# Improvement of Hardness of Hydroxyapatite by the Addition of Silica from Tin Tailings

F Afriani[1*], Evi.J[1], Zaitun[2] and Y Tiandho[1]

[1] *Department of Physics, Universitas Bangka Belitung, Kampus Terpadu UBB, Balunijuk, Kecamatan Merawang, Kabupaten Bangka, Provinsi Kepulauan Bangka Belitung, Indonesia*
[2] *Department of Precision Machinery and Precision Instrumentation,, University of Science and Technology of China, 443 Huangshan Road, Hefei, Anhui, The People's Republic of China*
**Email: fitri-afriani@ubb.ac.id*

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***Abstract***

*The application of bone scaffolding in bone therapy is an alternative solution developed in bone tissue engineering technology to avoid bone donors' scarcity. The main requirement for a material that can be used as a scaffold is that it is biocompatible. Hydroxyapatite is a calcium phosphate ceramic that is often used as the primary material for scaffolding because it has good biocompatibility properties. However, like most ceramics, hydroxyapatite has low mechanical properties. In this study, we synthesized hydroxyapatite from cockleshell waste. To improve hydroxyapatite's mechanical properties (hardness), we added silica from tin tailings to hydroxyapatite. Through the analysis of the x-ray diffraction (XRD) pattern, it was found that hydroxyapatite was successfully synthesized from cockleshell using the co-precipitation method. Analysis of the diffraction pattern of tin tailings also shows that most of the crystals comprising tin tailings sand are silica in the α-quartz phase. The addition of silica to hydroxyapatite followed by compaction and sintering at a temperature of 800ºC did not produce a new crystal phase. The addition still has a diffraction pattern consisting of a combined XRD pattern of hydroxyapatite and silica. Based on the hardness test using the Vickers hardness method, it is known that the addition of silica can increase the hardness of hydroxyapatite.*

**Keywords:** *biomaterial, hydroxyapatite, silica, tailing.*

## I. INTRODUCTION

IN recent years, scientists in the field of bone tissue engineering have developed a scaffold that is applied to the bone therapy process to overcome the shortage of donors. It is hoped that the bone scaffold development can be an alternative to the bone therapy process [1], [2]. Conventional bone therapy methods such as allografts and autographs have several disadvantages, such as being prone to experiencing donor shortages, possible rejection, and viral infections [3].

One of the absolute conditions that must be met when a material is to be used as scaffolding is that the material must have good biocompatibility [4]. It is essential because the scaffolding will interact directly with human tissue when applied to the human body so that the use of materials with good biocompatibility will minimize the occurrence of side effects and accelerate the healing process. Hydroxyapatite is one material that is widely known to have good biocompatibility properties [5]. Hydroxyapatite is a bioceramic calcium phosphate family with the chemical formula $C_{10}(PO_4)_6(OH)_2$. The biocompatibility of hydroxyapatite is well understood because hydroxyapatite is the primary building block of human bones [6], [7].

One of the fascinating natural material sources to be synthesized into hydroxyapatite is cockleshells, especially *Anadara granosa* [8]. It is because the shells contain high amounts of calcium. Also, as an archipelago country, the production is abundant and can be obtained easily [9].

When applied to a porous scaffold, hydroxyapatite has drawbacks mainly related to its mechanical properties [10], [11]. Hydroxyapatite tends to be brittle, so it has mechanical properties that are feared not to bear the body's burden during the healing process. Whereas on the other hand, pores in the scaffold have an essential role, especially related to the transfer of nutrients to cells and space for cells to develop [12].

This article proposes an innovation to improve hydroxyapatite's mechanical properties, particularly hardness, by adding silica to hydroxyapatite. Silica is a material that is known to be used to improve the mechanical performance of a material [13], [14]. On the other hand, silica is a material that has good biocompatibility and can increase a scaffold's bioactivity [15], [16]. The source of silica to be applied comes from tin tailings sand silica. It is because the amount of tin tailings is abundant, considering that Indonesia is one of the primary tin producers in the world [17], [18].

## II. MATERIALS AND METHODS

To synthesize hydroxyapatite in this study, we used cockleshell waste from Pangkalpinang, Bangka Belitung Islands. The synthesis of hydroxyapatite was carried out by the co-precipitation method, as we have developed in the previous paper [19]. Before being used, the shell powder was calcined at a temperature of 1000ºC to produce calcium oxide (CaO). The calcium oxide powder was dissolved in distilled water and added with $(NH_4)_2HPO_4$ to have a Ca/P ratio of 1.67. The resulting precipitate was then sintered at a temperature of 900ºC. The silica used in this study is the silica of post-mining land in Pangkalpinang, Bangka Belitung Islands. After cleaning and refining, the silica is added to the hydroxyapatite by mixing it with distilled water media. The samples synthesized were hydroxyapatite without silica, hydroxyapatite with 20% by weight of silica (silica-20), and hydroxyapatite with 40% by weight of silica (silica-40). The mixing powder is compacted and sintered at a temperature of 800ºC. We use the x-ray diffraction (XRD) method to determine the crystal phase, while the hardness value was determined using Vickers hardness test.

## III. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of hydroxyapatite synthesized from cockleshells powder. It appears that almost all peaks in the x-ray diffraction pattern correspond to the peaks belonging to the hydroxyapatite. Thus, it appears that this research has successfully synthesized hydroxyapatite from cockleshells. The hydroxyapatite produced has a hexagonal crystal system with a space group: P63/m. The lattice parameters of hydroxyapatite are: $a = b =$ 9,432 Å and $c$ = 6,881 Å. The XRD pattern of hydroxyapatite synthesized in this study is similar to the XRD pattern in Azis et al. (2018) with eggshells as the raw material [20].

In Figure 2, the XRD pattern of tin tailings is presented. It appears that through the analysis of the XRD pattern, it is known that the majority of tin tailing is composed of silica crystals. Most of the XRD peaks correspond to α-quartz type silica (PDF-2: 01-083-0539). Tin tailings silica has a hexagonal crystal system with space group P3121. The silica lattice parameters are a = b = 4,921 Å and c = 5,416 Å. This XRD analysis results follow the previously carried out XRF measurements, stating that the tin tailings contain high silica amounts, reaching 89.35% [21].

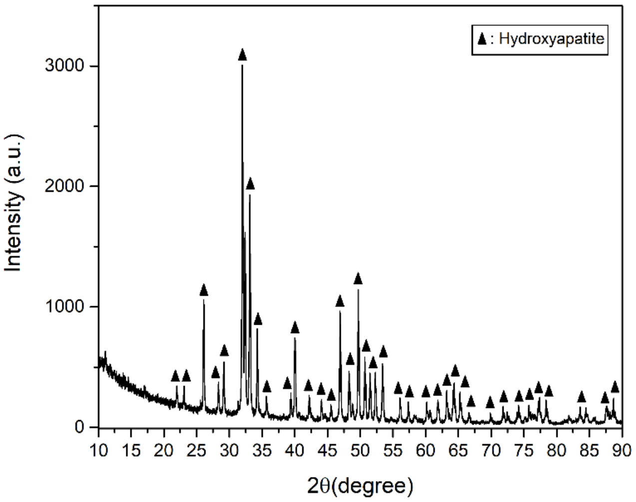

**Figure 1.** XRD pattern of hydroxyapatite

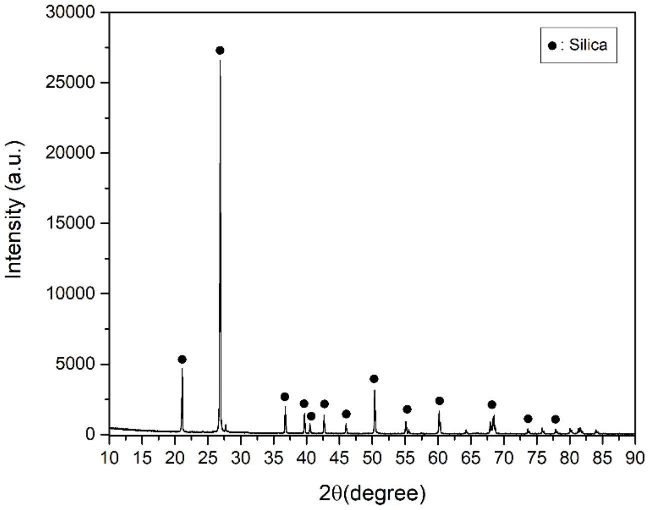

**Figure 2**. XRD pattern of silica tin tailings

The XRD pattern is obtained after adding silica to hydroxyapatite and continuing with the compaction and sintering process, as shown in Figure 3. It appears that the compaction process and the sintering process at a temperature of 800ºC do not change the resulting hydroxyapatite phase. Based on the XRD pattern, it is known that the addition of silica to hydroxyapatite does not form a chemical reaction. The mixture between hydroxyapatite and silica is still composed of the two materials without any peaks forming associated with the impurity crystal phase. Therefore, this indicates that the synthesized mixture does not interfere with the two constituents' biocompatibility properties. The absence of a chemical reaction between hydroxyapatite and silica in this study is related to the low thermal energy given to the sintering process [22]. Also, the hydroxyapatite and silica phases in the quartz type have good stability.

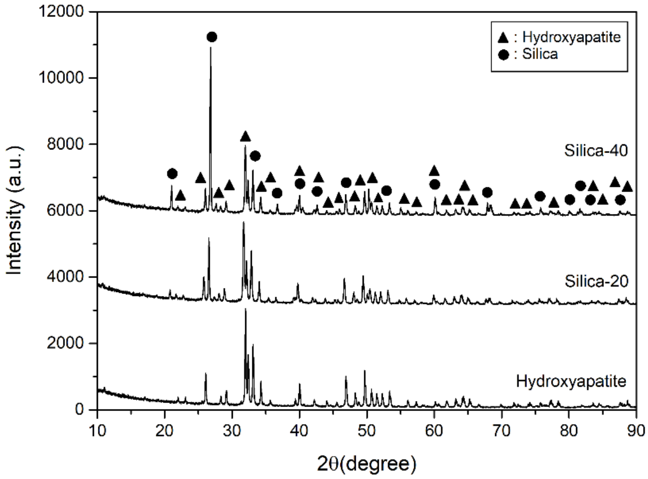

**Figure 3**. XRD pattern of the sample after adding silica to hydroxyapatite

In Figure 4, the results of hardness testing using the Vickers hardness method are presented. It appears that the indentation has a diamond shape. The indentation of hydroxyapatite without silica addition has a larger diagonal size compared to hydroxyapatite added with silica. It indicates that the addition of silica can increase the hardness of the hydroxyapatite mixture.

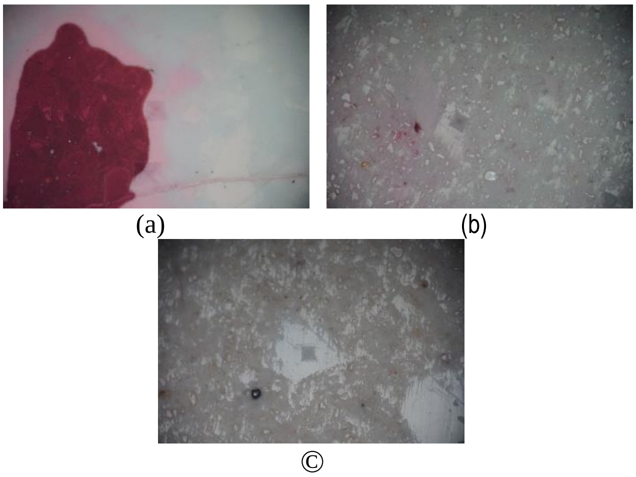

**Figure 4**. The results of the indentation micrograph: (a) hydroxyapatite without silica; (b) silica-20; and (c) silica-40

Quantitatively, the calculation of Vickers hardness (HV) is:

$$HV = \frac{1.8544F}{d^2} \quad (1)$$

where F is the load applied, and d is the diagonal of the indentation. Using this formula, the hardness test results of the mixture of hydroxyapatite and silica synthesized in this study are shown in Table 1. Without the addition of silica, the hardness of the compacted and sintered hydroxyapatite is 32 HV. The addition of silica to hydroxyapatite will increase the hardness of 72 HV for silica-20 and 54 HV for silica-40. The increase in hardness due to silica in hydroxyapatite can be understood as an analogy with the appearance of the second phase in hydroxyapatite. This second phase can increase the stress in the material and is related to the hardness of the material. However, it appears the hardness of hydroxyapatite with the addition of 20% silica is higher than that of 40% addition of silica.

**Table 1**. Hardness testing results

| Silica percentage (wt%) | Hardness Vickers (HV) |
|---|---|
| 0 | 32 |
| 20 | 72 |
| 40 | 54 |

## IV. CONCLUSIONS

This study has succeeded in synthesizing hydroxyapatite with a hexagonal crystal structure from shells through the co-precipitation method. Based on XRD analysis, it is known that the composition of tin tailings sand is dominated by quartz silica. The addition of silica from tin tailings to hydroxyapatite followed by the compacting and sintering processes at a temperature of 800 °C did not produce new impurities. The XRD pattern resulting from the mixing still contains hydroxyapatite and silica compounds. Through the hardness test results, it appears that the addition of silica to hydroxyapatite is effective in increasing the hardness. Without silica addition, the hydroxyapatite’s hardness was 32 HV, and after adding silica, the hardness reached 72 HV.

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