Solid-State Sintering Synthesis of Biphasic Calcium Phosphate/Alumina Ceramic Composites and Their Mechanical Behaviors

Hartatiek1, a, R Kurniawati1, Yudyanto1, N Hidayat1, R Kurniawan1, Masruroh2

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, East Java, Indonesia
2Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Brawijaya Malang, Jl. Veteran, Malang 65145, East Java, Indonesia

*Corresponding author’s email: hartatiek.fmipa@um.ac.id

Abstract. In this present study, we report the fabrication of biphasic calcium phosphate (hydroxyapatite-tricalcium phosphate), abbreviated as BCP. The BCP was compositied with alumina by grinding process and continuously sintering at 1200 °C for 2 hours. The sintering triggered the partial changes of crystalline phase from hydroxyapatite to tricalcium phosphate. Some fundamental characterizations were conducted to reveal the crystal structure, microstructural morphology, and mechanical strength, by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), and Vickers hardness test, respectively. Our results clearly showed that the desired crystalline phases of the composites have been successfully formed. The SEM data captured compact ceramic composites of BCP/alumina. On top of that, introducing of alumina into BCP leads to enhancing the mechanical strength of the composites, having maximum Vickers hardness of nearly 0.38 GPa. Therefore, the composites meet the criteria for load-bearing application in human dentin.

Keywords: Solid-State, BCP, ceramic composites, hydroxyapatite, tricalcium phosphate

1. Introduction
The large number of bone damage cases are caused by infection, bone tumors, and congenital diseases has motivated researchers to develop materials that could be used as bone replacements. Previously, autograft and allograft bone grafts were considered for bone regeneration [1, 2]. The autograft has the advantages of being biocompatible, osteoconductive, and osteoinductive, but it requires an additional surgical procedure and has a high price [3-5]. The allograft is non-immunogenicity and effective for bone regeneration. However, it has a limited availability. In order to solve the problems, a synthetic material becomes a potential alternative for bone regeneration. Nowadays, bioceramics biphasic calcium phosphate (BCP) has received great interest as graft or scaffold material in bone tissue engineering [6]. Currently, the BCP is used as a gold standard in bone reconstruction surgery [7].
Biphasic calcium phosphate (BCP) is formed from a mixture of hydroxyapatite (HA: Ca$_{10}$(PO$_4$)$_6$(OH)$_2$) and tricalcium phosphate (TCP: Ca$_3$(PO$_4$)$_2$) [8,9]. The BCP is widely used as a scaffolding material because it is more effective for bone repair than each HA or β-TCP, as well as its degradation rate can be controlled [10, 11]. Despite the excellent bioactive and biocompatible properties, usually, the CPS (calcium phosphate ceramics) included BCP has a low fracture resistance and load-bearing capacity, which limit their application in the monolithic form [12]. In order to solve this problem, we employed other biocompatible materials as reinforcement. The alumina is one of the bio-inert materials [13] which has excellent mechanical properties and is widely used in orthopedics [14]. The addition of alumina to biomaterials, such as HA and BCP can improve the structure and morphology, which further promote the enhancement of thermal and mechanical properties of the material [16, 17]. In fact, the alumina particles can increase the HA hardness and demonstrate the role of reinforcement [18,19].

The previous study reported that the BCP was synthesized by a hydrothermal method using marine algae with the variation of HA/β-TCP ratio [20]. The BCP was also successfully synthesized by using calcinated bovine bone mixed with a P$_2$O$_5$ solution at room temperature [21]. Natural cuttlefish bone was also used as starting material on the synthesis of porous BCP using a variation of the HA/β-TCP composition and sintering at a high temperature [22]. Moreover, the BCP powder was successfully prepared by CDHA (calcium-deficient hydroxyapatite) as a precursor with the wet chemical method, followed by decomposition into HA and β-TCP after calcination [23-24]. A different method was also used to synthesize BCP. Here, the solid-state reaction technique and sintering at a high temperature were used for the preparation of BCP from DCPD (CaHPO$_4$.2H$_2$O) and CaCO$_3$ [25]. However, the preparation of the BCP with a simple method by utilizing natural calcite has not been reported. In this study, we synthesized BCP by using calcite (CaCO$_3$), which is one of the abundant materials in Indonesia.

Related to the mechanical application, the BCP has poor mechanical properties and it is difficult to be applied as a load-bearing. Therefore, in this work, we propose to prepare BCP composites with alumina to solve the mechanical problem. Here, the synthesis of the BCP/alumina composite was performed in two steps. The first step is synthesizing hydroxyapatite by precipitation method (step I) and following by synthesis of BCP/alumina composites by using HA/alumina composites. To obtain high-quality phase sample, the sintering at a temperature of 1200 °C to promote a partial phase transformation of HA into TCP (step II) was conducted [26]. Furthermore, the phase composition, morphology, and mechanical properties of the samples are investigated in this paper.

2. Methods

The CaCO$_3$ was ground and calcinated at a temperature of 1000 °C for 6 hours to form CaO phase. Furthermore, distilled water was used to change the CaO powder to become Ca(OH)$_2$. Here, the Ca(OH)$_2$ was sieved with 200 mesh and characterized by X-Ray Fluorescence (XRF) and X-Ray Diffraectrometer (XRD) to determine the content of the element in the calcite and Ca(OH)$_2$ phase, respectively. The HA was synthesized by mixing the Ca(OH)$_2$ and HNO$_3$, continued by stirring at 700 rpm at a temperature of 35 °C by following reaction as shown in Equation 1.

$$\text{Ca(OH)}_2 + 2\text{HNO}_3 \rightarrow \text{Ca(NO)}_3\cdot2\text{H}_2\text{O} \quad (1)$$

The Ca(NO)$_3$.2H$_2$O was mixed by the (NH$_4$)2HPO$_4$ and stirred at 700 rpm at a temperature of 35 °C for 3 hrs, with pH of the solution was maintained at 9 – 10 by dripping the NH$_4$OH. Here, the reaction occurs with the following Equation 2.

$$10(\text{Ca(NO)}_3\cdot2\text{H}_2\text{O} + 6(\text{Na}_2\text{HPO}_4 + 8\text{NH}_4\text{OH} \rightarrow \text{Ca}_{10}((\text{PO}_4)_6(\text{OH})_2 + 20\text{NH}_4\text{NO}_3 + 46\text{H}_2\text{O} \quad (2)$$

Based on Equation 2, the Ca(NO)$_3$.2H$_2$O as sources of calcium were mixed with the (Na$_2$)HPO$_4$ as sources phosphate and NH$_4$OH (7.5 M) as controlling pH, to generate HA. The solution was precipitated for 24 hrs, followed by washing of the deposited materials using DI water until the pH was neutral
(pH = 7). The deposited material was further dried at a temperature of 100 °C for 6 hrs. The HA powder was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS).

BCP/alumina composite was synthesized by mixing HA and alumina powders (Sigma-Aldrich) with the ratio of 90:10, 70:30, and 50:50 in % wt for sample A, B, and C, respectively. All of the samples were sintered at a temperature of 1200 °C for 2 hrs. Here, the structure and morphology of the samples were characterized by XRD, SEM, and EDS. Furthermore, the hardness of the samples was characterized by hardness Vickers with a load of 10 gf and detention for 10 s.

3. Results and Discussion

BCP/Alumina composite has been successfully synthesized by solid-state sintering using the starting material of Ca(OH)$_2$ from calcite stone (CaCO$_3$) by calcined at 1000 °C for 5 hrs to converting into CaO and then soaked in aquades to generate Ca(OH)$_2$. Here, the initial characterization was performed to investigate the content of the element in the Ca(OH)$_2$. The detail of the elements in Ca(OH)$_2$ is presented in Table 1.

| Compound | Ca (%) | Fe (%) | Co (%) | Er (%) | Yb (%) |
|----------|--------|--------|--------|--------|--------|
| Conc. Unit | 98.8   | 0.2    | 0.1    | 0.1    | 0.8    |

Table 1 shows the high calcium concentration of 98.84 % in the Ca(OH)$_2$ from calcite stone. The high concentration of calcium in the calcite stone is almost the same as the eggshells [25], which gives a favorable condition to calcite stone as the precursor to synthesize the HA. Furthermore, the obtained Ca(OH)$_2$ and HA were analyzed using XRD to investigate the crystal phase. Here, the XRD results are presented in Figure 1. Figure 1(a) confirms that the CaO phase exists in the Ca(OH)$_2$, with the Miller indices of (010) and (110). Figure 1(b) shows the HA peaks are observed in diffraction angle of 25.9º, 31.7º, 39.9º, 46.7º, 49.5º, 53.3º, and 64º, which has a good agreement with AMCSD model: 0001257. Here, the monetite (CaHPO$_4$) phase existed in the system.

Figure 2 presents the XRD pattern of HA-alumina composite sintered at a temperature 1200 °C with different HA: alumina ratio, labeled with A (90:10), B (70:30) and C (50:50). The result shows that the HA phase is partly transformed to become TCP. The composite with higher alumina concentration exhibits the lower peak intensity. This result reveals that the addition of alumina promotes the decrease of the HA crystallinity.
Table 2. Phase percentage of the composite analyzed from XRD data

| Composite | HA phase (in %wt) | β-TCP phase (in %wt) | Alumina phase (in %wt) |
|-----------|-------------------|----------------------|------------------------|
| BCP\(^1\)/alumina | 15.85 | 79.09 | 5.06 |
| BCP\(^2\)/alumina | 5.53 | 68.56 | 25.91 |
| BCP\(^3\)/alumina | 3.64 | 54.19 | 42.17 |

Figure 2 shows the XRD pattern of the HA/alumina composite with different HA: alumina ratio: A (90:10), B (70:30) and C (50:50).

Table 2 presents phase percentage of the composite after sintering at a temperature of 1200 °C. The sintering treatment at a temperature of 1200 °C promotes a phase transformation from HA to become TCP phases and further forms the BCP phase with HA/β-TCP ratio decrease with the increase of alumina concentration in the BCP/alumina composite. Furthermore, Brown et al. reported that the sintered HA above the temperature of 1200 °C leads the HA phase change into α-TCP, which stable at above temperature of 1300 °C [27].

Figure 3 shows the SEM image of the BCP/alumina composite with different BCP: alumina ratio. In addition, the BCP/alumina composite shows the dense morphology, with all exhibit the homogeneous shape and size. This condition is mainly related to grain growth due to high-temperature sintering. This result has a good agreement with the previous report by sintering at a temperature of 1100 °C [27] and 1200 °C [24]. Furthermore, the relation between morphology and hardness of the sample is explained. Table 3 presents the percentage of phase composition and a hardness value of the samples.

The results confirm that the hardness of the BCP/alumina increases with the higher alumina concentration. These results are presumably due to the enhancement of mechanic properties contributed by alumina. The pristine alumina is one of ceramics with high mechanic properties, which has an important role in the load-bearing application. This characteristic allows the BCP/alumina composite to have a high hardness number. Our results will provide a favorable condition of BCP/alumina composite to be applied to load-bearing in human dentin [28, 29, 30].
Figure 3. SEM image of BCP\(^1\)/alumina (a) BCP\(^2\)/alumina (b), BCP\(^3\)/alumina (c)

Table 3. The percentage of the phase composition and hardness of the samples.

| Composite          | HA phase (%wt) | TCP phase (%wt) | Alumina phase (%wt) | HVN (GPa)     |
|--------------------|----------------|-----------------|---------------------|---------------|
| BCP\(^1\)/alumina  | 15.85          | 79.09           | 5.06                | 33.5 (0.33)   |
| BCP\(^2\)/alumina  | 5.53           | 68.56           | 25.91               | 36.3 (0.36)   |
| BCP\(^3\)/alumina  | 3.64           | 54.19           | 42.17               | 38.8 (0.38)   |

4. Conclusion
The BCP/alumina has been successfully synthesized by sintering of the HA at a temperature of 1200 °C. Our results reveal that the BCP/alumina composites have the hardness at a range of 0.033–0.38 GPa, which fit with the hardness value of the human dentin with a range of 0.28–0.80 GPa.

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