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Synthesis and sintering of hydroxyapatite derived from eggshells as a calcium precursor

P. Kamalanathan[a], S. Ramesh[a,*], L.T. Bang[a], A. Niakan[a], C.Y. Tan[a], J. Purbolaksono[a], Hari Chandran[b], W.D. Teng[c]

[a]Center for Advanced Manufacturing and Materials Processing, Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia
[b]Division of Neurosurgery, Faculty of Medicine, University of Malaya, Kuala Lumpur 50603, Malaysia
[c]Ceramics Technology Group, SIRIM Berhad, Shah Alam 40911, Malaysia

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Abstract

In the present work, phase pure hydroxyapatite (HA) was successfully prepared using calcined eggshells as a calcium precursor via the wet chemical precipitation method. The sintering of eggshell-derived HA (EHA) compacts was carried out in air over a temperature range of 800–1400 °C. The sintered HA samples were evaluated in terms of phase stability, relative density, grain size, Vickers hardness and fracture toughness. The results showed that phase pure HA was obtained and remained stable after sintering at 1250 °C. However, secondary phases such as α-TCP and TTCP were obtained at 1300–1350 °C and melted upon further sintering at 1400 °C. A relatively high density of 97.4% was achieved in pure HA at 1250 °C whilst a maximum fracture toughness of 1.14 MPa $m^{1/2}$ was attained at 1000 °C due to the small grain size of 0.33 μm obtained at this temperature. The study found that a combination of relative density, the reverse Hall–Petch relationship and grain growth affected the hardness of the HA samples, where the highest value of 4.96 GPa was achieved at a sintering temperature of 1250 °C.
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1. Introduction

Up to now, large bone defects still represent a major problem in orthopaedics [1]. Being similar to bone structure in terms of its mineral composition, as well as its highly biocompatible and bioactive nature, hydroxyapatite (HA) has made its mark in the medical and health-related fields as a bone graft substitute [2–5]. However a distinctive drawback of HA lies in its poor mechanical properties, particularly its low fracture toughness (K_{Ic}) of < 1 MPa $m^{1/2}$. This limits its usage to non-load bearing applications [6,7].

Various methods have been developed to synthesize HA from synthetically derived precursors in which the parameters were varied to produce HA with significant purity and good mechanical properties [8]. Some of these synthesis methods include the wet chemical precipitation method [9,10], mechanochemical method [11,12], sol–gel method [13,14], and hydrothermal method [15,16]. However, stoichiometric HA prepared from these methods lack the presence of trace amounts of ions in its lattice structure. Bone itself is regarded as a non-stoichiometric HA due to the presence of minor amount of ions in its HA lattice which benefits its own structure as well as calcium phosphate based implants [17,18]. On the other hand HA derived from natural resources and bio-wastes such as eggshells [19–21], seashells [22,23] and animal bones [24–26] are non-stoichiometric due to the trace amount of ions incorporated in its crystal structure, such as Fe^{2+}, Mg^{2+}, Si^{2+} and F^{-} [26,27]. Therefore, the development of HA from natural resources is of great importance in its usage as bone-like implants.

High content of calcium carbonate ($CaCO_3$), as well as the presence of trace amount of ions such as Na^{+}, Sr^{2+}, and Mg^{2+}, in eggshells makes it an attractive waste material to be

*Corresponding author.
E-mail address: ramesh79@um.edu.my (S. Ramesh).

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used as a calcium precursor in the synthesis of HA [28,29]. The first research on the usage of eggshells as a calcium precursor in the synthesis of HA was reported by Rivera et al. [30], where a hydrothermal route was employed. Numerous methods have been adopted in the synthesis of HA from eggshells, such as the wet chemical precipitation method [31–33], hydrothermal method [19,34,35], and wet mechanochemical method [36,37], as well as the microwave irradiation method [17,38]. Different calcium precursors and synthesis methods employed can lead to the production of HA with different chemical and physical properties. These variations are evident in terms of the thermal stability of as-synthesized HA.

The wet chemical precipitation method is the most common synthesis route due to its simple and low-cost processing technique. This method generally produces larger particles in the micro-scale region [8,39,40]. However, some of the physical and chemical characteristics of the final product depend on the specific method used in the synthesis process. For example, the synthesis of fine nano-sized HA particles by Ibrahim et al. [33] was attributed to the steady addition of the phosphorous precursor to the calcium precursor derived from eggshells at a rate of 200 ml/h. This was to ensure a maintained pH in the mixture, translating to the dissolution, formation and maturation of the reactants at an effective rate, thereby contributing to the formation of fine nanoparticles. On the other hand, the nano-sized HA particles synthesized by Chaudhuri et al. [41] was owing to the length of the reaction period between the calcium and phosphorous precursor, ranging from 1 to 7 days.

An effective and efficient usage of synthetic HA in biomedical applications requires the produced powder to be morphologically well defined [12,42]. Synthesis of HA based on eggshells (EHA) has been shown to produce a number of powder morphologies. Rod-like and needle-like morphologies are commonly found in the human hard tissue whereas flower-like morphologies are known to be beneficial in drug loading and releasing [43–46]. In addition, it is postulated that the presence of needle-like particles in the bulk material is capable of enhancing fracture toughness. EHA with flower-like morphologies have been synthesized via a microwave irradiation route with the assistance of ethylenediaminetetraacetic acid (EDTA) as a chelating agent to control powder morphology [47]. On the other hand, EHA with rod-like [35] and needle-like morphologies [34] have also been produced. In these studies, an additional morphological controlling agent was always employed. For instance a cationic surfactant such as cetyltrimethyl bromide (CTAB) was added to the phosphorous precursor prior to synthesis [35], whilst fruit extract solutions such as pomelo peels were incorporated into the calcium precursor solution in order to manipulate the powder morphology of EHA [34]. Besides these, variations in synthesis durations have been shown to alter the morphology of EHA. This is highlighted in the study conducted by Wu et al. [34], where EHA particles with a needle-like morphology evolved to resemble a rod-like structure when the hydrothermal reaction time increased from 24 to 72 h. This is an inherent characteristic of the hydrothermal treatment, which manipulates the growth and morphology of the crystalline HA nuclei formed during the ionic reaction between precursors [8].

In the synthesis of EHA, eggshells have been converted to various forms of calcium precursor such as calcium oxide (CaO) [41], calcium hydroxide ($Ca(OH_2)$) [39], calcium nitrate ($Ca(NO_3)$) [48], and calcium chloride ($CaCl_2$) [34]. The study conducted by Ahmed and Ahsan [49] highlighted the effect of different precursors, where EHA was synthesized using Ca (NO_3) – derived from CaO (route 1) and $CaCO_3$ (route 2). The latter required an additional calcination procedure, resulting in as-synthesized EHA with a higher crystallinity as compared to route 1. Based on available resources, most of the research works conducted on EHA have been limited to the synthesis and characterization efforts on as-synthesized and sintered EHA samples whilst a full evaluation in terms of mechanical properties of sintered EHA samples has hardly been explored. Although the mechanical strength of sintered EHA samples has been investigated previously [38], only the relative density and Vickers hardness were evaluated. Thus, a thorough mechanical property evaluation on sintered EHA samples is necessary. Therefore, the aim of the present research is to synthesize and sinter phase pure HA using waste eggshells as a calcium source. Mechanical characteristic investigations of sintered EHA samples were evaluated through density, hardness and fracture toughness.

2. Experimental procedures

2.1. Powder preparation and sintering EHA compacts

Waste eggshells were thoroughly cleaned and air-dried prior to the removal of the inner membrane layer. Cleaned and dried eggshells were crushed to a fine powder consistency using a pestle and a mortar. The raw eggshells were then calcined at elevated temperatures to convert $CaCO_3$ inherent in eggshells to CaO. In order to determine the most suitable calcination temperature based on purity and the crystallinity of the CaO produced, the temperatures of 700, 800, 850, 900, and 1000 °C were employed with a 10 °C min^{-1} ramp rate (heating and cooling) for 1 h. The CaO obtained via calcination of eggshells were added to a pre-determined amount of distilled water to produce a $Ca(OH)_2$ solution, hereafter referred to as the calcium precursor. EHA was then synthesized using the calcium precursor and H_3PO_4 (85% purity, Merck) via a wet chemical precipitation (WCP) route [50]. The molar ratio of Ca $(OH)_2$ to H_3PO_4 was 1.67:1, where the H_3PO_4 solution was added to the calcium precursor at a rate of 10–20 drops/min. The pH of the solution was maintained at a level greater than 10.5 by using ammonium hydroxide (NH_4OH) (25% purity, Sigma-Aldrich).

After the reaction was complete, the produced EHA suspension was then allowed to mature for 24 h. Subsequently, it was filtered and washed with distilled water before being dried in an oven at 60 °C for 24 h. The dried EHA powder was crushed and sieved using a 212 μm sieve to produce uniform EHA particles. Disk samples were then made by uniaxial pressing at 13.5–14.0 MPa followed by cold isostatic pressing

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