Synthesis and characterization of CaCO₃/CaO from Achatina Fulica in various sintering time

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Abstract. Snail shell is an abundance of waste in Indonesia, particularly from snail or Achatina fulica snail. Snail shell has high calcium content; thus, it can be used as an alternative replacement for CaO/CaCO₃. This research aimed to make CaCO₃ and CaO from the Achatina fulica snail shell waste as the base material of hydroxyapatite. The synthesis process of CaO/CaCO₃ used the ball milling method for 6 hours in various sintering temperature of 850 °C, 950 °C, 1050 °C. The synthesised samples were then characterized using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM-EDX) and Fourier transform infrared (FTIR). The XRD results showed the successful synthesis of snail shell waste into CaCO₃ and CaO with the smallest particle size from each temperature variation were 17.60 nm, 30.16 nm, and 53.30 nm. The SEM images showed agglomeration and porosity in all samples. The EDX test results displayed the highest Ca (calcium) was found in the sample with 1050°C sintering temperature, and the highest O (oxygen) level was found in the sample with 850 °C sintering temperature. The FTIR test results presented the functional group transformation from CaCO₃ into higher CaO along with the increase of the sintering temperature.

Keywords: achatina fulica, calcium carbonat, ball milling, morphology, phase
1. Introduction
Achatina fulica snail or AF snail is the pest in the rice field and is often used to feed the animal such as ducks. The snail shell is an invertebrate exoskeleton that consists of 95–99% calcium carbonate (CaCO\(_3\)) and other components [1]. CaCO\(_3\) is the highest component in the snail shell, and it affects the shell hardness. CaCO\(_3\) is one of the essential materials in the application of orthopedy because of its similar properties with human bone and has the potential to replace the metal and ceramic in the implantations [2]. The process to turn the snail shell into hydroxyapatite powder is an alternative to resolve the waste [3].

Hydroxyapatite (HA) with the molecule formula of Ca\(_{10}(PO_4)_{6}(OH)_2\) is the primary inorganic component of teeth and bones which has been widely used as a carrier for drug delivery, bone replacement for bone defect fillers, scaffolding matrices for tissue engineering, and coatings on metal implants due to excellent biocompatibility and bioactivity [4]. Besides, all apatite minerals exhibit excellent properties as ion exchangers [5]. HA can also be used to remove heavy metals in wastewater [6].

The previous research aimed to find the effect of sintering temperature in obtaining HA powder or calcium phosphate biphasic through the wet chemical precipitation method. The ratio of HA formation was confirmed using means of energy-dispersive X-ray spectroscopy (XRD) analysis. While SEM determines structural and morphological, bonding compounds that arise in the formation of HA are observed using Fourier transform infrared spectroscopy (FTIR) such as biomaterials that are expected to find potential applications in the orthopaedic and biomedical industries. This research was the development of previous research. To reached the goals, innovations are needed in processing the HA, particularly in the base material, that was Achatina fulica snail shell, and the various sintering temperature to gain the advantages such as the character and properties of AF powder [7].

2. Method
The synthesis of AF powder was performed using the ball milling method to a combination of 300 g snail shell, five 33.3 g zirconia ball and 100 ml acetone. The mill was conducted for 6 hours at 800 rpm speed rotation to produce micro to nanometer powder. The mixing involved dispersion phase in a liquid form that was acetone. Acetone was added to provides lubrication in the milling process that unites and ties snail shells. The snail shell powder was mixed with the acetone in the zirconia container homogenously. The mixture was milled in wet condition in the planetary ball mill (QM-3SP2) machine. Next, the powder was calcinated in the microwave at 110 °C for 1 hour. The calcination process aimed to remove the moisture and produce a dry powder. The calcinated powder, then, was pounded for 1 hour to reduce the powder size. The pounded powder then was sintered at temperature variations of 850 °C, 950 °C, and 1050 °C for 1 hour to release the moisture inside the powder. The phase identification used the PanAnalytical XRD with Cu Ka (λ = 1.5406 Å) radiation, while morphology and element analysis were observed using the SEM-EDX FEI Inspect-S50 type. The molecule group was examined using the FTIR.

3. Result and Discussion
The phase identification was performed using the XRD to compare the crystal phase in the AF powder and to analyse the grain size, crystal orientation, phase structure, and crystal defect from each phase. The crystal size of the AF powder was calculated using the Scherrer equation as below.
Where \( d \) is crystal diameter, \( k \) is the constant (0.89–0.9), \( \lambda \) is the wavenumber (1.5406 Å), and \( \beta \) is the Full-width Half Maximum (FWHM). Table 1 displays the calculation of AF powder that was characterized using the XRD.

Table 1: Intensity, FWHM, D-spacing, and crystal size of the AF powder

| AF Powder Sample | X-Ray Diffraction (Correspond to major peak) |  |
|------------------|------------------------------------------|--|
|                  | Intensity (count) | FWHM (rad) | \( d \)-spacing (Å) | Crystallite Size (nm) |
| Sintering 850°C  | 200            | 0.00824319  | 2.61393       | 17.60347132       |
| Sintering 950°C  | 271            | 0.004808382 | 2.61864       | 30.17312781       |
| Sintering 1050°C | 783            | 0.002747148 | 2.39634       | 53.30589425       |

Figure 1. The XRD Pattern of Achatina fulica Snail Shell Powder at 850 °C, 950 °C, and 1050 °C Sintering Temperature for 1 hour.

Table 1 shows a significant difference in the crystal size from the various sintering temperature. The crystal sizes of the powder that was sintered at 850 °C, 950 °C, and 1050 °C for 1 hour were 17.60 nm, 30.17 nm, and 53.30 nm. Figure 1 displays the XRD chart of the formation of CaH₂O₂ and CaO in the AF sample. The highest intensity peak of CaH₂O₂ was found in the AF powder at \( 2\theta = 34.32° \) in the sample with 850°C sintering temperature. Meanwhile, the highest CaO peak was shown at \( 2\theta = 37.36° \) in the sample with 1050°C sintering temperature. In the sample with 850°C sintering temperature, almost all peaks presented CaH₂O₂ formation. The sample with 950°C sintering temperature shows the initial formation of CaO. However, several peaks still contain CaH₂O₂. In the AF powder sample with 1050°C sintering temperature, almost all peaks had CaO, corresponded with the previous research [7] that stated that the CaH₂O₂ decomposition into CaO and H₂O occurs in the minimum temperature of 954°C. The MATCH software was utilized to analyse the crystal shape from the AF powder sample that was tested with the XRD. The samples
with 850 °C and 950 °C had trigonal (hexagonal axes) crystal while the sample with 1050 °C sintering temperature had cubic crystal.

The AF powder morphology was observed using the SEM. Figure 2 displays the morphology difference in the AF powder with various sintering temperature. Figure 2 shows the SEM test results from the AF powder sample with sintering temperature variations. Figure 2a is the SEM test results with 850 °C that displays irregular network structure after sedimentation due to the milling process [8]. Figure 2b is the sintered AF powder at 950 °C that presented porosity after CO₂ release due to the sintering. Moreover, Figure 2c shows the AF powder sintered at 1050 °C that displayed more porosity than previous samples, following the previous research that stated that CaO formation occurs at 850 °C–1000 °C [7]. The CaO formation was followed with the CO₂ release that creates porosity in the sample.

\[ \text{Table 2. Comparison Ca and O elements in the AF powder.} \]

| Sample          | Ca (Calcium) | O (Oxygen) |
|-----------------|--------------|------------|
| Sintering 850°C | 51.77%       | 48.23%     |
| Sintering 950°C | 51.98%       | 48.02%     |
| Sintering 1050°C| 59.12%       | 40.88%     |

\[ \text{Figure 2. AF powder morphology: a) sintered at 850 °C with 25k enlargement, b) sintered at 950 °C with 25k enlargement, c) sintered at 1050 °C with 25k enlargement.} \]
The test used the EDX to analyze and compare the Ca and O elements in the AF powder. The goal in the analysis was to find the percentage level of Ca and O in the samples with various sintering temperature and presented in Table 2. Based on the EDX test, the sample with 850℃ consisted of 51.77% Ca and 48.23% O. Meanwhile, the sample with 950 ℃ sintering temperature had 51.98% Ca and 48.01% O. The sample with 1050 ℃ consisted of 59.12% Ca and 40.88% O. The results followed the research of [8] that proved that sintering process decreased the O (oxygen) level and increased the Ca (calcium) level.

Figure 3 shows the FTIR spectrum of the AF powder with the sintering temperature variations ranged between 500 cm\(^{-1}\) and 4000 cm\(^{-1}\). The spectrum displays an identical pattern and little changes during the increasing temperature. The samples with 850 ℃ and 950 ℃ had 879 cm\(^{-1}\) wavenumber that indicated all carbonate groups and natural dolomite characteristic in the samples [9].

The 3542 cm\(^{-1}\) peak in all samples signed OH group stretch during water absorption of CaO [10]. The 875 cm\(^{-1}\) peak on the samples with 950 ℃ and 1050 ℃ sintering temperature and also the 1456 cm\(^{-1}\) in each sample were correlated with the asymmetric C–O with the carbonate group vibration [9]. The 875 cm\(^{-1}\) peak also shows Ca–O group. Small spectrum peaks in 875 cm\(^{-1}\) in each sample showed different combinations of CaCO\(_3\) bands [11].

![Figure 3. The FTIR results of AF powder with sintering temperature variations](image)

4. Conclusion

Synthesis and characterization of CaCO\(_3\) and CaO from Achatina fulica snail shell using the ball milling method for 6 hours and sintered at various temperature was successfully conducted. The smallest CaO crystal size was found in the sample with 850 ℃ sintering temperature for 17.6 nm. The decomposition of CaH\(_2\)O\(_2\) into CaO was successfully performed at sintering temperatures of 950 ℃ and 1050 ℃. In the 850 ℃ temperature, CaH\(_2\)O\(_2\) was yet to decompose because the minimal composition temperature should be 954 ℃. The morphology showed irregular network...
structure; higher sintering temperature meant higher porosity. The increasing sintering temperature also influenced the decrease in the oxygen level and the increase in the calcium level. The wavenumber of 875 cm\(^{-1}\) had Ca–O groups in its functional group. Based on this research, the CaO made from Af powder and sintering temperatures of 950 °C and 1050 °C were ready to be utilised as hydroxyapatite base material.

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6. References
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