

# Porosity control of hydroxyapatite implants

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Conformation of hydroxyapatite (HAp) bodies was carried out using a multiple slip-casting technique, in order to obtain dual-layer samples with differential sized porosities. The external layer, because of its porosity, controlled by the addition of organic compounds (polyvinyl polyacrylate, PVC), will promote bone ingrowth. The internal denser layer, due to the addition of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) as sintering additive, will give mechanical resistance to the implant. HAp aqueous suspensions were characterized by rheological measurements. Scanning electron microscopy (SEM) and intrusion mercury porosimetry (MP) were used to characterize sintered bodies. It can be concluded that it is possible to introduce gross porosity in HAp bodies by the addition of organic compounds. The results show that a compatible shrinking of the layers during the sintering process and a good frequency of pores with an appropriate size in the external layer can be achieved with the use of organic additives. © 1999 Kluwer Academic Publishers

## 1. Introduction

Hydroxyapatite (HAp) is an attractive material in clinical use because of its chemical composition near to that of bone, its high bioactivity and biocompatibility.

A bone implant requires biocompatibility, mechanical strength and porosity to promote the interactions between the biomaterials and the host tissue without undesirable reactions. The creation of a porous structure relating the pore size, shape, distribution and their relative orientation is one of the most important problems of biomaterial engineering. On considering biocompatibility, porous sinters of calcium phosphates have the advantage of being completely osseointegrated, if the implant possesses the correct morphology, where bone completely penetrates the internal porosity, although their application is restricted to places that are not subjected to high stress [1]. The design of the porous fraction in HAp implants has the potential of controlling implant bioactivity and bone ingrowth with stable interfaces and the progressive substitution of the implant by newly formed bone tissue. Macroporosity must be present (open pore diameter higher than  $100\ \mu\text{m}$ ) in order to allow the regeneration of human bone by its growth into the porosity of the ceramic (osteointegration).

The objective of this research is to obtain HAp implants with differential porosities. A porous external layer will promote bone ingrowth and a denser internal layer will give mechanical resistance to the implant. Slip casting was the processing route chosen, as it enables the production of complex forms and a good homogeneity of the material. It was then necessary to study the factors that influence the porosity of the cast walls. The main thought was that, whereas deflocculated suspensions lead to dense cast walls, flocculated ones give rise

to porous walls. It is then necessary to control the rheological properties of the suspensions. If the suspension is flocculated, the particles will combine to form flocs and floc networks (aggregates) and a dynamic equilibrium is established between the aggregate growth and destruction at any given shear rate. The characteristics of the flocs in suspension are determined, among other factors, by the energy of the links between the particles. It can be said that the structure in suspension is a determining factor of the samples obtained by slip casting [2, 3].

The behavior of HAp aqueous suspensions is quite complex because of the changes in the concentration of the hydroxylic groups on the surface due to the suspension parameters or to the thermal treatment, as was pointed out by Galassi *et al.* [4].

In order to optimize the slip-casting process, deflocculants must be used, allowing the use of higher density HAp slips. The addition of compounds that after burnout origin pores allow the control of the porosity during the sintering of the slip-cast bodies. From previous results [5] it was concluded that it is possible to obtain HAp bodies with differential-sized porosity using two different slips: one prepared with the powder as received (internal layer) and the other with the powder after calcination (external layer). Although this pore size in the external layer is still not large enough. It was decided to add polyvinyl polyacrylate (PVC) to HAp slips, in order to obtain an external layer with pore size around  $100\ \mu\text{m}$ . For the production of the denser internal layer HAp slips with an addition of lithium phosphate ( $\text{Li}_3\text{PO}_4$ ) were used, which increases the degree of densification and the mechanical resistance of the sintered implant.

## 2. Experimental procedure

### 2.1. Materials

The starting material was an HAp powder (Merck). It was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IR) and specific surface area (Brunauer–Emmett–Teller; BET). Ammonium polyacrylate (Dolapix CE 64, Zschimmer & Schwarz) was added as deflocculant and PVC was used to create pores with diameter higher than 100  $\mu\text{m}$ .  $\text{Li}_3\text{PO}_4$  was used as the sintering additive to HAp slips to increase densification in the internal layer.

### 2.2. Equipment and procedure

Rheological properties of aqueous suspensions with a 60 wt % concentration were measured with a cone and plate viscometer (Carri-Med).

Solid casting on plaster molds with a water/plaster ratio of 50/100 was used as the conformation process. Cylindrical pellets with differential porosities were obtained by pouring first a suspension of HAp with addition of PVC (20 wt %) into the mold; after wall formation the excess suspension was drained out and a suspension of HAp with addition of  $\text{Li}_3\text{PO}_4$  (1 wt % of Li in HAp suspension) poured in, and the excess of suspension drained out after secondary layer formation. After mold release the samples were dried at 40  $^\circ\text{C}$  for 2 h and then at 110  $^\circ\text{C}$  to constant weight. Sintering was performed at 1150  $^\circ\text{C}$  for 1 h, following a previous heating schedule (heating rate of 2  $^\circ\text{C min}^{-1}$  until 200  $^\circ\text{C}$ , 1 h at 200  $^\circ\text{C}$ , heating rate of 2  $^\circ\text{C min}^{-1}$  until 310  $^\circ\text{C}$ , 1 h 30 min at 310  $^\circ\text{C}$ , heating rate of 2  $^\circ\text{C min}^{-1}$  until 1150  $^\circ\text{C}$  and 1 h at 1150  $^\circ\text{C}$  and cooling down until room temperature), to account for the decomposition of PVC particles. Sintered densities were determined by Archimedes' principle. Samples were characterized by SEM and MP. The processing route is summarized in Fig. 1.

## 3. Results and discussion

### 3.1. Rheological results

The variation of plastic viscosity of suspensions with the amount of deflocculant can be observed in Fig. 2. It can

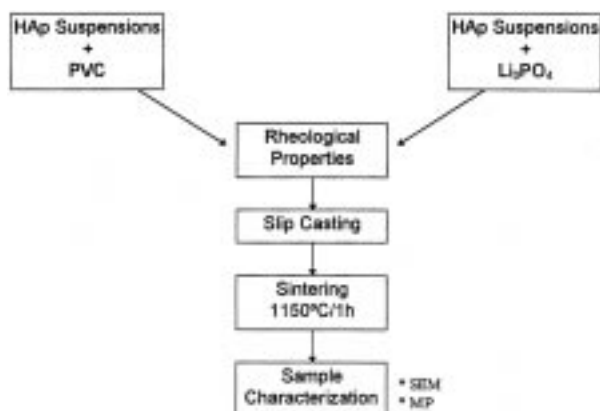


Figure 1 Processing route.

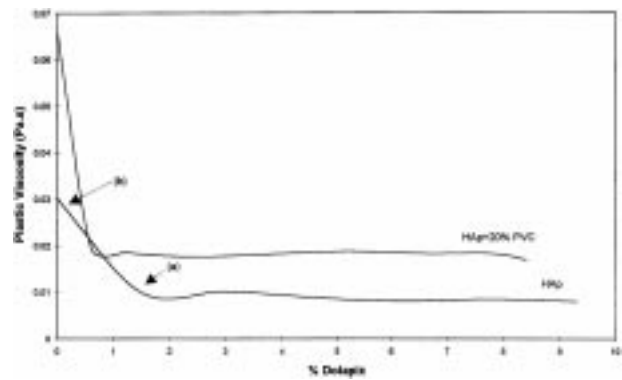


Figure 2 Variation of plastic viscosity of suspensions with the amount of deflocculant.

be concluded that the addition of PVC increases the viscosity of HAp suspensions. It is expected that samples obtained from those suspensions will show a more open structure, when compared with the ones from slips of HAp without additives. For HAp suspensions point (a) corresponds to optimum deflocculation degree whereas point (b) corresponds to a more flocculated stage and a more porous structure is expected in samples when a suspension with this degree of flocculation is used in the slip casting process.

### 3.2. Porosimetry results

#### 3.2.1. HAp samples

Fig. 3 shows the mercury porosimetry results for sintered pellets obtained from suspensions of HAp with an amount of deflocculant corresponding to the optimum point of deflocculation and from suspensions at a more flocculated stage.

It can be seen that samples obtained from slips with an amount of deflocculant corresponding to point (b) on Fig. 2 show a more porous structure. Total porosity is higher than for samples obtained from suspensions with an amount of deflocculant corresponding to the optimum point. Although there are only a small amount of pores of larger size in the external layer. It can be concluded that the variation of the deflocculation degree of suspensions

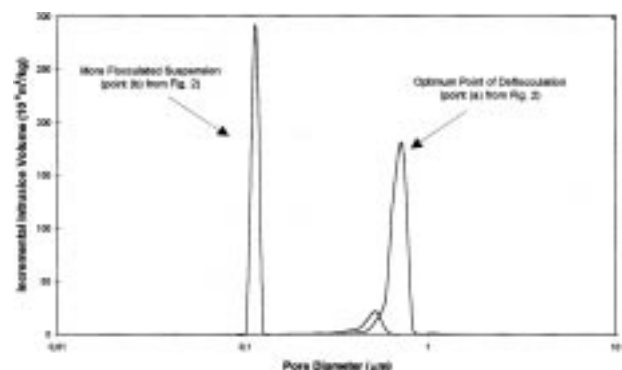


Figure 3 Porosimetry results for sintered pellets of HAp obtained from suspensions with an amount of deflocculant corresponding to the optimum point of deflocculation and from suspensions at a more flocculated stage.

allows the control of the microporosity of HAP samples obtained by slip casting.

### 3.2.2. External layer

Fig. 4 shows the mercury porosimetry results for samples obtained from suspensions of HAP with addition of PVC. It can be seen that there are a significant amount of pores with diameter around 100  $\mu\text{m}$ . The addition of PVC to HAP suspension increases its viscosity and during sintering of the cast bodies PVC is burned out leaving pores.

These results are corroborated by SEM, as can be seen in Fig. 5. Samples show 60% of theoretical density (TD).

### 3.2.3. Internal layer

$\text{Li}_3\text{PO}_4$  was added to HAP suspensions used for the internal denser layer. Fig. 6 shows the micrograph of this layer. Samples show 90% of TD.

### 3.3. Dual layer samples

Fig. 7 shows a micrograph of a dual layer sample where the external layer was obtained from HAP suspension with addition of 20 wt % PVC and the internal layer was obtained from HAP suspension with addition of 1 wt % of

Li. A good compatibility shrinking between the two layers can be observed. The addition of  $\text{Li}_3\text{PO}_4$  increases the relative density of samples, in agreement with results presented in [6]. It was suggested that the HAP will decompose into  $\beta\text{-Ca}_3(\text{PO}_4)_3$  in the presence of  $\text{Li}_3\text{PO}_4$  above 900  $^\circ\text{C}$ . Furthermore, above 1010  $^\circ\text{C}$ , the formation of an eutectic compound between  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Li}_3\text{PO}_4$  is suggested as possible [7]. The liquid phase causes the sudden densification through the arrangement process of HAP particles. During the sintering process Li reacts with PVC, which explains the Li deficiency in the interface between the two layers, originating a gradient in the degree of densification that is responsible for the good compatibility between the external (porous) and the internal (denser) layer.

## 4. Conclusions

From the present investigation the following conclusions can be derived:

1. It is possible that the introduction of gross porosity in HAP bodies can be obtained by slip casting, by

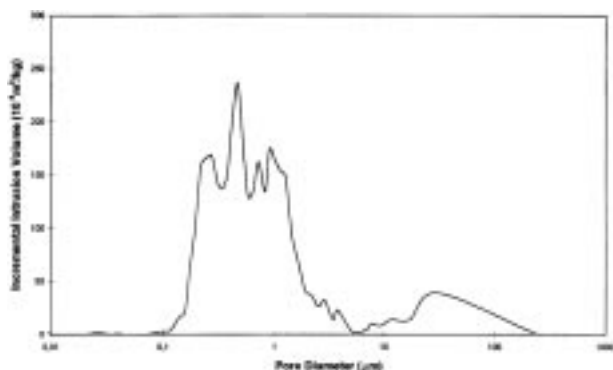


Figure 4 Porosimetry results for sintered pellets obtained from suspensions of HAP with addition of PVC.

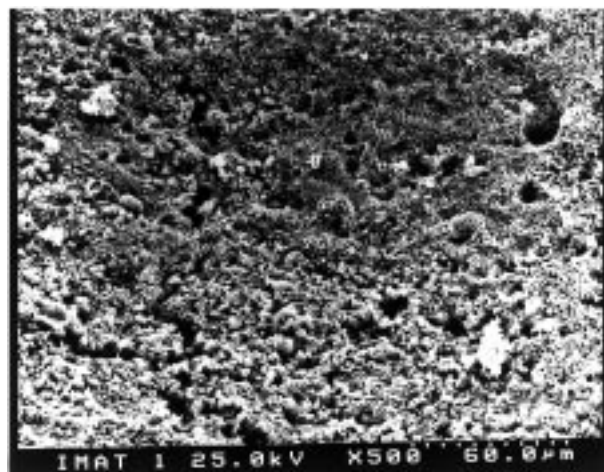


Figure 6 Scanning electron micrograph (internal layer).

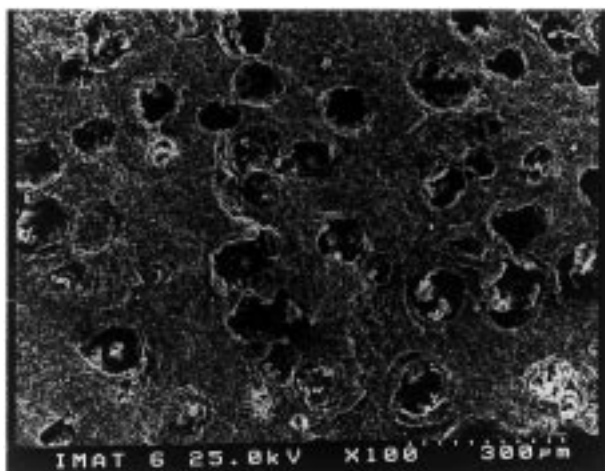


Figure 5 Scanning electron micrograph (external layer).

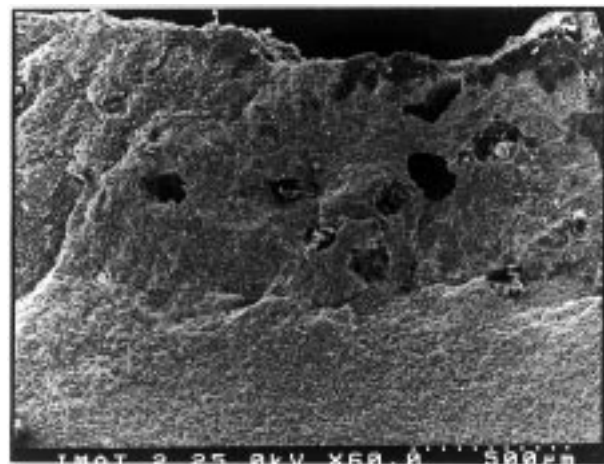


Figure 7 Scanning electron micrograph (interface between internal and external layer).

controlling agglomerate size distribution and by the addition to the slurries of organic compounds that are burning out during the sintering step;

2. A multiple slip casting procedure produces HAP dual layer samples with differential sized porosity and compatible shrinking between the multiple layers.

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