Polyvinylpyrrolidone Matrix as an Effective Reducing Agent and Stabilizer during Reception of Silver Nanoparticles in Composites

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Abstract – The use of polyvinylpyrrolidone matrix as an effective reducing agent and stabilizer during reception of silver nanoparticles in composites is substantiated. The influence of various factors on patterns of obtaining silver nanoparticles and their size.

Key words – polyvinylpyrrolidone, silver nitrate, reducing agent, stabilizer, nanoparticles.

I. Introduction

The polymer-mineral composites based on calcium-phosphate materials (which are similar to bone by their composition) and biocompatible polymeric matrix, namely on the basis of 2-hydroxyethylmethacrylate (HEMA) and glycidylmethacrylate (GMA) with polyvinylpyrrolidone (PVP) copolymers are perspective for use in osteoplastics [1]. However long or even lifelong being of the composites in the human or animal organisms is very often accompanied by inflammation or rejection and requires the constant introduction of preparations (including antibiotics) into the organism. The decision of this problem may be partially solved by using the composites with micro-, nano- or colloid silver particles as the materials with antibacterial and antiseptic properties. Therefore it is necessary to introduce argentums salts into the initial compositions. The salts interact with PVP polymeric matrix containing tertiary nitrogen and allow to obtain silver nanoparticles directly during composite formation without additional toxic reducing agents.

II. Result and Discussion

However long or even lifelong being of the composites in the human or animal organisms is very often accompanied by inflammation or rejection and requires the constant introduction of preparations (including antibiotics) into the organism. The decision of this problem may be partially solved by using the composites with micro-, nano- or colloid silver particles as the materials with antibacterial and antiseptic properties [2]. Therefore it is necessary to introduce argentums salts into the initial compositions. The salts interact with PVP polymeric matrix containing tertiary nitrogen and allow to obtain silver nanoparticles directly during composite formation without additional toxic reducing agents.

Copolymers were obtained *via* block-copolymerization under previously determined conditions [3]. The polymerization kinetics was studied by determination of non-reacted HEMA and GMA amount in the composition [4]. The average diameter of pores *(d_p)* and polydispersivity index (PDI) were determined by size measuring of at least 100 pores using MBS-9 microscope. The total porosity and composites density were determined using a Manehold method described in [5]. The mechanical properties were studied in accordance with general standards. The structure of the composites was studied using transmission electron microscope (TEM) JEOL JEM 200 CX.

Silver nanoparticles were received by argentum nitrate reduction reaction with tertiary nitrogen of PVP in water or water-alcohol mixture in the dark. PVP in this case plays also the role of an effective nanoparticles stabilizer.

The formation of silver by this reaction is confirmed with the presence of peak (420...430 nm) at UV spectra of products of interaction between $AgNO_3$ and PVP (Fig. 1) and with the results of the chemical analysis of reaction products.

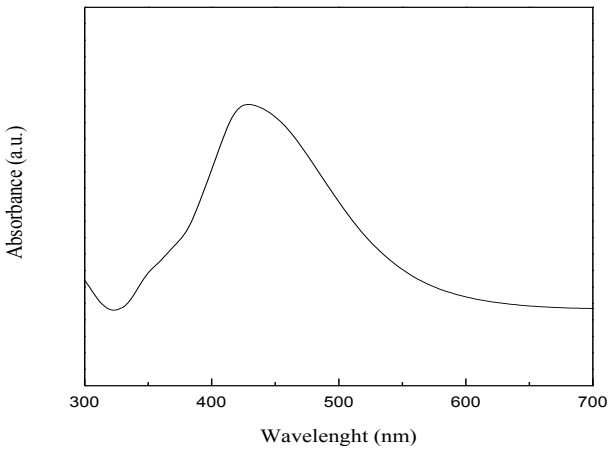
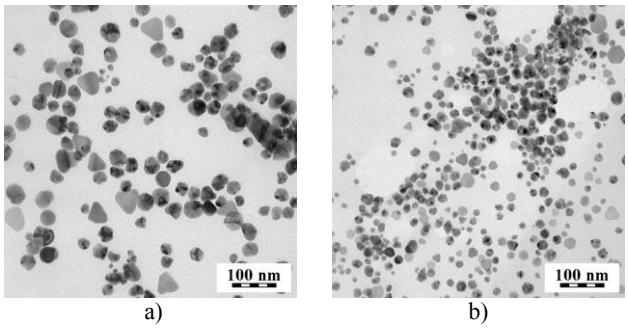


Fig. 1 UV spectra fragment of the solution of products of $AgNO_3$ interaction with PVP.

The results of electron microscopy studies have shown that Argentum nitrate forms silver nanoparticles in the shape of different size polyhedrons (Fig. 2). The degree of completeness of the reduction reaction, under conditions that are listed in the caption to Figure 2, is 85 % after 1 h.



a) b)

Fig. 2 TEM images of silver nanoparticles after centrifugation.
[$AgNO_3$]:[PVP] = 1:10 mass. parts, MW PVP = 10^4 g/mole, T = 348 K, reaction time 1 h. Solvent: a – water, b – aqueous ethanol (50%).

The size of nanoparticles depends on the nature of the reaction medium. In aqueous solution there are formed silver particles of 40...60 nm, whereas in mixtures of water with ethanol – 10...30 nm.

In the process of nanoparticles affects the nature of used silver salts. The results of electron microscopic studies show that argentum nitrate formed as spherical silver nanoparticles and as polyhedra of different sizes. During recovery arhentum acetate formed nanoparticles are mostly spherical. If argentum nitrate larger average size of nanoparticles (10...60 nm , the contents of the main fraction of 30 nm – 40 %), and the size distribution is much wider than in the case arhentum acetate under the same conditions (5...20 nm, core content of fraction 7 nm – 74%). With increasing temperature regardless of the nature of the salt particle diameter increases. With increasing content of PVP average diameter of argentum nanoparticles decreases, indicating that PVP but as an active reducing agent is also a stabilizer of nanoparticles formed. The size of nanoparticles also significantly affect the nature of the reaction medium. In aqueous solution when formed silver particles of 40...60 nm, in mixtures of water with ethanol – 10...30 mm. Thus, the selection of nature reagents and temperature conditions can be directed to resize silver nanoparticles.

Reaction of Argentum reduction by interaction of its salts with tertiary nitrogen of PVP was used to provide antibacterial properties of composites during the composite formation. Temperature conditions of composites synthesis were justified on the basis of kinetic studies of polymerization.

To impart antibacterial properties to the composites the silver nanoparticles are obtained during composite formation *via* the argentum nitrate reduction by tertiary nitrogen in the dark. The reaction completeness was estimated using the method described in [5]. During the synthesis composites with PVP and argentums salts change their color from weak-yellow to brown. It is also the indirect confirmation of silver nanoparticles formation while interaction between argentums nitrate and PVP tertiary nitrogen.

One of the main bioplastics requirements is the presence of through porous structure with controlled micro- and macropores sizes necessary for implant composite growth by bone tissue.

The value of porosity considerably depends on the components ratio. The proportional dependence of material porosity on PVP amount is observed (Table).

Porosity increases from 37 % for polyHEMA to 67…70 % for copolymer HEMA-PVP with PVP content of 30 mas %. This fact reveals that PVP positively affects not only the kinetics of composite curing but pores forming as well. The addition of crosslinking agent – ethylene glycol dimethacrylate (EGDMA) – does not change the general porosity but increases compression strength by 50 %. It means that such mixtures may be effectively used because the material substituting the bone tissue undergoes considerable mechanical load. Argentum salts do not affect the general porosity, though the polydispersivity index increases with the increase of their amount.

TABLE

EFFECT OF PVP AMOUNT AND CROSSLINKING AGENT EGDMA ON THE COMPOSITE PROPERTIES ([HA]=70 % MAS, CYCLOPENTANE (THE PORES FORMING AGENT) – 10 % MAS., [BP]=1 % MAS.)

Composition of the polymer-monomer mixture, mass parts			Porosity, %	d_p, mm	PDI
HEMA	PVP	EGDMA			
10	0	-	37.3	1.75	1.70
9	1	-	44.3	1.26	1.35
8	2	-	53.0	1.12	1.89
7	3	-	67.4	0.93	1.27
7	3	10	70.3	1.81	1.38
7*	3	-	66.4	1.58	1.32
7**	3	-	66.7	1.50	1.45

The composition contains additionally:

- – 1.2 mas % of $AgN0_3$; ** – 1.5 mas % of $AgNO_3$.

Conclusion

In this paper the silver nanoparticles research regularities obtain using povinilpirolidonu as an effective reducing agent and as stabiatora is given.

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