PREPARATION AND CHARACTERIZATION OF POROUS BLOCKS OF SYNTHETIC HYDROXYAPATITE

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***Abstract*— Porous structures were conformed by pressing and heating of hydroxyapatite powders. Samples were obtained in the form of blocks with 47 % porosity. An interval of pore sizes interconnected among 50-120 μm was obtained. The diametrile tensile stress of evaluated samples oscillated between 4 and 21 MPa, according to what has been reported for porous ceramics. The diffraction studies of x-ray of heated samples indicated an increase of hydroxyapatite crystallinity. The microstructure was studied by scanning electronic microscopy. Statistical techniques were employed to determine the certainty of the answer.**

***Keywords*— hydroxyapatite, porous, blocks, preparation, characterization.**

I. INTRODUCTION

The development reached by hydroxyapatite (HAp) ceramic as bone substitute is well known, for its high biocompatibility and good bioaffinity which stimulates the bone reconstruction. These ceramics, in the form of powders or blocks, dense or porous, are widely employed in certain surgical treatments that require bone substitution (Bucholz et al, 1987; Hench, 1991 and Jarcho, 1981).

The ideal artificial implant demands a good biocompatibility and excellent linking with the active bone. It needs also a certain resistance to mechanical load on the implanted bone. However, none of the materials developed so far contain all of these properties. The synthetic HAp, similar in composition to the inorganic part of the bone, presents good biocompatibility and osteoconductivity. But, their fragility is a restrictive condition which limit its use in areas not requiring high mechanical resistance (Abdel-Fattah et al, 1994; Radin and Ducheyne, 1994 and Zyman et al, 1998). The structure of dense bodies is stronger and very capable of uniting with bone but its use limited due to its high brittle character and low osteoconductivity. Despite its weak resistance, the porous HAp is considered as good substitute, due to its better osteoconductivity and quick colonization for the new bone (Boyne, 1987; Hench, 1991, Pilliar et al, 2001).

The biodegradation or bioresorption of implants materials is characterized by changes in their chemical and physical properties after being implanted. In case of the calcium phosphate ceramics, the physical changes include disintegration, lost of the mechanical strength and changes in the porosity; as long as the chemical changes include the formation of other phases and possible transformation of these in the surface of the ceramic (Guillemin et al, 1987; Holmes et al, 1986 and LeGeros, 1993).

Material factors as the structural configuration of the HAp affect the biological answer of implants (Kent et al, 1986 and Schmitt et al, 1997). The porous HAp is more re-arsorbable and more osteoconductive than dense HAp, and it is used as implant material in many experimental and clinical assays (Boyne, 1987; Jarcho, 1981 and Tsuruga et al, 1997). HAp with wide porosity ranges has been used; although there is not general agreement with respect to size, forms, interconnection and classification of pores (El Deeb, 1988); although usually it accepts a size range of grain of 100-300 μm (Ohgushi et al, 1989 and Yamamura, 1992).

Several methods of inducing porosity in the ceramic of HAp have been described in the literature. The simplest methods involve the incorporation of volatile compounds, during the heating process. Materials, as naphthalene and calcium stereate have been used with this purpose. The porosity degree is controlled by the quantity of degradable material added. The pores in calcium phosphate blocks have also been conformed by the addition of hydrogen peroxide (H_2O_2) to the powder, allowing the pores interconnection formed by the gases when escaping. The volume and size of the pores are controlled by the quantity of H_2O_2 added and the heating temperature.

In the present work, we study the influence of such parameters as the pressing pressure and temperature of thermal treatment in the physical mechanical properties of porous blocks of HAp using a variant (dry milling) of the traditional procedures reported in the literature (wet milling) and naphtalene as porogenic agent (Chang et al, 2001).

II. METHODS

2.1 Preparation of the HAp powder

The stoichiometric HAp was synthesized by the reaction between $Ca(OH)_2$ and H_3PO_4, obtaining powders that later on were dried 100°C, milled in ceramic mortar and sifted until achieving a grain size among 150-250 μm.

2.2 Preparation of the blocks

The samples were prepared weighing the HAp and naphthalene as porogenic agent (BDH with particle size smaller than 250 μm) necessary to obtain the desired height and porosity (50 %) and mixed in a porcelain mortar, adding 4 drops of solution 1% of polyvinyl alcohol (BDH). The mixture was pressed in cylindrical

die of stainless steel to pressures of 110 and 220 MPa, for being heated finally in a Termiber furnace with temperature programmable control, to temperatures of 1000, 1100 and 1200°C for 3 h, in air.

2.3 Characterization of porous structures

The microstructure of the HAp blocks was determined by scanning electronic microscopy (SEM) in Hitachi 200 equipment. The samples were also analyzed by x-ray diffraction (XRD) in a Philips X-ray difractometer, using the Kα of Co radiation source. This analysis was used to assure that the heated samples crystallized in the desired structure. In the same way a Nicolett FTIR equipment of infrared was used. The obtained spectra were compared with the data published in the literature (McIntosh and Jablonski, 1956), confirming that the formed structure was the crystalline HAp.

2.4 Mechanical properties

Once the briquettes were obtained, the corresponding study of densities was carried out. The density of the "green" and heated blocks was calculated starting from the weight and dimensions of the sample respect to theoretical density of HAp (3.156 g/cm^3). The bulk density was then calculated from Equation 1 (Ishikawa and Asaoka, 1995).

$$\rho = \frac{4m}{\pi d^2 h} \quad (1)$$

When block is heated, naphthalene was lost, and based on this fact, the porosity (P, expressed in %) was then calculated by Equation 2,

$$P = \left(1 - \frac{\rho_{sample}}{\rho_{HApure}}\right) \bullet 100 \quad (2)$$

Assays of diametral compression (Rudnick and Hunter,1963) were carried out to determine the blocks resistance, using 5 test tubes for sample. They were carried out at room temperature, at a bolster speed of 1 mm/min, like Thomas reports for similar compositions (Thomas et al, 1980).

Table I. Experimental design of the studies

Exp.	X1 (h)	X2 (p)	X3 (T)
1	0.5 cm	110 MPa	1000°C
7	0.8 cm	110 MPa	1000°C
4	0.5 cm	220 MPa	1000°C
10	0.8 cm	220 MPa	1000°C
2	0.5 cm	110 MPa	1100°C
8	0.8 cm	110 MPa	1100°C
5	0.5 cm	220 MPa	1100°C
11	0.8 cm	220 MPa	1100°C
3	0.5 cm	110 MPa	1200°C
9	0.8 cm	110 MPa	1200°C
6	0.5 cm	220 MPa	1200°C
12	0.8 cm	220 MPa	1200°C

The statistical treatment of the results (polynomial multivariable analysis) was carried out by means of the program Statgraphics Plus 2.1 according to the experimental design 2^2x3 (Spiegel, 1977), as described in Table I.

III. RESULTS AND DISCUSSION

The porous blocks of HAp were initially analyzed by IR (Figure 1). The characteristic bands of the $\nu_2(PO_4^{3-})$ is observed at 566 and 601 cm^{-1}, $\nu_1(PO_4^{3-})$ at 954 cm^{-1}, and the $\nu_3(PO_4^{3-})$ to the 1087 and 1022 cm^{-1}. These reflections indicate the classification of the polyhedrons of PO_4^{3-} in the structure of the glass. Besides, at 3566 cm^{-1} a main vibration $\nu(OH^-)$ is observed, joined to bands at 3400 and 1629 cm^{-1} (H-O-H) from water absorption of synthesis process. The band at 628 cm^{-1} is attributed to the OH^- groups (Fowler, 1974).

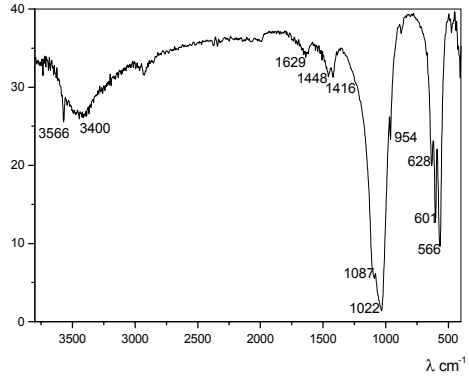

Fig. 1: FTIR spectrum of Hap porous blocks.

Figure 2 shows the XRD pattern of the HAp blocks. The most intense peaks appear in the range of 20-60, 2θ; characteristic of the apatitic phase (JCPDS #9-432). The characteristic peaks (211), (112) and (300) suggest the acceptable crystallinity of the apatitic structure.

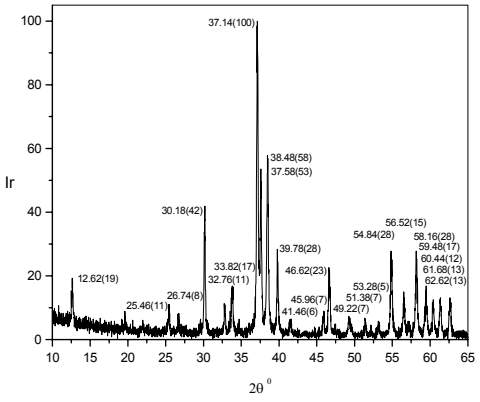

Fig. 2: XRD Diffraction pattern of the HAp blocks.

The Ca/P ratio was 1.65 according to values for stoichiometric hydroxyapatite. There is a good agreement (Table II) between the calculated unit cell parameters and the volumes for both samples (synthesized by us and reported in ASTM).

Table II. Cell parameters

Sample	a=b (Å)	c (Å)	V (Å^3)
HAp (9-432)	9.418	6.884	528.8
HAp (exp)	9.412	6.886	528.3

The HAp blocks porous were examined by SEM (Fig. 3a-b). The pore size of the HAp heated blocks was determined. The total porosity estimated by measure of the blocks density was 47% approximately, and in the case of microporosity, 13%.

The density of the sintered porous HA block was calculated measuring weight and dimensions and the relative density was determined by the ratio of the measured density over the theoretical density of HA (3.156 g/cm^3). The total porosity (P_T) of porous HA is determined by Equation 2.

The macroporosity (P_{MA}) of cylindrical-type porous HA was evaluated from the ratio of areas of pores, produced by the burned naphthalene, to total area in light micrographs made on at least 10 fields of cross-section (Chang et al, 2001). The microporosity (P_{MI}) is:

$$P_{MI} = P_T - P_{MA}$$

Additionally, a much finer microporosity was observed (pore size <5 μm) and a macroporosity among 50-120 μm between the particles inside the heated block. The expected structure, with its porosity three-dimensionally interconnected, is evident for all the samples. The structure seems uniform, from the periphery to the center of the disks, without indications of a gradient.

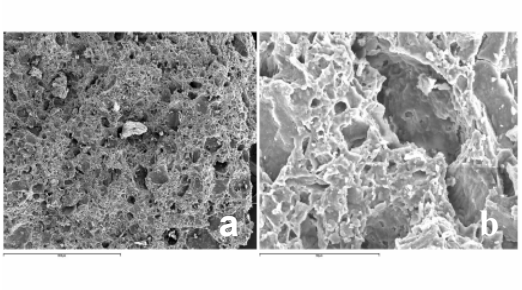

Fig. 3: Scanning electronic microscopy of the HAp blocks showing the interconnected porosity

The results of the statistical study referred to diametral compression stress (DTS) and the density are shown in Table III, where ρ_v represents the density in green of the prepared briquettes and ρ_s the density of the heated blocks and %ρ indicates the porosity percent with respect the theoretical density of the HAp, DTS the diametral tensile stress in MPa and σ_{DTS} its standard deviation.

Table III. Density, porosity and DTS of the samples

Exp.	ρ_v(g/cm^3)	ρ_s(g/cm^3)	P_T	$\overline{P_T}$	DTS ± σ_{DTS} (MPa)
1	1.577	1.083	34.3	34.5	9 ± 1
7	1.609	1.095	34.7		9.4 ± 0.7
4	1.408	0.764	24.2	24.6	4 ± 1
10	1.440	0.787	24.9		5 ± 2
2	1.553	1.493	47.2	46.4	11 ± 2
8	1.521	1.442	45.6		8.2 ± 0.9
5	1.513	1.484	47.0	46.9	5.6 ± 0.6
11	1.543	1.476	46.7		4.4 ± 0.2
3	1.577	1.510	47.8	49.1	21 ± 4.
9	1.599	1.592	50.4		19.2 ± 0.9
6	1.633	1.493	47.2	47.5	16 ± 4
12	1.617	1.506	47.7		19 ± 2

It is observed that good strength results are obtained by the compression to low pressures, what can suggest us that we are in the pressures frontier that causes "overpressing" in the material after the sintering process.

The proposed polynomial was: $Y = ß_0 + ß_1X_1 + ß_2X_2 + ß_3X_3 + ß_{12}X_1X_2 + ß_{13}X_1X_3 + ß_{23}X_2X_3 + ß_{123}X_1X_2X_3 + ß_{33}X_3^2 + ß_{133}X_1X_3^2 + ß_{233}X_2X_3^2$. For DTS we thought about quadratic terms of temperature, only variable with three levels, what presupposes their importance in the analysis. The resulting polynomial DTS = 7.2575 - 1.86 p + 6.03375 T + 5.68125 T^2 shows the temperature influence, because the linear and quadratic terms are significant to the statistical analysis. Besides, a small inverse influence of the pressure is observed. A slight increment of the DTS exists as the pressure value decreases. The biggest values of DTS were obtained at 1200ºC.

For density, the resulting polynomial was $\rho = 1.47375 + 0.2965\ T - 0.245\ T^2 + 0.0655\ PT + 0.01625\ hT^2 - 0.09125\ PT^2$, where the influence of the temperature is emphasized even more. The most significant terms are those containing temperature only, both linear and quadratic. The term following in importance is the one where the square temperature is accompanied by pressure, as we saw before. It is remarkable the fact that one obtains the biggest porosity percent in the case of 110 MPa and 1200°C, predictable condition as better in case of DTS.

IV. CONCLUSIONS

Our objective in this study was to develop porous blocks of HAp with an orderly structure of pores to facilitate bone integration. The conditions of the described process gave the desired structure, that is to say 47% of pores volume interconnected with a diameter average of 100 μm approximately and a DTS maximum of 21 MPa. From the obtained results and the statistical analysis, the best conditions for obtaining Apafill-BP would be to use low pressures and high temperatures, that is to say: 110 MPa and 1200ºC, the height and density values having no influence on the DTS.

These results indicate that porous structures of calcium phosphate can be manufactured, formed by heating to high temperatures with convenient porosity and geometry for the growth of bone, with the resistance required for certain applications of bone substitutions. The use of dry milling represent a substantial profit in time and money because reduce the prepararion of samples in two pases at least, and eliminate the process of drying (electric power including). The employment of animal models is recommended to confirm the utility of the proposed structures. The results exposed in this work represent the initial phase of investigation of an interesting material as bone substitute which in later studies will be evaluated in its biological perfomance.

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