up to complete solvent removal. The obtained film (thickness of about 70 micrometers) was transparent and had reddish tint.

The morphology of the powder and the polymer composite was determined by an EMV-100 transmission electron microscopy (TEM) with an accelerating voltage of 50–100 kV, resolution of 3 Å and magnification from 2000 to 50000. The prepared powder suspension in ethanol was sprayed on copper grids covered with carbon films using a supersonic dispenser nozzle.

IR spectra of the modified and unmodified polymer films were recorded by Avatar ESP-360 spectrometer in the range from 4000 to 600 cm^{-1}.

X-ray investigation was performed using a DRON-3M diffractometer using CuK_α radiation. The determination of the chemical composition was carried out by correlation of the parameters of the studied object's diffraction lines with reference data [13].

Antibacterial efficiency of the nanocomposites against colon bacillus and staphylococcus was checked by bacterial inoculation of "lawn" type in Petri dishes. 1.5–2 ml of the bacterial dredge containing 500 million microbial cells per ml was placed on the surface of beef-extract agar. Then above it the samples of the films under study were placed. The dredge was distributed evenly. Its excess was removed by a pipette. The dishes were kept in thermostat for 24 h. Inhibition of bacteria growth is the criterion of antibacterial efficacy.

3. Results and Discussion

Histogram showing the size distribution of the copper nanoparticles prepared from aqueous ethanol (0.1 mol·kg^{-1} $CuSO_4$, 0.04 mole fractions of the alcohol) is presented in Fig. 2. The histograms were obtained directly from the TEM images.

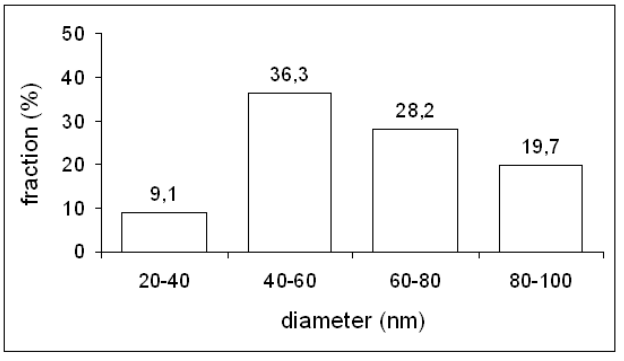

Fig. 2. Size distribution of copper particles in the powder

As can be seen from Fig. 2, ~ 93 % of the particles have the diameter from 20 to 100 nm and ~ 7 % are larger aggregates (100–500 nm). The obtained powder contains also unoxidized copper, Cu (I) and Cu (II) oxides.

Fig. 3 shows the TEM micrographs of the nanoparticles of the copper containing powder.

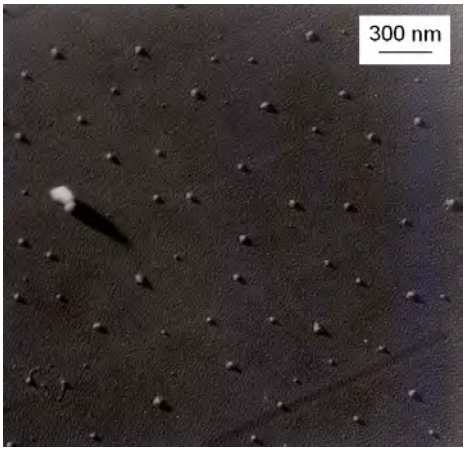

Fig. 3. The TEM micrographs of the nanoparticles of the copper containing powder

Histogram of size distribution of the copper particles in HEC matrix is presented in Fig. 4. As can be seen, the particles of the nanocomposite have sizes in the range of 20–100 nm. The amount of the larger aggregates (100–500 nm) is not greater than 10 %.

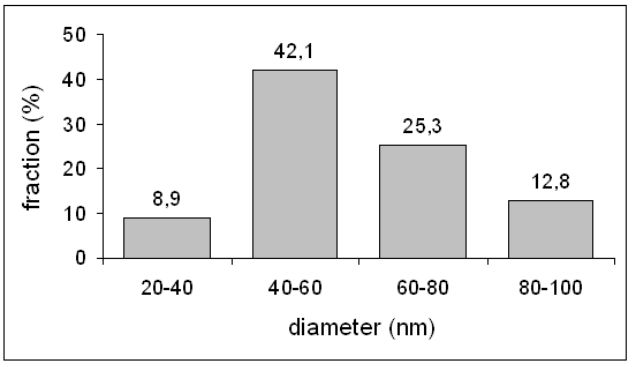

Fig. 4. Histogram of size distribution of the copper particles in HEC matrix

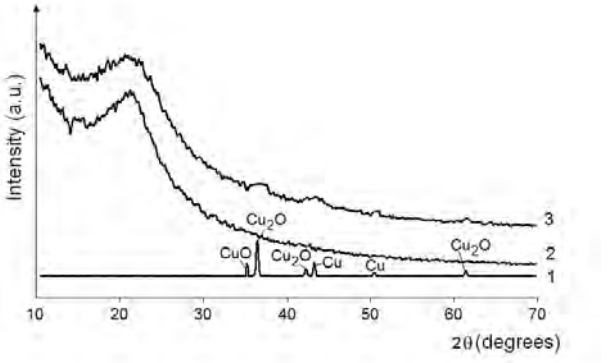

Fig. 5. The X-ray diffraction patterns of the nano-sized copper powder (1), the initial (2) and the modified (3) HEC films

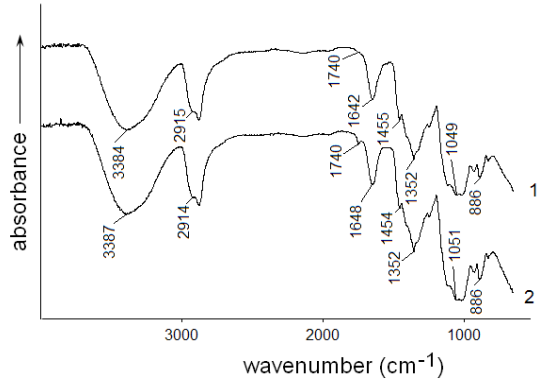

Fig. 6. IR spectra of the unmodified (1) and modified (2) HEC films

Thus, the size distribution of the copper particles in the copper containing powder and in the HEC nanocomposite is slightly different. It is likely that the observed increase of the particles fraction with the size of 40–60 nm and decrease of the particle fraction with the size of 80–100 nm in HEC matrix as compared with the copper powder is associated with intensive mixing at preparation of the nanocomposite.

X-ray diffraction can give information about the structure of the studied objects. The diffraction patterns of the nano-sized copper powder (1), the original (2), and the modified (3) HEC films are shown Fig. 5. The reflections of nano-sized powder on the diffraction pattern are observed. The most intense of them are ($2\theta^o$ = 35.73 (CuO); 36.63 (Cu_2O); 42.59 (Cu_2O); 43.90 (Cu); 50.35 (Cu); and 61 and 32 (Cu_2O). Thus, the nano-sized copper powder is multidimensional and includes unoxidized copper and copper oxides (I, II).

The diffraction pattern of the initial HEC film (2) contains only the amorphous halo. The center of its broad maximum is located at $2\theta \sim 22^o$. On the diffractogram of the modified HEC film (3) the narrowing main halo and new reflexes are observed. Their locations coincide with the reflections of nano-sized copper-containing powder. So it is likely that the introduction of nano-sized copper particles into the amorphous HEC film leads to changes in its structure and formation of crystalline areas.

To obtain information about changes upon modification of HEC by the copper nanoparticles, IR spectra of the films obtained were recorded (Fig. 6).

In the IR spectrum of the unmodified HEC a broad band at 3600–3000 cm^{-1} is assigned to stretching vibrations of H-bonded OH groups. A band at 2900 cm^{-1} is assigned to stretching vibrations of CH_2 and CH groups of the polymer. O–H deformation vibrations at 1352 cm^{-1} are a part of a broad band at 1450–1200 cm^{-1}. An intensive maximum at 1046 cm^{-1} is assigned to stretching C–OH vibrations. A band at 1642 cm^{-1} is associated with crystallization water. A shoulder at 1745 cm^{-1} indicates a small amount of C=O groups in the polymer [14].

The IR spectra of the unmodified and modified films of HEC differ from each other. In the spectrum of the modified film the pronounced increase of intensity of the band at 1747 cm^{-1} is observed. The band at 1046 cm^{-1} exhibits a shift of 7 cm^{-1} to high-frequency region. It should be noted that the interpretation of these spectra is not an easy task because of superposition of some bands in different regions of the spectrum. In this work an attempt of semi-quantitative analysis of the IR spectra using method of base line and internal standard [15] was undertaken. A band at 827 cm^{-1} assigned to C–H vibrations was chosen as the internal standard. Ratios of transmission density of a series of the characteristic bands in the IR spectra of the films to the transmission density of the band at 827 cm^{-1} are listed in the Table. In the spectrum of the modified film the relative intensities of the bands at 3384, 1352, and 1046 cm^{-1} decrease significantly. It is well known that copper oxides are

efficient catalysts of oxidation of organic compounds. It is likely that the decrease of the relative intensities characterizing different modes of vibrations of O–H bond indicates the oxidation of hydroxyl groups of the polymer and formation of C=O groups. This is confirmed by the appearance of the weak $\nu_{C=O}$ band at 1745 cm^{-1}.

Table

Infrared data of the unmodified and modified HEC films

Vibration bands	Unmodified HEC			Modified HEC		
	ν, cm^{-1}	*D*	D/D_{827}	ν, cm^{-1}	*D*	D/D_{827}
ν_{O-H}	3384	0.24	4.00	3387	0.21	3.42
$\nu_{C=O}$	1745	shoulder	-	1747	0.015	0.25
δ_{O-H}	1352	0.32	5.33	1351	0.28	4.67
ν_{C-OH}	1046	0.52	8.67	1053	0.44	7.33
δ_{C-H}	827	0.06		827	0.06	

The results of the tests of antimicrobial efficiency of the obtained films against colon bacillus and staphylococcus showed absolute death of the bacteria under the modified film. It should be noted that dynamics of inactivation of the bacteria persists during a month.

The effect of the unmodified (a) and the modified (b) films on staphylococcus is presented in Fig. 7.

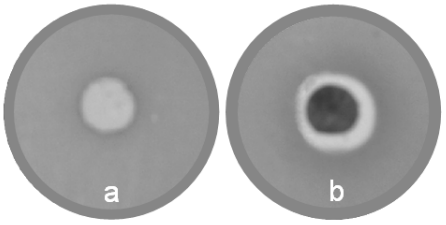

Fig. 7. The effect of the unmodified (a) and the modified (b) films on staphylococcus

It is likely that one of the reasons of bacteria death is interaction of the metal nanoparticles with functional groups of the amino acids composing bacterial proteins. This results in the cell membrane damage and destruction of the cell wall leading to their death.

4. Conclusions

Nano-sized copper containing powders were prepared by electrochemical cathode precipitation from solution of copper (II) sulphate in water-ethanol mixtures. The immobilization of the copper containing nanoparticles in hydroxyethyl cellulose matrix was realized. Size distribution of the copper containing nanoparticles in hydroxyethyl cellulose matrix as well as their interaction with the polymer was studied. It was found that the obtained nanocomposites exhibit antimicrobial activity against colon bacillus and staphylococcus.

Acknowledgements

This research was supported by Russia Foundation for Basic Research (grant N 10-03-00305-a).

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МІДНОВМІСНІ НАНОКОМПОЗИТИ НА ОСНОВІ ПОХІДНИХ ЦЕЛЮЛОЗИ

Анотація. *Проведено модифікацію полімерної гідроксиетилцелюлозної матриці за допомогою механіко-хімічного методу з використанням мідновмісних наночасток, одержаних електрохімічним відновленням розчинів сульфату міді у середовищі вода-етанол. Досліджено взаємодію мідновмісних наночасток з гідроксиетилцелюлозою. Встановлено антимікробну дію отриманих нанокомпозитів.*

Ключові слова: *целюлоза, металеві наночастини, електроліз, нанокомпозити, антимікробні властивості.*