Mechanical and Microstructural Characterizations on Commercial and Synthesized by the Sol-Gel Method Using Chicken Egg Shells as Precursor Hydroxyapatite

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ABSTRACT

The purpose of this work is to determine one of the most important mechanical properties of brittle materials, the hardness. Our work material is called hydroxyapatite (HAP), in this case, using chicken egg shells as precursor. Once considering the experimental parameters of force and time of the indentation, the Vickers microhardness measurements were obtained for both for HAP, synthesized from chicken egg shells and commercial hydroxyapatite for comparison purposes. The microstructural characterization of the materials, as well as their specimens, has been performed by the microscope scanning, x-ray diffraction and thermogravimetric analyses.

Key Words: Hydroxyapatite, Chicken Eggshells, Vickers Microhardness, Mechanical and Microstructural Characterization.

1 INTRODUCTION

Considering the advances in research on biocompatible materials, hydroxyapatite (HAP) has proven to be an important alternative for bone repairs and orthodontics implants. Due to its similarity to the inorganic phase of bone tissue and its osteoconductive properties (Andrade, 1998), HAP is a ceramic material that does not have any rejection. In general, one of the most important characteristics of HAP researches is the search for improving the mechanical properties of synthesized HAP, obtained through the use of different chemical methods and precursor materials. Regarding measurements of

microhardness, other mechanical properties can be determined from them such as the coefficient of fracture toughness (K_{IC}), modulus of elasticity (E) and analysis of the effects of hardening (Muralithran & Ramesh, 2000) in plastic behavior.

2 MATERIALS AND METHODS

Using a uniaxial hydraulic press (M. Moutinho - Machine Operators, General Tools and Abrasives, model EVA 6052), we have produced from the hydroxyapatite powders (commercial and synthesized from egg shells) applying a compressive force of 4000 kgf during 20 minutes, 6 of chicken HAP from chicken egg shells and 3 of commercial HAP, a 4340 steel matrix with a diameter of 15.20 mm was used, totalizing an applied average tension of approximately 216.25 MPa. Subsequently, there was a sintering process, which occurred in a Muffla furnace of the manufacturer Quimis at 1000 °C for two hours. It is worth mentioning that the densities of the specimens were determined before and after the sintering process, by measuring the masses and the geometric dimensions of the specimens. The preparation of the test specimens for Vickers microhardness measurements consisted of polishing the surfaces to be tested. After this step, 36 microhardness measurements Vickers were obtained on the surfaces of the 6 HAP test specimens synthesized from chicken eggshells and other 36 measurements were obtained on the 3 HAP test specimens commercial. The measurements were performed in a microdurometer, brand Panambra model Pantec HDX-1000TM. Three procedures were carried out in order to structurally characterize the materials and specimens produced with them, the microscopic analyzes were carried out with two hydroxyapatites used in this research, x-ray diffraction in specimens and powders, and the thermogravimetric analysis of both powders. The microscopic analysis of the powders of the one two HAPs has been performed to determine the mean particle size of each of the powders used, SEM-FEG equipment, model JEOL JSM 7100F, from NanoFab, Laboratório de Nanofabricação do Programa de Pós-Graduação em Engenharia Mecânica da Universidade do Estado do Rio de Janeiro. The x-ray diffraction has been applied to demonstrate the present phases in the samples tested. The x-ray diffraction was carried out for both hydroxyapatite powders (the one from egg shell of chicken and commercial), for the non-sintered specimens of the two hydroxyapatites, for sintered and sintered specimens and also tested for these two materials to be confronted. The diffraction was performed in PANalytical equipment, XPD X'Pert PRO model from the Laboratório de Difração de Raios-x do Centro de Brasileiro de Pesquisas Físicas, and the refinements, were obtained with the help of the software TOPAS, which uses the Rietveld method. To complement the characterizations microstructures, a thermogravimetric analysis was performed on the thermo-balance of the Netzsch, model STA 449 F3 of the Laboratório de Análises

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3 RESULTS

The experimental parameters for determined Vickers microhardness tests were: 200 gf for the force of application of the indenter on the surface of the specimens (showed a better impression between the tested forces, 50 gf, 100 gf) and 15 s for the time of indentation in accordance with ASTM C1327-15 [28]. After setting these parameters the Vickers microhardness measurements were performed on the test specimens of the HAPs, derived from hen eggs and commercial chicken. In those, the results obtained were:

Average: 35,846 HV

Standard Deviation: 4,198

Amplitude: 19,347 HV

And in sequence, for commercial HAP it was obtained:

Average: 40,860 HV

Standard deviation: 5,952

Amplitude: 21,503 HV

It is noted that the mean of the measurements done on the HAP specimens of eggshells is contained in the dispersion in relation to the mean values determined for the bodies of commercial HAP test. The highest mean of commercial HAP values in relation to the mean calculated for the measured values in the samples of HAP synthesized from chicken egg shells, is associated with a greater compaction, density, of those in relation to these. It is seen, that the average particle size of commercial HAP powders is smaller than those of HAP from chicken egg shells.

3.1 GRAFICS

The histograms relating the number of measurements (vertical axis) with the respective ranges of Vickers microhardness measurements for each type of HAP (horizontal axis), are shown below:

Figure 1: Histogram for chicken egg shells HAP.

Figure 2: Histogram for commercial HAP.

Some of the main results of the tests related to microstructural characterization are commented and can be seen below: Scanning electron microscopy showed that the particles of commercial HAP powder are lower than those of HAP powder from egg shells, which are more compacted in commercial HAP test specimens. For the analysis of the x-ray diffraction, the phases obtained from the diffractograms

of HAP specimens synthesized chicken egg shells sintered and tested in the microdurometer, as well as the sintered and tested commercial HAP samples. Respectively, we obtained:

Chicken Egg Shells

HAP = 8.59%

Beta-TCP = 5.61%

Whitiloquita = 85.80%

Commercial

HAP = 39.32%

Beta-TCP = 9.64%

Whitiloquita = 51.04%

Figure 3 - Comparison between the diffractograms of synthesized chicken egg shells and commercial HAP sintered samples, and sintered and tested in the microdurometer HAPs samples.

The thermogravimetric analysis performed with the powders of the two HAPs showed hydroxyapatite synthesized from chicken egg shells close to 100 °C, process of vaporization of water, a dehydration of the material at this step, which was present in the material. Subsequently, there is a mass loss in around 1000 ° C, possibly associated with adsorption of gases during this stage of the test, raising the suspicion that this material is microporous. As there is a marked adsorption, the suspected microporosity of the hydroxyapatite synthesized from chicken eggs may be confirmed by a BET analysis

in a future work. All of the features of the thermogravimetric analysis highlighted above can be verified in the following graphs, which represent the analysis for synthesized HAP powder from chicken egg shells and commercial HAP powder, respectively.

4 CONCLUSION

The dispersion around the mean of the measurements made on the hydroxyapatite specimens is greater than the dispersion of the measurements performed on the HAP test specimens chicken egg shells as a precursor to Vickers microhardness values obtained for them. The observation of statistical data obtained still allows us to verify that the calculated average for microhardness values Vickers on the specimens of the synthesized material from eggshells, is contained within the dispersion around the mean obtained for the bodies of commercial hydroxyapatite, or the standard deviation observed in the measurements for commercial HAP for the values verified on the hydroxyapatite specimens from eggshells of chicken. The higher density of commercial hydroxyapatite specimens than the density of chicken egg shells hydroxyapatite specimens, helps to understand the highest mean value of Vickers microhardness for that material in relation to this. There is a reasonable congruence between the Vickers microhardness values measured for both materials, with the measures averages differing by only 12.27%. With respect to SEM analysis, it has been observed that the mean particle sizes of commercial HAP are generally smaller than those of HAP from chicken egg shells, it can be understood the higher compaction/density of the commercial HAP specimens and in consequence, the highest Vickers microhardness average observed in them. Due to the differences in the percentages of the phases observed in the samples used for microhardness measurement, the measurements could not have statistical data with greater congruence than that observed. For the thermogravimetric analysis, it could be observed a gradual loss of mass in commercial hydroxyapatite powder (commercial HAP powder shows a single phase) and for egg shell HAP powder, a significant mass gain around this same level of temperature with consequent mass loss at about 1000 °C is observed. This distinct behavior is related to the three phases present in the HAP powder from eggshells of chicken. In addition, it is suspected that the latter material is microporous due to an accentuated adsorption of gases around 1000 °C.

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