Characterization of Calcium Powders from Merauke Mangrove Crab Shells

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Abstract. In this study, we report the successful fabrication of calcium powders by utilizing mangrove crab shells originating from Merauke as a natural source of bio-ceramic. Calcium powders from Merauke mangrove crab shells were synthesized at different temperatures varying from 800 to 1000 °C for 5 h in ambient atmosphere. It is observed that the calcinations temperature plays a significant role in the formation of hydroxyapatite crystallite phase. From the XRD and FTI characterization, it is confirmed that hydroxyapatite crystal was well synthesized at temperature of 1000 °C with no more carbon phase remains. SEM image also shows better crystalline shape having crystal size of ~ 800 nm. However, due to long period of air exposed, samples may be hydrated to Ca(OH)2.

1. Introduction
Bio-ceramic is a class of ceramic that mainly applies on repairing or replacing damaged parts of musculoskeletal systems [1], and it is also used in different applications throughout the body. Based on its interaction with the hot tissue, bio ceramic can be categorized as bioinert, bioactive, and biodegradable materials [2]. However, research has mainly focused on bioactive material since it can react with physiological fluids and produce a strong bond between the material and bone. Hydroxyapatite (HAp) and Ca10(PO4)6(OH)2, are well known bioactive ceramics that common to be used for implantation purpose due to its chemical and crystallographic similarity to the carbonated apatite in human bones and teeth [3-4].

Large numbers of techniques have been developed to synthesize hydroxyapatite powders, it includes wet chemical method, sol-gel method, hydrothermal synthesis procedure, continuous precipitation, thermal deposition and solid-state reaction method [5]. Natural resources of biogenic structures and materials such as eggshell [5], corals [6,7], seashells [8], animal bones [9,10], and cuttlefish bones [11,12] have been widely developed for medical purposes. These natural materials were preferable due to its low production cost and it is environmentally friendly technology, particularly for waste management.

In the last decade, synthesis of hydroxyapatite derived from crabs’ shells has attracted a lot of attention [13-15], because it rich content in calcium carbonate and it is available in a large number. In this study, Merauke Mangrove crab shells (Scylla serrata) were selected as a raw material since this type of crabs were considered a waste for local households, hence the materials were easily available in the natural mangrove areas in Merauke and it is easy to obtain. Additionally, the crab shells of contained less harmful compounds due to its natural ecosystems that are less polluted from urban and industrial activities, particularly when it is compared to other type of mangrove area in Indonesia.
The purpose of this research was to synthesize calcium powders from Merauke mangrove crab shells and to study the effect of calcinations temperatures to the hydroxyapatite crystalline growth. The calcinations temperatures of calcium powders were range from 800° to 1000°C.

2. Experimental Method
The waste of crab shell was collected from local restaurants and home industries in Merauke, Papua Province, Indonesia. Subsequently, these shells were washed, dried, crunched and grinded, in order to obtain a raw powder. The powders were then calcined at different temperatures varying from 800 to 1000 °C for 5 h with a heating rate of 5 °C/min in ambient atmosphere. After the calcination process, each sample were stirred using a magnetic stirrer at 90 °C for 2 h.

After the previous process, the calcium powder was analyzed for its crystal structure, chemical constituents, and morphology characteristics using X-Ray Diffraction, Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscopy. The X-ray diffraction (XRD) patterns were collected using a Shimadzu 7000 X-Ray Diffractometer with CuKα radiation. The FTIR spectra (4000-4000 cm⁻¹) were recorded on a Shimadzu 8400 spectrophotometer. The SEM images were recorded on a JEOL JSM-IT 300 scanning electron microscope, operated at 20 kV accelerating voltage.

3. Result and Discussion
3.1. Crystal structure identification
Figure 1 shows the XRD pattern of samples calcium powder samples synthesized at temperatures of 800, 900, and 1000 °C. Peaks from the XRD pattern were identified using pattern data from Joint Committee on Powder Diffraction Standards (JCPDS). Peaks marked as # 1 was correspond to CaO (JCPDS file 77-2376); #2 was correspond to Ca(OH)₂ (JCPDS file 84-1264); #3 was correspond to calcite CaCO₃ (JCPDS file 86-174) and #4 was correspond to aragonite–CaCO₃ (JCPDS file76-606).

![XRD pattern of calcium powder synthesized at temperatures of 800 °C, 900 °C, and 1000 °C](image)

Figure 1. XRD pattern of calcium powder synthesized at temperatures of (a) 800 °C, (b) 900 °C, and (c) 1000 °C (1 CaO; 2 Ca(OH)₂; 3 calcite CaCO₃; 4 aragonite CaCO₃)
Patterns from calcium powders synthesized at temperatures of 1000 °C (sample c) clearly exhibit strong peaks corresponding to Ca(OH)$_2$ together with peaks from CaO. Granados report that Ca(OH)$_2$ phase may be originated from CaO hydrated [16]. This indicated that the calcium powder synthesized at temperatures of 1000 °C might be already hydrated due to air exposed. In contrast, patterns from calcium powders synthesized at temperatures of 800 and 900 °C (sample a and b) were exhibit strong peaks from calcite CaCO$_3$ and aragonite CaCO$_3$, means that there are carbon remains. Shells naturally contain organic matter and impurities in addition to calcium carbonate. The heating of calcium powders to high temperatures more than 900 °C may remove these organic matter and impurities [16]. Decomposed of both calcite and aragonite phase from samples (a) and (b) may originated from not sufficient calcinations temperature.

3.2. Chemical constituent characterization

Figure 2 shows the different FTIR spectra obtained. All sample show CaO spectrum confirmed by strong peak from 3643 cm$^{-1}$ and 1448 cm$^{-1}$. Other peaks, such as 1049 cm$^{-1}$ and 873 cm$^{-1}$, also confirmed that hydroxide is remains from the carbonation process. The wide and broad peaks between 3643 cm$^{-1}$ and 1448 cm$^{-1}$ shown from samples (a) and (b) were related to carbonate ion (C=O). In accordance with the crystal structure characterization, the calcium carbonate may remain from samples synthesized at temperatures of 800 and 900 °C. We can conclude from FTIR that the optimum of calcium powders came from sample synthesized at temperature of 1000 °C since it shows no more carbonate ion, however, the hydroxide confirmed that CaO was hydrated became Ca(OH)$_2$.

Figure 2. FTIR Spectra of calcium powder synthesized at temperatures of
3.3. **Surface morphology characterization**

Figure 3 (a) and (b) shows amorphous like particles and non-homogenous particle size. Both images also show some enormous size agglomerated particles. Low crystalline and amorphous nature should be improved via higher thermal treatment [17]. Furthermore, figure 3 (c) which representing calcium powder synthesized at 1000 °C, shows better crystalline with homogenous cylindrical shapes having crystal size of ~ 800 nm.

![Figure 3. SEM images of calcium powder synthesized at temperatures of (a) 800 °C, (b) 900 °C, and (c) 1000 °C](image)

**4. Conclusion**

Calcium powders from Merauke mangrove crab shells were successfully synthesized. It is clearly observed that the calcinations temperature plays an important role in the formation of hydroxyapatite crystallite phase. The crystalline identification and chemical constituent characterization confirmed that hydroxyapatite crystal was well synthesized at temperature of 1000 °C with no more carbon phase remains. The morphology characterization also confirmed better crystalline from calcium powders synthesized at temperature of 1000 °C. However, due to long period of air exposed, samples may hydrate to Ca(OH)$_2$. Storage method should be well considered in the future.

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