



Silver Nanoparticles Modification of Ultra High Molecular Weight Polyethylene in Non-Aqueous Medium

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ABSTRACT

A series of experiments for obtaining modified with silver nanoparticles ultra-high molecular weight polyethylene (UHMWPE) is done. Optimal precursors are silver trifluoroacetate, silver nitrate and silver methanesulfonate. Three variants of UHMWPE modification is studied: 1) the polyol synthesis, 2) polymer processing silver nanoparticle colloid and 3) reduction of silver salt solution in the UHMWPE polymer matrix. It is found that the last method is optimal. The specific surface of obtained nanoparticles is 7.1-7.6 m²/g and the size varies in the range of 60-110 nm. The antibacterial activity of the composite samples to *E. Coli* and *S. Aureus* is studied. Inhibition of bacterial growth occurs at the level 10⁴ cfu/ml and 10⁶ cfu/ml respectively.

Keywords: Silver nanoparticles, UHMWPE, Polyol synthesis, Reduction, Silver trifluoroacetate, Silver methanesulfonate, Silver laurate, Silver palmitate, Antibacterial activity.

INTRODUCTION

One of the objects of modern medicine is the creation and improvement of materials for joint implant production (coxas, knee joints, spinal bones, dentofacial joints) for improvement their tribological and antimicrobial properties. Nowadays due to a number of properties (low constant of friction, high wear resistance and high chemical resistance)¹

the ultra-high-molecular-weight polyethylene holds a leading position as a material for prosthetics. There is number of works in literature devoted to the modification of UHMWPE with the metal nanoparticles, where the great attention is paid to introduction the silver nanoparticles into the polymer because of their unique antibacterial properties to the modification gains and UHMWPE². The modified materials with silver nanoparticles have been already

successfully used for the filter production and they are allowed to harmless pathogens, contained in the water for creation the special fabrics, paints and varnishes, which have antiseptic properties³. At the moment, there is a number of works where the polymers modified with the silver nanoparticles are used to create a new generation of implants and prostheses⁴.

The improvement of the earlier known methods and the development of such methods of nanomaterials producing identified main requirements that they must correspond:

- To provide the obtain of controlled composition materials with reproducible properties;
- To provide the temporal stability of nanomaterials, primarily provide the surface protection against spontaneous oxidation and sintering in the manufacturing process;
- To have high production and economical efficiency;
- To provide the obtain of nanomaterials with a specific particle size or the obtain of grains which size distribution must be sufficiently narrow, if necessary.

In this work we proposed a method of modified UHMWPE with the silver nanoparticles, which corresponds these requirements. The number of silver salts of organic acids and silver nitrate is used as precursors.

Theoretical analysis

Up to date the developed methods of nanocomposites obtaining are very diverse. The most common among the chemical and physical methods are listed below.

- 1) Inorganic nanoparticles and polymer are synthesized separately and then the nanoparticles are dispersed in the polymer (in its solution or melt). These methods include the dispersion in polymers of coarse particles with the colloid mills, ultrasound, high-frequency or arc crushing⁵.
- 2) Inorganic particles and polymer are synthesized separately, and after that the polymer is grafted to the inorganic core. An example of such synthesis is the nanoparticles microencapsulation by various polymers when

applied surfactant on the particle, and then polymer grafts to the surfactant molecule⁶.

- 3) Inorganic nanoparticles which are obtained preliminary, serve as centers of heterophase polymerization of organic monomer⁷.
- 4) Inorganic nanoparticles are synthesized *in situ* in the polymer solution. By this strategy various chemicals belong, including photochemical and thermal methods of nanoparticles synthesis in polymers (recovery precursors, the decomposition of metal carbonyls in polymer matrices, etc.)⁸.
- 5) Synthesis of inorganic nanostructures is combined with the polymerization of the organic monomer (creation of organic-inorganic copolymers based on organometallic compounds that are compatible with organic monomers)⁹.

One of the main tasks in the developing polymer nanocomposites sphere is studying the nanoparticles formation processes *in situ* in a polymer matrix. There are various methods for nanoparticles forming in a polymer matrix, such as chemical synthesis methods in an organic solvent¹⁰, vacuum precipitating on the viscous polymeric materials¹¹, with a plasma polymerization with the metal spatter¹².

An important obtain aspect of the composite polymeric materials modified with nanoparticles, is the choice of introducing nanoparticles technology into the polymer structure. This also applies to the obtain of polymeric materials modified with silver nanoparticles. However, it is known that due to the strong hydrophobicity of UHMWPE the introduction of silver in its polymer matrix is complicated. Therefore, the preferred method of introducing silver to UHMWPE is dispersion in organic solvents.

To starting precursors for the impregnation of the polyethylene must correspond the certain requirements. First, they must have a solubility which is necessary to produce the desired concentration in the chosen solvent type, and a sufficiently high chemical stability under the chosen conditions.

As the precursors they selected: halogenated acetic acid salt (silver trifluoroacetate), sulfonic acid

(silver methanesulfonate) salts of fatty acids (laurate, palmitate, and silver), and also the most used for this purpose - the silver nitrate.

For the silver nanoparticles modification of UHMWPE there were selected following methods from the literature:

- 1) Polymer impregnating with colloidal solution of silver nanoparticles¹³;
- 2) Synthesis of silver nanoparticles in the polymer matrix:
 - a) with agent presence¹³;
 - b) polyol synthesis¹⁴⁻¹⁷.

An ascorbic acid was selected as the reducing agent, and its effectiveness has been confirmed in previous works^{18, 19}.

Experimental part

Reagents and solvents

They used powdered UHMWPE of Ticona company (GUR-4120) with the molecular mass of 5.0 million g/mol.; silver nitrate - 99.9%, trifluoroacetic acid - 99%, methanesulfonic acid - 99%, lauric acid - 99%, palmitic acid - 99%, ethylene glycol - 99%, ethanol - 95%, methanol - 99%, ascorbic acid - 99%, silver carbonate - 99% in these experiments.

Obtain of silver salts

Silver trifluoroacetate CF_3COOAg (1a)

To 5.0 g (18 mmol) of silver carbonate is added 60 ml of trifluoroacetic acid and is stirred for 30 minutes. The reaction mixture is boiled down to dryness and is received 7.0 g (72%) of a white crystalline solid. Calculated: C - 10,874. Found C - 10,861.

Table 1: Atomic emission spectroscopy and SEM data in the modification of UHMWPE with silver nanoparticles by polyol

Method	Silver salt	Silver content, %	Size distribution of nanoparticles of dispersion
1.1	1a	0.05	A significant amount of silver nanoparticles with the size of 60-110 nm was found.
1.2		0.07	
1.1	1c	0.04	There is an aggregation of silver.
1.2		0.07	

Table 2: Atomic emission spectroscopy and SEM data in the modification of UHMWPE with impregnation with colloidal solution of silver nanoparticles

Method	Silver salt	Solvent 2	Silver content, %	Nanoparticles size, nm
2.1	1a	ethylene glycol	0.22	65-100
2.2			0.35	60-100
2.1	1b		0.11	65-90
2.2			0.30	70-95
2.1	1c		0.19	70-110
2.2			0.33	70-110
2.1	1d	methanol	0.14	65-100
		ethanol	0.12	70-110
	1e	methanol	0.04	70-100
		ethanol	0.03	65-95

Silver methanesulphonate $\text{CH}_3\text{SO}_3\text{Ag}$ (1b)

5.0 g (18 mmol) of silver carbonate is dissolved in 30 ml of methanesulfonic acid. To this solution is added 50 ml of isopropanol, after which there is the precipitate. The reaction mixture is cooled to 0°C and the precipitate is filtered off, after which it is washed with 10 ml of isopropanol and winded. Obtained 5.91 g (80%) of silver methanesulfonate. Calculated: C - 5,917; H - 1.499; S - 15.798. Found: C - 5,978; H - 1.517; S - 15.826.

Silver laurate $\text{C}_{11}\text{H}_{23}\text{COOAg}$ (1c)

To 5.0 g (22.4 mmol) of the sodium salt solution of lauric acid in 300 ml of distilled water is added dropwise a solution of 3.8 g (22.4 mmol) of silver nitrate in 170 ml of distilled water. The reaction is stirred for two hours, white precipitate. The precipitate is filtered off, washed with 100 ml of water and dried in a desiccator. Obtained 4.14 g (60%) silver laurate. Calculated: C - 46,925; H - 7,548. Found: C - 46,931; N - 7.530.

Silver palmitate $\text{C}_{15}\text{H}_{31}\text{COOAg}$ (1e)

To 5.0 g (13.8 mmol) of the sodium salt suspension of palmitic acid in 300 ml of distilled water is added dropwise a solution of 2.34 g (13.8 mmol) silver nitrate in 170 ml of distilled water. The reaction is stirred for two hours, white precipitate. The precipitate is filtered off, washed with 100 ml of water and dried in a desiccator. Obtained 5.8 g (89%) of silver palmitate. Calculated: C - 52,850; H - 8,531. Found C - 52,939; H - 8,510.

The received silver salt was used to modify UHMWPE

The polyol synthesis**Method 1.1**

To 10 ml of ethylene glycol was added 0.5 g of UHMWPE, then it was heated to 115°C and stirred for one hour. After that was poured 20 micromole of the solution silver salt of **1a, c** in 10 mL of ethylene glycol and kept at this temperature for 1 hour. UHMWPE is filtered off, washed with 250 ml of distilled water and dried at 110°C.

Table 3: Atomic emission spectroscopy and SEM data in the formation of silver nanoparticles in a polymer matrix UHMWPE

Method	Silver salt	Solvent2	Silver content, %	Nanoparticles size, nm
3.1	1a	ethylene glycol	0.27	65-100
3.2			0.44	60-100
3.1	1b		0.15	65-90
3.2			0.35	70-95
3.1	1c		0.24	70-110
3.2			0.37	70-110
3.1	1d	methanol	0.26	65-100
		ethanol	0.22	70-110
	1e	methanol	0.07	70-100
		ethanol	0.06	65-95

Table 4: The effect of UHMWPE powder on the antibacterial activity

Samples	<i>S. aureus</i> , CFU/ml				<i>E. coli</i> , CFU/ml		
	10^2	10^4	10^6	10^7	10^4	10^6	10^7
Silver methanesulfonate	-	±	+	+	-	±	±
Silver trifluoroacetate	-	±	+	+	-	±	±
control	+	+	+	+	-	+	+

Method 1.2

To a solution of 20 micromole of silver salt **1a, c** in 10 mL of ethylene glycol was added 0.5 g of UHMWPE and heated to 115°C and sonicated with frequency 20000 Hz for 30 minutes. UHMWPE was filtered off, washed with 250 ml of distilled water and dried at 110°C.

Processing of polymer with colloid silver nanoparticles**Method 2.1**

To a solution of 20 micromole of silver salt **1a-e** in 20 ml of solvent **2** ($C = 10^{-3}$ M) solution with stirring, was poured 1.76 mg (10 micromole) of ascorbic acid in 10 milliliters of solvent **3** ($C = 10^{-3}$ M). Then was added 0.5 g of UHMWPE which is pre-impregnated with ethanol and is stirred for 2 hours. The suspension is filtered on a Shott filter, washed the precipitate with 500 ml of distilled water and dried at 110°C.

Method 2.2

To a solution of 40 micromoles of silver salt **1a-e** in 20 ml of solvent **2** ($C = 2 \cdot 10^{-3}$ M) was poured with stirring the solution 3.52 mg ($2 \cdot 10$ micromoles) of ascorbic acid in 10 milliliters of solvent **3** ($C = 10^{-3}$ M). Then was added 0.5 g of UHMWPE, which is pre-impregnated with ethanol and stirred for 2 hours. The suspension is filtered on a Shott filter, the precipitate is washed with 500 ml of distilled water and dried at 110°C.

Recovery of silver salt solution in the polymer matrix UHMWPE**Method 3.1**

To a solution of 20 micromole **1a-e** of silver salt in 20 ml of solvent **2** ($C = 10^{-3}$ M) was added 0.5 g of UHMWPE, which is pre-impregnated with ethanol. To the resulting suspension under stirring solution is poured 1.76 mg (10 micromole) of ascorbic acid in 10 milliliters of solvent **3** ($C = 10^{-3}$ M) and stirred for

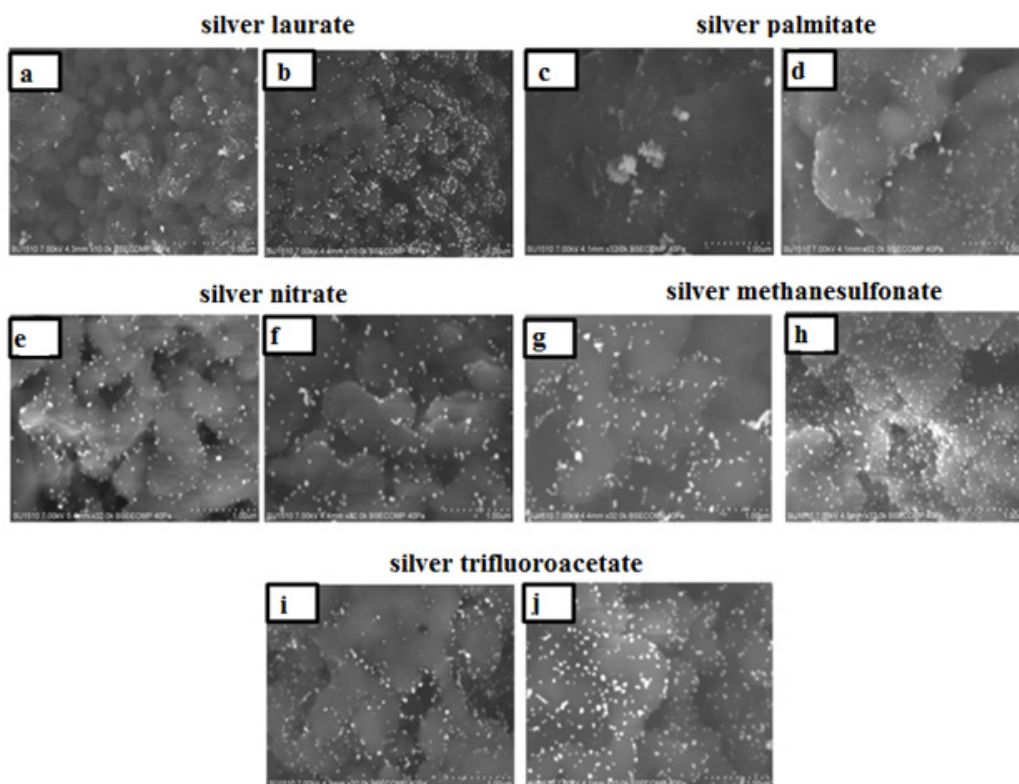


Fig. 1: The SEM image of UHMWPE powder, which is obtained by impregnating a dispersion in the reduction of silver laurate (a), silver palmitate (c), silver nitrate (e), silver methanesulfonate (g), silver trifluoroacetate (i); obtained by reduction with of silver laurate UHMWPE (b), silver palmitate (d), silver nitrate (f), silver methanesulfonate (h), silver trifluoroacetate (j)

2 hours. The suspension was filtered on a sintered glass filter, the precipitate was washed with 500 ml of distilled water and they dried at 110°C.

Method 3.2

To a solution of 40 micromoles 1a-e the silver salt in 20 ml of solvent 2 ($C = 2 \cdot 10^{-3}$ M) was added 0.5 g of UHMWPE, which is pre-impregnated with ethanol. To the resulting suspension was poured under stirring solution 3.52 mg (10 micromole) of ascorbic acid in 10 milliliters of solvent 3 ($C = 2 \cdot 10^{-3}$ M) and stirred for 2 hours. The suspension was filtered on a Shott filter, the precipitate was washed with 500 ml of distilled water and dried at 110°C.

Antimicrobial activity

Antimicrobial activity of the samples was determined towards to gram-positive bacteria *Staphylococcus aureus* and to gram-negative bacteria *Escherichia coli*. Test organism *E. coli* was cultured on meat-peptone broth, and *S. aureus* on meat-peptone broth with 6% NaCl. To assess the antibacterial activity of microbial of UHMWPE powder they seed the microorganisms cultures in the meat-peptone at a concentration from 10^2 to 10^7 CFU/ml, after that they add the test samples of composite powders, which activity qualitatively was assessed

by the presence or absence of meat-peptone broth turbidity due to bacteria propagation. The samples were incubated at 37°C during the day.

RESULTS AND DISCUSSIONS

There were considered three modification methods of UHMWPE with silver nanoparticles: 1) the polyol synthesis 2) Processing of polymer with colloid silver nanoparticles polymer processing silver nanoparticle colloid and 3) Recovery of silver salt solution in the polymer matrix UHMWPE.

The polyol synthesis

According to the first method the recovering of silver salt is getting with glycol aldehyde, which is forming under the influence of a high temperature from the glycol. According to the atomic-emission spectrometry with inductively coupled plasma the silver content of UHMWPE is not more than 0.07%, according to scanning electron microscopy (SEM) there is a significant amount of aggregated silver in polymer (data shown in Table 1).

The second method is that the UHMWPE powder which is previously wetted with ethanol, is impregnated with stirring for 2 hours by the

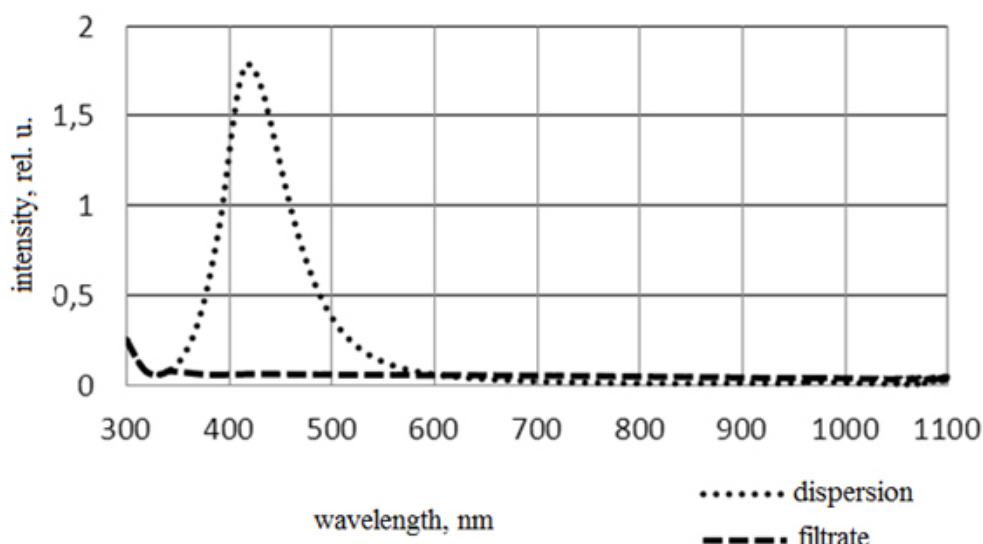


Fig. 2: The comparison of the absorption spectra of silver nanoparticle dispersion, which is obtained by recovery of silver methanesulfonate and filtrate after UHMWPE impregnation

silver colloidal solution, which is obtained previously^{18,19}. Then the powder is washed with distilled water and dried (see Table 2). Thus stable dispersion was obtained previously with the reduction of silver trifluoroacetate¹⁸ and silver methanesulphonate¹⁹.

According to the third method, to a solution of a silver salt in an organic solvent they add UHMWPE powder, which is impregnated with ethanol previously, and then they add a reducing agent (table 3). It should be noted that pre-impregnation of ultra-high molecular polymer powder with ethanol ensures quick absorption of solution in volume of the polymer matrix.

Figure 1 shows the received with the SEM method, the image of UHMWPE powder, which is modified with silver nanoparticles. With using trifluoroacetate, methanesulfonate, laurate, silver nitrate there was found a significant amount of silver nanoparticles with the size of 60-110 nm equally spaced in the UHMWPE matrix. In the samples obtained by treating of UHMWPE powder with a dispersion of nanosilver is observed nonequilibrium distribution of silver nanoparticles by using the fatty acid there is the presence of aggregating. With

recovering silver palmitate in both cases there is an aggregation of silver, the colloidal solution is poor, and therefore there is only a small amount of nanoparticles on the UHMWPE matrix.

The content of silver nanoparticles in the polymer ranges by using different salts, salt concentration, the reducing agent and the reaction conditions. According to the atomic-emission spectrometry with inductively coupled plasma, the best results is observed when they use as precursors the silver trifluoroacetate - in this case, the content of silver in the polymer is 0.22 - 0.44%; silver nitrate - 0.19 - 0.37%, silver methanesulfonate 0.11 - 0.35%. In view of the low solubility of silver salts of fatty acids it is impossible to increase the salt concentration in the organic solvent. Thus, when using silver laurate, silver content can not exceed 0.26%, silver palmitate - 0.07%.

The specific surface of nanoparticles according to the data obtained by the analyzer nanoparticle surface area is 7.1-7.6 m²/g.

To monitor the transfer completeness of passage nanosilver from the solution into the UHMWPE matrix there had been taken spectra of

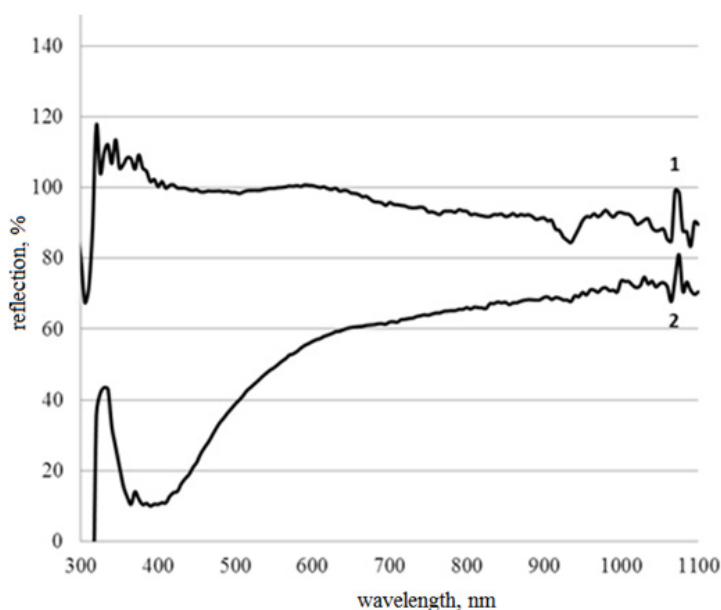


Fig. 3: Diffuse reflection spectrum of the UHMWPE (1) and spectrum of the UHMWPE modified by silver nanoparticles (2)

the filtrate absorption. Figure 2 shows that on the absorption spectrum of the filtrate there is no peak at a wavelength of 400-420 nm, which corresponds to the peak of the plasmon resonance of silver nanoparticles, it indicates about complete or almost complete absence of silver nanoparticles in the filtrate and their sorption on the polymer matrix.

Also, using an integrating sphere there were read spectra of the reflectance diffuse UHMWPE powders, modified with the silver nanoparticles (Fig. 3). When there is a comparison with the spectrum of the original powder UHMWPE there is minimum at a wavelength of 400 nm, which allows to judge about the presence of silver nanoparticles. Also it should be noted that this minimum corresponds to the peak of the plasmon resonance of silver nanoparticles in dispersion (Fig. 2).

Samples, which were obtained by reduction of silver trifluoroacetate and methanesulfonate were investigated for bactericidal activity. The results are shown in the Table 4.

Table 4 shows that UHMWPE powder containing silver nanoparticles in a varying degree have a antimicrobial activity. The full growth inhibition of *S. aureus* with the samples obtained by reduction of silver trifluoroacetate and methanesulfonate is

at an initial concentration of 10^2 CFU/ml but at the initial concentration of 104 CFU/ml there is a partial suppression of bacterial growth.

The growth of *E. coli* in the control is observed at an initial concentration of 10^6 CFU/ml. At the initial concentration the both samples completely inhibit bacterial growth, and at a concentration of 10^7 CFU/ml - in part.

CONCLUSION

There were considered approaches to modification of ultrahigh molecular weight polyethylene with silver nanoparticles. It was found, that for the best way of modification of UHMWPE with silver nanoparticles, the most suitable are precursors such as trifluoroacetate, methanesulfonate, nitrate and silver, and the recovery of silver salt solution should be carried out in the matrix of UHMWPE. The obtained samples have antibacterial activity towards to *E. Coli* and *S. Aureus*.

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