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POLYMERS MODIFIED BY SILVER NANOPARTICLES AS DISPERSANTS FOR HYDROXYAPATITE IN AQUEOUS SYSTEMS

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In this article a new class of polymer dispersants, which are very important for preparation of polymer–ceramic composites is presented. The polymer matrix contains silver nanoparticles, thereby received suspensions are characterized with high antibacterial activity and low toxicity to the human organism. Hydroxyapatite (HAp), which is a ceramic material with a chemical composition similar to the mineral component of bone, was added to the colloidal solution. Ceramic biomaterials are nowadays commonly used in the biomedical field, because of their high biocompatibility and bioactivity. In the preliminary researches the effect of dispersant type on particles stabilization were investigated. For complete characterization of received dispersions the following methods were applied: viscosity and sedimentation height measurements, pH determination, X-ray diffraction (XRD), UV - VIS and IR spectroscopy.

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1. Introduction

Polymer biomaterials are widely used in tissue reconstruction and bone regeneration. Such applications enclose poly(methyl methacrylate)-based bone cement, poly(glycolic acid)-based degradable sutures and poly(ethylene glycol)-based drug carriers, which extend the circulation half-life of some drugs. A new class of polymer dispersants, especially polyelectrolytes, are widely used in colloidal processing of ceramic powders, because they improve suspensions' properties. Particles appearing inside of colloidal solution can be stabilized through electrostatic interactions [1-3]. Presence of additional particles in polymer matrix, such as silver nanoparticles, cause that obtained suspensions exhibit specific and unique characteristics. In fact, the use of silver metal as a material to overcome infections is known from ancient times. Silver is well-known antibacterial agent and nowadays is commonly used in biological and medical applications [4-8].

The most important application of such suspensions is synthesis of composite materials based on hydroxyapatite (HAp). The chemical composition of hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is similar to mineral component of bone. Calcium phosphate-based bioceramics have been used in medicine and dentistry for nearly 20 years. Mainly they are applied in dental implants, periodontal treatment, alveolar ridge augmentation, orthopedics, maxillofacial surgery and otolaryngology. This extensive interest in medical field is a result of high biocompatibility and bioactivity of hydroxyapatite [9-13].

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This paper explores the influence of polymer additives on dispersion of HAp particles. The dispersants we have selected include poly(acrylic acid), poly(ethylene glycol) and sliver nanoparticle combined in various compositions to disperse HAp in aqueous systems.

2. Experimental procedures

2.1 Materials

In this study polymer matrix based on poly(acrylic acid) (PAA) modified with poly(ethylene glycol) (PEG) (15%) and nanosilver (Ag) (5% solution) was used [14]. The PAA/PEG/Ag matrix (SAP) was obtained under microwave irradiation [14]. Next, the colloidal solution was mixed with natural origin hydroxyapatite (HAp) (size 0.20 mm) made of pork bones [15].

2.2 Preparation

In the first research step a solution of polymer matrix containing 1 wt% of PAA/PEG/Ag composition was prepared by dissolving it in deionized water. Then this solution was poured to 100ml containers and mixed with 1, 2, 3, 4 and 5g of hydroxyapatite (HAp), respectively. Obtained suspensions were characterized with the use of X-ray diffraction (XRD), UV - VIS and IR spectroscopy. The viscosity measurement, sedimentation behavior and pH determination demonstrated that the addition of dispersants improved particle stabilization.

2.3 Dispersion stability system

The stability of dispersions was determined through pH measurements, which were carried out for 10 days period for all obtained suspensions including constant concentration of polymer solution (1wt.%) and different amounts of hydroxyapatite (HAp) (1–5g), respectively.

2.4 Viscosity measurement

The viscosity of obtained suspensions was measured at room temperature with the use of Anton Paar DV-2 P viscometer.

2.5 Sedimentation behavior

Particle stabilization in suspensions was studied by means of sedimentation experiments. The colloidal solutions were placed in test tubes and sedimentation behavior was observed after 1h and 24h.

2.6 XRD investigation

The phase composition of HAp was determined with the use of X-Ray method on Philips X'Pert diffractometer equipped with PW 1752/00 graphite monochromator.

2.7 FT-IR investigation

The FT-IR investigations were carried out with the use of BioRad FIS 165 spectrophotometer in the range of middle infrared at 400–4000 cm^{-1}. A 0.0007 g of sample was pressed with 0.2000 g of KBr. 16 scans and the resolution of 4 cm^{-1} characterized these measurements.

2.8 UV–visible absorption

All UV-visible extinction spectra were recorded at room temperature with the use of Marcel S330 spectrometer with quartz cuvettes (1 cm optical path) as the containers.

2.9 Dynamic light scattering measurements

Particle size distribution of silver nanoparticles was determined on DLS analyzer (Zetasizer Nano ZS Malvern particle sizing system) at temperature 25°C.

3. Results and discussion

3.1 UV–visible absorption

The optical properties of metal nanoparticles are highly dependent on the size and shape of the particles. This matter has been extensively explored experimentally on PAA/PEG dispersants including silver. The absorption of dispersants with Ag nanoparticles are presented in the Figure 1.

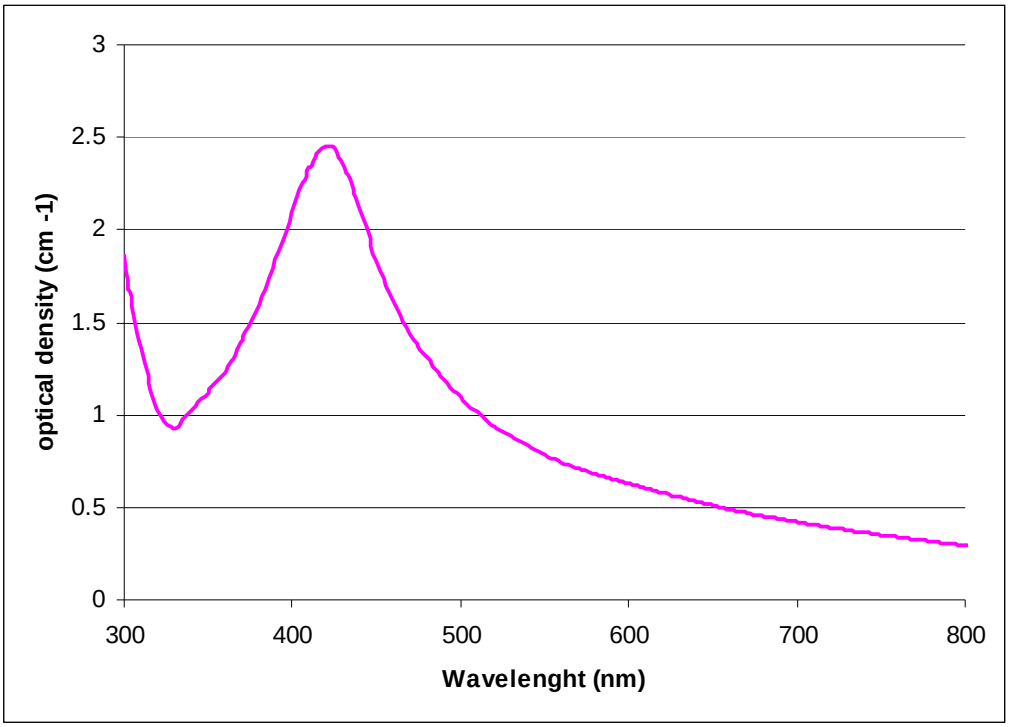

Fig. 1. UV-Vis absorption spectra of the PAA/PEG/Ag dispersion

The optical properties of silver nanoparticles depend on shape as shown in the Figure 2. The Figure 1 demonstrates a UV–Vis absorption band centered at 418 nm for PAA/PEG/Ag where the characteristic absorption of spherical silver nanoparticles is presented.

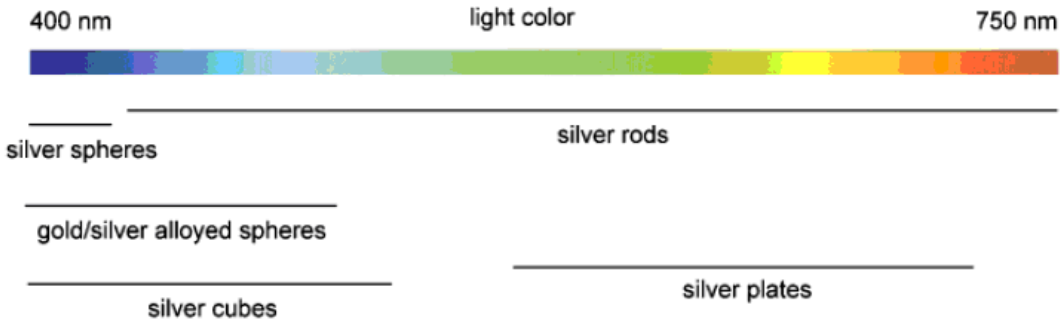

Fig 2. Silver nanoparticles having various morphologies, compositions, and structures, together with their typical locations of surface plasmon resonance (SPR) bands in the visible regime. Adopted from [16]

3.2 Dynamic light scattering measurements

Obtained dispersants contain metallic silver nanoparticles which size distribution can be determined by DLS measurement - Figure 3. It can be observed that nearly 97% of particles have an average diameter between 3 -10 nm. The silver nanoparticles in dispersants do not seem to form aggregates and remain stable, although it is known that nanosilver in a smaller size has higher surface energy, and thus the reactivity is higher.

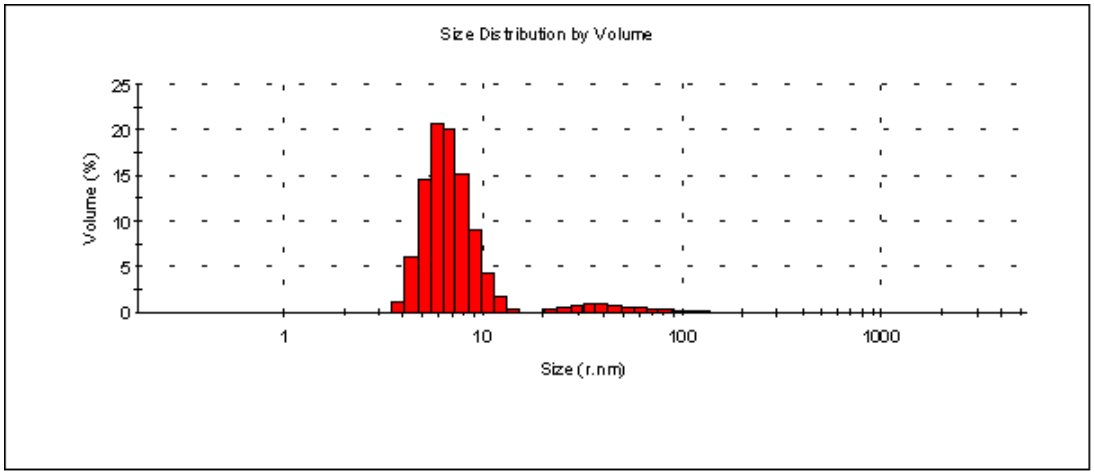

Fig. 3. Nanosilver size distribution histograms in dispersants

3.3 Dispersion stability system

The results of pH measurements are presented in the Figure 4. The concentration of polymer solution was constant (1wt%), but obtained suspensions contained different amounts of hydroxyapatite (HAp) (1 – 5g). The dispersion without hydroxyapatite (HAp) exhibits the lowest pH value (about 6). The suspension containing 5 g of hydroxyapatite (HAp) has the highest pH value (pH = 7.6 to 10). Figure 4 illustrates that progressive addition of hydroxyapatite (HAp) caused increase of pH values. This dependence results from strong basicity of HAp. The pH measurements carried out for 10 day period allowed to conclude that all obtained suspensions are very stable systems. It is possible due to the presence of carboxylic groups (-COOH) from PAA. The anionic polymer (PAA) is very effective in the alkaline pH range due to ionization of carboxylic group, which gradually increased from the acid range to pH 10.

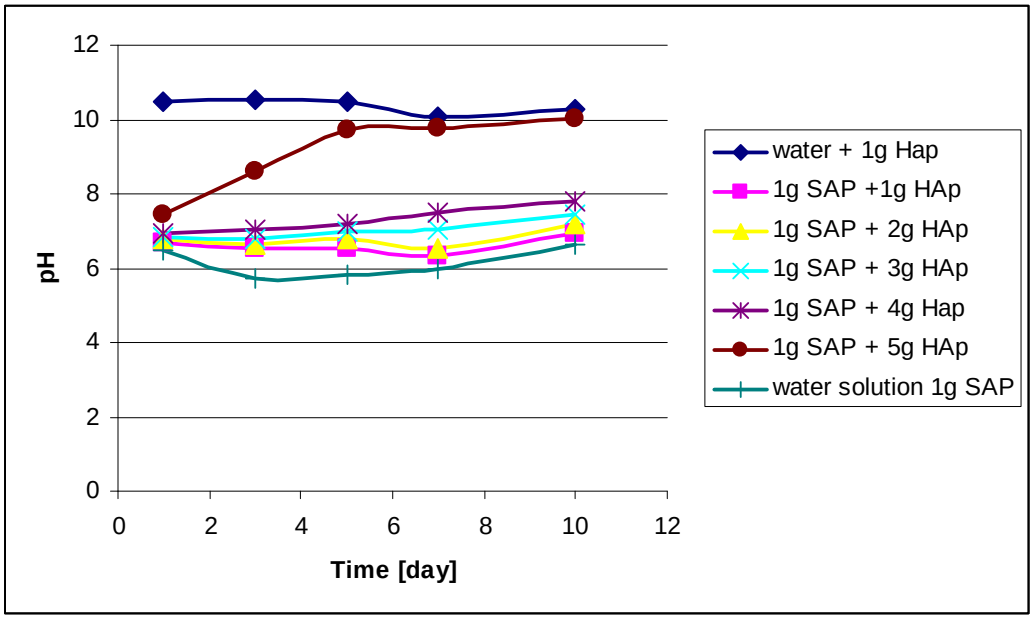

Fig. 4 The changes of dispersants pH during 10 days

3.4 Viscosity measurement

The change of viscosity is illustrated in the Figure 5. The viscosity decreased with increasing pH for all suspensions. This dependence was caused by the differences in dissociation

degree of carboxylic groups in each dispersant at various pH values. In this case the changes of viscosity are not so significant, because of the presence of silver nanoparticles what improves dispersion stability. The polymer matrix PAA/PEG/Ag (SAP) comprises short chains, that is why additional electrostatic interactions occur inside polymers.

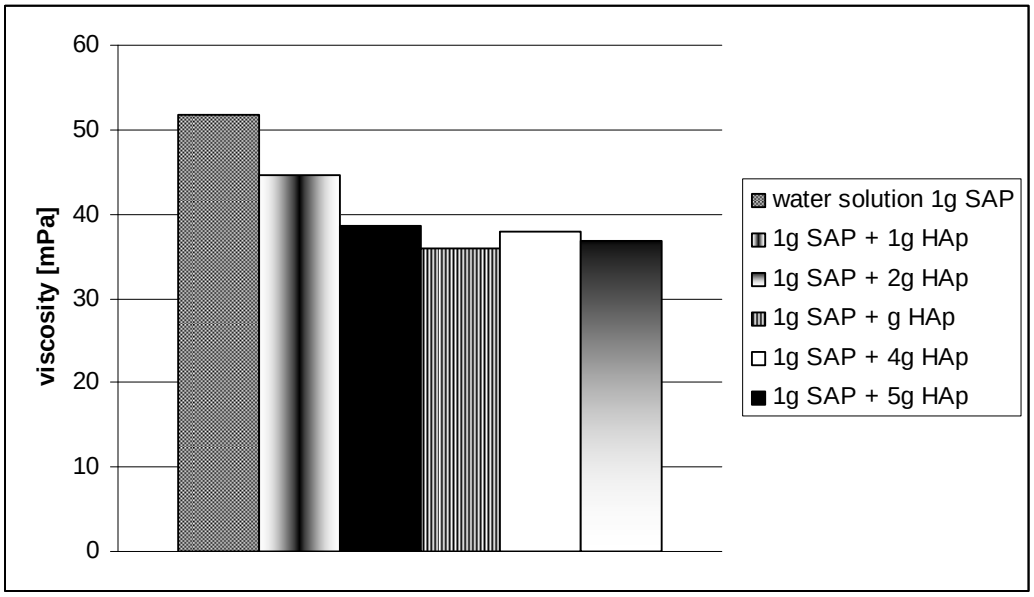

Fig. 5 The results of viscosity measurement

3.5 **Sedimentation behavior**

The sedimentation behavior was examined for all suspension containing different amounts of hydroxyapatite (HAp) (1 – 5g). First, initial suspension height (h_0) and sedimentation height (h) after 1h and 24h were measured. Sedimentation coefficient for each sample can be calculated from received results and is presented in the Figure 6:

$$S = h/h_0$$

Initially, the h/h_0 ratio is the same for all suspensions, what is characteristic for well-dispersed and highly stable suspensions. After 24h the change of sedimentation behavior was observed. The h/h_0 ratios increased with increasing amount of hydroxyapatite (HAp) and with increasing pH of suspensions. Therefore colloidal solutions are highly stable, what is very important for preparation of polymer–ceramic composites. Such high suspensions stability is possible because of dispersants abilities to de-aggregate hydroxyapatite (HAp) particles in PAA/PEG/Ag matrix.

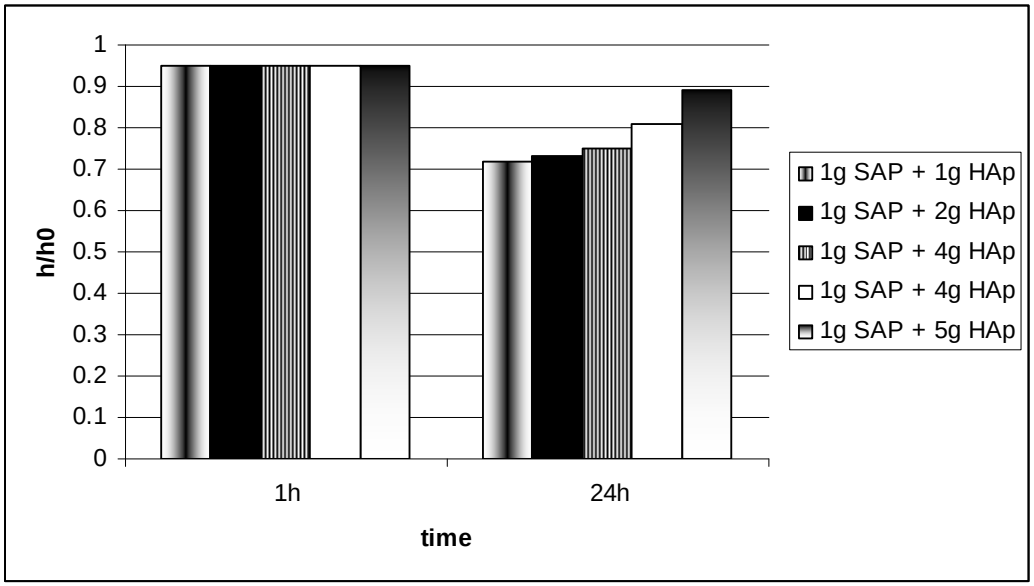

Fig. 6 The results of sedimentation behavior after 1h and 24h

3.6 XRD investigation

The X-ray analyses confirmed that hydroxyapatite was the only phase indicated in all samples immersed in polymer solution. Silver nanoparticles are not detected because of low concentration. It was found that in all samples no degradation of hydroxyapatite ceramic structure was observed. Figure 8 demonstrates the X-ray diagram of HAp particles immersed in PAA/PEG/Ag dispersions.

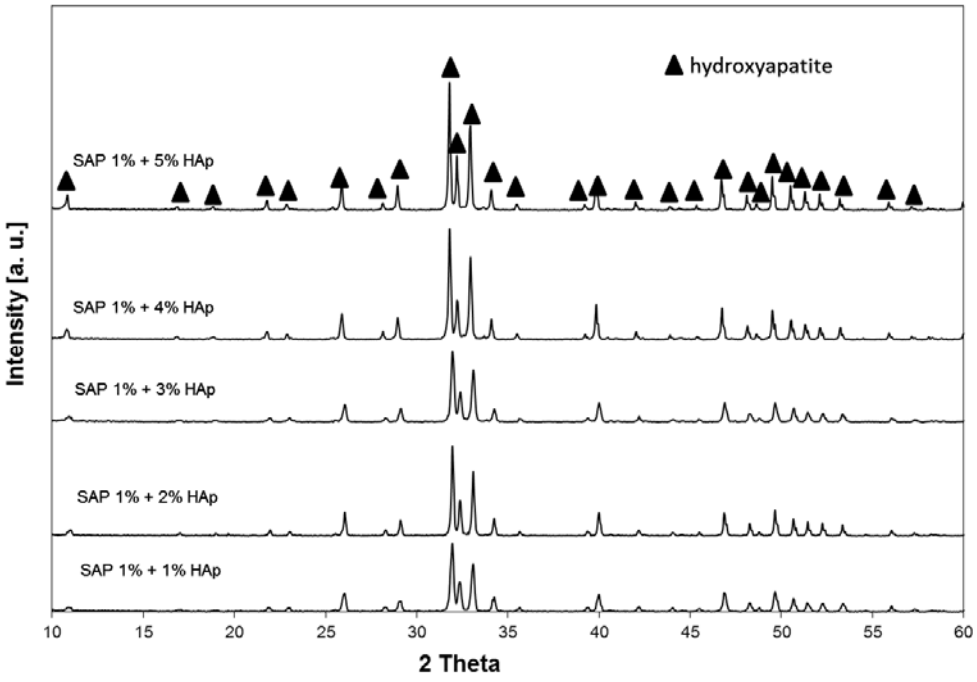

Fig. 7. The X-ray diagram of hydroxyapatite immersed in PAA/PEG/Ag dispersions

3.7 FT-IR analysis

Infrared analyses of confirmed that the polymer solution did not cause formation of other phases (Figure 8). The most intensive band at 1034 cm^{-1} corresponded to asymmetric stretch vibrations of P-O bond, whereas the maximum of absorption at 964 cm^{-1} from the symmetric vibration of P-O bond, can be observed. The vibrations of O-P-O bonds were assigned to absorption bands in the range of 604 – 563 cm^{-1}. The broad bands at wave numbers 1400 and 3300 cm^{-1} are corresponded to vibrations of organic compounds. The band at high wave number range (3427 cm^{-1}) resulted from the vibration of O-H bonds.

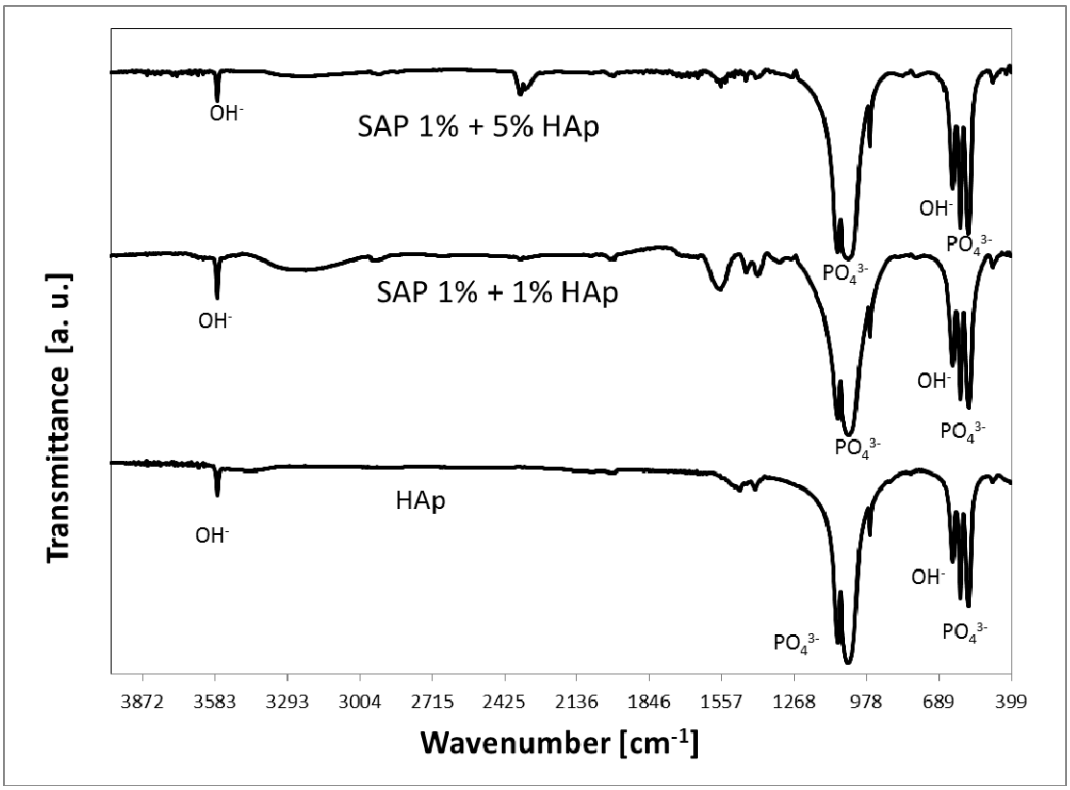

Fig. 8. Infrared spectra of hydroxyapatite immersed in PAA/PEG/Ag dispersions

4. Conclusion

In this research new suspensions containing hydroxyapatite (HAp) were prepared. The dispersion systems are characterized by high stability and homogeneity, what was confirmed by pH determination, viscosity measurements and sedimantation behavior. The high stability of PAA/PEG/Ag-HAp suspensions is a result of appropriate selection of dispersants, which minimize agglomeration between HAp particles. It is possible due to presence of anionic polymer containing carboxylic groups (-COOH), which are the source of additional electrostatic interactions. It turned out that addition of silver nanoparticles influenced significantly the dispersion stability and improved properties of obtained suspensions. The presence of silver nanoparticles in polymer matrix is very beneficial because of silver high antibacterial activity. Therefore, PAA/PEG/Ag dispersants are able to become interesting for biomedical applications.

The investigations were carried out with the use of natural origin hydroxyapatite (HAp), which is commonly used as ceramic biomaterial in biomedical fields, because of its osteoconductivity, biocompatibility and bioactivity. On the basis of our investigations it was confirmed that obtained PAA/PEG/Ag-HAp suspensions are charaterized by very interesting properties and can be used for biomedical applications.

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