

BIOACTIVE CARBON-CERAMIC COMPOSITES

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Abstract

Bioactive carbon-ceramic composites may constitute a new group of materials that combine bioactivity of calcium phosphates (HAP, TCP) or bio-glass, and the mechanical properties of carbon-carbon composites, comparable to those of natural bone tissue. Both mechanical and biological properties of these composites are affected by the type and the way of introducing the bioactive particles. The presence of bioactive phases in the examined composites considerably enhances their ability of bonding with bone tissue, while their mechanical properties remain at the level typical for carbon-carbon composites. These observations create good prospects for development of multifunctional implants designated mainly for bone surgery.

[Engineering of Biomaterials, 34, (2004), 3-5]

Introduction

Carbon-carbon composites are very useful in bone surgery. They are biocompatible, they have satisfactory strength, low modulus of elasticity and suitable density and porosity, therefore they are capable of creating good mechanical scaffold for bone tissue rebuilding [1]. Low-porosity carbon-carbon composites form mechanical bond with the bone. When the size of pores is larger than 100 μm , the biological bond is formed, where the bone's tissue ingrows into the implant's pores. Much better chemical bond is formed with the bone by bioactive materials, like hydroxyapatite (HAP) or bioglass [2, 3]. The type of bond has an influence on strength of bone-implant interface. This strength of bio-active implants is about 5 times higher than that of C-C composites (FIG. 1). Introducing the HAP or bio-glass into

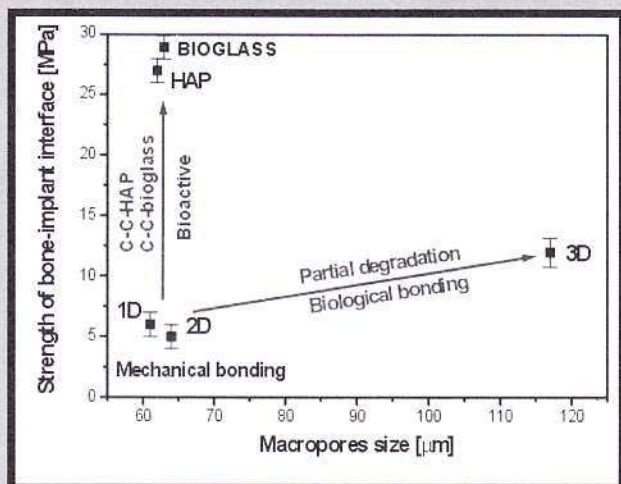


FIG. 1. Bone-implant interface in C-C composites.

the C-C composite brings about the increase of interface's strength [4, 5].

Therefore, an idea has been developed of obtaining the carbon-ceramic composite, which would be capable of combining the good mechanical properties of carbon-carbon composites with bioactivity of hydroxyapatite or bioglass.

Materials and methods

The carbon-ceramic composites were obtained in two ways, schematically shown in FIG. 2. The bioactive phase can be introduced into the composite either during the first production step, together with the precursor into the entire volume of the composite, or during the densification step, into the open pores of the composite. The phenolic resin was used as a precursor and low modulus carbon fibres (T-300 by Torayca) were applied as a reinforcing phase. Bioactive phases consisted of synthetic stoichiometric hydroxyapatite (made by AGH) [6], and bioglass A2 (40%mol SiO_2 , 54% mol. CaO, 6% mol. P_2O_5) obtained by the sol-gel method developed by AGH [7].

Results

Some variations of mechanical properties and biological behaviour may be expected as a consequence of different microstructures, due to application of different fabrication method applied. In this study the changes of mechanical properties, phase transformations as well as the growth of hydroxyapatite in SBF were examined.

FIGURES 3 and 4 show the mechanical properties of the examined composites. Figure 3a illustrates the values of bending strength measured on different composite samples in comparison with the bone material and pure hydroxyapatite. The differences of properties of 2D composites obtained in two different ways are visible. When the bio-active phase is introduced into composites' microstructures in the last step of processing, (i.e. during densification) higher bending strength can be observed than for composites with bioactive phase introduced in first stage of processing. In each case the bending strength of obtained composites is higher than the same parameter for the bone material and the hydroxyapatite.

From the point of view of bone fixation it is beneficial when Young's modulus of the implant is similar to Young's modulus of the bone. Such situation occurs in carbon-ceramic composites with 2D structure. It is worthwhile ment-

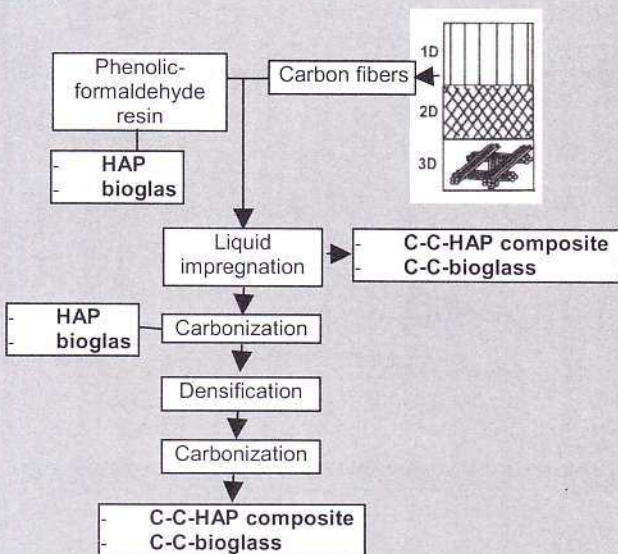


FIG. 2. The scheme of manufacturing of carbon-ceramic composites.

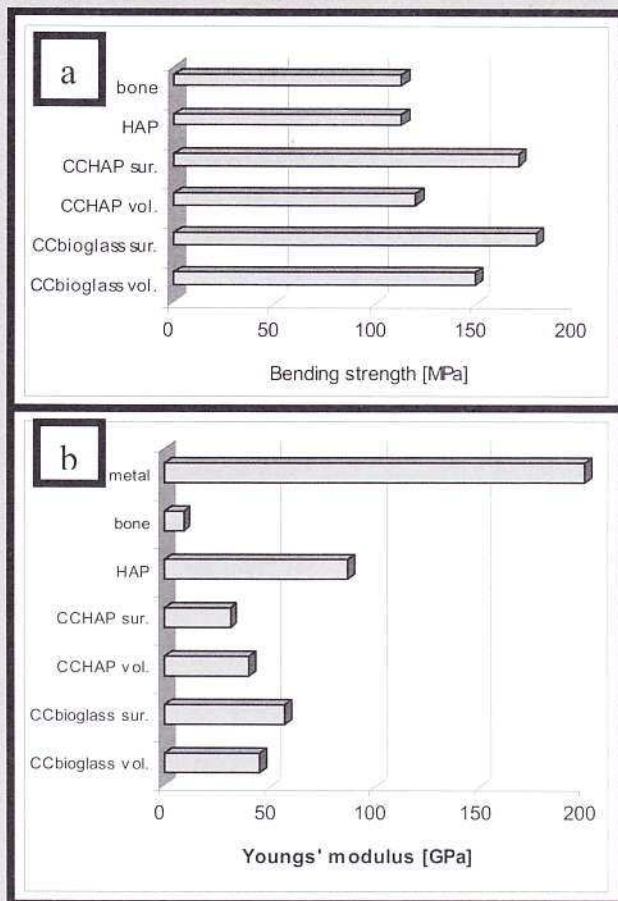


FIG. 3. The bending strength and Young's modulus of 2D composites, hydroxyapatite and bone.

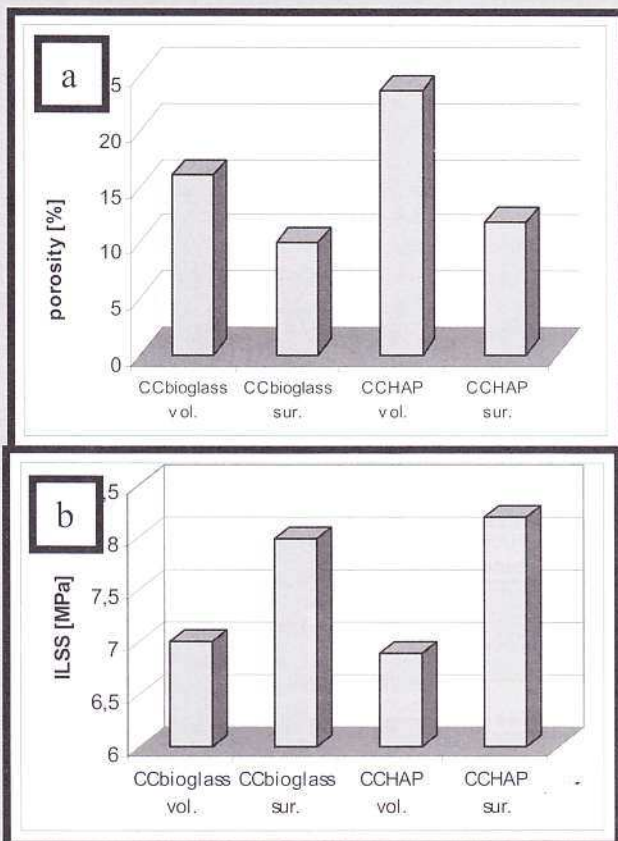


FIG. 4. Porosity and interlaminar shear strength of 2D.

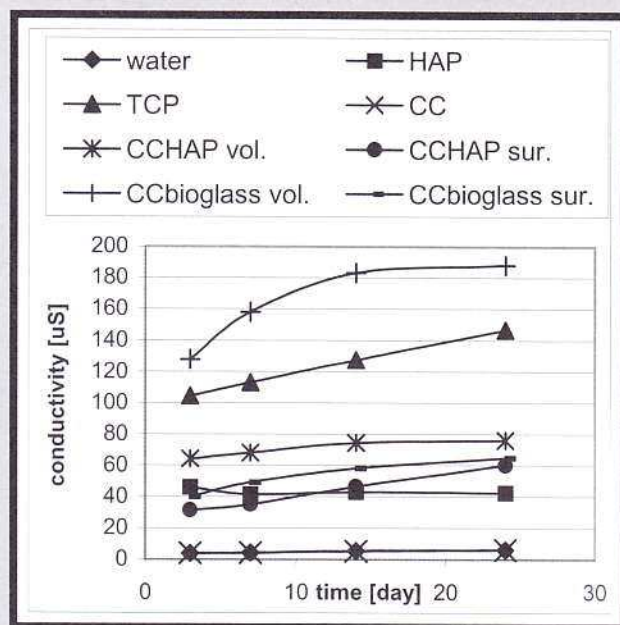


FIG. 5. Variations of water conductivity after incubation.

tioning here that Young's modulus of HAP and widely used metal implants are too high, which causes undesirable effect of excessive stiffness and growth problems (FIG. 3b).

There are differences in porosity as well as in inter-laminar shear strength of obtained composites (FIGs. 4a and 4b). Materials with bulk addition of bioactive phase are more porous and have lower fiber-matrix interface strength. The values for C-C-HAP and C-C-bioglass composites are similar.

Introduction of HAP into C-C composites affects the phase transformation of HAP and changes biological behavior of the materials. At the processing temperature of 1000°C the phase transformation of HAP occurs in these composites. Besides HAP, the TCP and the carbonate phase appear. The presence of these new phases causes the implemented synthetic HAP to behave like a natural bone apatite in a living organism. There are no changes in bio-glass structure at the temperature of 1000°C.

In order to investigate the biological behavior of examined materials, the experiments in distilled water were carried out. The electrical conductivity of water after the incubation of different samples was measured. FIGURE 5 illustrates the dependence of electrical conductivity on the incubation time. The most pronounced changes are observed for pure TCP, which is related to its dissolution in water. The effect of increasing conductivity is also observed in the case of C-C-HAP composites, which confirms the presence of the resorbable TCP phase, and also C-C-bio-glass composites. For the C-C composite alone, the electrical conductivity is independent of the incubation time. For HAP sample only the preliminary increase was noticed, but after 1 week the conductivity remained at the same level.

The composites were incubated in SBF at 37°C for two weeks. In order to ensure the constant supply of Ca^{2+} and PO_4^{3-} ions, the liquid was replaced every three to four days. Figure 6 shows an SBF influence on incubated materials. After 14 days of soaking in SBF the surfaces of C-C-HAP and C-C-bioglass composites were covered by precipitates of calcium-phosphates. For the purposes of comparison, the same soaking experiments were performed on C-C composite alone, as well as on C-C/nanoHAP (composite with nano-hydroxyapatite obtained from natural bone). The samples of C-C composites did not contain the phosphate phase, due to which their surface was inactive towards the nuclea-

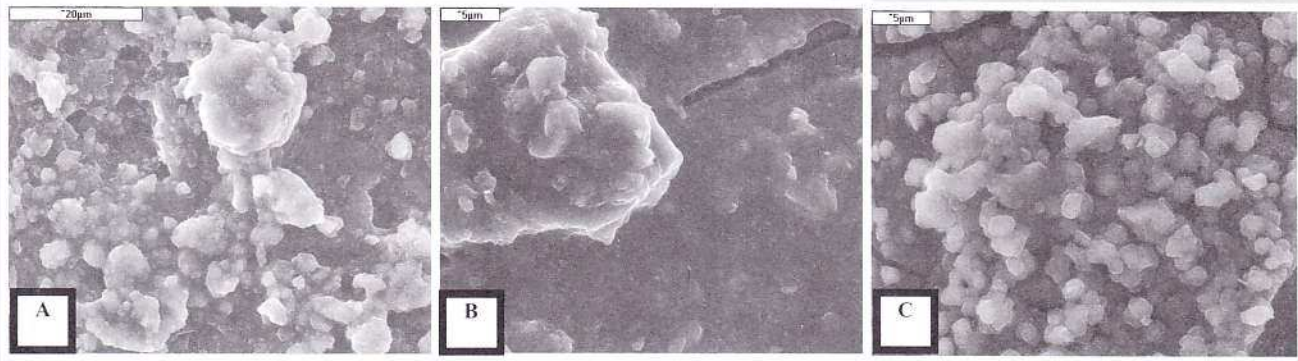


FIG. 6. SEM images after 14 days incubation in SBF a) C-C-HAP, b) C-C-bioglass, c) C-C-nanoHAP.

tion of apatite. The most active C-C-nanoHAP composite was very densely covered with fine particles of freshly formed hydroxyapatite.

Conclusions

1. The way of introducing the bioactive ceramic phase influences the mechanical and biological properties of carbon-ceramic composites.
2. Composites with bulk addition of bioactive phase are more porous and have lower fiber-matrix interface strength.
3. Good conditions for growth of bone apatite occur in the case of carbon-HAP and carbon-bioglass composites, in particular containing the bioactive particles located on the surface.

Acknowledgements

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