CALCIUM PHOSPHATE CERAMICS PREPARED FROM NATURAL WASTE MATERIALS

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Calcium Phosphate Ceramics Prepared from Natural Waste Materials

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Abstract. Calcium phosphate bio-ceramics have widely been developed in biomedical applications due to their excellent biocompatibility, bioactivity and osteoconduction characteristics. These materials may be employed in many ceramic forms such as porous blocks, dense body, granular forms and hybrid composites to fill bone defects or voids. The main component of calcium phosphate ceramics is calcium. One of the means to produce calcium phosphate is by extracting it from natural sources such as eggshells, animal bones, cockles and coral as biogenic materials that are naturally available. Finer particles of the resulting powder promises better bioactivity and mechanical properties of bio-ceramic materials. This present research aims to synthesize calcium phosphate powders from raw materials, such as egg shell and bovine bone. The chemical and morphological properties of the materials are studied and the phase stability and mechanical characteristics of the resulting granulated bio-ceramic material are evaluated. The final products are porous bio-ceramics used as ceramic scaffolds for spongy bone application and dense ceramics used for load bearing applications.

Introduction

Calcium Phosphates. Bioceramics and their potentials have recently been explored particularly in the applications of bone tissue engineering as scaffolds that encourage regeneration of diseased and damaged hard tissues [1]. Calcium phosphates (CP) as hydroxyapatite (HA) and tricalcium phosphate (TCP) are accepted bioceramics due to the bioactive and biocompatible properties of HA that allows bonding with the surrounding tissues whereas TCP has a higher rate of biodegradation compared to HA which induces faster bone growth [2]. Hard tissue or bone replacements are synthesized mainly from bioactive and strong materials, which have similar chemical and phase structures with our natural bone minarals, biological HA [3].

Biogenic Raw Materials. CP can be synthesized from calcium extracted from calcium carbonate-based natural materials such as eggshells [4], cockles [5], seashells [6], snail shells [7], oyster shells [8], cuttlefish shells [9] and coral [10]. These raw materials are processed to obtain pure calcium oxide (CaO) and then used as starting materials to synthesize calcium phosphates. Other biogenic materials from calcium-based wastes are animal bones [[11], 12, 13], teeth [14] and fish scales [15] where natural calcium phosphates are extracted through calcination procedures.

Hydrothermal Synthesis Method. There are many methods to prepare synthetic CP. They include hydrothermal [[16], 17], wet chemical precipitation [18], sol-gel process [[19],

20] and bio-mimetic synthesis [21]. Hydrothermal synthesizing method is currently one of the preferred methods to prepare nanoparticles of biomaterials [22]. High degree of crystalline production is shown by the small-sized single crystals [23] and whisker-like [3] CP developed through hydrothermal synthesizing method. Hydrothermal synthesis procedure involves single or heterogeneous phase reactions in aqueous at temperatures more than 25 °C and pressures exceeding 100 kPa to initiate crystallization directly from solutions [24].

Porous and Dense Ceramics. Our bones are created in multi structural levels. Implant scaffolds should have structures that mimic our bones because of their function as matrix for tissue growth. From the macroscopic view, our bones are generally categorized as; cancellous or porous bone and cortical or dense bone [1]. Both types have a degree of porosity to support osteoconductivity and assure bone vascularization [25], likewise porous parts of bones except that the pores are visibly seen with our naked eyes. Moreover, both HA and TCP are used in the form of dense granules, porous blocks and scaffolds and sintered bioceramics [3]. Dense ceramics CP are preferred for the mechanical properties compared to porous ceramics [6].

This current work aims to report the preparation procedures of dense and porous ceramic bodies from biogenic raw materials, which are egg shells and bovine bone. The raw materials are processed to obtain HA powders before being calcined and formed into ceramic bodies and comparing them with the structural and mechanical properties of TCP ceramic bodies.

Methodology

Materials. Eggshell wastes were collected from household kitchens. Di-ammonium hydrogen phosphate, $(NH_4)_2HPO_4$ (R&M Chemicals, UK) was chosen as the phosphate ion source. While other chemicals used were Duramax (Dow Chemical, Philadelphia) and polyvinyl alcohol, PVA (Merck, Germany).

Waste Material Preparation. Eggshells were washed thoroughly before being dried and crushed into powder. The prepared eggshell powders were thermally treated in air atmosphere at 1000 °C for 3 hours of holding time and 5 °C/min of heating and cooling rate to convert calcium carbonate ($CaCO_3$) to calcium oxide (CaO) and eliminate the organic substances. The resulting calcium oxide will be used as one of the starting material during hydrothermal synthesis of HA.

Hydrothermal Synthesis. HA powder from eggshells (*HA-ES*) was prepared hydrothermally (Fig. 1). $(NH_4)_2HPO_4$ was dissolved in dH_2O and was continuously stirred until a homogeneous solution was obtained. The CaO slurry was prepared and was continuously stirred using magnetic stirrer. $(NH_4)_2HPO_4$ was added drop-wise to the CaO slurry by stoichiometric amounts with 300-350 rpm constant stirring for 5 hours at 85-90 °C until paste was obtained. The mixture was dried overnight at 120 °C before calcined in a Carbolite UK chamber furnace at 600 °C for 2 hours constant temperature and heating rate of 10 °C/min. The hydrothermal synthesis process may be represented by Eq. 1 below:

$$10\ CaO + 6\ (NH_4)_2HPO_4 + H_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12\ NH_3 + 9\ H_2O \quad (1)$$

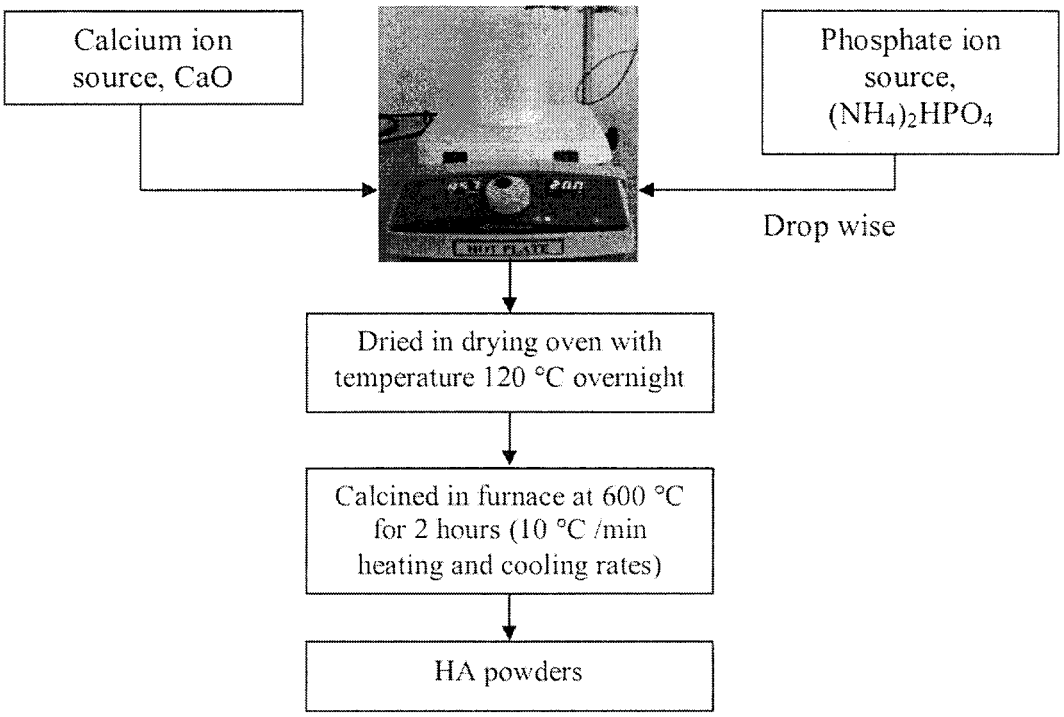

Figure 1. Flowchart of hydrothermal synthesis of HA powder from eggshell waste.

Porous Ceramics Bodies. Polymeric sponge was the method chosen to form the porous HA ceramic bodies. A slurry of *HA-ES* powders (70% of powder loading), PVA as binding agent and Duramax as dispersing agent was prepared in dH_2O on a hotplate stirrer. The cellulose sponge was used to create the pores. The sponge was cut into small circular shapes of 10 mm in diameter and immersed into the slurry until the sponge was completely soaked. The soaked sponges were dried at room temperature for 72 hours. The dried cellulose cylinder sponges were sintered at 1250 °C for 2 hours. Fig. 2 shows the progress of cellulose sponges to form the porous scaffold.

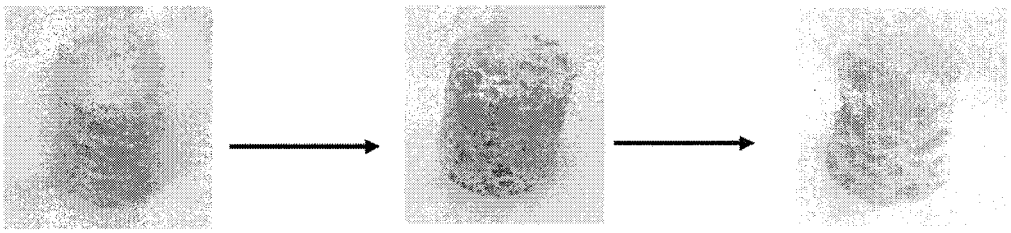

Figure 2. Development of porous ceramic (A) 10 mm cellulose sponge (B) Dried cellulose sponge after soaked in HA slurry (C) Porous ceramic after sintering.

Dense Ceramics Bodies. Dense test specimens were formed using Manually Hydraulic Press (Specac) machine. 1.5 gram of *HA-ES* powders was weighed and inserted into the mould (13 mm diameter) to form dense cylinders (Fig. 3). Pressing load used was constantly 3 tones for all samples. Dense test bars (4 x 3 x 45 mm^3 [26]) were form using 1 gram of HA powders to evaluate their mechanical properties using the universal material testing machine. All pressed samples were sintered at 1250 °C for 2 hours before testing.

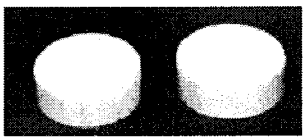

Figure 3. Dense HA-ES

Characterization. The white powder samples obtained were characterized by several methods. Chemical and morphological characterization was examined by Scanning Field Emission Scanning Electron Microscopy (FESEM, JEOL, JSM – 6700F). The thermal transformation process of raw materials of HA-ES sample and the thermal stability of HA-BB were studied by using a Thermogravinomety and Differential Thermal Analysis (TG/DTA, Perkin Elmer, Pyris Diamond). Fourier transformed infrared (FTIR) spectroscopy (Jasco, FT/IR 6100) was also performed in order to understand the phase changes upon annealing and to determine HA stoichiometry deviations, i.e. the presence of anions and substituting PO_4^{3-} and OH^- groups. The crystallinity and phase identification was analyzed using X-ray Diffraction (XRD, PANalytical, System X'Pert Pro) by comparing the experimental XRD patterns to the provided Joint Committee on Powder Diffraction Standards (JCPDS) code number HA, 09-0432.

Result and Discussion

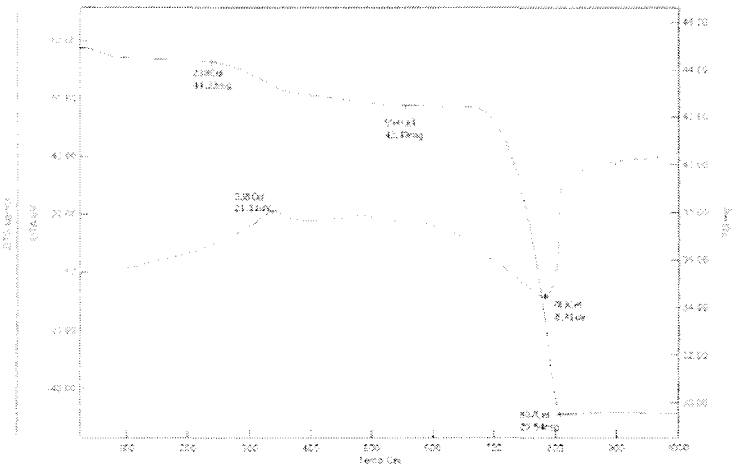

Figure 4. TG/DTA of calcium carbonate powder from eggshell waste.

Fig. 4 shows the TG/ DTA of crushed eggshell waste which composed of calcium carbonate. The first dropped as shown in above figure attributed to the evaporation of water at 100°C. The degradation of organic compounds occurs at ~200°C up to ~300°C. Between 300°C-700°C, the eggshell waste contains mainly the calcium carbonate as the main component. The TG/DTA thermogram shows a sharp drop of the mass at temperature between 700°C to 807°C .This mass loss attributed to decomposition of calcium carbonate to calcium oxide about 30.5%. At this temperature, the crushed eggshell experienced an endothermic process as the combustion take place. However, the chosen temperature to convert calcium carbonate to calcium oxide is 1000°C since the XRD results shows that calcium carbonate was completely converted to calcium oxide at this temperature (Fig. 5). However, there is still intermediate product (34°) which likely belong to amorphous element. The XRD pattern for the synthesized HA powder, calcium oxide and calcium carbonate is shown in Fig. 5. It

shows that the major peaks is the HA peaks in the synthesized powder. The highest HA peak found in the powder is at ~32° as illustrated in the figure.

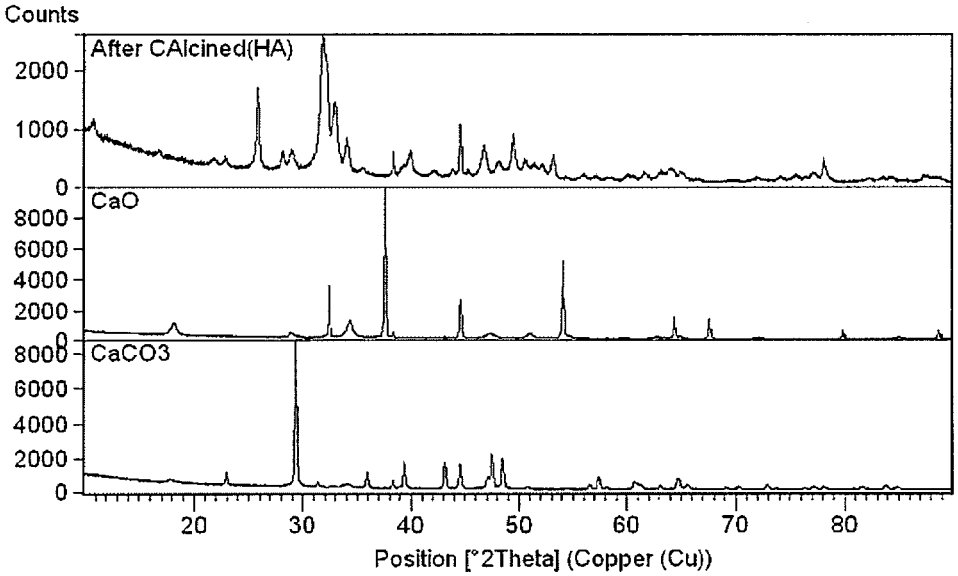

Figure 5. XRD Patterns for calcium carbonate from eggshell waste, calcium oxide obtained after burning at 1000°C and HA powder.

FTIR spectra of HA powder, CaO and CaCO3 is illustrated in Fig. 6. this study shows the presence of phosphate bands at ~950 cm^{-1}, ~1040cm^{-1} and ~1100 cm^{-1}. The band at ~630 cm^{-1} is derived for OH group in HA powder from synthesized eggshell.

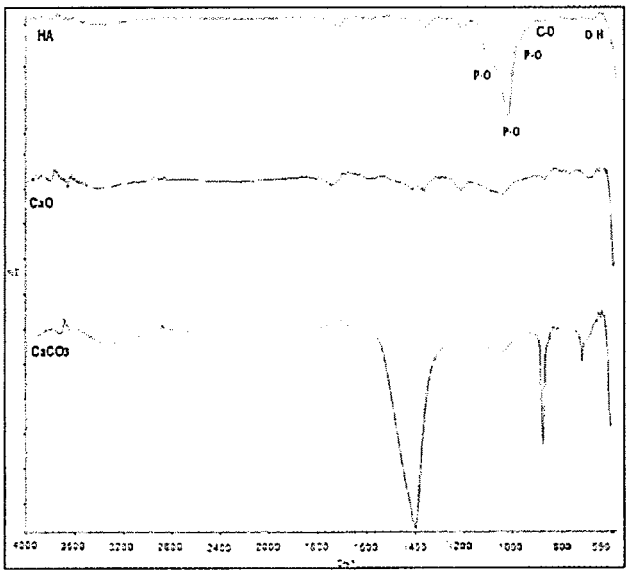

Figure 6. FTIR spectra of calcium carbonate from eggshell waste, calcium oxide obtained after burning at 1000°C and HA powder.

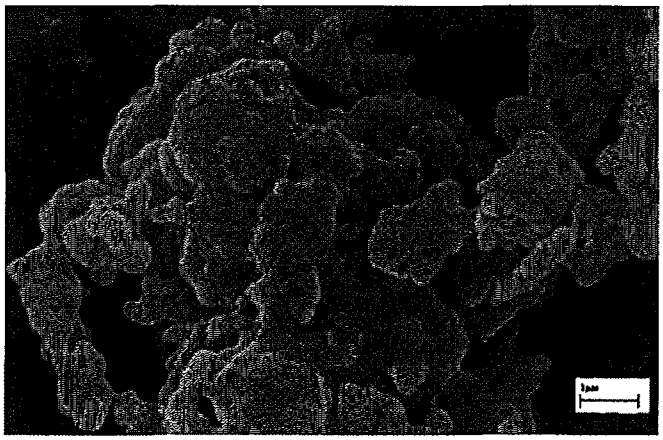

Figure 7. SEM image of hydroxyapatite powder derived from eggshell waste.

Fig. 7 shows the SEM picture for eggshell derived HA at 900°C. The figure shows that the HA powder is tightly agglomerated in globular shape with primary particles having a diameter of 100nm in average.

Dense and porous samples were prepared to evaluate the performance of the synthesized HA-ES powder that obtained from eggshell waste. Porous bodies of HA-ES were prepared via polymeric sponge method with HA-ES and PVA contents. Fig. 8 shows the resulting macrostructure of porous HA-ES. The figure shows that the macrospores were interconnected through cell walls. From the SEM image, it was observed that the pore size of the HA-ES scaffold in the range ~50-500μm. The average sintering shrinkage of the porous bodies of HA-ES is about 35 vol.%. Porosity of the samples prepared is in the range of 54-85%. The compressive strength of porous HA-ES is in the range 0.5-1.2MPa. However, the micrograph of porous HA-ES shows residual porosity due to incomplete densification of structure during the sintering process. This residual porosity adversely influenced the mechanical performance of the porous ceramics.

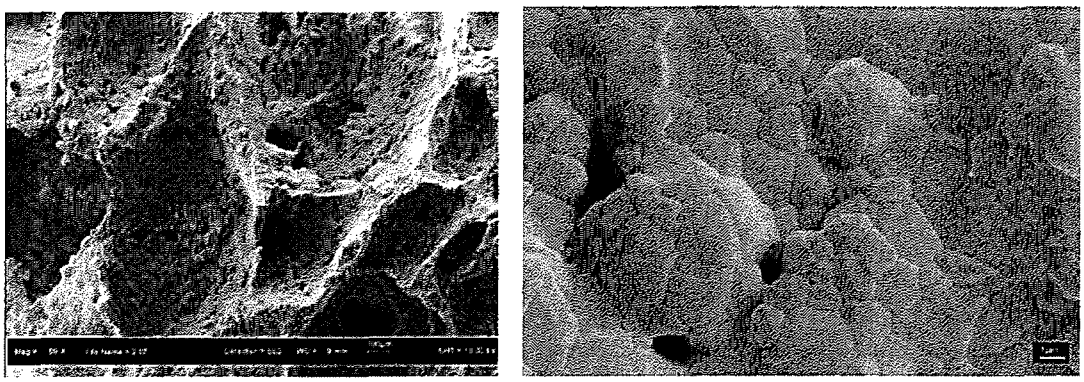

Figure 8. Microstructure of porous hydroxyapatite

The sintered dense bodies of HA-ES at 1250°C for the hydrothermal derived HA-ES powder showed hardness value of 3.9-5.8 GPa. Fig. 9 shows a SEM image of sintered HA-ES. The sample shows excellent mechanical properties at this sintering temperature. It was observed that densification has occurred at this temperature which has eliminated the porosity in the microstructure which resulted in complete sintering process. The dense HA-ES samples also experienced grain growth which due to improvement in the homogeneity of the powder.

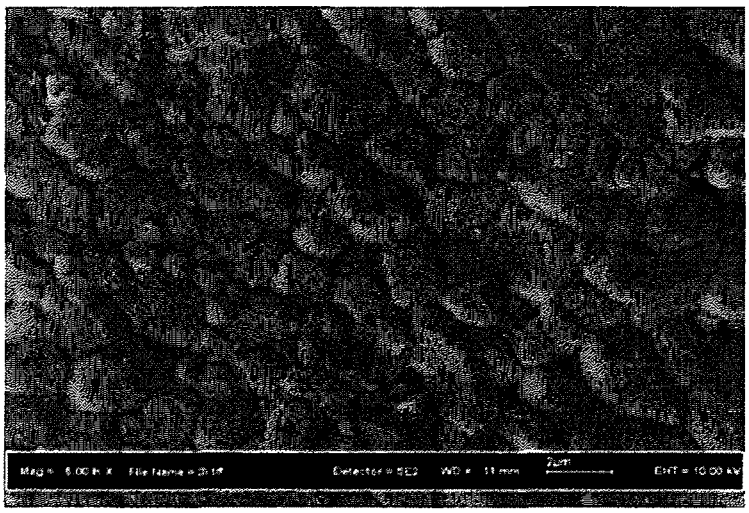

Figure 9. SEM image of dense HA-ES.

Summary

Hydrothermal method was able to produce pure and crystalline HA from waste eggshells. FT-IR spectra and XRD analysis shows that the purity and crystallinity of the hydroxyapatite powder and the FESEM shows that nano-sized HA is produced. These methods provide an environmentally beneficial and cost effective technique of producing medical grade hydroxyapatite materials utilizing organic by-products such as, eggshell waste.

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