Synthesis and characterization of hydroxyapatite/silica composites based on cockle shells waste and tin tailings

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Abstract. Hydroxyapatite is a biocompatible material that has great potential in the development of scaffold in the bone tissue engineering. To satisfy the needs of mechanical properties and the time of degradation to support the bone growth, currently hydroxyapatite-based composite material is being developed. One of the fillers that can be used is silica because it also has excellent biocompatible properties. In this study, hydroxyapatite/silica composites were prepared using cockle shell waste and tin tailings as raw materials. The study aims to utilize the waste produced in the maritime and mining sectors to move towards sustainable industries. The characteristics observed in this study are crystal characteristics and degradation properties of composites.

1. Introduction

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) (HAp) is a bioceramic that has been widely researched in tissue engineering as a bone scaffolding or grafting material. This is because HAp has good biocompatibility and has biodegradable properties which can be decomposed by body solutions [1]. Also, the bone is composed of 22% protein, 8% water, and the remaining approximately 70% is the HAp nanoparticle [2].

However, although HAp has properties that are almost the same as bone characteristics and good biocompatibility there are several disadvantages such as poor mechanical properties [3] when applied to the bone and poor bioactivity. Therefore, HAp-based material development and other calcium phosphate families have led to doped HAp material or HAp-based composite material. Some materials that are often used as additional material in the synthesis of HAp are silica. Basically, silica is a bioglass-based material that has been known to be accepted by the human body. In addition, silica can increase the mechanical strength of HAp scaffolds. In vitro testing has also shown that HAp/silica composites have higher bioactivity properties than pure HAp. The presence of silica in the composite HAp/silica can provide an ion exchange effect on the surface of the material which can induce nucleation and precipitation of the HAp layer [1, 4].

To support the sustainability program, the use of material derived from waste as a base material has attracted a lot of attention. Similarly, the development of waste material-based HAp synthesis. Some wastes that can be utilized in the HAp synthesis include eggshells [5] and shells of oysters and cockle [6, 7]. The selection of waste material is because it contains high levels of calcium, thus with the addition of phosphate at certain levels, it allows the formation of calcium phosphate. As a maritime
country, one of the abundant wastes in Indonesia is cockle shells. This is because shells can be easily found along coastal paths in various islands in Indonesia [8-10].

2. Methods

2.1. Calcium Oxide Preparation from Cockle Shells
The cockle shells that will be used in this study were previously cleaned and dried in room temperature for 24 hours. Next, the calcination process was carried out at 1000°C for 3 hours to decompose calcium carbonate into calcium oxide. The calcium oxide powder is then stored in a dry container which is then used as a source of calcium in the synthesis of hydroxyapatite (HAp) powder.

2.2. HAp synthesis
Calcium oxide powder from cockle shells dissolved in aquadest 100 mL, then (NH4)2HPO4 was dissolved in 100 mL aquadest with a Ca/P ratio of 1.67. Precipitation and homogenization of calcium and phosphate solutions were carried out at room temperature for 150 minutes with a stirring speed of 300 rpm, then continued with aging for one night. The precipitation results are then filtered using filter paper and washed with distilled water and then sintered at 900°C with a holding time of 5 hours.

2.3. Silica preparation from tin tailings
The tin tailing sand used in this study came from the post-mining area in Pangkalpinang. Before use tailing sand is washed and dried at a temperature of 110°C to remove macro-impurities. Furthermore, tailing sand was crushed using a mortar and sifted using a 200 mesh sieve. The fine tailing sand that passes the sieving process is used as a source of silica.

2.4. Composite HAp/silica synthesis
Synthesis of HAp and silica composites was carried out by combining HAp and silica with a mass ratio of 50/50. Furthermore, HAp and silica are dissolved into water and stirred until homogeneous. Then filtering is done using a vacuum machine to separate solid and liquid material. The filtering results were then sintered at 110°C for 3 hours to obtain HAp/silica powder.

2.5. Simulated Body Fluid Preparation
Simulated Body Fluid (SBF) is a synthetic solution that has an ionic composition close to the composition in blood plasma. The SBF composition is shown in Table 1.

| Material      | Mass/Volume |
|---------------|-------------|
| NaCl          | 8,035 g     |
| NaHCO3        | 0,355 g     |
| KCl           | 0,225 g     |
| K2HPO4.3H2O   | 0,231 g     |
| MgCl2.6H2O    | 0,311 g     |
| HCl 1 M       | 35 mL       |
| Aquadest      | 965 mL      |

2.6. In vitro Testing
In vitro testing was carried out by preparing 10 mL bottles of 10 pieces and preparation of 2 pieces of HA pellet samples, 2 pieces of SiO2 and 2 pieces of HAp/SiO2. The SBF solution will be put into each bottle as much as 40 mL. The SBF solution used for testing is 490 mL. Data retrieval starts on the 3rd day, namely the measurement of sample mass and the solubility of particles in SBF solution measured using TDS Meter. The SBF solution without pellet sample is used as a control. Furthermore, samples in the form of pellets were added to each bottle containing SBF solution. Then the bottle is closed and
stored in a closed room. Data retrieval was carried out on day 3 and day 7. Before weighing, the sample was drying for 2 hours at 70°C

3. Results and Discussions

In Figure 1, the results of the XRD analysis of cockle shells-based Hap, tailing sand-based silica, and Hap/SiO2 composites are presented. Through the XRD results, it appears that the Hap powder synthesized in this study has a peak that is almost entirely related to the reference XRD pattern of the reference Hap (PDF-2 01-084-1998). The synthesized Hap has a hexagonal crystal system with space group P63/m and lattice parameter (Å): \(a = 9.4148, \ b = 9.4148, \ c = 6.8791\). Whereas for silica sand tin tailings used in this study are related to the XRD silica pattern with the \(\alpha\)-quartz phase (PDF 01-085-1053). The crystalline system of silica from tin tailings is hexagonal with space group P3221 and lattice parameter (Å): \(a = 4.9128, \ b = 4.9128, \ c = 5.4042\). When synthesizing composites of Hap/silica, it appears that the peak of XRD pattern of the composite is related to the two peaks of the constituent material: Hap and silica. This indicates that the process of combining Hap and silica does not change the compounds of both. Each constituent material retains its characteristics.

![Figure 1. XRD patterns of Hap, SiO2, Hap/SiO2](image)

In Figure 2, the results of the changes in the mass of silica, Hap, and Hap/silica samples were obtained which had been pelleted with a load of 5 kN for 3 minutes in SBF solution. The immersion results for 3 days showed that the mass changes for silica, Hap, and Hap/silica were 4.35%, 11.86%, and 11.59% respectively. Whereas after 7 days the mass change from these samples in the sequence was 5.13%, 28.13%, and 16.67%. Through these results, it appears that silica has a lower biodegradable property than Hap. Hap is more soluble than silica. As for composites Hap/silica has biodegradable properties that are between the two. The addition of silica into Hap slows down the degradation process by SBF solution thus it can be used to regulate the times of degradability of the Hap scaffold when it applied to the bone.
In Figure 3, the results of TDS analysis are presented in SBF solutions after immersing the pellet samples for 3 days and 7 days. It appears that the entire sample experienced a decrease in the number of dissolved particles in the SBF. This can be understood because of the exchange of dissolved compounds/ion particles with a pellet sample. Some of the ions in SBF that have the potential to undergo ion exchange with pellet samples are Na⁺, K⁺, Mg⁺, HCO₃⁻, HPO₄²⁻, and Cl⁻. The value of silica dissolved particles has a higher value compared to Hap/silica and Hap. The lowest of the number of dissolved particles in Hap can occur due to the release of Ca²⁺ ions into the solution and substituted by 2 ions with an oxidation number of 1+ (i.e. Na⁺, K⁺, Mg⁺). Thus it reduces the number of dissolved particles in the SBF. This also corresponds to the results of mass changes in Figure 2 which shows that Hap has the greatest mass loss compared to others.

Figure 3. The number of total dissolved particles in SBF after silica, Hap, and Hap/silica immersion

4. Conclusions
According to the results, it can be stated that the addition of silica powder into Hap will produce a Hap/silica composite. The addition of silica does not change the compound in Hap. The results of mass change analysis show that silica is more difficult to degrade in SBF solutions than Hap. Addition of silica into Hap to form a composite of Hap/silica is also effective to slow down the degradation process. The results of the analysis of the level of material degradation based on mass changes are also in accordance with the analysis of
dissolved particles in SBF. As a result of ion exchange between samples with ions in SBF, the number of dissolved particles in SBF with immersion Hap has the lowest value compared to silica and Hap/silica.

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