Carbon - phosphate nanocomposites

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Abstract

In this work the effect of size and origin of hydroxyapatite particles on mechanical and biological properties of carbon-carbon composites was analyzed. To obtain carbon-phosphate composites hydroxyapatite powder with micro- and nano-particles was used. Microsized HAp was synthetic and nanosized HAp was both synthetic and natural. IR and X-ray tests showed that hydroxyapatite after heat treatment changed its chemical composition towards natural one containing carbonate groups. In vitro study revealed that the presence of natural HAp nanoparticles in the composites enhanced their biological activity. Tests performed in Simulated Body Fluid proved that the process of hydroxyapatite's building becomes the most intensive only in the case of composite modified with nano-particles originating from natural hydroxyapatite. The size as well as origin (chemical composition) of HAp has a great influence on biological behaviour of composites. These composites with good mechanical properties and bioactivity are proposed to be used as implants for bone defects fulfil.

Introduction

The resemblance between fibrous material and tissue is a reason why in this very group of materials intensive research is carried [1,2]. The research is done for medical purpose on properties and structure optimisation. Carbon-carbon composite is a good example that illustrate long-lasting research and its outcome carbon-carbon composites are very useful in bone surgery [3,4]. They are biocompatible, have got satisfactory strength, low Young's modulus as well as suitable density and porosity. Carbon-carbon composites can form mechanical or biological bond with bone. First kind occurs in case of low-porous structures and the second one in case of porous systems, when bone tissue ingrowths into implant's pores more than 100 um. Strength of such a bond is still much lower than in the case of bioactive materials which form chemical bond with bone. Bioactive materials like hydroxyapatite or bioglass have low toughness and therefore they cannot be used as biomechanical implants [5]. Attempts to improve their toughness have not succeed. That is why nowadays there is a tendency to do modification in different type of synthetic material like polymers with bioactive powders [6,7]. The modification is done in order to improvement material integration with bones. On one hand polymer-ceramic composites obtained in that way are bonding with bones faster and stronger but on the other hand their low mechanical resistance does not allow to fulfil mechanical requirements. Introducing of bioactive HAp into fibrous material with good mechanical properties like carbon-carbon composite let obtain bioactive composite for structural implants [8]. Because of the fact that HAp activity depends on its structure as well as microstructure in following work there will be compared three types of carbon- phosphate composites modified by different kind of HAp powders – the difference is in particles size and origin.

Materials and methods

Carbon-carbon composites modified by hydroxyapatite were investigated. All composites were produced using the pre-preg method. Medium stiffness carbon fibres T300 made by Torayca, phenol-formaldehyde resins Nowolak MR made by Zaklady Chemiczne 'Organika – Sarzyna', and three kinds of hydroxyapatite powder were used. The fibres were impregnated with phenol-formaldehyde resin (as the precursor of the carbon matrix). Composites were carbonized at the temp. of 1000°C (with temperature increase 5°C/min) in an atmosphere of inert gas, followed by impregnation with the mixture of phenol-formaldehyde resin with hydroxyapatite powder [9] under vacuum as well as under pressure, and then they were re-carbonized at the same conditions as before. Used hydroxyapatites differ in grain size, an origin and oxide composition. Natural one (HAp-nn) was obtained from bones of animals at the Department of Special Ceramics WIMiC – AGH [10] and composed of particles with size in a nanometer range (fig. 1a). The remaining two HAP powders were synthetic and vary from size of grains: a synthetic one made by Mitsubishi (HAp-sn) contained nanometric grains (fig. 1b) while hydroxyapatite made at the Department of Technology of Ceramics and Refractories of AGH (HAp-sm) was micrometric.

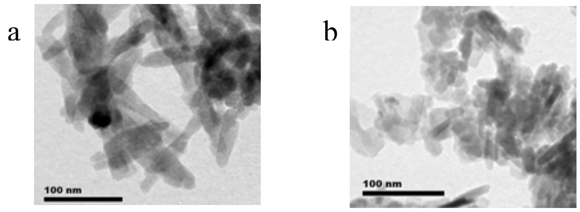

Figure 1**.** TEM microphotographs of hydroxyapatite powders a) HAp-sn, b) HAp-nn

Both kind of synthetic HAp powders, as it may be distinguished from FTIR spectra (Fig. 2), does not reveal the fact of containing carbonaceous groups. Vibrations of this group is visible in the spectrum of natural HAp. Considering that the very group is present in natural bones apatite and influenced its bioactivity, it can be assumed samples with this powder will be more biologically active than the rest of the samples with synthetic hydroxyapatites.

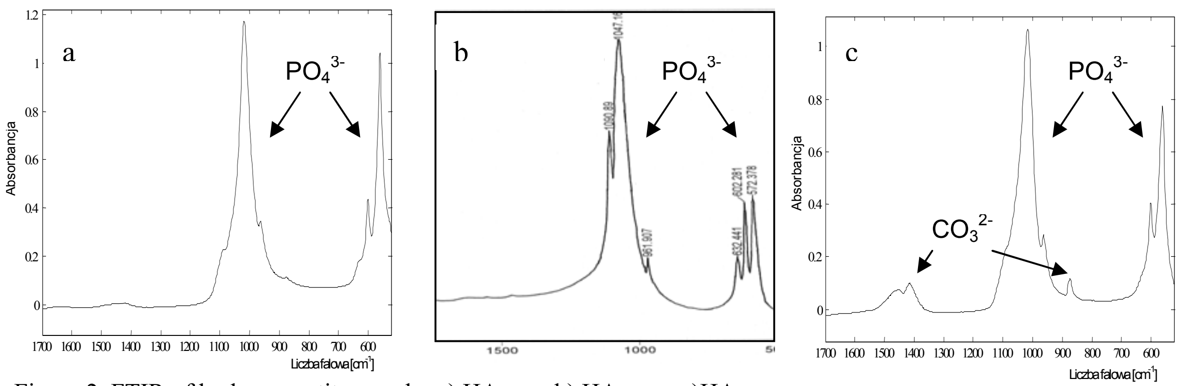

Figure 2. FTIR of hydroxyapatite powder a) HAp-sn, b) HAp-sm, c)HAp-nn.

To confirm that thesis, moulders incubation in simulated body fluid (SBF) was carried at temp. 37C for one month. During that time observation was done under scanning microscope Jeol JSM-5400 joined with chemical analyzes EDS LINK ISIS Seria 300, changes occurred on samples' surface. In order to ensure constant delivery of Ca^{2+} and PO_4^{3-} ions, within 3-4 days liquid was changed. Similar observation was done for carbon composites modified by hydroxyapatite powders. During three-point bending test performed on Zwick 1435 machine Young's modulus and bending strength were measured. In order to identify phases created in composites during thermal treatment infrared spectroscopy (FTIR) and X- ray diffraction were used.

Results

Incubation of hydroxyapatite samples in SBF confirmed higher activity of natural HAp. Synthetic nanometric hydroxyapatite are not an active basis for the process of calcium phosphates nucleation and after a month of incubation on its surface only some chlorides were visible. Meanwhile surface of the sample with natural hydroxyapatite was covered with calcium phosphates densely (fig. 3).

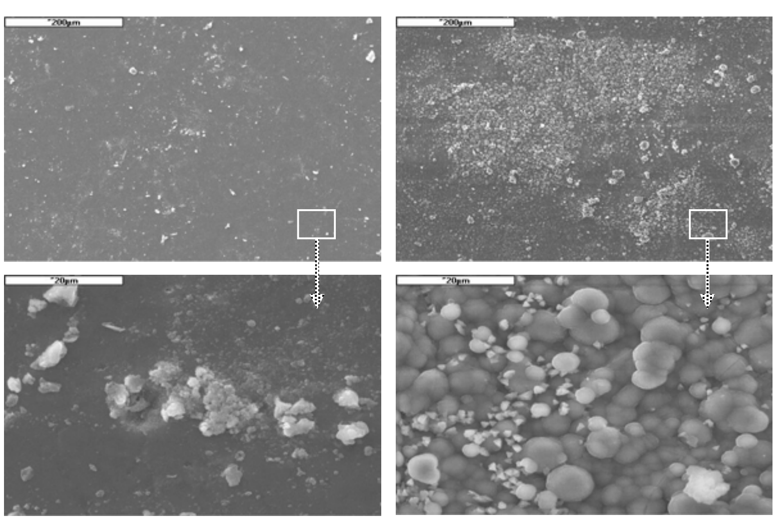

Figure 3. SEM micrographs of surfaces of nano-HAp a) synthetic b) natural.

Mechanical properties measurements for calcium-phosphate composites revealed that addition of hydroxyapatite, both micro and nanosized, to carbon-carbon composites in amount 3-5 vol.% did not change their strength or Young's modulus (fig.4). However it can influence their activity in biological environment. This phenomena is observed in case of composites modified by natural hydroxyapatite (nano-) as well as micrometric synthetic HAp (fig.5).

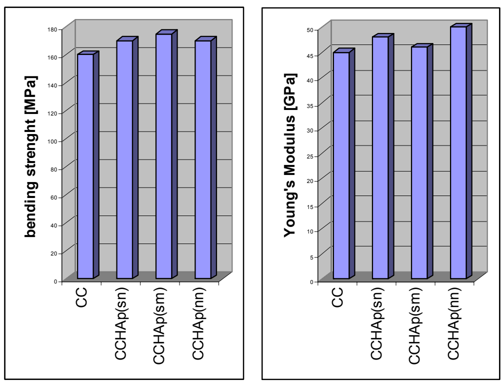

Figure 4. Mechanical properties of carbon-phosphate composites.

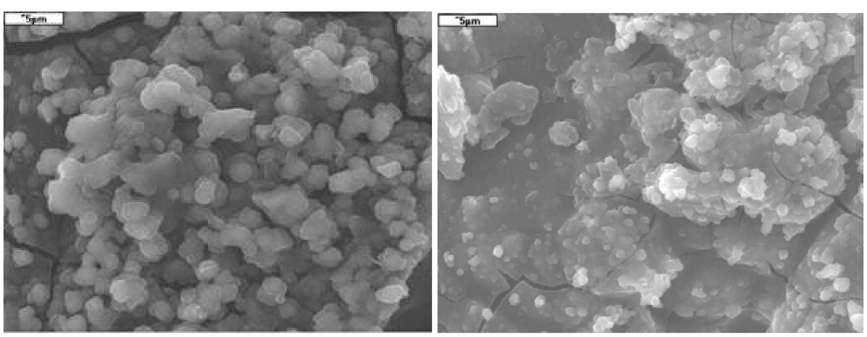

Figure 5. SEM micrographs of surfaces of carbon-phosphate composites modified with natural and synthetic hydroxyapatite after incubation in SBF.

Improvement of biological activity of synthetic hydroxyapatite is connected with HAp transformations during thermal treatment while obtaining carbon-phosphate composite. At the temperature 1000C there is a phase transformation of HAp in this composites. Besides HAp there TCP appears and carbonate, what is proved by FTIR and X-ray diffraction (fig. 6). The presence of these new phases causes that synthetic HAp behaves like natural bone apatite.

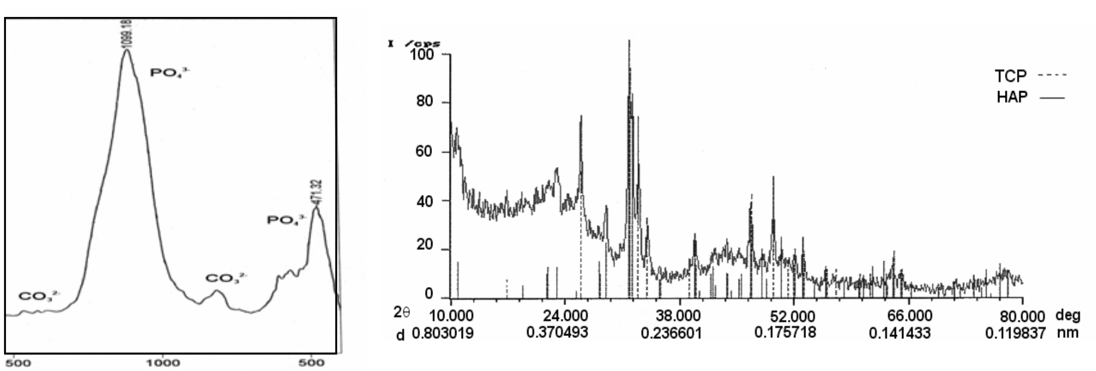

Figure 6 . FTIR and XRD of carbon-phosphate composite CC-HAp(sm).

Thanks the presence of such bioactive phase as hydroxyapatite it is possible to create strong bonding with bones. Additionally fibrous structure enable tissue ingrowth into material and creation biological fixation.

Conclusion

1. HAp implementation to carbon-carbon composites does not affect mechanical properties nevertheless may increase its biological activity.
2. Process of hydroxyapatite's building becomes the most intensive in the case of a composite modified with use of nano-particles originating from natural hydroxyapatite. Bioactivity should be connected with the presence of the carbonate phase and amorphous TCP.
3. Synthetic HAp may change its structure during carbonization of carbon-carbon composites towards natural one.
4. Bioactive carbon-phosphate composites can be used as implants to fulfil biomechanical functions.

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