Effect of Composition and Temperature to the HA/β-TCP Composite

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Abstract. The aim of this study is to fabricate hydroxyapatite (HA) and beta-tricalcium phosphate (β-TCP) composite by varying the HA/β-TCP compositions (100% HA, 80% HA with 20% β-TCP, 60% HA with 40% β-TCP, and 50% HA with 50% β-TCP) and sintering temperatures (1000°C and 1200°C). The powders are mixed with ethanol by using agate mortar, dried in oven (80°C, 24 hours) and uniaxially pressed into 16 mm diameter pellets followed by sintering. Samples are characterized by bulk density testing, phase analysis using X-ray Diffraction (XRD) and Vickers hardness test. Pure HA powder sintered at 1200°C shows the highest density and hardness with 3.090 gcm⁻³ and 421.70 HV respectively. XRD phase analysis show decrease of HA phase at higher sintering temperature due to phase decomposition of HA into β-TCP and alpha-tricalcium phosphate (α-TCP). Both HA/β-TCP composition and sintering temperature are significant factors to the hardness with sintering temperature the more dominant factor.

1. Introduction

Calcium phosphates ceramics are well known in the field of biomaterials due to their occurrence in normal bone and their association with the formation and progression and of enamel and dentin caries. Hydroxyapatite ((Ca₁₀(PO₄)₆(OH)₂, HA) with Ca/P stoichiometric ratio of 1.67 is one of the common calcium phosphate used in medical applications [1]. It is considered as a high strength and non-resorbable material. Beta-tricalcium phosphate (Ca₃(PO₄)₂, β-TCP) with Ca/P ratio of 1.5 is also another type of calcium phosphate that have bioresorbable ability [2]. HA/β-TCP composite; known as biphasic calcium phosphate (BCP) consist of an intimate mixture of HA and β-TCP with varying Ca/P ratios from 1.5 up to 1.67. By varying HA/β-TCP ratios, the properties such as compressive strength, macroporosity, dissolution behavior and the bioresorbable ability of the HA/β-TCP composites can be modified [3]. The lack of bioresorbability of HA in body fluid is unfavorable to the host tissue surrounding the implant. Therefore, β-TCP is being introduced but the presence of β-TCP alone causing too fast resorption in an uncontrollable way. However, by combining HA and β-TCP together, the properties can be combined and their properties can be customized [4]. Despite that, HA/β-TCP composite is still lacking in its mechanical properties such as hardness and fracture toughness which is a major drawback for load bearing applications [5]. Sintering process can enhance the densification of HA/β-TCP composite and thus improving its mechanical properties. In this research, the main objectives are to fabricate and characterize the HA/β-TCP composite with varying the composition of HA/β-TCP and sintering temperature.
2. Materials and method

2.1 Sample preparation

Four different compositions of HA/β-TCP were made based on weight percentage (wt%); namely 100% HA, 80% HA with 20% β-TCP, 60% HA with 40% β-TCP, and 50% HA with 50% β-TCP (tabulated in Table 1). The powders were mixed homogeneously using agate mortar with the aid of ethanol as medium. The mixing process was carried out until ethanol solution had evaporated. The mixture was dried for 24 hours at 80°C in oven to completely remove excess ethanol. 1.5g of each powder was pressed into 16 mm diameter pellets using Specac hand press machine. The pellets were sintered at 1000°C and 1200°C for two hours soaking time with heating rate fixed at 5°C/min.

Table 1. Variation of initial composition with subjected sintering temperature

| Sample | Sintering temperature (°C) | Initial composition (wt%) | HA | β-TCP |
|--------|----------------------------|---------------------------|----|-------|
| R1     | 1200                       | 100.0                     | 0.0 |       |
| R2     | 1200                       | 80.0                      | 20.0|       |
| R3     | 1200                       | 60.0                      | 40.0|       |
| R4     | 1200                       | 50.0                      | 50.0|       |
| Q1     | 1000                       | 100.0                     | 0.0 |       |
| Q2     | 1000                       | 80.0                      | 20.0|       |
| Q3     | 1000                       | 60.0                      | 40.0|       |
| Q4     | 1000                       | 50.0                      | 50.0|       |

2.2 Sample characterization

The bulk density of the pellets after sintering was determined using Archimedes principle. The sintered pellets were subjected to XRD phase analysis with 2θ used between 10°-90° (XRD machine: model Bruker AXS D8 Advance). The phase of pellets was analysed with X’pert Highscore Plus software and Rietveld refinement was used to determine the changes in phase composition of pellets. The result obtained was compared with the International Center for Diffraction Data (ICDD). The hardness of pellets was measured via Vickers hardness test model from Future Tech Corporation. Before performing hardness test, pellets were grind with silicon carbide paper and then polished using alumina to obtain a smooth flat surface. All pellets were subjected to 3 kgf indentation load with 10 second dwell time.

3. Results and discussion

3.1 Bulk density analysis of HA/β-TCP composite

It is essential to determine the density of pellets because it can greatly affect the mechanical properties of composite. Bulk density of HA/β-TCP composite are determined and tabulated in Table 2. Density plays an important role as it can affect the mechanical properties of HA/β-TCP composite. Pellet with the composition of 100% HA shown to have the highest density value when sintered at 1200°C with 3.090 g/cm³ (sample R1). Conversely, composition 50% HA 50% β-TCP has the lowest density values at 1000°C with 1.975 g/cm³ (sample Q4). By comparing in terms of sintering temperature factor, an
increasing trend can be observed where the density values increase as sintering temperature increases (refer Table 2). Highest density value obtained from sample R1 while the lowest density value obtained from sample Q4. From this finding, densification process is expected to occur but the stage of densification varies at different sintering temperature. At the early of sintering process, pellets have successfully entered the first stage of densification process where only inter-particle necks form and grow, reaching up to 65% of its theoretical density (~1.63 gcm\(^{-3}\)). During intermediate stage, the pores in the pellet will start to shrink but remain open and connected, reach up to around 90% theoretical density (~2.26 gcm\(^{-3}\)). Then, in the final stage of densification, the pores become isolated or eliminated, leaving a fully or nearly fully dense structure (~3.14 gcm\(^{-3}\) HA/β-TCP full density) [6].

It can be concluded that pellet sintered at 1200°C (sample R1, R2, R3 and R4) have entered the final stage by having a denser structure compared to samples sintered at 1000°C (sample Q1, Q2, Q3 and Q4). A study reports that approximately 95% of theoretical density was achieved when calcium phosphate – mullite composite was being sintered in the range of 1300\(^\circ\)-1350\(^\circ\)C [7]. Another study reported that the density of HA increase as the sintering temperature being increased [8]. It was also reported that different holding time during sintering gives different density of HA where longer holding time resulted in higher density of HA. However, the effect of holding time was not being investigated in this study.

Table 2. Variation of bulk density, final composition (obtained via Rietveld refinement) and hardness value of sintered pellets

| Sample | Sintering temperature (°C) | Bulk density, gcm\(^{-3}\) | Final composition (%) | Hardness value (HV) |
|--------|---------------------------|-----------------------------|-----------------------|---------------------|
| R1     | 1200                      | 3.090                       | 56.1 19.0 24.9        | 421.70             |
| R2     | 1200                      | 3.039                       | 4.5 91.8 3.7          | 340.60             |
| R3     | 1200                      | 2.891                       | 0.0 100.0 0.0         | 256.37             |
| R4     | 1200                      | 2.709                       | 0.0 100.0 0.0         | 231.80             |
| Q1     | 1000                      | 2.243                       | 73.6 26.2 0.2         | 70.67              |
| Q2     | 1000                      | 2.145                       | 2.8 97.2 0.0          | 68.43              |
| Q3     | 1000                      | 2.005                       | 0.0 100.0 0.0         | 57.37              |
| Q4     | 1000                      | 1.975                       | 0.0 100.0 0.0         | 55.07              |

3.2 Phase analysis of HA/β-TCP composite via XRD

Rietveld refinement is used to determine the percent of phase composition exist in the pellets. These data are presented in Table 2. The diffraction pattern with identified phases for pellets sintered at 1200°C and 1000°C are shown in Fig. 1 and 2 respectively. The presence of α-TCP (ICDD #98-007-8160) in R1 and R2 indicates that HA (ICDD #98-007-7628) had lose its OH functional group through dehydration process and decompose into α-TCP after sintering process [9]. The formation of α-TCP can suppress the densification process thus lowering mechanical strength of HA. The formation of α-TCP probably due to the sintering of β-TCP at 1200°C resulting in the decomposition of HA through dihydroxylation [10]. The complete transformation of HA to β-TCP as in sample R3, R4, Q3 and Q4 is due to the presence of β-TCP (ICDD #98-007-6561) in the initial composition that able to promote thermal decomposition of HA [10]. Thus, higher decomposition of HA into β-TCP is observed with the higher initial amount of β-TCP in the sample. Subsequently, the variation of phase composition is difficult to be controlled, and the large difference in phase composition before and after sintering can be explained via pressureless sintering fabrication route; where the HA/β-TCP mixture is unstable during pressureless sintering, thus altering the final composition of composite [10]. On the other hand,
Q1 which initially has 100% HA have transformed into triphasic calcium phosphate comprises 73.7% HA, 26.2% β-TCP, and 0.2% α-TCP. Q2 pellet which has an initial composition of 2.8% HA and 97.2% β-TCP, remained as a biphasic calcium phosphate with 2.8% HA and 97.2% β-TCP, after sintering. The formation of triphasic calcium phosphate in Q1 when sintered at 1000°C are due to the unstable mixing of HA/β-TCP composite [11]. For the case in pellet R3 and Q3, the complete decomposition of HA also comes to a good agreement with some studies whereby 60% HA can completely transformed to β-TCP [10–12].

![Figure 1. XRD diffraction pattern for pellets sintered at 1200°C](image)

![Figure 2. XRD diffraction pattern for pellets sintered 1000°C](image)

**3.3 Vickers hardness test**

The hardness value obtained is tabulated in Table 2. Higher initial composition of HA in sample R1 resulting in high hardness after sintering. It is due to the better mechanical properties of HA than β-
TCP which relate to the highest bulk density and highest HA present in R1 as mentioned in Table 2 and Fig. 1 and 2 respectively. This had contributed to its high hardness properties. By referring to Rietveld refinement data in Table 2, it is noticeable that both R1 and Q1 has HA phase while R4 and Q4 has only β-TCP phase. These explain the high hardness in R1 with 421.74 HV and low hardness in Q4 with 55.07 HV. However, Q1 (70.67 HV) exhibit lower hardness when compared to R4 (231.80 HV) although Q1 have higher HA initial composition than R4. Such findings are unable to be explained only by the initial HA composition factor; therefore, this finding will be evaluated based on the sintering temperature factor. An increasing trend is seen in Fig. 3; where hardness value increases with increasing sintering temperature. Highest hardness value is obtained from sample R1 with the highest sintering temperature of 1200°C, highest initial HA composition of 100% and highest density, while the lowest hardness value is obtained from sample Q4 with lowest sintering temperature of 1000°C, lowest HA initial composition of 50% and lowest bulk density of 1.975 gcm$^{-3}$. It shows that temperature plays a significant role in affecting the density which also influences the hardness of pellets. Higher sintering temperature would result in better densification; increasing density of pellets, hence increasing pellets’ hardness. It can be claimed that sintering temperature is the more influential factor in producing high hardness HA/β-TCP composite compared to the initial HA composition in pellets.

4. Conclusion

HA/β-TCP composite has been successfully fabricated. Based on characterization results, hardness value increases with higher HA initial composition and sintering temperature. From the XRD phase analysis, most HA will convert into β-TCP after sintering at 1000°C. The increase of hardness of the composite is due to the decomposition of HA to β-TCP observed in samples sintered at 1000°C and 1200°C. Sample with high HA composition after sintering provides higher hardness. However, it should be noted that the effect of sintering at higher temperature is more significant towards increasing the composite hardness compared to the effect of initial HA composition.
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