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Preparation of Poly(vinyl alcohol) Based Composites Filled with Biocompatible Nanoparticulate Silver Containing Fillers for Highly Efficient Bactericidal Materials

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Polymer composites based on poly(vinyl alcohol) filled with silver nanoparticles containing biocompatible fillers, such as silica and hydroxyapatite, have been prepared and tested for potential antimicrobial application. An effect of silver content on the properties of prepared polymer composites was evaluated. The results show that defined bactericidal activity of the elaborated materials was observed silver nanoparticles concentration of ~ 61 ppm.

Keywords: Silver nanoparticles, Polymer, Polymer composites, Films and coatings, Bactericidal activity.

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1. INTRODUCTION

Recent development of health care technologies initiates searching new materials with improved safety properties. One group of such materials is antimicrobial polymer composites with highly active antimicrobial agents -. There are many types of polymer have been used for preparation of such composites, like polyacrylics, vinyl polymers, polyurethanes, polyamides etc. However, for faster release an active components into environment the highly hydrophilic polymer matrices are more preferable.

In this work we elaborated poly(vinyl alcohol) based composites filled with biocompatible fillers, such as modified fumed silica and hydroxylapatite, which contain silver nanoparticles and tested for bactericidal activity. The structural characteristics and the properties of prepared polymer composites have been studied also.

2. EXPERIMENTAL

2.1 Materials

Poly(vinyl alcohol) (PVC Celvol 103, $M_a = 1{,}3\text{-}2{,}3 \times 10^4$), silver nitrate ($AgNO_3$), fumed silica ($SiO_2$, Aerosil™ A-300), γ-aminopropyltriethoxysilane (ATS) and other chemicals were uses as received.

2.2 Synthesis of Silver Nanoparticles Loaded Biocompatible Fillers

Polymer-stabilized silver nanoparticles (AgNP) have been prepared in aqueous solution according to previously described synthetic approach [1]. Hydroxyapatite $Ca_5(PO_4)_3(OH)$ (HAP) has been synthesized from $Ca(CH_3COO)_2{\cdot}xH_2O$ and H_3PO_4 by conventional solution deposition technique [2]. To improve an adsorption capacity of SiO_2 and as-prepared HAP a surface functionalization of the fillers via grafting of ATS layer [3] was carried out by partially modified approach in aqueous solution at a temperature of 70-80 °C. Quantitative analysis of NH_2 groups content shows the follow results: 4.3×10^{-4} and $1.8 = 10^{-4}$ mol/g for SiO_2 and HAP, respectively.

Deposition of AgNP onto a surface of the fillers was carried out by mixing aqueous dispersions of fillers and AgNP at ambient conditions for appropriate time. This approach is allowed to achieve a maximum value of AgNP load of 4.1 wt %.

2.3 Preparation of PVA Based Polymer Composites

For preparation of polymer composites the fillers with concentration of AgNP of 2 wt % have been prepared and used. Polymer composites were prepared by introducing silver-containing filler into 15 wt % aqueous solution of PVA followed by film casting of obtained compositions. Concentration of AgNP in composites films was varied from 61 to 180 and 760 ppm. Composition and AgNP content in the samples were identified in superscript indexes of the sample code. The samples PVA^{AgNP61}, $PVA^{HAP\text{-}AgNP61}$, $PVA^{SiO2\text{-}AgNP61}$, $PVA^{HAP\text{-}AgNP180}$, $PVA^{SiO2\text{-}AgNP180}$, $PVA^{AgNP760}$ were prepared.

2.4 Characterization

FTIR spectra have been recorded by Bruker Tensor® 37 spectrometer in the spectral range of 4000-400 cm^{-1}. Morphology of the samples was studied by scanning electron microscopy (SEM) via JEOL JSM 6060 LA equipment at accelerating voltage of 30 kV. TGA experiments were performed via TA Q-1500D instrument in the temperature range of 20-500 °C.

Samples for bactericidal testing were prepared by dip-coating technique on a glass slides (17 × 17 × 0.17 mm). Thickness of composite films was 0.05 ± 0.01 mm. Samples activity was evaluated by *Escherichia coli DH5a strain* (Invitrogen, USA) grown on LB-agar at 37 °C for 16 hrs. Comparative bactericidal efficiency of the composites was tested by measuring a zone of bacteria lysis.

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3. RESULTS AND DISCUSSION

Functionalization of fillers surfaces and their loading with AgNP were studied by FTIR spectroscopy. FTIR spectrum of HAP (Fig. 1) is characterized by complex broad stretching vibration bands of "free" and H-bonded OH groups in the range of 3500-3100 cm^{-1}, vPO_4^{3-} of phosphate ions with maxima at 1095, 1038, 959, 602 and 564 cm^{-1}. A presence of intensive bands at 1576 and 1425 cm^{-1} (v_{as} and v_sCOO^-, respectively) is related to excess of CH_3COO^- ions of calcium precursor adsorbed by HAP surface.

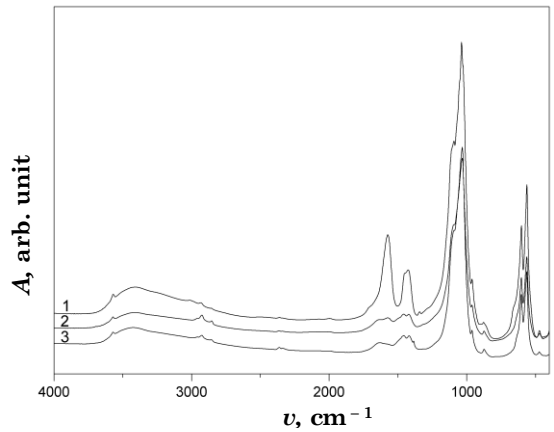

Fig. 1 – FTIR spectra of HAP (1), HAP-APS (2) and HAP-APS-AgNP (3)

Modification of HAP surface by APS decreases the intensities of νOH and increases the intensities of νCH bands in the range of 3000-2800 cm^{-1} due to their interaction of the filler with APS modifier. An appearance of $-NH_2$ groups on a filler surface is not clearly identified by FTIR analysis because of overlapping νNH and γNH with νOH and vPO_4^{3-} bands, correspondingly. Adsorption of AgNP has minor effect on spectral characteristics of HAP due to relatively low AgNP content.

In the FTIR spectrum of SiO_2 (Fig. 2) a broad νOH band of surface hydroxyls at 3700-3200 cm^{-1}, νOH of H_2O molecules with maximum at 1630 cm^{-1}, complex absorbance band of Si-O-Si groups in the range of 1300-950 cm^{-1} with maxima at ~ 1200 and ~ 1097 cm^{-1}, as well as stretching vibrations band of O-Si-O fragments at 810 cm^{-1} have been identified.

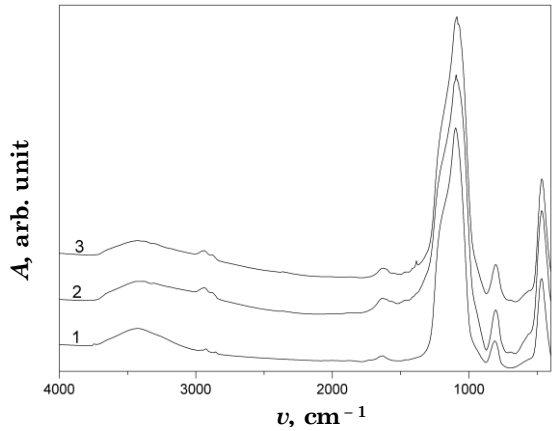

Fig. 2 – FTIR spectra of SiO_2 (1), SiO_2-APS (2) and SiO_2-APS-AgNP (3)

Functionalization of SiO_2 by APS leads to decreasing intensities of νOH band of hydroxyl groups on SiO_2 surface and appearance of νCH and weak γC-N bands at 3000-2800 and 1414 cm^{-1}. Due to relatively low level of AgNP adsorption on SiO_2 surface there are no changes in the FTIR spectrum of silver-containing filler was found also.

When the AgNP loaded filler was introduced into hydrophilic PVA matrix the morphology analysis of obtained composites was carried out by SEM. It was found that $PVA^{SiO2\text{-}AgNP180}$ sample (Fig. 3a) is characterized by uniform distribution of the nanosized filler (AgNP loaded SiO_2) in polymer matrix and absence of large aggregates (≥ 1 μm) of the particles. Otherwise, $PVA^{HAP\text{-}AgNP180}$ composite (Fig. 3a) have clearly heterogeneous structure due to filler peculiarities (HAP consist of the particles with a size of 1-8 μm).

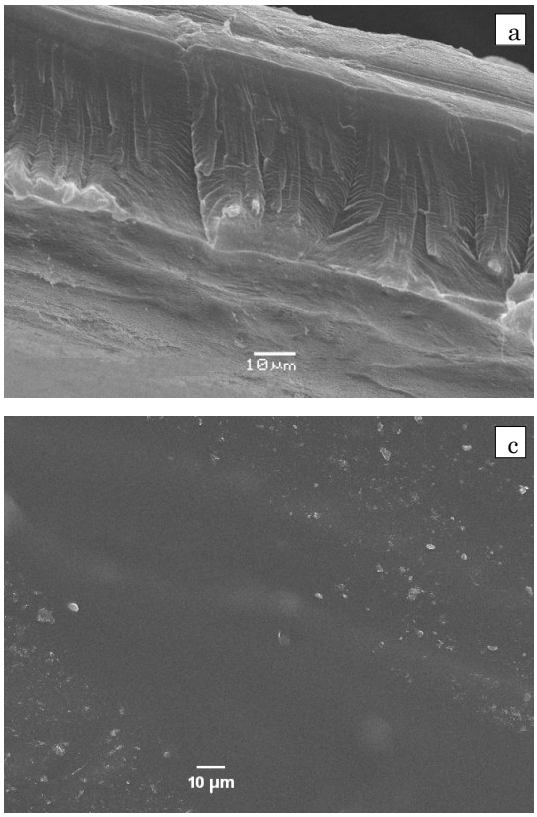

Fig. 3 – SEM photographs of $PVA^{SiO2\text{-}AgNP180}$ (a) and $PVA^{HAP\text{-}AgNP180}$ (b) composites

Comparative analysis of thermal properties of pure PVA and PVA in the presence of AgNP was performed using TGA technique. The temperatures of onset and maxima as well as weight loss at each stage of termooxidative destruction (T_{onset}, T_{max} and Δm, respectively) were found and analyzed.

Typical PVA is characterized by multistage degradation behavior: *1-st stage* at 70-160 °C (desorption of H_2O and beginning of dehydratation process); *2-nd stage* at 240-280 °C (dehydratation of PVA macrochain and formation of poly-ene structures); *3-rd stage* at 320-410 °C (Diels-Alder condensation of poly-ene fragments that leads to formation of aliphatic, cycloaliphatic and aromatic structures in the matrix); and *4-th stage* at 420-480 °C (formation of charcoal with high aromatics content).

Presence of AgNP in PVA changes the thermooxidative behavior of polymer matrix. It was found that narrowing the temperature intervals of basic stages of thermooxidative destruction and shift of T_{onset} to low temperatures by 10-40 °C, as well as an appearance of new degradation stages at 170-210 °C and 280-310 °C is probably due to catalytic effect of AgNP on termodestruction of PVA matrix (catalytic properties of AgNP on different chemical reactions are well known and applied in organic synthesis [4, 5]). Moreover, AgNP reduces a weight loss rate of PVA in some degradation stages probably due to inclusion some volatile products of PVA degradation in catalytic reactions with matrix macrochains.

The results of antimicrobial tests of prepared composites are presented in Table 1.

Table 1 – Antimicrobial properties of PVA based composites

No	Sample	AgNP content, ppm	Zone of bacteria lysis, mm
1	PVA	0	0
2	PVA^{AgNP61}	61	< 0.2
3	$PVA^{HAP\text{-}AgNP61}$	61	0.5-0.7
4	$PVA^{SiO2\text{-}AgNP61}$	61	0.5-1.0
5	$PVA^{HAP\text{-}AgNP180}$	180	2.0-2.5
6	$PVA^{SiO2\text{-}AgNP180}$	180	2.5-2.8
7	$PVA^{AgNP760}$	760	3.0-4.0

The pure PVA and PVA with 61 ppm of AgNP (PVA^{AgNP61}) have no bactericidal effect in selected test conditions. However, the HAP or SiO_2 filled composites with 61 ppm of AgNP content ($PVA^{HAP\text{-}AgNP61}$ and $PVA^{SiO2\text{-}AgNP61}$) are characterized by zone of bacteria lysis of 0.7-1.0 mm. A difference in bactericidal activity of unfilled and filler-containing composites with 61 ppm of AgNP content could be interpreted as filler-induced ionization of AgNP on a fillers' surface which possess improved diffusion of bactericidal agent (Ag^+) to the environment.

High antibacterial activity (zone of bacteria lysis reaches 2.8 mm) was found for PVA-based filled composite films with 180 ppm of AgNP content. A slightly lower bactericidal activity of $PVA^{HAP\text{-}AgNP180}$ compared to $PVA^{SiO2\text{-}AgNP180}$ sample is due to larger HAP particle size that not allowed to provide uniform diffusion of Ag^+ from a bulk and a surface of composite films to environment. A direct correlation between bactericidal activity of the composites and AgNP content was detected from experimental results.

Thus the proposed approach is allowed to produce efficient bactericidal polymer composites based on hydrophilic poly(vinyl alcohol). Using silver nanoparticles loaded biocompatible fillers, like hydroxyapatite and nanosilica, was found to be perspective to possess high bactericidal activity of obtained materials. Surface functionalization of fillers improves its adsorption capacity to nanoparticulate silver. Polymer composites, which contain AgNP loaded filler, have stronger bactericidal effect in comparison with AgNP containing PVA without filler at the same concentration of silver nanoparticles.

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