CHARACTERIZATION OF HYDROXYAPATITE SCAFFOLD USING CORN STARCH AS POROUS AGENT

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Abstract. *The searching for new biomaterials for increasing the life quality of people that had had accidents have been increasing everyday, and makes researchers have been developing new materials, since technology have advanced on this area. Hydroxyapatite is a bioceramic based on calcium phosphate and very utilized for bone substitution due to its excellent biocompatibility that makes it an excellent biomaterial for long time implants. As a porous material, it has a large range of applications, permitting a large contact area between implant and host tissue and then increases interface strength and avoid implant mobility. Interconnected macroporosity presence provides a permeable reticulate that allows incorporation and bone tissue growth in its interior. The aim of this research was evaluate the structural characteristics of porous ceramics made by hydroxyapatite and corn starch synthesis sintered at three different temperatures. Samples were made with 100% hydroxyapatite and 70% hydroxyapatite – 30% corn starch. Samples were sintered at 1250ºC, 1300ºC and 1350ºC and characterized by x ray fluorescence, x rays diffraction and scanning electronic microscopy plus essays using Archimedes method. It was possible to obtain porous hydroxyapatite samples using corn starch as veicule for porosity and that the better temperature for this end was 1300ºC, due to energy saving reasons, also because the project aims the use of economic and durable means, in order to make the scaffolds manufacture feasible as a medical implant.*

Keywords*: Hydroxyapatite, Corn Starch, Porosity.*

1. INTRODUCTION

Along of years, mankind has witnessed an improvement of technology applied to human health, increasing life expectancy, even though not every part of the body can maintain their functions with the aging process. It is necessary that bones and cartilage support the body's aging, even if the cells that produce them become less active with time. Other organs, such as kidneys, heart and liver must be operated to have a higher lifetime. The researchers' challenge is to develop new biomaterials able to replace damaged organs or tissues, and thus increasing people life quality "Ratner, (1996)".

Tissue engineering has been developed in order to replace, repair or rebuild tissues or organs lost or damaged due to accidents or serious diseases through the use and development of new materials that are biocompatible, bioabsorbable, with porosity among other characteristics "Park, (1992)"; "Langer, (2000)"; "Lanza, (2000)".

Scaffolds are a kind of porous tridimensional net and they are used on tissues regeneration to their natural state and functions, which is fundamental for tissue engineering. They can be classified as scaffolds that induce migration and cell growth and as carrier scaffolds for autogenous ostheogenic cells, which were colonized inside bioreactors and then redeployed on the patient. Those scaffolds can be natural or synthetic. "Park, (1992)"; "Langer, (2000)"; "Lanza, (2000)".

One of the biomaterials used to bone growth is hydroxyapatite, a bioceramic based on calcium phosphate due to its excellent biocompatibility, once it's similar to bone tissue, making it an excellent biomaterial for long permanent implants "Le Geros; Le Geros (1990)".

As porous material, hydroxyapatite is used for bone implants, mainly on reconstitution, repairs and bone cavities filling, due to inflammatory processes, accidents and osteoporosis "Liu, (1996)"; "Fabri, (1995)"; "Ravaglioli and Krajewaki, (1992)"; "Hench, (1998)", which permits a higher contact area between the implant and the host tissue, improving the interface strength and avoid implant mobility. Interconnected macroporosity presence provides a permeable reticulated that permits a bone tissue incorporating and growth on its interior "Ravaglioli and Krajewski, (1992)"; "Hench, (1998)".

There are many methods to produce porous ceramic bodies based on organic materials addition, such as potato peel, corn starch, wax spheres, almond crust, etc. "Prado da Silva *et al.* (2002a e b)"; "Lemos, (2000)", to obtain homogeneous microstructure of pores.

This research aimed to evaluate structural characteristics of porous hydroxyapatite bodies made by adding corn starch and sintered at different temperatures. Samples were characterized by scanning electronic microscopy (SEM) and X rays diffraction (XRD), thus physical properties such as density and post-sintering porosity.

2. MATERIALS E METHODS

2.1. Hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) obtained by precipitation method.

Figure 1 indicates the used method to obtain hydroxyapatite by precipitation method.

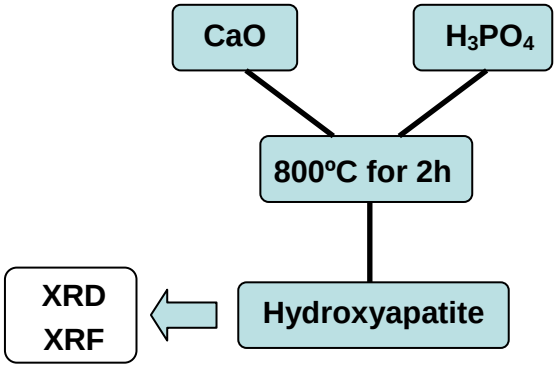

Figure 1 – Flowchart of obtained hydroxyapatite method.

Precipitation occurs by mixing CaO (Vetec, Brazil) and H_3PO_4 (Lafan, Brazil) with 0.5 mol/L concentration. Initially solution was heated and stabilized at 90ºC with constant agitation. After stabilization phosphoric acid was slowly added to solution, permitting that a precipitation occurred. This precipitated was filtrated, dried at stove and calcined at 800ºC for 2 h "Rigo, (1995)".

2.2. Making samples.

Samples were fabricated with 70 % of hydroxyapatite plus 30% of commercial corn starch and for comparison were produced samples with 100 % HA. The mixtures were prepared by ball mill during four hours.

After homogenization, powder was sifted through 80 mesh sieve, uniaxially pressed (± 3 t) as tablets with 6 mm thickness and 12 mm diameter. For each analysis was used ten samples and then measured the size with a high precision caliper ± 0,005mm and also, were weighed using a digital scales with precision ± 0,001g.

After pressing, samples were heated at 500ºC at 10ºC/min for corn starch evaporation for two hours and then sintered at 1250ºC, 1300ºC and 1350ºC during two hours.

HA powder was characterized by XRD and XRF, using the standard JCPDS for the first analysis. Samples density and porosity were analyzed by water absorption test using the Archimedes method and pores morphology was observed by SEM after sintering.

3. RESULTS AND DISCUSSION

3.1. Hydroxyapatite X Ray diffraction (XRD) and X Ray Fluorescence (XRF).

It was possible to analyze the hydroxyapatite powder using the X Ray Diffraction, and when compared with the JCPDS (09-0432) standard, HA powder presented main diffraction peaks, as shown in Figure 2.

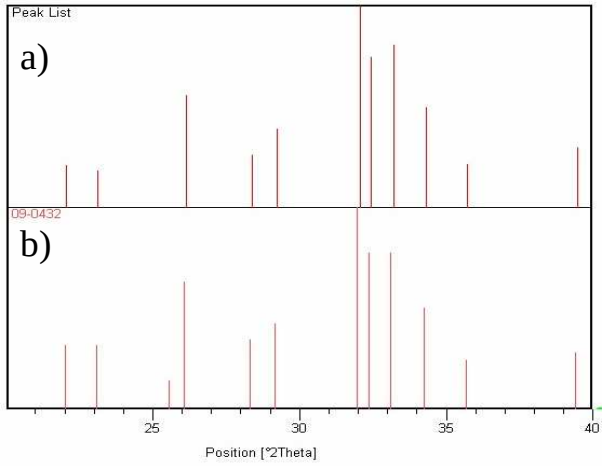

Figure 2 – X Ray diffraction, [a) Peak List] sample; [b) 09-0432] JCPDS standard.

XRF was performed to analyze of obtained HA chemical composition, as shown in Table 1. There's no evidence of impurities and Ca/P ratio equals to 1,67. This result is in accordance to the literature "Fulmer *et al.* (1992)".

Table 1 - Ca/P ratio results of the XRF.

Elements	**HA (%)**
Ca	38,00
P	17,50
O	44,00
Ca/P	1,67

3.2. Density and Porosity

The comparative physical properties results between the pre-sintering relative density (PSRD) and the post-sintering relative density (PoSRD) can be observed at Table 2 and Figure 3.

Pre-sintering relative density values for pure hydroxyapatite were near 63%, which contributed for decreasing density and porosity after the synthesis. For samples with corn starch, those values presented less than 60%, once corn starch was burned out at 500ºC, leaving more pores at samples.

Table 2 – Comparative physical properties results between pre-sintering relative density (PSRD) and the post-sintering relative density (PoSRD).

Samples	**PSD (1) (g/cm3)**	**PSRD (%)**	**PoSD (2) (%)**	**PoSRD (%)**
	1250ºC			
HA	1,47 ± 0,01	61,97 ± 0,37	2,28 ± 0,07	91,29 ± 3,07
HA+ CS	1,40 ± 0,01	58,68 ± 0,35	2,10 ± 0,06	88,37 ± 2,70
	1300ºC			
HA	1,47 ± 0,01	61,75 ± 0,29	2,04 ± 0,26	85,64 ± 11,15
HA+ CS	1,39 ± 0,01	58,57 ± 0,36	1,37 ± 0,07	57,56 ± 3,09
	1350ºC			
HA	1,48 ± 0,01	62,20 ± 0,50	1,89 ± 0,08	79,46 ± 3,33
HA+ CS	1,40 ± 0,01	58,71 ± 0,23	1,47 ± 0,13	61,67 ± 5,48

Where: (1) Pre-sintering density (PSD); (2) Post-sintering density (PoSD)

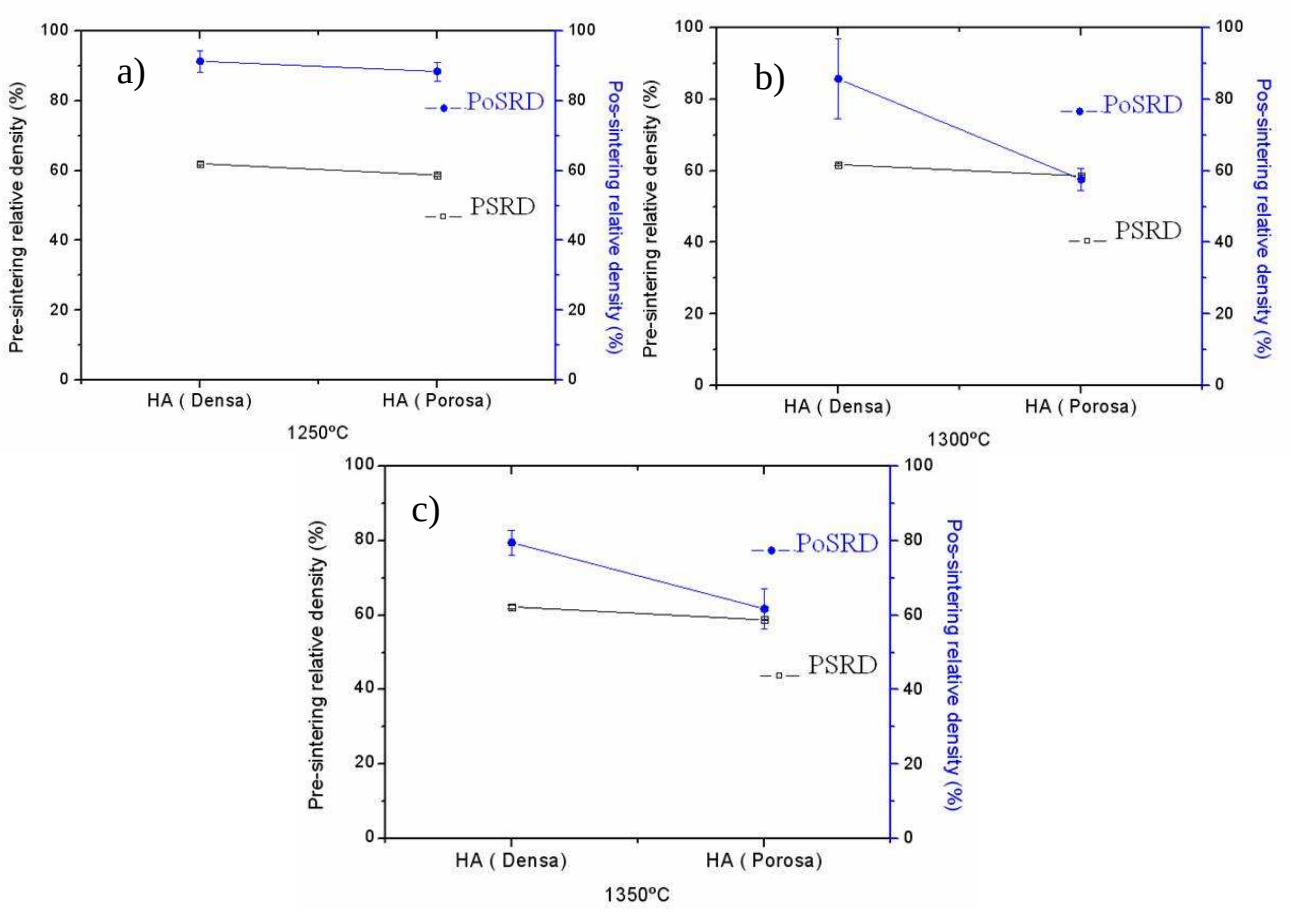

Figure 3 – Pre and post-sintering relative density of the samples analyzed at: a) 1250ºC; b) 1300ºC; c) 1350ºC

Results of post-sintering porosity (PoSP), water absorbtion (WA), post-sintering density (PoSD) and post-sintering relative density (PoSRD) are indicated on Table 3 and Figure 4 shows results concerning the post-sintering porosity (PoSP) and post-sintering density (PoSD).

Table 3 – Post-sintering porosity (PoSP), water absorption (WA), post-sintering density (PoSD) and post-sintering relative density (PoSRD) of the samples.

Samples	PoSP (%)	WA (%)	PoSD (%)	PoSRD (%)
	1250ºC			
HA	0,58 ± 0,36	0,26 ± 0,17	2,28 ± 0,07	91,29 ± 3,07
HA + CS	0,47 ± 0,51	0,23 ± 0,25	2,10 ± 0,06	88,37 ± 2,69
	1300ºC			
HA	2,82 ± 1,71	1,38 ± 0,88	2,04 ± 0,26	85,64 ± 11,15
HA + CS	11,65 ± 0,72	8,51 ± 0,25	1,37 ± 0,07	57,56 ± 3,09
	1350ºC			
HA	1,07 ± 0,45	0,57 ± 0,24	1,89 ± 0,08	79,46 ± 3,33
HA + CS	14,18 ± 0,89	9,68 ± 0,38	1,47 ± 0,13	61,67 ± 5,48

As sintering temperature increase, porosity and water absorption increase also, whereas relative density decreases. This behavior happened for both pure HA and HA + CS. Those results are in accordance with literature.

Therefore it is advisable to use temperature max of 1300ºC at sintering, for reasons of economizing electric power, as well the results has been close to the result of 1350ºC, the project seeks to use economic means and durable so that it is feasible manufacturing as a medical implants.

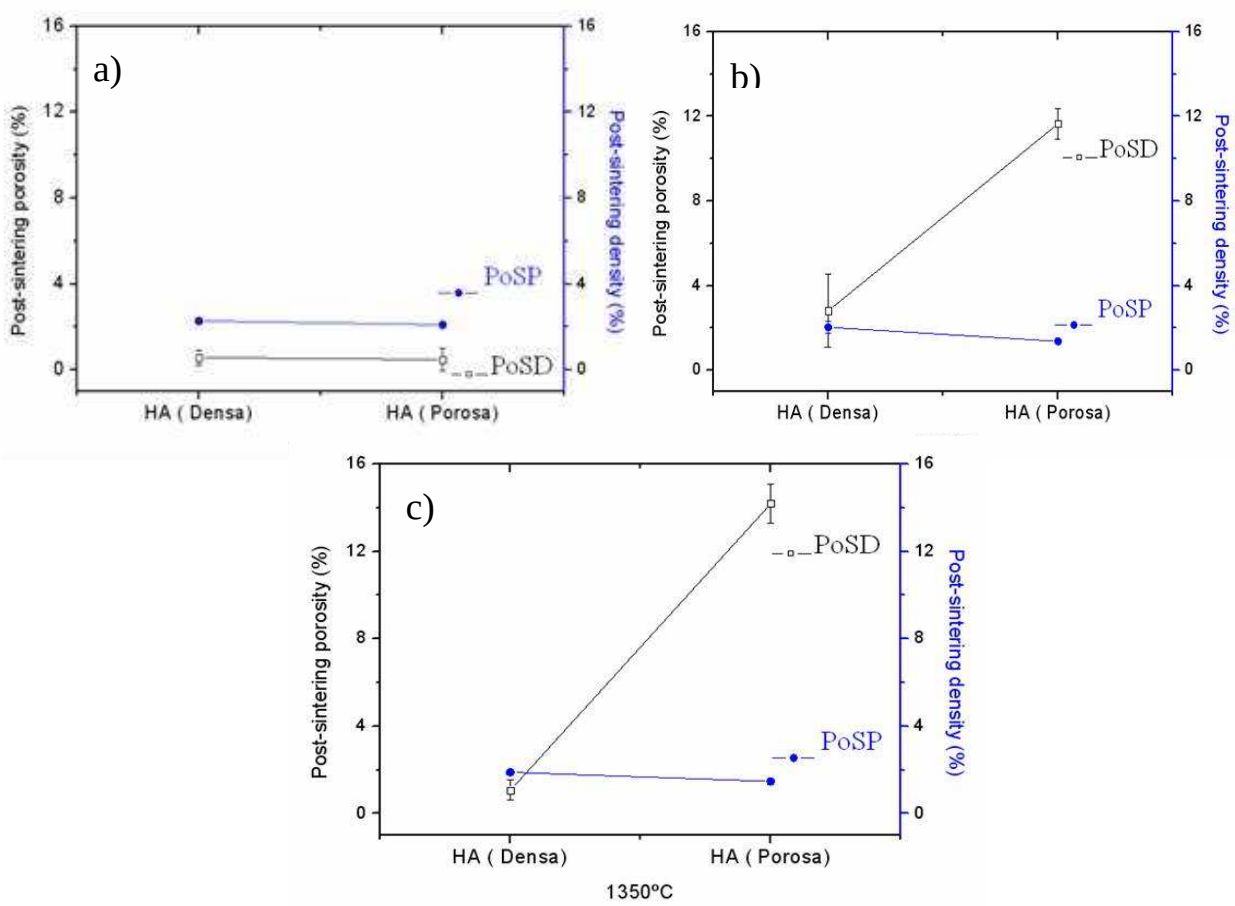

Figure 4 – Porosity and post-sintering density of samples analyzed at: a) 1250ºC; b) 1300ºC; c) 1350ºC.

3. 3. Scanning Electron Microscopy (SEM).

Scanning Electronic Microscopy (SEM) was performed to study samples microstructures and micrographs can be seen in Figures 5, 6 and 7, with the following increases: (a) 500x and (b) 1000x. It is observed that samples sintered at 1250 °C were not possible to visualize pores morphology. As the sintering temperature increases, it can be observed no significant changes on dense HA samples at 1300ºC and 1350°C respectively, unlike the samples of HA + CS (porous HA) where pores are rounded, interconnected and well distributed.

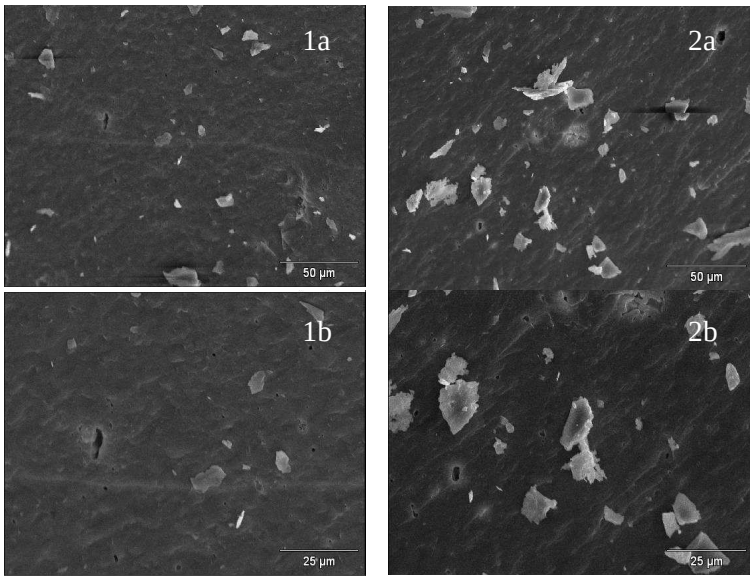

Figure 5 – SEM imagens; samples sintered at 1250 ºC ; (1) Dense HA; (2) Porous HA.

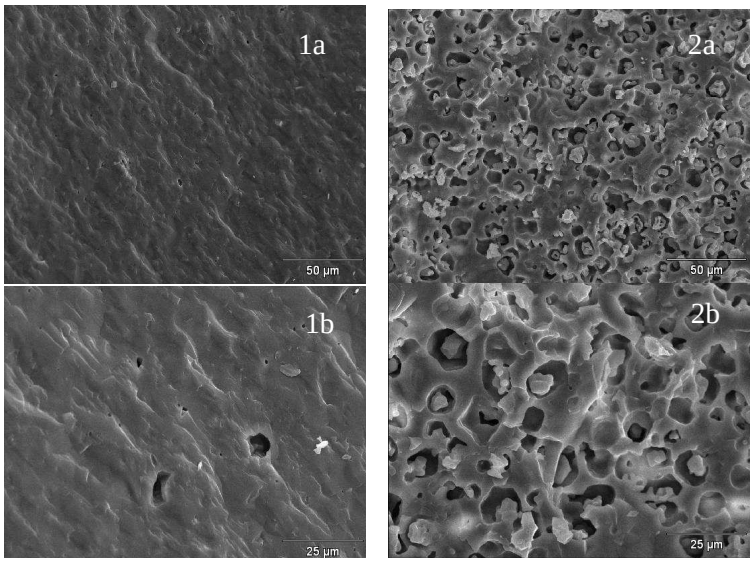

Figure 6 – SEM imagens; samples sintered at 1300ºC; (1) Dense HA; (2) Porous HA.

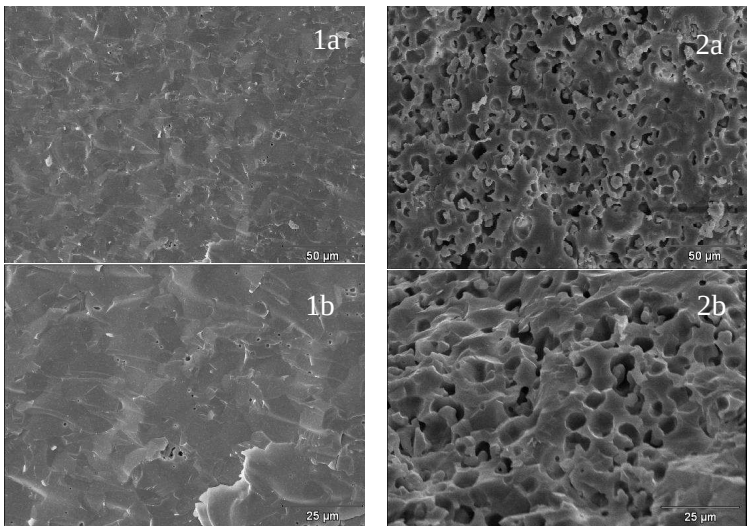

Figure 7 – SEM imagens; samples sintered at 1350ºC; (1) Dense HA; (2) Porous HA.

The reason of the use of porous ceramics is to provide location for bone tissue growth and implant fixed biologically, where pore size should be large enough to accommodate cells, leaving around 100 to 200 µm in diameter and pore minors between 75 to 100 µm resulting in growth of non-mineralized osteoid tissue. Even smaller pores, between 10 - 75 µm only allow penetration of fibrous tissue, which helps in determining the mechanical part. "Hulbert *et al.* (1971)"; "Karageorgis and Kaplan, (2005)".

Pores with different diameters can be used to allow neovascularization, fibroblasts growth and for osteoid matrix for bone regeneration "Klawiter, *et al*. (1971)" and "Whang, *et al.*(1999)".

It can be observed in Figures 5, 6 and 7 that obtained pores in samples sintered at 1300°C and 1350°C are in appropriated size for penetration of fibrous tissue, which helps in setting mechanical part.

4. CONCLUSIONS

The hydroxyapatite sintered at the laboratory showed similar with the JCPDS standard, when compared the crystalline planes. The best temperature for the achieve porous tablets was the 1300ºC, because the density showed lower than 63%, and the morphology was very similar with the samples at 1350ºC and for reasons of economizing electric power, and the project aimed at the use of economic means and durable, so they are viable to manufacture the same as a medical implant.

Is possible to observe those results analyzing the graphics and the SEM images, where is possible observe the porous, which showed interconnectivity and well distributed.

5. FINAL CONSIDERATIONS

The results were possible to identify an optimum temperature and show that it is possible to obtain a porous block HA using commercial corn starch as a porous medium. In continuation of this work will be added to different proportions of a bioinert ceramic material to improve the mechanical properties of the samples and analyze them through mechanical characterizations.

6. ACKNOWLEDMENTS

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8. RESPONSIBILITY NOTICE

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