The Effect of Sonication Duration on the Characteristics of Nano Hydroxyapatite-Silica (nHAp/SiO2) Composite and its Mechanical Properties

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Abstract. In this present study, we report the fabrication of nano-hydroxyapatite/silica (nHAp/SiO2) composite with the sonochemical method from Bojonegoro natural minerals, i.e. onyx stone and quartz sand. The nano-HAp was synthesized from Ca(OH)2 and H3PO4 solutions. The nHAp was successfully composed with silica by using sonication role. The sonication process was done in 1, 2, 3, and 4-hour variations at 20 % wt filler composition of Silica. The crystal structure properties of nHA were evaluated by X-ray diffraction (XRD). The ratio of Ca/P was evaluated by scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX). The microstructural characterization of the sample was captured by scanning electron microscopy (SEM). Vickers hardness test was also conducted to identify the hardness (mechanical properties) of the sample. On the other hand, the porosity of the sample also was reported. The results of this study show that hydroxyapatite has a size of 30.57 nm and the ratio of Ca/P was 1.57. The variations of sonication affect the mechanical properties of nHAp-SiO2 composite. The increasing sonication duration influences the hardness properties and porosity. The porosity of HAp (31.58 %) is still suitable to be applied for biomedical applications.

Keywords: Nano-hydroxyapatite, silica, hardness, porosity, natural material.

1. Introduction

Hydroxyapatite (HAp) has been extensively investigated and used in the bone clinical application for more than four decades. The increasing interest in HAp is due to its similar chemical composition to that of the inorganic component of natural bone [1] on account of its outstanding properties like biocompatibility, bioactivity, osteocoductivity, non-toxicity and non-inflammatory nature [2].

Synthetic HAp is often stochiometric with a chemical formula of Ca10(PO4)6(OH)2, and a specific atomic Ca/P molar ratio is 1.67. HAp is generally highly crystalline with the lattice parameter of a=0.95 nm and c = 0.68 nm and display a hexagonal symmetry typically (S.G. P63/m) with the preferred orientation along the c axis [3]. HAp exists as nanocrystals with dimensions of 4 x 50 x 50 nm whereby the nanocrystals are embedded in organic collagen fiber matrix which comprises 90 % of the protein...
content [4]. HAp is manufactured in many forms that can be prepared as a dense ceramic [5], powder [6], ceramic coating [7] and porous ceramic [8] as required for particular applications.

The chemical composition, crystallinity, size, and morphology of the HAp crystals and their aggregates play critical roles in determining their properties and potential applications [9-13]. Nano-hydroxyapatite (nHAp) crystals possess excellent sintering ability due to their high surface energy [14]. HAp nano-ceramics with enhanced mechanical properties can be fabricated using HAp nano-powder as raw material [15].

Even though HAp is biocompatible, the mechanical properties of HAp such as brittleness, low tensile strength, and poor impact resistance have restricted its compatibility in load-bearing applications [16]. This study proposes two methods to improve the mechanical properties of HAp. First, HAp was fabricated in nano scale because the nano-sized ceramic is bigger than the micro-sized one [17]. Moreover, Hap nano-bioceramics exhibit better bioactivity than those in micro-scale sizes [15]. Second, nHAp is composed of other materials that have better mechanical properties of silica. Silica (SiO$_2$) is biocompatible, non-toxic and has good mechanical properties, i.e. strong, hard and tough. In addition, silica also offers the advantages of its ability to increase the density of the structure and to exhibit excellent hardness [18]. Silica results in stronger and harder composites [19] so silica is selected to be a composite material with Hap. In this study, the nHAp-SiO$_2$ composites were synthesized through the sonochemical method by varying the duration of sonication to examine their effect on mechanical properties.

2. Materials and Methods

2.1. Synthesis of Nano-Hydroxyapatite from Onyx Stone

Onyx stone from Bojonegoro East Java was selected as a source of calcium to produce HAp. Onyx stone was grounded and sieved, and then it was used further in the laboratory. The powder was calcined at 500 °C for 1 h to obtain CaO powder. The CaO was then dissolved in distilled water to obtain Ca(OH)$_2$. The solution was stirred at a rate of 700 rpm and 50 °C for 60 mins to be subsequently incorporated in an ultrasonic bath and disonicated at 50 °C for 60 mins. During the course of the sonication, H$_3$PO$_4$ 6M was dripped. NH$_4$OH was dripped to control the pH of the solution (9 ~ 10). The produced HAp was then filtered and dried at 100 °C for 24 h to remove H$_2$O, and then crushed again to obtain homogeneous powder. The powder was characterized by XRD, SEM, and EDX to identify the phase, surface morphology and Ca/P ratio, respectively. Vickers hardness test and porosity were measured to determine the mechanical properties (hardness) and porosity of the samples.

2.2. Synthesis of nHA/SiO$_2$ Composite with Sonochemical Methods

The powder of nHAp and silica was dissolved in DI water. The solution was stirred at a rate of 1000 rpm at 50 °C for 1 h. Furthermore, the solution was incorporated in an ultrasonic bath and was sonicated for various durations of 1, 2, 3 and 4 h at 50 °C. The solution was filtered and dried in a furnace at a temperature of 100 °C for 24 h. The powder was characterized by XRD and SEM-EDX to study the phase and surface morphology of composite, respectively. Vickers hardness test and porosity test were also measured to determine the mechanical properties (hardness) and porosity of nHA/SiO$_2$ composite.

3. Results and Discussion

The result of XRF test on onyx stone is shown in Table 1. According to the Table 1, the onyx stone contains a dominant element of calcium, which reached 94.33 % of the compound, and other elements such as Ti, Mn, Fe, Cu, Sr and Ba present in a low percentage within the compound.
The XRD pattern of HAp analyzed by Highscores Plus software shows a good match with the crystallographic open database code of AMCSD 0002299. The presence of Ca₃(PO₄)₂ or whitlockite impurities in HAp and whitlockite phase shows a ratio of 94.26 % : 5.74 %. This result indicates that Ca₃(PO₄)₂ (tri calcium phosphate) is biocompatible and biodegradable [20]. We obtained the crystal size of HAp by using the Scherrer equation of 30.57 nm. The size of these crystals shows a compatibility of the sample with the size of crystals within the human bones of 20-80 nm [21]. Furthermore, the EDX result shows a Ca/P ratio of about 1.57 that represented the non-stoichiometric sample and this corresponds with the apatite bone characteristic.

The XRD pattern for HAp and HAp-SiO₂ composites with various sonication durations can be seen in Figure 2. The PCW analysis for HAp-SiO₂ composite produced the same diffraction pattern as that of the HAp with the 002297 AMCSD code. The peak of SiO₂ is not clearly observed on the XRD pattern of HAp-SiO₂ composite. These results show that silica has amorphous properties. The HAp-SiO₂ composite did not affect the crystal structure of HAp but impacted the intensity of each peak. The high and sharp peak could be attributed to the crystallinity of the samples. The peak intensity and FWHM increased along with the increasing duration of sonication. This implies that the size of the HAp crystals in the composite is decreased while the duration of sonication is prolonged. This result is in line with a previous report [22].
Table 2. The lattice parameters and crystal size of HAp-SiO₂

| Duration of sonication | Lattice Parameters (Å) | The size of crystal (nm) |
|------------------------|------------------------|--------------------------|
|                        | a          | b          | c          |                |
| 1 h                    | 9.4301     | 9.4301     | 6.8314     | 36.35          |
| 2 h                    | 9.4352     | 9.4352     | 6.8205     | 30.24          |
| 3 h                    | 9.4771     | 9.4771     | 6.8513     | 29.96          |
| 4 h                    | 9.4404     | 9.4404     | 6.8297     | 29.72          |

Figure 2. XRD pattern of HAp and HAp-SiO₂ with various sonication durations

Table 2 illustrates the values of lattice parameters and crystal size of nHAp-SiO₂ composite for different sonication durations. According to Table 2, the experimental lattice parameter of nHA-SiO₂ composite is in good agreement with the theoretical lattice parameter, which is \(a = 9.432\ Å, c = 6.881\ Å\) [22-24]. On the other hand, Figure 3 shows the hardness of nHAp-SiO₂ composite for various sonication durations. Sonication duration linearly increase along with the increasing hardness of nHAp-SiO₂ composites with a high correlation rate \(R^2 = 0.995\).

Figure 3. Graph of the hardness of nHA-SiO₂ composite in various sonication durations
To characterize of hardness of the HA and HA-SiO$_2$, a material of HA and HA-SiO$_2$ was synthesized via sonochemical method within ranges of 26-30 HVN or 0.26-0.3 GPa. This value is significantly too high for implant application which requires 3.43 GPa but this is suitable for human tooth dentin application with the hardness standard is 0.25 -0.8 GPa [19]. The different result of hardness of HA and HA-SiO$_2$ materials might be caused by too low sintering temperature used, i.e. 500 °C for 1-hour detention. Lim et al. [24] reported that the sintering temperature affects the hardness of HAp-Zirconia.

![Figure 4](image)

Figure 4. Graph of the porosity of nHA-SiO$_2$ composite for various sonication durations

Figure 4 shows the effect of sonication duration on the porosity of nHAp-SiO$_2$ composite. The porosity of nHA-SiO$_2$ for sonication duration of 1, 2, 3, and 4 hours were 25, 20, 14.29, and 10 %, respectively. The sonication duration linearly decreases the porosity of nHA-SiO$_2$ composite with the correlation $R^2 = 0.997$. The porosity of nHAp-SiO$_2$ is lower than the porosity of HAp which is 31.58 %. These results implied that the addition of SiO$_2$ (20 % of composite weight) as a filler can close the pores of HA. Whereas, the porosity of bioceramic materials for biomedical applications can be tolerated in a range of 10-40 % [25] so the obtained porosity of HAp 31.58 % is still suitable for biomedical applications.

Figure 5 shows the photographs of HA-SiO$_2$ with the variations of sonication duration, i.e. 1 to 4 hours. Based on Figure 5, all of the samples have high homogeneity. These results confirmed that the porosity of the sample with the 4-hour sonication duration has the highest porosity and is well confirmed by the graphs of the sample porosity illustrated in Fig 4.
Figure 5. SEM photographs of HA-SiO$_2$ (sonication duration $a=1$ h, $b=2$ h, $c=3$ h, and $d=4$ h) and (e) pure HA.
4. Conclusion
This work has successfully synthesized nano-hydroxyapatite by using naturally Onyx stone from Bojonegoro East Java as the source of calcium with sonochemistry method. Sonication duration influences the hardness and porosity of nHA-SiO$_2$. The hardness of nHA-SiO$_2$ is significantly increased as along with the increasing the sonication duration. On the other hand, the porosity of nHA-SiO$_2$ is slightly decreased along with the increasing sonication duration. It means that natural materials are potential to synthesize more benefits from biomaterials. Moreover, the porosity of HAp (31.58 %) that shown by this research is suitable biomedical applications.

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