Filling of polymer hydrogels by nanoparticles of the hydroxyapatite

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***Abstract* – In this work was development of new methods of synthese the hydrogel composites with nanoparticles of hydroxyapatite using sol-gel synthesis. At first the nanoparticles were synthesized in the presence of the peroxide oligomers which at the next stage provided polyacrylamide grafting on to the surface nanoparticles; that resulted in formation of the powder-xerogels capable to turn in to hydrogels. In accordance with other approach, the hydrogels filled were formed via in situ synthesis of the hydroxyapatite nanoparticles directly inside of the crosslinked polyacrylamide gels. The shape, composition and structure of the hydroxyapatite nanoparticles as well as polymer composites were investigated applying gas-liquid chromatography, X-RD analysis, scanning electron microscopy.**

Key words – hydroxylapatite, hydrogel, nanopartikel, polymer composite.

I. Introduction

Hydroxyapatite (HA) is the main inorganic component of bone and tooth tissue of the humans and animals. Therefore materials based on hydroxyapatite lately attracted considerable attention due to their high biological compatibility and biological activity, particularly in rehabilitation surgery, dentistry and as components of toothpastes and gels, cosmetics and hygiene products, food additives. To solve the problem of fragility of these materials for biomedical applications using their compositions with polymers. The problem of the obtaining high full composites caused by the poor adhesion (compatibility) of the polymer matrix to the surface of the bioceramics, which can lead to premature separation at the interface and as the consequence to deterioration of the mechanical properties of the composite material. Therefore, the use as surface modifiers, heterofunctional oligo peroxides (HFO), which are composed of functional groups on the one hand, that are capable to chemical interaction with the surface of fillers, and on the other hand - with the polymer, including peroxide groups that are capable to free radical reactions, opens new prospects for creating polymer composites.

II. Page Setup

During the work were used the following materials: calcium chloride, calcium nitrate, three monofosfat and differently substituted sodium phosphates (clean for analize), polymers of acrylamide – kation and anion active polymer product, and acrylamide polymer A-1510. Heterofunctional peroxide containing copolymers on the basis of peroxidic monomer 5-tert-butyl peroxy-5-methyl-1-hexene-3-yne (PM) and maleic anhydride (MA) was synthesized and cleaned in accordance with the technique [1].

Hydroxyapatite nanoparticles were obtained using sol-gel method as described in accordance with the reaction:

$$10\,CaCl_2 + 6\,(NH_4)_3PO_4 + 2\,NH_4OH \rightarrow$$
$$Ca_{10}(PO_4)_6(OH)_2 + 20\,NH_4Cl$$

Method of the synthesis was the next: were prepared 5% water solutions of CaCl2 and $(NH_4)_3PO_4$ in the molar ratio of Ca/P = 1.67. The HFO in the amount of 5% by weight. (by weight CaCl2) was pre-dissolved in a solution of $(NH_4)_3PO_4$. Calcium chloride solution was thermostatic at 40 ˚C in the reactor, with vigorous stirring of the reaction mixture. Then slowly, drop by drop added the solution of $(NH_4)_3PO_4$ and HFO, with the following incubation of the reaction mixture for 7 hours. pH was 8.5. After the end reaction mixture was filtered and washed three times with distilled water. Obtained precipitate was dried at room temperature to a constant weight.

III. Page Setup

Getting polymer hydrogel. For obtain hydrogel used polymers based on acrylamide of different chemical composition. The synthesis was performed as follows: selected samples were dissolved in two separate containers with the concentration of polymer 3% by weight. After complete dissolution of the polymers, solutions were mixed with the addition of 1M NaOH for increased activity of the cation polymer, the pH value was adjusted to 8.5 under stirring to receive the homogeneous system.

After that obtained hydrogel dried at 90 ˚C during the 12 hours to remove excess moisture. After that the dry hydrogel was prepared for further research.

The formation of the hydrogels with particles of hydroxyapatite. The formation of calcium phosphate containing polymer composites performed by the following procedure.

In a glass tube hydrogel layer is placed (thickness ≈ 1 cm). from bouth sides of the tube are added solutions of the $CaCl_2$ and $(NH_4)_3PO_4$. This system was left for 15 hours for the diffusion of cations and anions in to the free space between the hydrogel macromolecules . This leads to the formation of hydroxyapatite structure.

The hydrogel is formed as follows. In reactions take the part anionic and cationic polymers containing acid and amino groupes, respectively. During the mixing of this two polymers salt connections begin to form in the system, making thus crosslinked, three-dimensional structure of macromolecules between the initial polymers.

After the filling tube and adding solutions carried out the second stage of the process. A layer of hydrogel creates the semipermeable barrier for salt solutions Ca^{2+} and PO_4^{3-} ions. Due to the effect of ion diffusion in free space between macromolecules of the hydrogel they undergo chemical interaction and, as a result, the particles of hydroxyapatite is formed as the final product.

To select the optimal synthesis conditions, there were obtain different samples of the hydroxyapatite. The synthesis of the hydroxyapatite was done as in the presence of peroxide modifier, and without it. The best results are seeing, when as initial reagents are used $CaCl_2$ and $(NH_4)_3PO_4$ in the ratio 1: 2, at pH 8.5.

The structure of the HA samples, synthesized by the sol-gel method, using $CaCl_2$ and $(NH4)_3PO_4$ was confirmed by X-ray analysis. Radiographs HA samples is shown in Figure 1.

The results of X-ray analysis shows that some samples contain traces of unwanted impurities present in the reaction. These impurities often observed at higher pH. This should be taken into account when washing the reaction products.

The shape and size of the hydroxyapatite samples were investigated by the SEM microscope.

Results of the samples of HA are shown in micrographs (Figure 2).

In the above picture seeing a significant difference between the samples of modified and not modified HA.

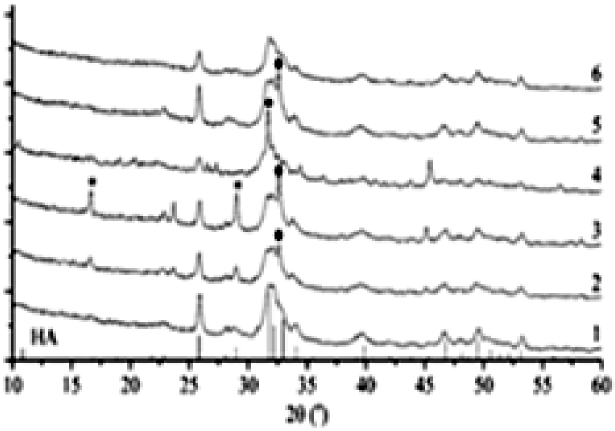
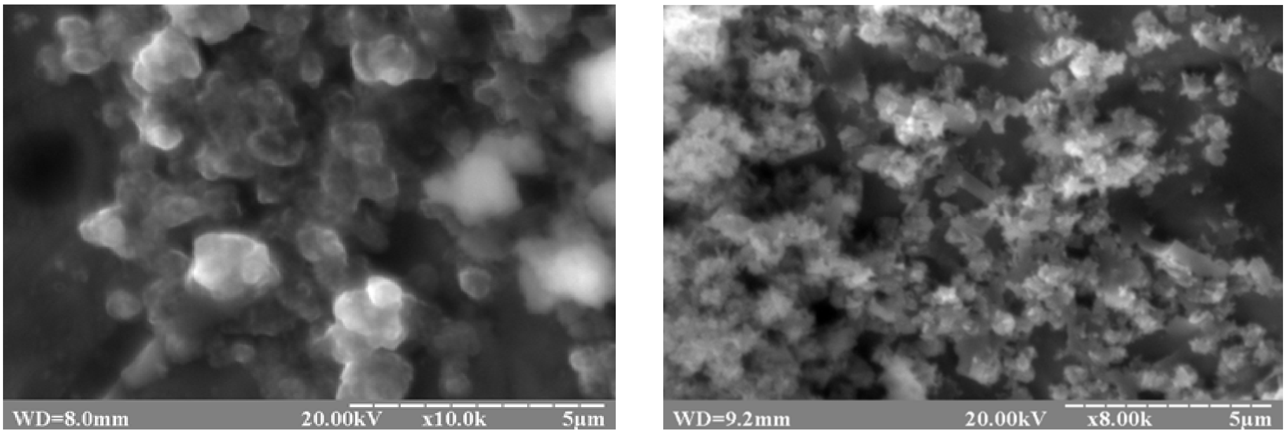


Fig. 1. XRD patterns of the HA samples: ♦ - ammonium chloride phase; ● - sodium chloride
* - ammonium phosphate

Figure 2 (a) no needle particles that correspond to form particles of the hydroxyapatite, which are clearly visible on the Figure 2 (b). There are also significant differences in the sizes of the samples.



a

b

Fig. 2. Microphotograph of the hydroxyapatite

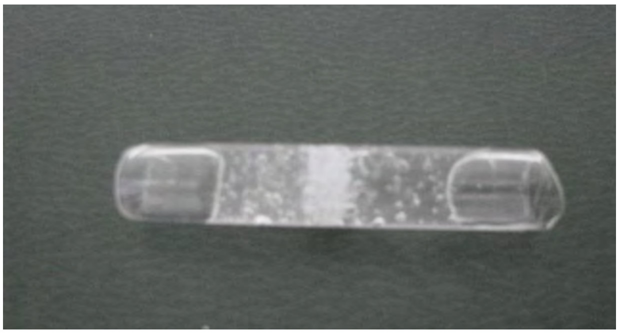


Fig. 3. Obtaining of the particles of hydroxyapatite in hydrogel

The studies were used to select the optimal conditions for the formation composites of the hydrogel. Figure 3 shows that composite hydrogel particles of the hydroxyapatite are formed in it by the method that is described above.

Conclusion

The results of the HA peroxidation indicate that the optimal conditions for the synthesis are pH = 8.5, as the using of these reagents gives the highest value of contents HFO. However, we can also state that the tri-substituted salts of phosphoric acid are characterized smallest content of the peroxide oligomer in HA. By increasing the pH decreases the amount of adsorbed modifier on the HA surface, probably, due to the better solubility of the last one. Managed to get a hydrogel with the HA crystals in the gel structure.

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