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Characterization of the Calcium Phosphate Porous Ceramic Obtained by Foam Consolidation using Albumin

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Abstract. In many *in-vivo* and *in vitro* studies, the behavior of calcium phosphate ceramics like β - tricalcium phosphate in biological environments has been reported to be predictive and positive. In terms of bone tissue growth, this ceramic can be more attractive presenting a porous microstructure. To obtain biomaterial quality ceramics, in this investigation β- TCP porous ceramics were prepared by a special consolidation method with albumin as a foam generating agent. This technique enables preparation a variety of formats with complex geometries. To obtain porous samples using albumin, heat had to be introduced into the system during the consolidation stage. After consolidation, the samples were sintered at 1250^{o}C for 30 minutes and characterized using X-ray diffractometry, scanning electron microscopy and mercury porosimetry. The foams that were obtained by this method exhibited spherical and interconnected pores, characteristics desirable in biomedical implants.

Introduction

In the last years, various processing techniques have contributed towards the development of porous biomaterials. The potential of porous ceramics for applications in the medical, engineering and pharmaceutical fields has been widely reported [1, 2]. Tricalcium phosphate (TCP) ceramic exhibit interesting properties such as biocompatibility, osteoconduction and resorbable nature. The later allows the incorporation and release of different drugs or biologically active substances to stimulate cell function [3]. The β - TCP, obtained by foam consolidation, have features that are ideal for use as bone implants and scaffolds [3, 4].
The colloidal processing for near net shape ceramic has been incorporated into the biomedical field, to obtain more reliable grafts and implants [2]. The consolidation method by protein action, such as albumin of egg white (ovalbumin) is used as a promising alternative to obtain porous ceramics. Albumin, under specific conditions (thermal and chemical), has the ability for pore formation and gelation in water. The use of ovalbumin in ceramics shape forming has many advantages in porous ceramic processing. Ovalbumin is nontoxic, biodegradable, cheap, and widely available. In the other techniques of foams obtention, like the traditional gel casting of foams, the neurotoxic nature of the monomers is a limiting factor [5, 6, 7]. Hence, this new methodology to produce porous biomaterials is considered to be promising as it does not pose any danger with respect to handling of additives and does not require controlled atmospheres for foam consolidation and the pores are spherical.
This paper presents the characterization of β-tricalcium phosphate ceramic foams obtained by direct consolidation method with ovalbumin.

Materials and Methods

To prepare the suspensions, 69 wt% of solids in the form of β-TCP (Fluka) and ovalbumin (Schettert) powder were used. To obtain the foams, 0.6 mg/m^2 of dispersant (Dispex A 40), a non-ionic surfactant (Genaminox) and 0.08 wt% of amine dimetil alkyl oxide were added to the β-TCP aqueous suspension. Albumin (5, 6 and 7 wt%) was added to the ceramic suspensions to form the gel and stabilize the foam. The foams were kept in oven at 60^oC/12 h. This temperature was chosen based on rheological studies that were carried out to determine the gel point. Subsequently the foams were annealed at 600^oC/2h using a heating rate of 3^oC/min, in order to degrade the organic material. The samples were sintered in oxidative atmosphere, with heating rate of 5^oC/min up to 1250^oC/30 minutes and characterized by XRD, SEM and mercury porosimetry.

Results and Discussion

The X-ray diffraction profiles of the β-TCP samples in the different states are presented in the Fig. 1. The starting material, the sintered ceramic and the sintered foam obtained with the higher albumin content (7 wt%) are showed. The diffractograms were analyzed using the JCPDS 9169 card.

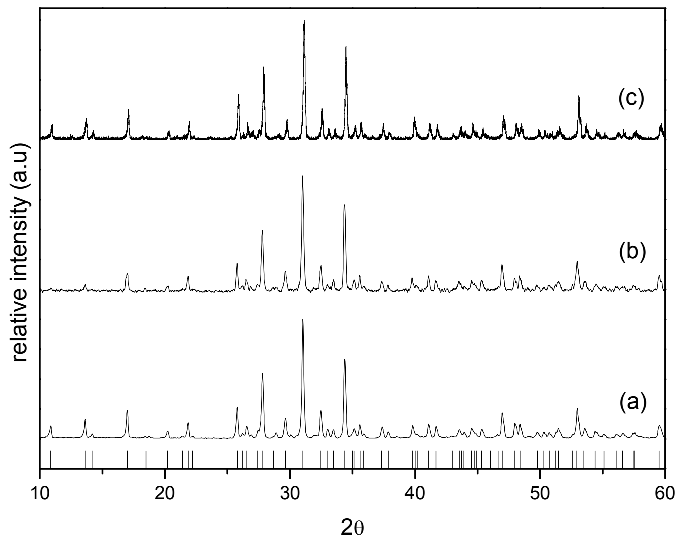

Figure 1 - X-ray diffractograms of the TCP different specimens: (a) starting powder; (b) the sintered ceramic (1250^oC/30 min.); (c) ceramic foam obtained with albumin and sintered (1250^oC/30 min.), compared with JCPDS 9169 card.

β-TCP was the only phase identified in starting material and in sintered samples. The presence of albumin, as a foaming agent in suspension, did not result in any new phase and the diffractogram was identical to that of the specimen sintered without albumin.

The total porosity results determined by mercury porosimetry technique are shown in Table 1. The Fig 2 shows pores distribution of samples with different amount of albumin. The porosity is expressed as volume of intruded mercury as a function of pore diameter.

Table 1 - Total porosity values of foams obtained by mercury porosimetry technique.

Samples	*Total porosity (volume)*
TCP 5	58 %
TCP 6	62 %
TCP 7	51 %

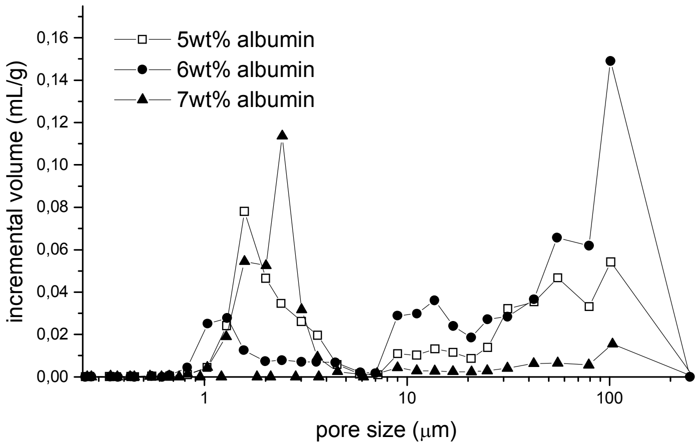

Figure 2 – Curve of pore size distribution frequency as a function of volume intruded mercury of the TCP samples.

The ceramic foams analyzed exhibit a particular behavior in function the amount of albumin, resulting in different pore size distribution.
For foams, derived from suspensions with 7wt% albumin, it was observed a reduction in porosity of the sample. This effect is related to the exponential increase in viscosity in the presence of albumin, due to its tendency to absorb water. This characteristic confers higher resistance of the suspension, to form foam and results in a decrease of total porosity. However, when 5 wt% of albumin was added, the foam didn't exhibit a suitable stability, due fast draining between cells. This phenomenon promotes a previous collapse of the bubbles and leads to TCP foams with undesirable handling mechanical resistance. The foams with 6 wt% of albumin has suitable draining and high superficial viscosity, leading to a higher elasticity of the cells and consequently, improving their stability.
The micrographs of the samples obtained with 6wt% of albumin shown in Fig. 3 reveal that the structures consist of a permeable porous network and spherical geometry of the pores.

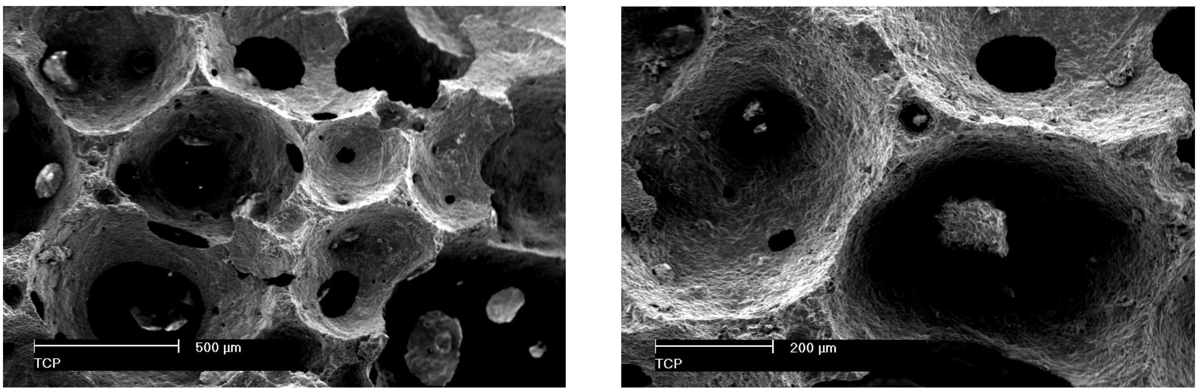

Figure 3 - SEM micrographs of TCP foams (fractured surfaces) based 6wt% of albumin.

Albumin is efficient to obtain interconnect pores, according to results observed by mercury porosimetry. Pore dimension higher than 200 μm, observed by SEM, was not detected in porosimeter results due to the low pressure used in this range measures.
The foams were consolidated in maturation stage, in order to maintain cells with spherical shape and absence of poliedric geometry in foams. This characteristic indicates that the rheology and dispersion condition of the suspension were well adjusted to have suitable stable foam, which is

able to persist during solidification stage. These conditions were optimized according to a previous study [8, 9].
Interconnected pores are an important feature and various studies show that this microstructure contribute and maintain bone tissue growth, by transport of nutrients and drainage of interstitial fluids. The small pore fraction seen in the specimens and observed in the micrographs is also important in terms of capillarity and permeability of body fluids, which could contribute to dissolution of the ceramic. The microporosity is morphologically functional by contributing to surface roughness. The roughness induces more bone formation compared to smooth surfaces, due to increased anchoring of fine osteoblastic type of cells [10].
The macropores in these specimens provide paths for bone tissue growth, as these easily penetrate the pores and establish the osteoconduction process. The filling of these pores with new bone tissue brings about strong interlaced bone-implant and confers increased strength to the implant.

Conclusions

The results obtained in this study demonstrated that:
The foaming action, along with the consolidation effect of this albumin methodology is the main attribute of this technique and this improves porous ceramic processing.
The presence of albumin did not alter the crystalline phases in sintered ceramic foams.
TCP suspensions obtained with 6 wt% albumin are more suitable than others albumin concentrations to produce foams with good stability and pore distribution.
Albumin promotes formation of micro and macro pores with characteristics such as size, spherecity and pore interconnectivity that are interest for use as biomaterial.

Acknowledgements

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