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X-ray study of structural formation, thermomechanical and antimicrobial properties of copper-containing polymer nanocomposites obtained by the thermal reduction method

V. Demchenko[a,*], S. Riabov[a], N. Rybalchenko[b], L. Goncharenko[a], S. Kobylinskyi[a], V. Shtompel[a]

[a] Institute of Macromolecular Chemistry, The National Academy of Sciences of Ukraine, Ukraine
[b] Zabolotny Institute of Microbiology and Virology, The National Academy of Sciences of Ukraine, Ukraine

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ABSTRACT

Structural organization, morphology and thermomechanical properties of nanocomposites based on pectin, polyethyleneimine and Cu nanoparticles, formed by the thermal reduction method from interpolyelectrolyte–metal complexes (IMC) pectin–Cu^{2+}–polyethyleneimine have been investigated using WAXS (wide-angle X-ray scattering), SAXS (small-angle X-ray scattering) methods as well as TEM (transmission electron microscopy) and thermomechanical analysis. It is defined that thermal reduction of Cu^{2+} ions in IMC bulk (while films are heated to the temperature around 170 °C and higher temperatures) results in nanocomposites based on interpolyelectrolyte complexes "pectin–polyethyleneimine" and Cu nanoparticles being formed. In its turn, thermal reduction of copper ions is found out to take place owing to polyethyleneimine (namely, on account of electrons transfer from the amino groups' nitrogen atoms of polyethyleneimine to Cu^{2+} ions). It has been shown by thermomechanical analysis that the optimal time for complete thermal reduction of Cu^{2+} ions to metallic copper at $T = 170$ °C is 30 min. The antimicrobial investigations of the elaborated nanocomposites revealed they possess a high antimicrobial activity against *S. aureus* and *E. coli* strains.

1. Introduction

Interest to the investigations of polymeric composites, comprising nanoparticles of metals and metal oxides in their structure is rapidly growing within the recent years due to their unique physico-chemical, mechanical and biological properties [1–3]. Formation of metal-containing nanocomposites, involving macromolecular compounds is a current trend in the scientific searches because of their high-potential practical application.

Copper nanoparticles have interesting optical properties, high catalytic, antibacterial and fungicidal activities and this urges an interest for design and preparing a polymer-metal and hybrid composites, having controllable structure and particles of nano-size level [4].

In the last decade, researches dealing with elaboration of such hybrid materials, including synthesis of Cu-nanoparticles directly in polymers films [5–7], are intensively developed.

Nanohybrids based on synthetic and natural polyelectrolytes containing ultradispersed particles of noble metals, silver, and

* Corresponding author.
E-mail address: dvaleriyl@ukr.net (V. Demchenko).

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copper manifest antibacterial and fungicidal properties and show a promise as materials for medical applications [8–10].

The key problem to be solved, while synthesizing metal-containing nanocomposites, is in preparing of nanoparticles, having definite parameters, like size, distribution in bulk and morphology. Stabilization of nanoparticles in the polyelectrolyte complexes enables them to be protected from oxidation and aggregation processes [4]. At the present time, the widespread methods for nanocomposites' forming are as follows: chemical reduction and radiation-chemical reduction of metal ions in the interpolyelectrolyte–metal complexes [4,11].

The reduction of copper ions (Cu^{2+}) to copper nanoparticles (Cu) is conventionally achieved by chemical methods using reducing agents such as $NaBH_4$ [4], dimethylformamide [12], hydrazine [13], etc. Although such approach is simple and effective enough for getting nanocomposites with controlled structure and properties, however, the biological toxicity and the environmental hazard of the residual reducing agents are considered to be a problem.

The principal advantage of the radiation-chemical reduction of metal ions is that there is no need to introduce chemical reducing agents into reaction medium, thus allowing for nanoparticles to be obtained without admixtures [14]. But, this method requires application of special equipment for generating radiation.

Among the various techniques developed for the synthesis of copper-containing nanocomposites, thermal reduction is a novel method to produce polymer-metal nanocomposites. As compared to conventional methods, it is much faster, ecologically cleaner and economically reasonable.

So, the aim of this work is to study the structural organization, thermomechanical and antimicrobial properties of nanocomposites prepared involving natural and synthetic polymers – pectin, polyethyleneimine (PEI) and Cu nanoparticles, formed by the thermal reduction method.

2. Experimental

2.1. Materials

To obtain the interpolyelectrolyte complexes (IPEC), pectin–polyethyleneimine; the interpolyelectrolyte–metal complexes (IMC), pectin–Cu^{2+}–polyethyleneimine; and nanocomposites of IPEC–Cu the following reagents were used: anionic polyelectrolyte citrus pectin (Cargill Deutschland GmbH, Germany) with $M = 3 \times 10^4$, cationic polyelectrolyte anhydrous branched polyethyleneimine (PEI) (Aldrich) with $M_n = 1 \times 10^4$ and $M_w = 2.5 \times 10^4$ g/mol, copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) (Aldrich) with M = 249.69.

2.2. Preparation of polymer systems

IPEC samples were formed via mixing of 5% aqueous solutions of pectin and PEI taken at a molar ratio of 1:1, at $T = 20 \pm 2$ °C. IPEC as films were prepared via pouring their solutions onto polytetrafluoroethylene (PTFE) plates and then dried at $T = 20 \pm 2$ °C up to constant weight.

Dried (water insoluble) IPEC films were washed from unreacted components of oppositely charged polyelectrolytes in distilled water up to neutral pH and dried repeatedly at 20 ± 2 °C up to constant weight. The resulting films were 100 μm of thickness.

IMC samples were prepared via immersion of IPEC films into an aqueous solution of $CuSO_4$ with a concentration of 0.1 mol/L at $T = 20 \pm 2$ °C for 24 h. The colorless IPEC films became dark blue.

The absorption capacities of films, A (mmol/g), were calculated through the formula

$$A = (c_{init} - c_{eq})V/m,$$

where m is the weight of the absorbent, V is the volume of copper sulfate's solution, and c_{init} and c_{eq} are the initial and the equilibrium concentrations of copper ions. For IMC films $A = 2.9$ mmol/g.

Thermal reduction of Cu^{2+} ions in the IMC's volume was performed by heating of films up to 120–190 °C within 30 min, as well as at optimal temperature 170 °C within 5, 10, 20 and 30 min, respectively. Specimens were heated in the oven using precise thermal regulator VRT-3. Temperature regulation precision was ± 0.5 °C.

2.3. Experimental methods

The features of the structural formation of the IPEC (pectin–PEI); the IMC (pectin–Cu^{2+}–PEI); and nanocomposites of IPEC–Cu were studied by wide-angle X-ray diffraction on a DRON-4-07 diffractometer, whose X-ray optical scheme was used to "pass" primary-beam radiation through samples. The heterogeneous structuring of these polymeric systems (at the nanometer level) was studied via small-angle X-ray scattering with a CRM-1 camera, having a slit collimator of the primary irradiation beam made via the Kratky method. All X-ray diffraction studies were performed at $T = 20 \pm 2$ °C in CuK_α radiation monochromated with a Ni filter. The size of the Cu nanoparticles and their distribution in the polymer matrix were examined with a JEM-1230 transmission electron microscope (JEOL, Japan) at a resolution of 0.2 nm. Thermomechanical studies of polymer systems were conducted using the penetration method in the mode of a uniaxial constant load ($\sigma = 0.5$ MPa) on a UIP-70 M device. Linear heating of samples was performed at a rate of 2.5 °C/min in the temperature range −100 to +350 °C. The antimicrobial activity of IPEC–Cu (Cu/Cu_2O) nanocomposites, prepared by thermal and chemical reduction of Cu^{2+} ions in IMC was investigated using reference strains of opportunistic bacteria *Staphylococcus aureus* ATCC 6538 and *Escherichia coli* ATCC 35218 (as a model gram-positive and gram-negative bacteria) [15].