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Properties of calcium phosphates ceramic composites derived from natural materials

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ABSTRACT

In this study, ceramics containing mixed phases of hydroxyapatite/beta-tricalcium phosphate (HA/β-TCP) were fabricated by a solid-state reaction technique. The HA powder was synthesized from cockle shells while the β-TCP powder was synthesized from egg shells. Pure HA and β-TCP fine powders were successfully obtained. The HA and β-TCP were mixed and subjected to a thermal treatment up to 1100 °C. To form the mixed phase ceramics, the resulting powders were sintered at 1350 °C. Effects of HA concentration on the properties of the studied ceramic were investigated. X-ray diffraction analysis revealed that all samples presented multiphase of calcium phosphate compounds. Average grain size of the ceramics decreased with the HA additive content. The 75 wt% HA ceramic showed the maximum hardness value (5.5 GPa) which is high when compared with many calcium phosphate ceramics. In vitro bioactivity test indicated that apatite forming increased with the HA additive content. To increase antibacterial activity, selected ceramics were coated with $AgNO_3$. Antibacterial test suggested that an Ag compound coating on the ceramics could improve the antibacterial ability of the studied ceramics. In addition, the antibacterial ability for the Ag coated ceramics depended on the porosity of the ceramics.

1. Introduction

Calcium phosphate-based bioceramics have been widely investigated due to their excellent biocompatibility, bioactivity, and osteoconduction characteristics. These materials have potential for medical applications such as a bone graft substitute primarily. Calcium phosphate has many forms, depending on the amount of Ca and P in the molecule, such as hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$), alpha-tricalcium phosphate (α-TCP, $Ca_3(PO_4)_6(OH)_2$) and beta-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) where the Ca/P ratios in HA, α-TCP, and β-TCP are 1.67, 1.5 and 1.5, respectively. However, the most interesting used calcium phosphate-based bioceramics are HA and β-TCP. HA is the mineral component of bone which has been widely investigated for many years [1,2]. This material is appropriately used for artificial bones as it has excellent biocompatibility and its biocomponents are similar to natural bone and human teeth [3,4]. It has been developed for use as bone implants [5,6]. However, dense HA hinders bone ingrowth after implantation, due to its low biodegradability. Moreover, its brittleness and low fracture toughness limit its biomedical used especially for loading applications [7]. Therefore, there have been many attempts to improve the mechanical properties of sintered HA [8,9].

Recently, β-TCP has been proposed for bioceramic applications due to its better bioresorption rate [5,10,11]. It has been reported that β-TCP ceramics exhibit higher resorption comparing to pure HA. Since both HA and β-TCP are still of interesting, i.e. HA shows good performance for biological applications while β-TCP has high bioresorbability, and so in this work attempts to combine the advantages of both compounds were carried out. Thus, β-TCP and HA were used together to form biphasic composites to overcome the low biodegradability of pure HA.

Normally, many calcium phosphate-based compounds can be synthesized by chemical techniques such as co-precipitation [12,13], sol–gel synthesis [14,15], hydrothermal method [16] and thermal deposition [17]. However, costs of raw materials for these processes are quite high. In addition, the yield product from these methods is very small. There has been a constant quest to scale up any process to bulk processing. Therefore, the calcium phosphate powder produced from natural products, e.g. bovine bone, cockle

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shell and egg shell [14,18] by the conventional calcination method could be another candidate [19]. Therefore, the aim of this work is to fabricate biphasic ceramic composites of HA and β-TCP from natural products and investigate their properties. HA and β-TCP powders synthesized from natural products can reduce the cost of production. With their complementary features, composites between HA and β-TCP are expected to exhibit better properties than those of a single phase. Furthermore, the properties can also be tailored over a wide range by changing compositions to meet strict requirements for specific applications.

2. Experimental procedures

To fabricate the ceramics, calcium carbonate ($CaCO_3$) was synthesized from cockle shells and egg shells which were fired at 625 °C for 3 h. The calcium carbonate powders (fired cockle shells for HA synthesis and fired egg shells for β-TCP synthesis) were then reacted with diammonium phosphate ($H_9N_2O_4P$, Fluka ≥ 99%). After that the obtained HA and β-TCP were mixed in ethanol for 24 h by a ball-milling technique. The weight ratios of HA/β-TCP used in this work were 25/75, 60/40 and 75/25. The mixtures were then heated at 300 °C for 10 h followed by heating up to 900 °C for 2 h and then to 1000 °C for 12 h. The obtained powders were uniaxial pressed at 1 MPa into a disc shape. The green body samples were sintered at a temperature of 1350 °C for 2 h. The particle size distributions of HA and β-TCP powders were examined by a dynamic light scattering technique. The phase formation of powders and ceramics was carried out by X-ray diffraction technique (XRD, Phillip Model X-pert) in $2\theta = 20–65°$. Density of all sintering ceramics was determined by Archimedes' method. The microstructure of all samples was examined by scanning electron microscopy (SEM). In regard to apatite-forming ability evaluation, the samples were immersed in simulated body fluid (SBF) solution for 14 days (in vitro bioactivity test) [19]. For mechanical property, the samples were tested by a Vickers microhardness indenter. Antibacterial tests were performed by the LB broth method. Two types of microorganisms, *Escherichia coli* as Gram-negative bacteria and *Staphylococcus aureus* as Gram-positive bacteria, were used in the antibacterial tests. The bacteria were cultivated at 37 °C in a sterilized broth. The concentration of all the bacterial cell suspensions was about 10^4 colony-forming units (CFU)/ml. Based on the LB broth method, 10 mL of bacteria (10^4 CFU/ml) was cultivated at 37 °C and incubation was continued for another 24 h. The ceramics were placed into flasks at 37 °C for 24 h. The bacterial concentrations in the liquid cultures were determined by measuring the optical density as absorbance at 600 nm (OD_{600}) by a UV–vis spectrophotometer. The antimicrobial efficiency was calculated according to the equation: $\%IR = ((A-B)/A) \times 100$, where A is the absorption at 600 nm before incubation and B is the absorption at 600 nm for the tested sample after incubation for 24 h.

3. Results and discussion

X-ray diffraction patterns of $CaCO_3$ powders synthesized from cockle and egg shells are shown in Fig. 1. Based on XRD analysis, single phase of $CaCO_3$ was successfully obtained for both samples. The XRD data was found to match with JCPDS data file of $CaCO_3$ (File no. 01-085-1108). SEM micrographs of $CaCO_3$ powders synthesized from egg and cockle shells are shown in Fig. 1(b)–(e). Agglomeration of particles with porous structure was observed for both samples. Particles of $CaCO_3$ powder synthesized from cockle shells showed a round-shape while the product from egg shells displayed a plate-like shape. It should be noted that size of pore for

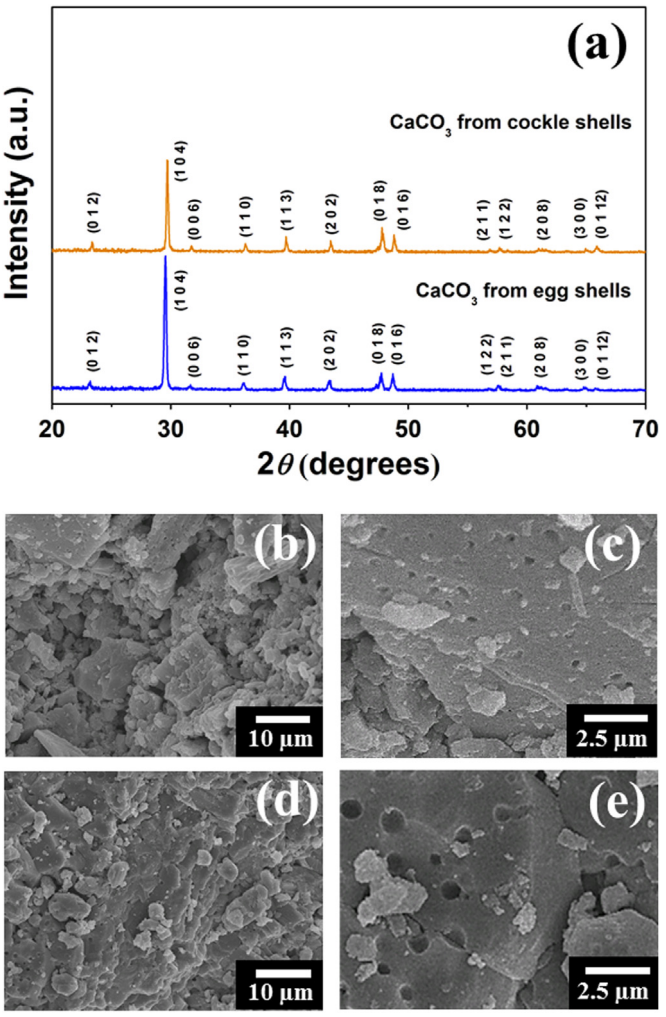

Fig. 1. (a) XRD patterns of $CaCO_3$ powders synthesized from different natural raw materials, (b, c) SEM micrographs of $CaCO_3$ powders synthesized from the egg shells (at low and high magnifications, respectively), and (d, e) SEM micrographs of $CaCO_3$ powders synthesized from cockle shells (at low and high magnifications, respectively).

the cockle shell sample (0.62 ± 0.18 μm) was larger than that the egg shell sample (0.28 ± 0.08 μm). This may affect the observed XRD data such as the presence of difference in intensity of XRD peaks between the samples. The obtained results suggested that type of natural raw material affected the characteristics of the $CaCO_3$ powder product.

X-ray diffraction patterns of the obtained HA and β-TCP powders at 2θ~20–65° are shown in Fig. 2. In this work, HA and β-TCP powders were derived from cockle and egg shells, respectively. Based on XRD analysis, a pure phase of HA and β-TCP powders were successfully obtained. XRD data for the HA powder was found to match with the stoichiometry of HA which correlated with JCPDS data File no. 01-073-1731. While, the β-TCP powder was successfully formed and characterized according to JCPDS File no. 01-073-1731.The particle size distributions of HA and β-TCP powders was examined by the dynamic light scattering technique and the results are shown in the inset of Fig. 2. It is clearly seen that the particle size distributions exhibit a mono-model distribution. This suggests no trace of particle agglomeration, implying that the method of powder preparation for the particle size analysis produced a well disperse particle. The average particle sizes of HA and β-TCP, as estimated from the particle size analysis, were 459 and 395 nm, respectively. Furthermore, the particle size ranges of HA and β-TCP were ~255–820 nm and 222–703 nm,