UDC 546.5.7:614.7

Comparative Evaluation of Antimicrobial Properties of Sintepon with Various Silver-Containing Coatings

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Abstract

Chemical and electrochemical methods of the application of nanolayers of silver metal and its poorly soluble compounds (silver chloride and oxide) on the surface of polymeric fibers were considered. The morphology and phase composition of coatings were studied. A comparative evaluation of the antimicrobial activity of the obtained materials on various bacterial cultures was presented. It was shown that the antimicrobial activity of coatings significantly increased with the rise of their solubility. Due to the developed surface and a high porosity, synthetic fibres with such coatings are particularly promising for the application as antimicrobial filters in the purification systems and air conditioning, as well as the water treatment system.

Key words: synthetic fibres, silver-containing coatings, antimicrobial properties

INTRODUCTION

Antibacterial properties of silver have been known to mankind already long ago. Historically, silver was used both in the metallic and ionic form. The increasing resistance of bacteria to various antiseptics and antibiotics in recent years makes researchers and practitioners refer again to oligodynamic properties of silver [1].

Various forms of antimicrobial preparations based on silver are known: ionic liquid – diluted solutions of silver nitrate (protargol) [2], ionic solid form – silver ions that are sorbed on powders of natural and artificial sorbents, for example, of zirconium aluminosilicates or phosphates [3], as well as fabrics modified with silver metal [4]. All these preparations are used more or less successfully in various areas of medicine. However, protection from microbes, in particular, in the treatment of respiratory organs and infected wounds remains one of the pressing world issues [5]. To disadvantages of protargol, one should attribute its low efficiency associated with the use of only dilute solutions to avoid chemical burns, excess moistening wound and the absence of prolonged action. Pulverous preparations fall into the wound and their retrieval at dressings is time-consuming and painful. The materials modified with silver metal are more convenient. A considerable attention is paid to the development of such functional materials.

Several methods for the modification of polymeric fibres with silver are known at the present time. Most radical from them envisage the preparation of specialized fibres due to the introduction of silver nanoparticles into the polymer mass before the extrusion of fibres [6] or inclusion of silver in the fibre during its formation by the electrospinning method [7]. Silver particles in this case are encapsulated inside the fibre; therefore, on the transfer of silver to the surface of threads and their ionization under the action of moisture, an additional time for the manifestation of their antimicrobial activity is required. Another group of methods of the modification of fibres is based on applying thin metal coatings on the surface of fibers. This can be achieved when using various physical methods of spraying or chemical metals reduction [8]. Herewith, the uniform application of coatings on fibres of three-dimensional fabrics or nonwoven materials is possible only with the use of chemical reduction methods.

The goal of the present work was the preparation of coatings from silver and its sparingly soluble compounds on synthetic fibres and investigation of their antimicrobial activity.

EXPERIMENTAL

Samples of sintepon covered by nanolayers of silver metal, chloride and oxide were used as object of research. Sintepon metallised with silver was obtained by the way of chemical silvering sintepon reducing ammoniac or sulphite silver complexes by glucose. Samples of sintepon with coatings from poorly soluble silver compounds were obtained by the way of the chemical (AgCl) and electrochemical (AgCl and Ag_2O) modification of sintepon metallised by silver. Reagents of the Kh. Ch. (chemically pure) grade were used for the preparation of solutions.

The morphology of coatings was determined by micrographs obtained on a scanning electronic microscope Carl Zeiss EVO 50 XVP (Germany, Carl Zeiss AG) in the high resolution mode. The X-ray phase analysis of the resulting coatings was performed by the method of diffraction using a diffractometer DRON-3 (CuK_{α} radiation).

To determine the antimicrobial activity of materials, suspensions of bacterial test cultures were used (*Staphylococcus aureus* – gram-positive non-sporiferous bacteria; *Escherichia coli* – gram-negative non-sporiferous bacteria; Candida *albicans* –

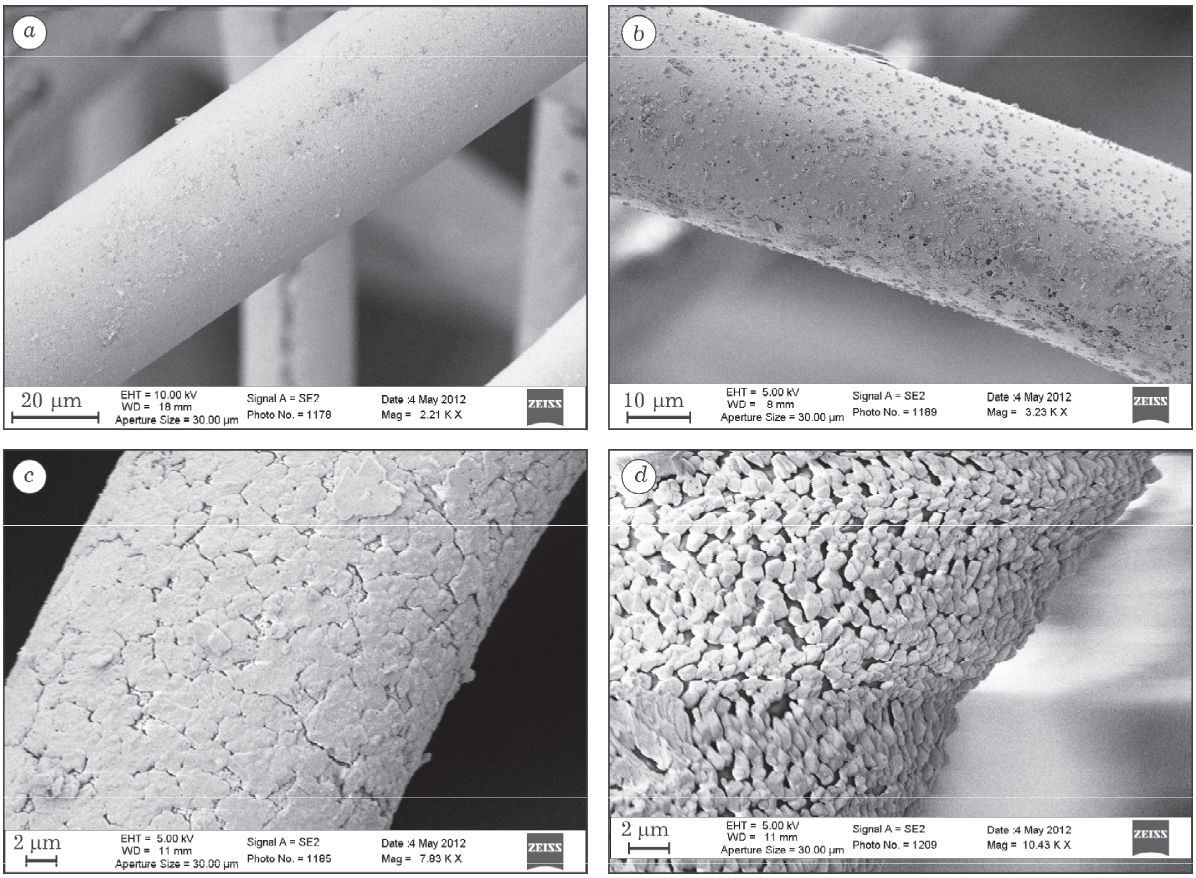

Fig. 1. Morphology of layers of AgCl obtained by the chemical treatment of sintepon previously metallised by silver in a solution of NaClO of various concentrations (mg/L): 0 (*a*), 4.6 (*b*), 9.38 (*c*), 62 (*d*).

yeast, the eukaryotic type of the cell structure) with the concentration of 10^3–10^4 CFU /mL.

RESULTS AND DISCUSSION

The method of chemical silvering of one of the most widely spread polyether non-woven synthetic materials – sintepon [9] was developed at the laboratory of electrochemistry of ISSCM, SB RAS (Novosibirsk). The average thickness of the coating, its integrity and electrical conductivity depend on the amount of applied silver and are regulated by the concentration of silver ions in the solution. For sintepon with the surface density of 100–120 g/m^2 at the consumption of silver of 10 g/m^2, the average coating thickness is 40–50 nm, conductivity – 3–5 Ohm/square. The morphology of silver coating of the sintepon thread is shown in Fig. 1, *a*.

Due to a high specific surface of the material and good contact with the air and liquid environments, as well sections of human skin, sintepon metalized by silver turned out to be promising for the treatment of infected wounds [10]. It can be used as antibacterial dressings, but given its high electrical conductivity, electrophoresis procedures turned out to more effective. As the anode, this material provides the generation of silver cations and allows relatively easy achieving the concentration of ions, necessary for the infection suppression. Trials conducted at the department of traumatology of Central Clinical Hospital, SB RAS (Novosibirsk) showed that these procedures ensured the dosed introduction of silver ions into the skin areas surrounding the wound and promote the acceleration of wound healing and reduce the need for antibiotics. A high antiviral activity of this material for the protection from the influenza virus type A at the use as the liner in medical masks was also established [11].

Silver ions are the active acting form of silver-containing preparations applied in medicine, therefore, the nanolayer transfer of silver metal on the surface of fibres of sintepon into its poorly soluble compounds (for example, into silver chloride or oxide) can significantly enhance the antimicrobial and antiviral activities of the material.

The chemical and electrochemical variants of such a transfer were proposed. At the chemical method of the preparation of the coating from AgCl, the reaction of the oxidation of silver metal by sodium hypochlorite was used. In order to prepare a homogeneous, uniform and dense coating, the effect of the concentration of a solution of sodium hypochlorite on the surface morphology and phase composition of the coating was studied. Micrographs of starting Ag-sintepon and after the treatment in solutions of sodium hypochlorite of various concentrations are shown in Fig. 1. It can be seen that the quantity, shape and size of AgCl aggregates on the sample surface are changed significantly. At a low concentration of NaClO, as was expected, coatings consisting of a mixture of silver metal and silver chloride are formed (see Fig. 1, *b*). The most uniform and dense coatings AgCl were obtained when treating Ag-sintepon in a stirred solution of NaClO with the concentration, equal or somewhat exceeding the stoichiometric amount

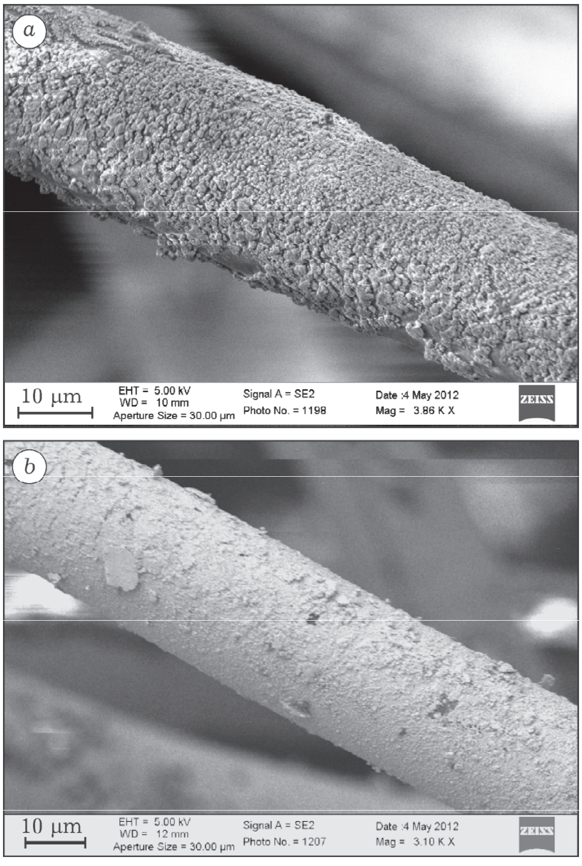

Fig. 2. Morphology of layers of AgCl (*a*) and Ag_2O (*b*) obtained by the anodic treatment of sintepon previously metallised by silver in a solution of NaCl and KOH, respectively.

of active chlorine that is required for a complete oxidation of silver on the surface of threads of sintepon. As an example, a micrograph of the coating (see Fig. 1, *c*) obtained at the treatment of Ag-sintepon in a solution of NaClO with the concentration of 9.4 mg/L, is presented, which corresponds to three-fold excess of the content of active chlorine. According to the XPA data, the coating mainly consists of AgCl and an insignificant amount of silver metal. From the data of Fig. 1, *d*, it follows that the increase of the concentration of NaClO leads to the coarsening of grains AgCl, the coating consists of AgCl.

The electrochemical method of the preparation of coatings from AgCl and Ag_2O consisted in the anodic treatment of sintepon metallised by silver in solutions of sodium chloride and hydroxide in the potentiostatic mode at the anode potential, on 50–300 mV more positive than the equilibrium potential of systems silver–silver chloride and silver–silver oxide, respectively. Micrographs of threads of sintepon with a coating from AgCl and Ag_2O are presented in Fig. 2. According to data of XPA, these coatings consist of a mixture of silver with silver chloride or silver with silver oxide. The study of the effect of the potential and

TABLE 1

Efficiency assessment of the antimicrobial action of sintepon samples with silver-containing coatings

Sample No.	Starting concentration of bacteria, CFU/mL	Concentration of bacteria after joint cultivating the preparation and test-strain, CFU/mL			
		One sample of the material of the size of 1 × 1 cm (25±2 mg)		Two samples of the material of the size of 1 × 1 cm (55±2 mg)	
		4 h	24 h	4 h	24 h
		Staphylococcus aureus			
1	$1.5 \cdot 10^4$	$1.5 \cdot 10^5$	$1.1 \cdot 10^9$	$8.2 \cdot 10^4$	$1.3 \cdot 10^9$
2	$1.5 \cdot 10^4$	0	0	0	0
3	$1.5 \cdot 10^4$	0	0	0	0
Control	$1.5 \cdot 10^4$	$1.3 \cdot 10^5$	$5.7 \cdot 10^8$	$1.3 \cdot 10^5$	$5.7 \cdot 10^8$
		Escherichia coli			
1	$4.5 \cdot 10^4$	$1.1 \cdot 10^4$	$2.8 \cdot 10^7$	$1.4 \cdot 10^3$	$3.0 \cdot 10^4$
2	$4.5 \cdot 10^4$	$2.5 \cdot 10^1$	0	0	0
3	$4.5 \cdot 10^4$	$1.3 \cdot 10^3$	0	$3.7 \cdot 10^2$	0
Control	$4.5 \cdot 10^4$	$6.0 \cdot 10^4$	$2.1 \cdot 10^9$	$6.0 \cdot 10^4$	$2.1 \cdot 10^9$
		Candida albicans			
		Microbial load $1.5 \cdot 10^2$ CFU/mL			
1	$1.5 \cdot 10^2$	$1.6 \cdot 10^3$	$1.0 \cdot 10^5$	$1.3 \cdot 10^3$	$4.7 \cdot 10^4$
2	$1.5 \cdot 10^2$	0	0	0	0
3	$1.5 \cdot 10^2$	0	0	0	0
Control	$1.5 \cdot 10^2$	$1.9 \cdot 10^3$	$1.7 \cdot 10^8$	$1.9 \cdot 10^3$	$1.7 \cdot 10^8$
		Candida albicans			
		Microbial load $4.2 \cdot 10^3$ CFU/mL			
1	$4.2 \cdot 10^3$	$4.7 \cdot 10^4$	$3.0 \cdot 10^5$	$2.8 \cdot 10^4$	$5.7 \cdot 10^5$
2	$4.2 \cdot 10^3$	$1.1 \cdot 10^2$	0	0	0
3	$4.2 \cdot 10^3$	$7 \cdot 10^1$	0	$2.5 \cdot 10^2$	0
Control	$4.2 \cdot 10^3$	$9.0 \cdot 10^4$	$3.4 \cdot 10^8$	$9.0 \cdot 10^4$	$3.4 \cdot 10^8$

Notes. 1. 0 indicates the absence in the sample of viable bacteria, *i. e.* bactericide action of preparations under the conditions of testing. 2. CFU – colony-forming unit. 3. CFU/mL – indicator of the number of viable microorganisms in the volume unit.

concentration of the solution on the morphology of coatings showed that the increase of the anode potential promoted milling grains of a poorly soluble compound, and the concentration change has no effect on the morphology.

Comparative trials of the antimicrobial activity of sintepon samples with various coatings were carried out at the testing laboratory of the NPTs "Vektor-Vita" Ltd.

Three samples of materials were tested: No. 1 – sintepon metallised with silver, No. 2 – sintepon with coating from silver oxide, No. 3 – sintepon with coating from silver chloride. The antimicrobial activity of the material was determined by the way of the calculation of the number of viable bacteria in colony-forming units (CFU/mL) at the cultivation of the test-strain on the liquid nutrient medium in the presence of various sample weights of the material under study (25 and 55 mg, which corresponds to 1 and 2 cm^2). As the control, a suspension of the test-strain without a silver-containing material (the control of the nutrient medium) was used. In order to evaluate the effect of the microbial load on the antimicrobial activity of the materials tested in case of the test-strain *Candida albicans*, the experiment was conducted at two values of the concentrations of microbes: $1.5 \cdot 10^2$ and $4.2 \cdot 10^3$ CFU/mL.

Comparative data on the antimicrobial activity of silver-containing materials are presented in Table 1. It can be seen that the studied samples differ markedly in their antimicrobial activity. Sintepon metallised with silver turned out to be the least active: none of the studied test-strains revealed its bactericide effect, only to this or that extent, a bacteriostatic effect on the cultures *Candida albicans* and *Escherichia coli* was found. Sintepon covered with silver oxide demonstrates the highest activity. This material exhibited the bactericide effect on all the three studied cultures. Sintepon with the coating from Ag_2O demonstrated a strong bacteriostatic effect in two cases only – on cultures *Escherichia coli* (at the sample weight of 25 mg and 4 h of cultivating) and *Candida albicans* (at the increased microbial load). Sintepon covered with silver chloride was inferior to sintepon with a coating from silver oxide on the activity but exceeded significantly sintepon metallised with silver. Additionally, it should be noted that test-strains differ on their sensitivity to the action of the silver-containing coating, and quantitative indicators of the antimicrobial activity depend on such parameters, as the duration of cultivation (contact), sample weight of the material and microbial load.

CONCLUSION

Thus, from the results of the tests carried out it follows that the antimicrobial activity of coatings increases with the rise of their solubility in the row $Ag \ll AgCl < Ag_2O$. This agrees well with the suggestion about the decisive role of silver ions. On the assumption of the obtained results, one can expect a high efficiency of the application of synthetic fibers with coatings from slightly soluble compounds of silver as antimicrobial filters in purification and air conditioning systems, as well as for water processing.

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