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CHARACTERIZATION OF POLYMERIC SUSPENSIONS CONTAINING HYDROXYAPATITE PARTICLES FOR BIOMEDICAL APPLICATION

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In this article a method of dispersion system preparation where a polymeric matrix is used as a dispersant, is presented. Stability, homogeneity and rheological properties of such systems are improved by interactions with macromolecules. Therefore polymeric materials are more and more frequently used for production of ceramic dispersions. In this research natural origin hydroxyapatite (HAp), which is highly bioactive and osteoconductive, is used. For that reason biomaterials based on a HAp are widely used in medicine.

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1. Introduction

Polyelectrolytes are more often used in production of ceramic dispersions. The content of electrolyte in aqueous colloidal system highly affects its stability. The higher concentration of potential determining ions and lower ionic strength, the higher system stability. Moreover, dissociable groups in macromolecules increase the range of electrostatic repulsion forces due to formation of macromolecular adsorption layer. Dispersion systems stabilized by macromolecules are insensible to electrolyte addition, mainly because of weak dispersive attraction forces [1, 2].

Nowadays highly biocompatible and bioactive materials, as well as durable and resistant to body fluids, are explored. Among others ceramic biomaterials are well known as implants, materials stimulating osseous tissue regeneration, bone cements in surgery and dentistry. Such materials exhibit ample porosity enabling tissue to grow into, high compressive strength, great corrosion resistance and are highly bioinert [3-6].

Ceramic biomaterials based on a hydroxyapatite (HAp; $Ca_{10}(PO_4)_6(OH)_2$), which is a main component of bone and teeth, are commonly obtained. Such materials demonstrate supreme biological properties: bone jointing, osteoconductivity and biocompatibility [3, 7-10]. However, some disadvantages are also observed: fragility, low bending resistance and no dynamic load resistance. Therefore, new phases are incorporated into HAp structure to improve mechanical properties and form new composite materials. In the eighties of the 20th century the chemical method of materials' preparation from solution, described as gel casting method, was developed

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[7]. Selection of the appropriate dispersion of ceramic material is extremely important in the gel casting method, therefore our research is concentrated on this issue.

2. Experimental part

2.1. Materials

In this research a PAA/PEG polymer matrix synthesised by modification of poly(acrylic acid) (PAA) with poly(ethylene glycol) (PEG, 10% by weight) under microwave irradiation [12], was applied. A natural origin hydroxyapatite (HAp, particle size below 100 μm), obtained in 3-step process from pork bones [7, 13], was used.

2.2 Samples preparation

In the first research step a colloidal solution containing 0.3% SAP (polymeric superabsorbent = PAA/PEG) in 500 ml of distilled water, was prepared. Afterwards the solution was divided into five parts to 100 ml containers, where 1, 2, 3, 4, and 5% by weight of HAp was added, respectively. For a comparison a reference sample containing 100 ml of distilled water and 1% by weight of HAp was prepared. Received dispersions were studied in stability, rheological and sedimentation experiments.

2.3 Dispersion stability experiments

Dispersion stability was examined by solution pH determination during 10 days. The experiment was carried out for samples containing constant amount of SAP (0.3%) and different amount of HAp (1 - 5%), respectively.

2.4 Rheological experiments

Rheological experiments were carried out on the Anton Paar DV-2 P viscometer with R2 spindle. The viscosity of all colloidal solutions was examined.

2.5 Sedimentation experiments

Sedimentation experiments were carried out in 30ml containers. The results were observed after 1h and 24h.

2.6 XRD investigation

The phase composition was determined with the 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 a BioRad FIS 165 spectrophotometer in the range of middle infrared of 400-4000 cm^{-1}. A 0.0007 g sample was pressed with 0.2000 g of KBr. 16 scans and the resolution of 4 cm^{-1} characterized these measurements.

3. Results and discussion

3.1 Dispersion stability experiments

In the Figure 1 the solution pH determination for all dispersions containing constant amount of SAP (0.3%) and different amount of HAp, is presented. The solution pH changes during 10 days are shown.

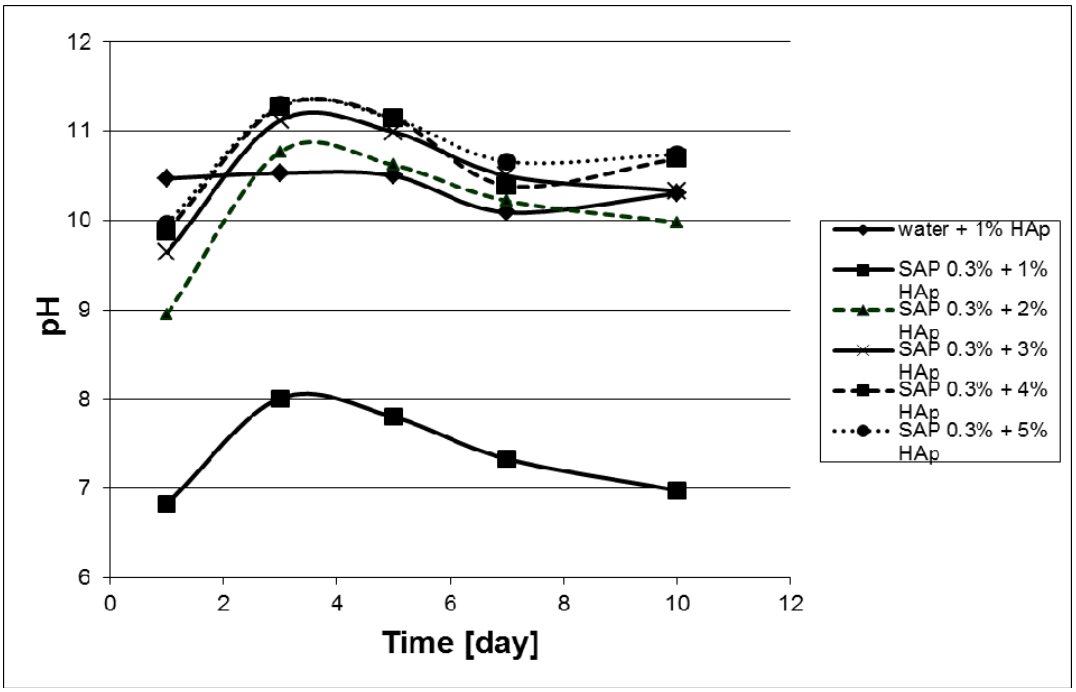

Fig. 1. The solution pH changes during 10 days

Results demonstrate that the increase of HAp amount in dispersion elevates solution pH, due to hydroxyapatite basic character. Figure 1 demonstrates that all obtained dispersions are stable to some extent, what is a great advantage. The solution pH ranged from 6.8 to 8.0 for dispersion with 1% of HAp, and from 9.0 to 11.3 for remaining samples.

3.2 Rheological experiments

Results from rheological experiments are presented in the Figure 2.

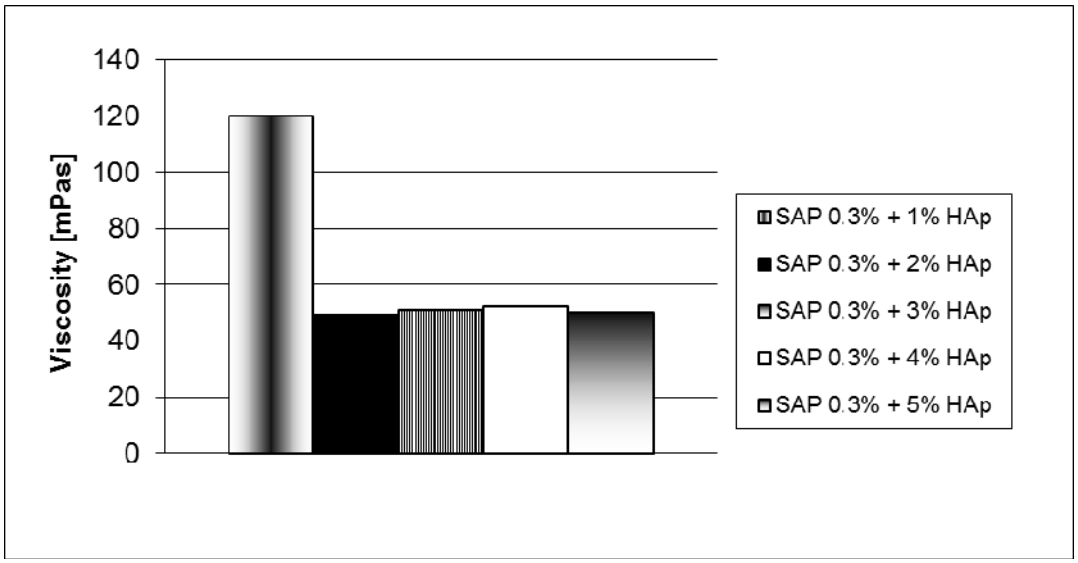

Fig. 2. Results of rheological experiments

The highest viscosity demonstrates the 0.3% SAP solution, without HAp addition. The pH of solution directly influences on the rheological properties of dispersion. Higher concentration of

carboxyl groups –COOH from poly(acrylic acid) reduces solution pH. Hydrophilic groups of polymer interact rather with water molecules than hydroxyapatite particles, what increases dispersion viscosity because of macromolecules swelling process. An addition of hydroxyapatite in amount of 1 – 5% by weight significantly reduces dispersion viscosity because of HAp basic character.

3.3 Sedimentation experiments

Sedimentation experiments demonstrate significant improvement of dispersion system stability after addition of polymer matrix, what is a result of electrostatic interactions between macromolecules and HAp particles.

In the Figure 4 a considerable difference between sedimentation coefficient of reference sample and obtained dispersions, can be observed. For the water with 1% of HAp after 1h the coefficient equals 0.128, while for the rest samples is close to one. There is no significant difference between samples in gravitational fall of particles after 1h, nevertheless after 24h such difference can be observed (Figure 3a and 3b).

Sedimentation coefficient for each sample can be calculated from received results and is presented in the Figure 4:

$$S = h/h_0$$

h – the height of a liquid column after time t (1h, 24h),
h_0 – the initial height of a liquid column.

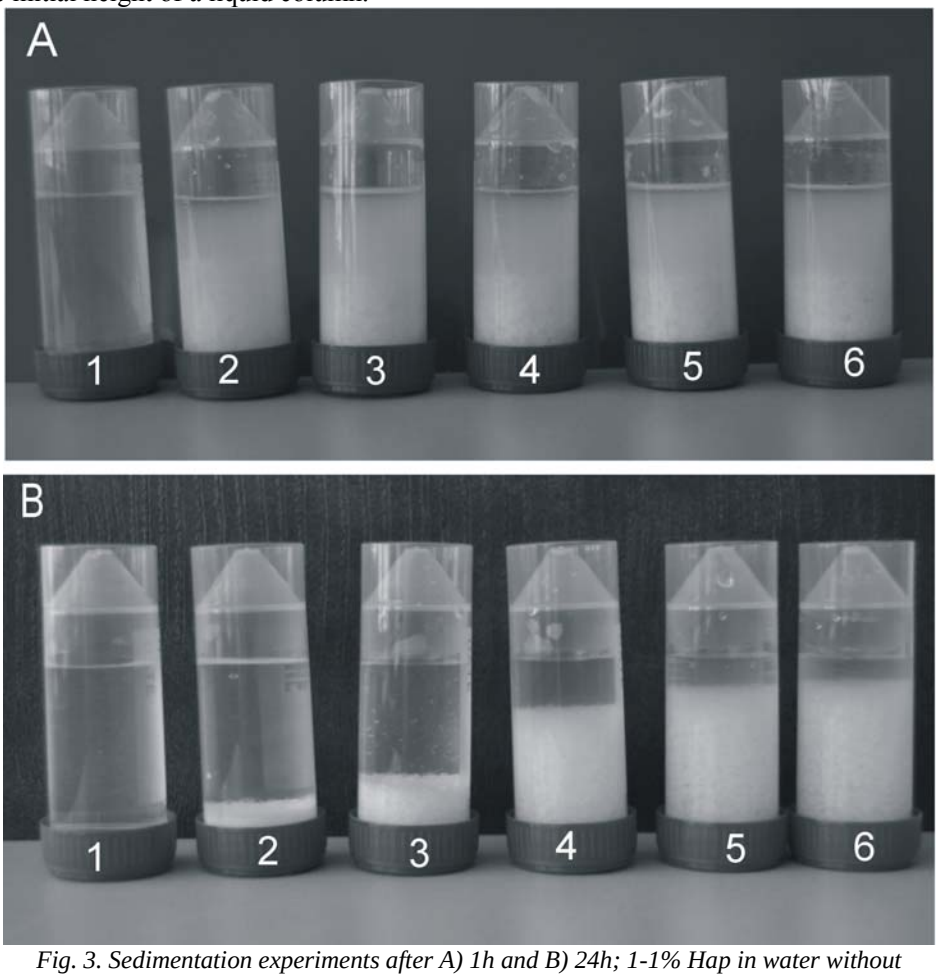

Fig. 3. Sedimentation experiments after A) 1h and B) 24h; 1-1% Hap in water without SAP, 2-SAP 0.3% + 1% HAp, 3- SAP 0.3% + 2% HAp,4- SAP 0.3% + 3% HAp, 5-SAP 0.3% + 4% 6-HAp, SAP 0.3% + 5% HAp

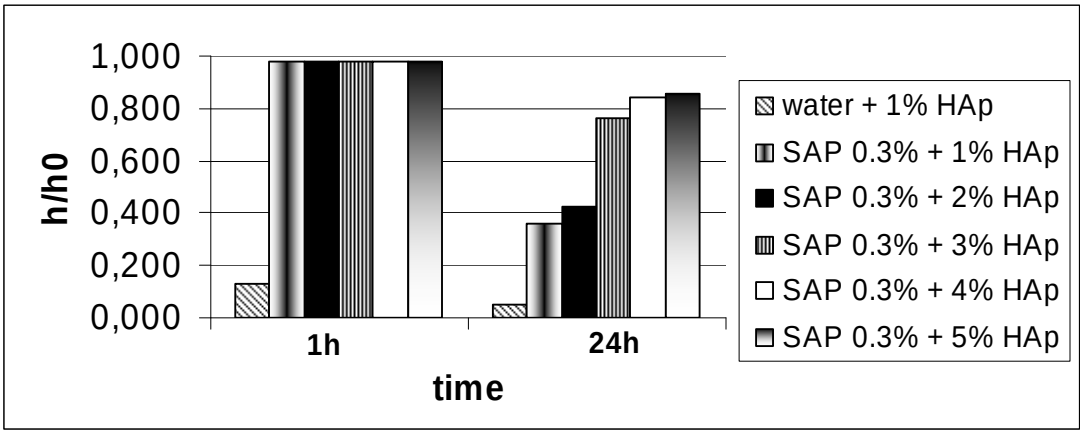

Fig. 4. The dependence of sedimentation coefficent (h/h_0) on HAp content (1 – 5%) in colloidal solution after 1 and 24h

3.4. FT-IR investigations

FT-IR spectrum (fig. 5) of the dried samples exhibited the characteristic absorption peaks of hydroxyapatite. It was noticed that for all spectra the absence of bands corresponding to the vibrations of C–H and C–C bonds of organic compounds was observed. The vibrations of O–P–O bonds corresponded to the absorption bands within the wave number ranging from 570 to 636 cm^{-1}. The most intensive bands in the range of 1047–1095 cm^{-1} corresponded to asymmetric stretching vibrations of P–O, whereas the maximum of absorption at the wave numbers of 964 cm^{-1} came from the symmetric vibration of P–O. The low-intensity bands at 1427 and 885 cm^{-1} observed for the material obtained in the preliminary calcination could correspond to the stretching vibrations of CO_3^{2-}. The band with high wave number range corresponded to the vibration of O–H bonds.

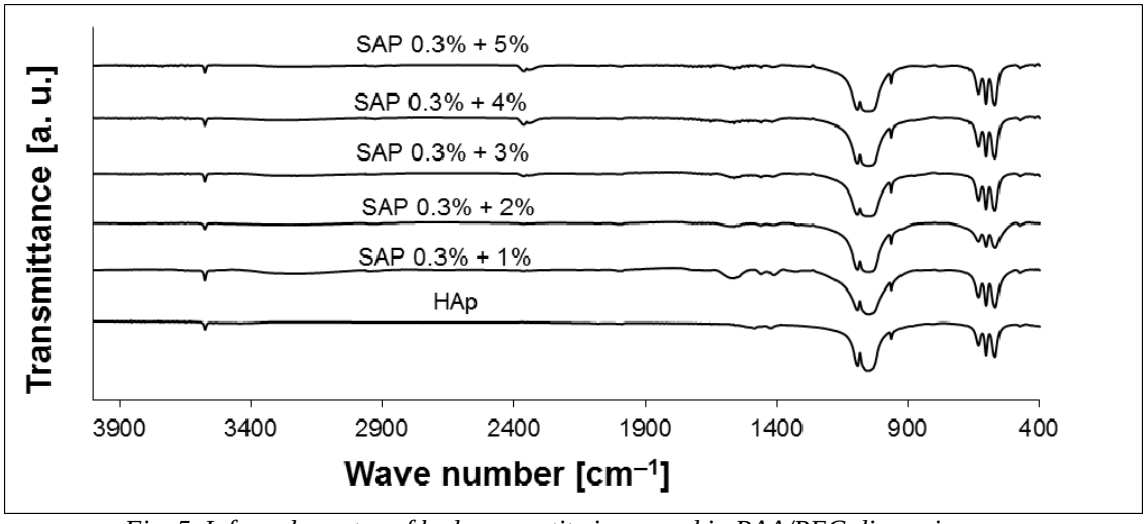

Fig. 5. Infrared spectra of hydroxyapatite immersed in PAA/PEG dispersions

3.5. XRD analysis

The X-ray analyses confirmed that hydroxyapatite was the only crystalline phase indicated in all the samples immersed in the polymer solution environments. It was found that in all the cases the degradation of hydroxyapatite ceramic structure was not observed. Figure 6 shows a X-ray diagrams of the materials immersed in PAA/PEG dispersions.

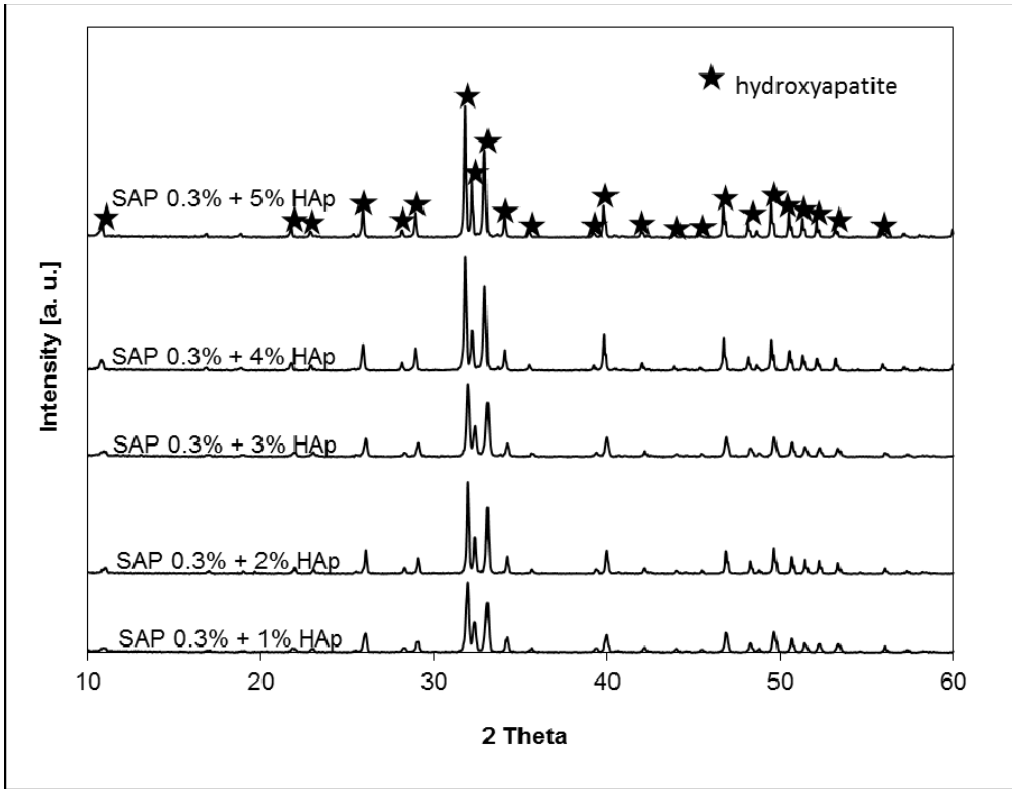

Fig. 6. The X-ray diagram of hydroxyapatite immersed in PAA/PEG dispersions

4. Conclusions

The studies concerning preparation of dispersion containing hydroxyapatite particles were carried out. PAA/PEG dispersants were evaluated for their potential to be used as biocompatible dispersants in the synthesis of biomimetic composites with a dispersed mineral phase. Stability, sedimentation and rheological experiments were confirmed that addition of the PAA/PEG polymers solutoins improve durability and homogeneity of the coloidal system.

Consequently, aggregation and sedimentation of HAp mineral phase was reduced considerably. FT-IR spectrum of the PAA/PEG/HAp suspensions exhibited the characteristic absorption bands of hydroxyapatite. Dried products contained hydroxyapatite as the only crystalline phase identified with the X-ray method.

On the basis of the research results it could be inferred that suspensions PAA/PEG/HAp has a great potential to be used as a viable and economical biomaterial for medical application.

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