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Preparation of macroporous ceramic based on beta – $Ca_3(PO_4)_2$. Preliminary results

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The aim of this study was to elaboration of β- TCP foams with good compressive strength, by the polymeric sponge technique that typically produces open-cell structures: polyurethane impregnated with ceramic slurry, is burned out leaving a porous ceramic. For experiments was used two type of the polyurethane with different pore sizes. Porous samples were characterized with optical Microscope Carl Zeiss NU2, Material Testing Machine Zwick T1-FR005TN, and the β-TCP suspensions with the ZetaPlus Brookhaven type. The preliminary results evidenced a macroporous structure formed (with pose size between 150-450 μm) characterized by good compressive strength in the range of the cancellous bone. Future work will focus on improving the strength of these open porous calcium phosphate ceramics.

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1. Introduction

In medical applications where bone ingrowth is intended it is beneficial to have bioresorbable phase like beta tricalcium phosphate, as this phase are know to be more soluble than HAP. Tricalcium phosphate $Ca_3(PO_4)_2$ (β-TCP), an osteoconductive as well as bioresorbable ceramic, has found applications as bone cement and bone implant material, respectively.[1-4] This ceramics may by used in granular, dense or porous form. In recent years, attention was particularly placed on the fabrication of β-TCP with porous configuration because the porous network allows the tissue to infiltrate, which further enhances the implant-tissue attachment.[1]

The most currently used production method for these foam structures is the polymeric sponge technique wherein soft polyurethane foams (PU-foam) is dipped into ceramic slurry. After elimination of the excess slurry and drying, the Pu-foams are burnt off and, after sintering, ceramic foams are obtained. This method has the advantage that the cell size of such structures are be easily adapted by starting from another PU-foam having the appropriate cell size. The proprieties of the ceramic slurries are crucial for the characteristics of the foams. Firstly, they should have high content of solids, in order to reduce the shrinkage during firing, good homogeneity and must be stable in time.

In this work, in order to obtain stable slurry with solid content of 65wt% was used different additives like dispersant agents and binder. The binder provides strength to the ceramic structure after drying prevents collapse during sponge volatilization and promote the optimal polymeric sponge structure cover; a binder previously tested with good results was polyethylene oxide. The characteristics of the slurries like as zeta potential and iso-electric point (IEP) were determined with the ZetaPlus Brookhaven type. The results showed that the mechanical properties of the bioresorbable foams evidencieted with Material Testing Machine Zwick T1-FR005TN are in the range of the cancellous bone.

2. Experimental

The starting materials used in this study were: beta-TCP powders obtain in our laboratory, dispersing agents (sodium polyacrylic acid and di-sodium pyrophosphate made by Merk), binder (polyethylene oxide) and two types of the polyurethanes.

Preparation of the slurries

In order to obtain stable and homogenous suspensions with an initial solid content of 65wt%, two dispersant were tested: sodium polyacrylic acid and di-sodium pyrophosphate made by Merk.

The slurries were prepared by first mixing deionized water and dispersants (0-2 wt% based on dry solid mass) ultrasonic and mechanical. Then powders were progressively added for a period of 20 minutes and agitation for a 30 min to prepare a fluid system enable to all further utilizations. The binder is added at the end, as solution (polyethylene oxide).

Selection of sponge and impregnation

When the impregnation foam is heated to volatilize the sponge, the polyurethane relieving any thermal stress which might disrupt the unsintered ceramic. The sponge is totally decomposed at around 600°C. It was more favorable to realize the decomposition of the polymeric sponge at lower temperature, with a lower rate, so that stresses not to be induced in the unsintered ceramic structure.

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Typically, the sponge was compressed to remove air, immersed in the slurry and then allowed to expand. After the sponge has been infiltrated, it was being passed through pre-set rolls, in order to eliminate the excess, and also to homogenize the slurry distribution.

Drying and Sintering

After the excess slurry was removed, the infiltrated sponge was dried to deposit the ceramic particles. The drying was done in air, for 48 hour. The dry reticulated structure was heated in air to volatilize the polymeric sponge. Sintering cycles are shown in fig.1.

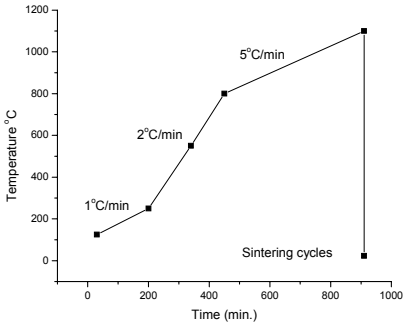

Fig. 1. Sintering cycles.

3. Results and discussions

3.1 Characterization of the suspensions

The suspensions containing 0.01wt% particles without and with two dispersants (sodium polyacrylic acid and di-sodium pyrophosphate made by Merk) was characterized with ZetaPlus Brookhaven type device. Fig.2. shows the zeta potential curves of the β-TCP powders as a function of pH, without and with dispersing agents (2% sodium polyacrylat acid and di-sodium pyrophosphate). The iso-electric point (IEP), in absence of dispersants, was found at pH 7.52. The addition of the different dispersants increases the negative zeta potential values leading to an increase of the repulsive force among particles, in conclusions more stable ceramic slurries.

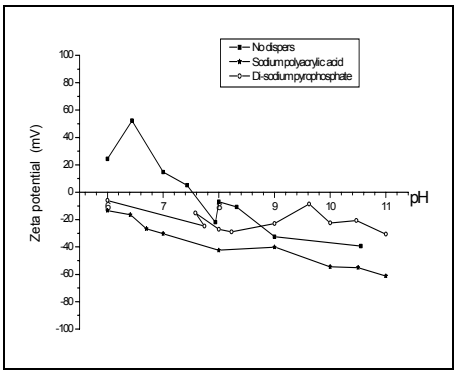

Fig.2. The zeta potential curves of β-TCP particles in the absence and presence of dispersing agents.

3.2 Characterization of the ceramic foams

The structure of samples was evaluated through optical images, using Optical Microscope Carl Zeiss NU2.

Observation by optical microscopy reveals a regular macrostructure of the PU-sponge with polyhedral geometry (fig. 3).The structure of the ceramic foams is very similar, it can be noticed that the pores becoming spherical or oval.

The walls of the struts are particularly thin, of about 50 microns. It can thus assumed that the strength of the ceramic struts, which can be achieved by proper sintering and appropriate choice of the affect the mechanical resistance of the foams, even more important than density.

Optical images shows (in figure 3.) that the pores size of the β- TCP foams after sintering were in the range 150-450 μm.

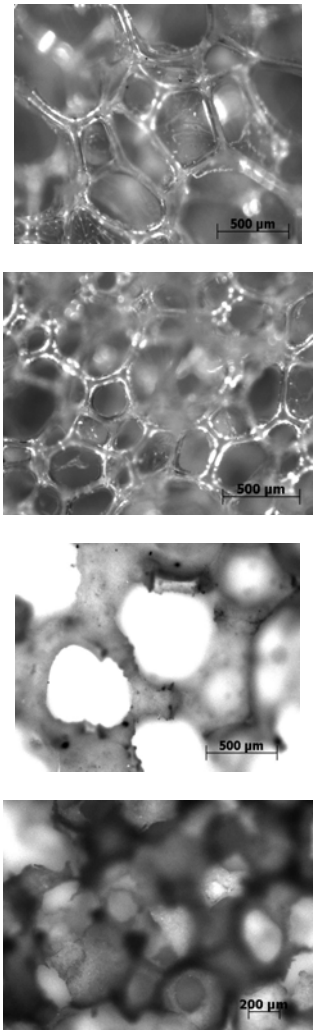

Fig.3. optical images a) PU-foam by A type b) PU-foam by type B c) final porous ceramic structure result after sintering of the PU-foam by A type impregnated with ceramic slurry d) final porous ceramic structure result after sintering of the PU-foam by B type impregnated with ceramic slurry.

Material Testing Machine Zwick T1-FR005TN device was used to characterize the compressive strength; it was observed a double value in case of the PU-foam by type B, but, in general both values for the samples are in the range of the cancellous bone (2-10 MPa).

Table .1. Compressive strength.

Samples	Compressive strength (MPa)
A	6.77
B	11.88
Cancellous bone	2-10

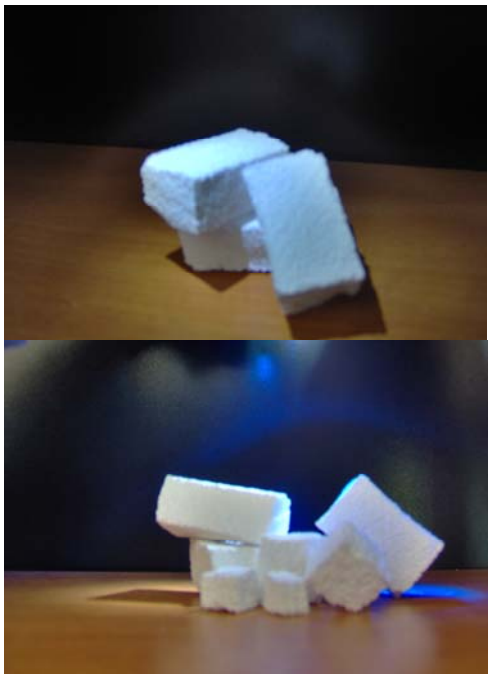

Fig. 4. Macroporous structures obtain by polymeric sponge technique.

4. Conclusions

In this preliminary study of the production of macroporous ceramic based on beta-$Ca_3(PO_4)_2$ we used polymeric sponge technique, which is very good way for the preparation of porous foams.

The β-TCP powders synthesized by precipitation, from salt solutions were highly flocculated when dispersed in aqueous medium; the iso-electric point (IEP), was found at pH =7.52. The type and amount of dispersing agent added revealed to be an important factor that determines the behavior of the β-TCP suspensions.

The most efficient dispersant used in this work was sodium polyacrylic acid enables to prepare a stable suspensions containing 65 wt% solid. It was determined that a 2 wt% dispersing agents with respect to the ceramic powders at a pH level between 10-11 was sufficient for deflocculating of β-TCP powders. Sodium polyacrylic acid produced the higher negative zeta potential values and it is recommended for further applications, because it is the most promising electrostatic stabilizers, and would enable to achieve high solids loading.

The products obtained by polymeric sponges technique were characterized by good compressive strength in the range of the cancellous bone. Optical images show that the pore size for ceramic foams obtain in our laboratory were between 150-450μm (the pore size acknowledged as that needed for osteogenesis).

The main results are in concordance with the data from specialty literatures.

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