The Effects of Calcium-to-Phosphorus Ratio on the Densification and Mechanical Properties of Hydroxyapatite Ceramic
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In this work, hydroxyapatite (HA) powders were synthesized using calcium hydroxide Ca(OH)$_2$ and orthophosphoric acid H$_3$PO$_4$ via wet chemical precipitation method in aqueous medium. Calcium-to-phosphorus (Ca/P) ratio was set to 1.57, 1.67, 1.87 that yield calcium-deficient HA, stoichiometric HA, and calcium-rich HA, respectively. These synthesized HA powders (having different Ca/P ratio) were characterized in terms of particle size and microstructural examination. Then, the densification and mechanical properties of the calcium-deficient HA, stoichiometric HA, and calcium-rich HA were evaluated from 1000 to 1350°C. Experimental results have shown that no decomposition of hydroxyapatite phase was observed for stoichiometric HA (Ca/P = 1.67) and calcium-deficient HA (Ca/P = 1.57) despite sintered at high temperature of 1350°C. However, calcium oxide (CaO) was detected for calcium-rich HA (Ca/P = 1.87) when samples sintered at the same temperature. The study revealed that the highest mechanical properties were found in stoichiometric HA samples sintered at 1100–1150°C, having relative density of ~99.8%, Young’s modulus of ~120 GPa, Vickers hardness of ~7.25 GPa, and fracture toughness of ~1.22 MPam$^{1/2}$.

Introduction

In the early year, transplantation was a promising method to replace damaged hard tissues such as bone and tooth, but it was later found to be inappropriate due to the scarcity of suitable donor tissues and risk of diseases transmission. 1 Owing to these issues, implantation was introduced to overcome the overall ineffectiveness of transplantation. Development of implantation has led to heavy demands on bioceramics because bioceramics possess good biocompatibility and ease of processing. 1,2 Hydroxyapatite (HA), having Ca/P ratio of 1.67, is the most renowned calcium-phosphate-based bioceramics because it forms a mechanically strong bond to bone and no fibrous particles were found encapsulated on the implant’s interface. 3 These superb properties make stoichiometric HA (Ca/P ratio = 1.67) as a potential material in clinical applications such as biomedical implants, 1,3 coating for metal-based biomaterials 4 and substitutes for the repair of damaged bones. 1,3

However, HA was later found to carry a major downside, which is its relatively low fracture toughness, restricting it to be used in load-bearing clinical applications. 5 Thereafter, extensive studies have been placed on the methods that enhance the mechanical properties of HA without compromising its biocompatibility. These methods included tailoring the powder processing techniques, adjusting the sintering atmosphere, and adding dopants into HA. 6–8 An effective bioceramic should have good biocompatibility accompanied by great mechanical strength. A few researchers 5,9 have reported on the importance of Ca/P ratio in affecting the biodegradation rate of hydroxyapatite in human body. Nonetheless, the literature on Ca/P ratio effects on the phase stability and mechanical properties of hydroxyapatite are found to be very limited. Therefore, the objectives of the present study are to synthesize HA having Ca/P ratio of 1.57, 1.67, and 1.87 by wet chemical method and to elucidate the effect of sintering temperature ranging from 1000 to 1350°C on the densification and mechanical properties of the synthesized HA of different Ca/P ratios.

Experimental Details

The hydroxyapatitic powders with different Ca/P molar ratio of 1.57, 1.67, and 1.87 were produced using the wet chemical method involving precipitation from aqueous medium through titration process, involv-
ing calcium hydroxide Ca(OH)₂ (98% purity, BDH) and orthophosphoric acid H₃PO₄ (85% purity, Merck). To synthesize HA powder with Ca/P ratio <1.67, less amount of calcium hydroxide (5% less as compared to when used to synthesize stoichiometric HA) was used as the initial reagent. In contrast, HA powder with Ca/P ratio >1.67 was synthesized by using 5% more of calcium hydroxide as compared to when used to synthesize stoichiometric HA. The amount of orthophosphoric acid H₃PO₄ used for the preparation of both powders was similar to that employed to prepare stoichiometric HA. The pH was maintained at about 10–12 by the addition of small amounts of ammonium (NH₄OH) solution. The as-synthesized powders were uniaxially compacted about 1.3–2.5 MPa into discs (20 mm dia. × 5 mm thickness) and rectangular bars (13 × 32 mm) followed by cold isostatically pressing (CIP) at 200 MPa. The CIP pellets were sintered via conventional pressureless sintering, over temperature range of 1000–1350°C, under soaking time of 2 h with heating and cooling rate of 2°C/min.

The calcium (Ca)-to-phosphorus (P) ratio was analyzed by the inductively coupled plasma -atomic emission spectrometry (ICP-AES) method. The particle size distributions of the HA powders were determined using a standard Micromeritics® SediGraph 5100 X-ray particle size analyzer (Norcross, GA). Subsequently, the microstructures of powders were detected through scanning electron microscope (SEM). X-ray diffraction (XRD) (Geiger-Flex, Rigaku, Tokyo, Japan) was carried out to investigate the phase change and decomposition of the HA sintered compacts. Next, the bulk densities of compacts were determined in accordance with the water immersion technique (Mettler Toledo, Greifensee, Switzerland) using Archimedes principle. Relative densities of the compacts were then determined by comparing the theoretical density of HA (3.156 g/cm³) with the measured bulk densities. The Young’s modulus was determined for rectangular samples via sonic resonance technique. Vickers hardness (H) and fracture toughness (K̅c) determination was done through Vickers indentation tester (Matsuwa, Japan). The indentations were made using a pyramidal diamond indenter with an applied load varying between 50–200 g. Since the crack system for hydroxyapatite ceramic is median type, the fracture toughness value was calculated using the equation derived by Ni injection et al.12:

\[
K̅c = 0.203 \left( \frac{E}{H(a)^{1.5}} \right) \left( \frac{2H}{L} \right)^{1.5},
\]

where K̅c is the fracture toughness, H is the Vickers hardness, e is the characteristics crack length, L is the average crack length, and a is the half diagonal of the indent.

**Results and Discussion**

The results of the chemical and particle size analysis that were carried out on all the HA powders are tabulated in Table 1. The average particle size of stoichiometric HA (Ca/P = 1.67) powder was slightly smaller than calcium-deficient HA (Ca/P = 1.57) and calcium-rich HA (Ca/P = 1.87) as indicated in Table 1. This was evident from the SEM micrographs of the powders shown in Fig. 1. Stoichiometric HA (Fig. 1a) consisted of a mixture of particles ranging from 0.5 to 2.5 μm in diameter while the particle size of calcium-deficient HA (Fig. 1b) and calcium-rich HA (Fig. 1c) ranges from 1.0 to 3.0 and 1.25 to 3.5 μm, respectively.

Figure 2 shows the XRD profile of all samples sintered at 1300°C. No secondary phases were formed in stoichiometric and calcium-deficient HA samples while CaO was detected in calcium-rich HA sample. This indicated that the phase stability of calcium-rich HA was disrupted when sintered at high temperature which is undesirable. Several authors have claimed that the CaO phase in hydroxyapatite hinders the mechanical performance of host material due to the built-up stress from CaO hydration.13,14 Besides, according to the literature, CaO should be excluded from biological application because it affects the biocompatibility of host material.15 Conversely, the stoichiometric HA in the current work did not decompose throughout the sintering regime employed (1000–1350°C) which is in agreement with the previous literature.16,17 The resistance toward the

<table>
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<th>Table 1. Properties of the HA Powders with different Ca/P Ratio</th>
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<tr>
<td><strong>Stoichiometric HA</strong></td>
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<tr>
<td>Calcium (Ca)%, w/w</td>
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<td>Phosphorus (P)%, w/w</td>
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<td>Ca/P ratio</td>
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decomposition at high temperature has made stoichiometric HA as a suitable material for biomedical application.

Figure 3 depicted the densification rate of all HA samples as a function of sintering temperature. Regardless of sintering temperatures, all samples for stoichiometric (Ca/P = 1.67) and calcium-deficient HA (Ca/P = 1.57) did not show any cracking or distortion after sintering. However, cracks were detected for calcium-rich HA (Ca/P = 1.87) samples sintered at 1000 and 1350°C. Thus, data could not be retrieved for samples sintered at these temperatures. In general, the relative density of stoichiometric HA showed an increment from 97.3% (at 1000°C) to a maximum of 99.8% (at 1100°C). Calcium-deficient HA and calcium-rich HA could only achieve maximum relative density of 98.4% and 97.5%, respectively, when sintered at 1200°C. The lower density exhibited by the calcium-rich HA as compared to stoichiometric HA and calcium-deficient HA could be attributed to the existence of CaO in the HA matrix.

The relationship between the Young's modulus (E) of the sintered body, sintering temperature, and Ca/P ratio is shown in Fig. 4. In general, the stoichiometric HA recorded higher value of Young's modulus as compared to nonstoichiometric HA. The highest E value of 121 GPa was recorded for stoichiometric HA samples when sintered at 1200°C. Calcium-deficient HA and calcium-rich HA could only attain a maximum stiffness of 109 and 106 GPa, respectively, when sintered at 1150°C. The relatively low Young's modulus in calcium-rich HA could be attributed to the presence of CaO phase as secondary phase.

The variation of the Vickers hardness and fracture toughness of HA samples sintered at various sintering temperatures is shown in Fig. 5 and Fig. 6, respectively.

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