Structure and antimicrobial properties of nanocomposites based on anionic β -cyclodextrin, chitosan and silver nanoparticles

V. Demchenko¹, S. Riabov¹, S. Sinelnikov¹, O. Radchenko¹, N. Rybalchenko²

1. Department of Polymers modification, Institute of Macromolecular Chemistry, the National Academy of Sciences of Ukraine, UKRAINE, Kyiv, 48, Kharkivske shosse, E-mail: dvaleriy@ukr.net

2. Department of Antibiotics, Zabolotny Institute of Microbiology and Virology, the National Academy of Sciences of Ukraine, UKRAINE, Kyiv, 154, street Zabolotny, E-mail: nrybalchenko@ukr.net

Abstract – *Structural organization and antimicrobial properties of nanocomposites based on chitosan, anionic β -cyclodextrin (β -CD) and Ag nanoparticles, being formed by the chemical reduction method from interpolyelectrolyte–metal complexes (IMC) chitosan–Ag⁺–anionic β -CD have been investigated. It is defined that chemical reduction of Ag⁺ ions by NaBH₄ in the interpolyelectrolyte complex results to formation silver-containing nanocomposites. The antimicrobial investigation of the elaborated nanocomposites revealed they possess a high antimicrobial activity against S. aureus and E. coli strains.*

Keywords – interpolyelectrolyte complexes; interpolyelectrolyte–metal complexes; silver-containing nanocomposite; structure; antimicrobial activity.

Nanoparticles of metals, such as copper, silver, zinc are in the focus of the researchers involved into development of effective antimicrobial agents due to their biocidal activity and high stability in extremal conditions.

To obtain the interpolyelectrolyte complex (IPEC), chitosan–anionic β -CD; the interpolyelectrolyte–metal complex (IMC), chitosan–Ag⁺–anionic β -CD; and nanocomposites of IPEC–Ag the following reagents were used: cationic polyelectrolyte chitosan, anionic functionalized β -CD, silver (I) nitrate (AgNO₃).

IPEC samples were formed via mixing of 5% aqueous solutions of chitosan and anionic β -CD taken at a molar ratio of 1:1, at $T = 20 \pm 2$ °C. IPEC as films were prepared via pouring onto PTFE plates and drying up to constant masses at the same temperature. Dry IPEC films were washed in distilled water up to neutrality and dried repeatedly at 20 °C up to constant masses.

IMC samples were prepared via immersion of IPEC films into an aqueous solution of AgNO₃ with a concentration of 0.1 mol/L at $T = 20 \pm 2$ °C for 24 h. The colorless IPEC films became dark red.

The chemical reduction of Ag⁺ ions in the IMC's was conducted with NaBH₄ (a molar ratio of [BH₄[−]] : [Ag⁺] = 2.0) in an alkaline medium (pH 10.8) in a solvent mixture of water–isopropanol (4 : 1 vol %) at $T = 20 \pm 2$ °C for 3 h (until the release of gaseous bubbles ceased). The concentration of NaBH₄ in the aqueous alcohol solution was 0.1 mol/L.

As a result of the reduction IMC films changed color from red to metallic.

After the chemical reduction of the Ag⁺ ions in the IMC with the use of sodium borohydride (a molar ratio of [BH₄[−]] : [Ag⁺] = 2.0) nanocomposite based on the IPEC and Ag

were prepared. In the diffractogram IPEC–Ag nanocomposite (curve 2) two intense maxima at $2\theta_m = 38.2^\circ$ and 43.8° are fixed, corresponding to the crystallographic plan of the face-centered cubic lattice of silver with (111) and (200) indexes respectively, confirming presence of metal silver in the polymeric system.

Fig. 1. Wide-angle X-ray diffractograms of (1) the IPEC; (2) the IPEC–Ag nanocomposites obtained via the chemical reduction of Ag^+ ions in the IMC at molar ratios of $\text{BH}_4^- : \text{Ag}^+ = 2$.

IPEC–Ag nanocomposites which created by chemical reduction of Ag^+ ions in IMC are found out to demonstrate highest antimicrobial activity against *S. aureus* and *E. coli* strains. After incubation proceeds for 24 hours at 37°C one can observe a clear zone around the films' contours, thus confirming inhibition of bacteria growth. The growth inhibition's zone diameter for *E. coli* are 14.0 mm and 18.0 mm, correspondingly (table 1).

Table 1

Antimicrobial activity of the IPEC–Ag nanocomposites, prepared via the thermo and chemical reduction of Ag^+ ions in the IMC

The method of obtaining nanocomposite films	Diameter of inhibition zone, mm	
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>
chemical reduction	IPEC–Ag 18.0 ± 1.2	IPEC–Ag 14.0 ± 1.2
control sample	IPEC 0	IPEC 0

Active growth of the test bacteria and absence of growth inhibition have been observed in the test specimens (polymer film without nanoparticles).