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PHASE TRANSFORMATION OF $CASO_4$ GRANULES TO $CACO_3$ GRANULES BY DISSOLUTION–PRECIPITATION REACTION WITH 12 HOURS IMMERSION TIME

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ABSTRACT
Background*: Synthetic bone graft is a material that resembles human bone phase and is developed due to clinical demand. Calcium carbonte ($CaCO_3$/Calcite) has been used as bone substitution one of the methods to fabricate calcite is phase transformation by dissolution–precipitation reaction. Previous study did the same method but with lower temperature (<100ºC). Calcium sulfate anhydrate ($CaSO_4$) granules used as precursor is immersed in 0.5 mol/L sodium carbonate (Na_2CO_3) solution at 100ºC for 12 h.* ***Objective****: This study aims to fabricate $CaCO_3$ granules from $CaSO_4$ granules when the temperature is higher than the previous study.* ***Methods****: Fabricate $CaCO_3$ granules using $CaSO_4$ granules as precursor by dissolution-precipitation reaction in Na_2CO_3 solution with 12 h immersion time with 100ºC temperature. Powder X-ray diffraction patterns and Fourier transform infrared spectra study will be performed to characterize the granules. Results: $CaCO_3$ granules are fabricated by dissolution-precipitation reaction in Na_2CO_3 solution with 12 h immersion time when the temperature was 100ºC. Conclusion: $CaSO_4$ granules used as precursor are a potential material to fabricate $CaCO_3$ by using dissolution-precipitation reaction with 12 hours immersion time and 100ºC temperature.*

Keywords*: Bone graft, phase transformation, dissolution–precipitation reaction, calcium sulfate anhydrate, calcium carbonate.*

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INTRODUCTION

Bone grafts are used for augmentation or stimulating new bone formation in the case of bone defects. Autograft is a bone graft originating from the patient itself, so it becomes the gold standard in bone grafting due to excellent osteoconductive and osteoinductive properties. [1] Due to limited availability of the bone part that can be taken and high clinical demand, a synthetic bone graft was developed. Synthetic bone graft must have characteristics similar to bones[2–4], one of which is calcium carbonate. Marine coral has been used as bone graft (CaCO3).[5] Calcium carbonate has three polymorphs: vaterite, aragonite, and calcite. Among the three polymorphs, vaterite is the most unstable, and calcite is the most stable.[5–7]Aragonite has been extensively studied since coral can be used as a bone filling material. Coral can affect nature, and produce impurities when used as bone fillers.[5] Therefore, research has been developed on the manufacturing of artificial calcium carbonate. Research that explains artificial calcium carbonate is still limited.

Artificial calcium carbonate has only been used in the form of blocks in the medical field. Blocks have dense structure, so the material resorption is longer than granules. As seen in the research conducted by Ishikawa, et al (2017) with the composition transformation method through precipitation dissolution reaction, which used $CaSO_4$ blocks as precursor to produce $CaCO_3$ blocks. By immersing $CaSO_4$ precursor in $NaHCO_3$ solution pure $CaCO_3$ can be produced in 14 days at 80ºC. The shape of the granule has a high surface area so that phase transformation can occur more quickly, as seen in Ishikawa's research, et al. (2015) making calcium carbonate granules by immersing $Ca(OH)_2$ granules in Na_2CO_3 solution, $CaCO_3$ granules can be produced within 4 days at a temperature of 80ºC.[8] The use of $Ca(OH)_2$ is considered to be unstable at high temperatures, so the stable precursor in high temperature is selected, $CaSO_4$.[5]

The use of $CaSO_4$ granules has been done before to make pure CO_3Ap granules by precipitation dissolution reaction within 24 hours at 100ºC, and if the temperature is increased to 200ºC pure CO_3Ap is obtained within 6 hours.[9] Based on the research, it is revealed that the temperature can accelerate precipitation dissolution reactions. Research on the manufacturing of $CaCO_3$ that has been done previously used temperature of lower than 100ºC. Based on the previous study, this study uses temperature at 100ºC, we speculate that higher temperature can accelerate phase transformation through dissolution of precipitation on the granule $CaSO_4$ to $CaCO_3$ by identification the characterization of the granules.

MATERIALS AND METHODS

This study was adapted from Ishikawa et al. (2017) using precipitation dissolution reaction method, by making precursor of CaSO4 blocks which are then crushed to granules and immersed in Na2CO3 solution, soaking for 12 hours to produce CaCO3 granules.

Calcite granule ($CaCO_3$)

This study used $CaSO_4$.½H_2O powder (Wako Chemicals, Osaka, Japan). $CaSO_4$.½H_2O powder was mixed with distilled water with 0.5 ratio. A mixture of paste was poured into a plastic mold with a diameter of 6mm and a height of 3mm. Left to set for 1 hour, then $CaSO_4.2H_2O$ block was produced. The $CaSO_4.2H_2O$ block was then burned in the furnace at 700ºC with an increase of 5ºC / min and left for 5 hours at 700ºC to form a $CaSO_4$ block. The $CaSO_4$ block was then crushed using mortar and was sieved using a siever to obtain granules with a size of 300–500µm. The $CaSO_4$ granules were immersed in a solution 0,5 mol/L Na_2CO_3 (Wako Chemicals, Osaka, Japan) at 100ºC for 12 hours, then dried at 80ºC.

Characterization of Calcite Granule

The composition of calcite granules was evaluated using Fourier Transform Infra Red (FTIR; thermoscientific, FTIR-ATR, Japan) which was carried out using the ATR method and X-Ray Diffraction (XRD; Xpert PRO, Pananalytical) and was analyzed using 40KV CuKα radiation tube voltage and 40 -MA tube current. The diffraction angle was scanned at 2θ with a range from 10º to 40º with continuous mode, then the graph was processed using HighScore software (HighScore suite, Malvern Panalytical)

RESULTS

This research produces $CaCO_3$ granules made through phase transformation based on precipitation dissolution reactions. As a result of the characterization with FTIR, CO3 groups are seen (fig. 1). Figure 1A shows the absorbance of the precursor CaSO4 before immersion in a solution of Na2CO3. In the figure, the absorbance peaks at the wavelengths of 1100 cm-1, 672 cm-1, 611 cm-1 and 592 cm-1, illustrating the form of sulfate groups (SO4). The cluster obtained corresponds to the research conducted by Nomura, et.al (2014).[9] Figure 1 (B) shows the FTIR spectrum of CaSO4 after immersion in a solution of 0.5 mol / L Na2CO3 for 12 hours. There is a new absorbance peak at wavelengths of 1417 cm-1, 875 cm-1 and 712 cm-1 which indicates the presence of CO32-groups. The three absorbances show the characteristics of calcite. In addition, the absorbance of SO42 groups at waves 1100 cm-1, 594 cm-1, 614 cm-1 and 676 cm-1 can also be observed.

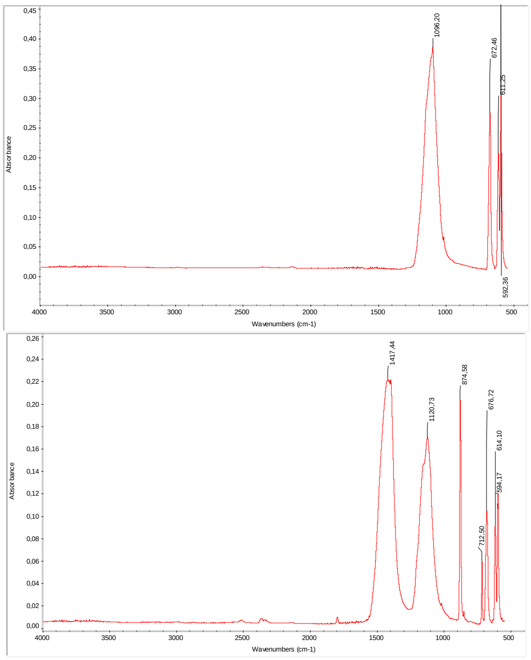

Figure 1. (A) FTIR spectrum of $CaSO_4$ before immersion. (B) FTIR spectrum of $CaSO_4$ after immersion for 12h at 100ºC

The results of FTIR spectrum analysis of CaSO4 samples before and after immersion in 0.5 mol / L Na2CO3 for 12 hours that calcite is formed. On the other hand, absorbance which shows CaSO4 is also still found after immersion.

This indicates that CaSO4 has not been completely converted into calcite under these conditions.

The results of XRD characterization in this study are the same as the research conducted (Ishikawa et al., 2015), namely the existence of the CaCO3 phase at 2θ 30º. The results of XRD analysis show that there are 2 phases formed after immersion, namely the phase of CaSO4 and CaCO3, evidenced in the diffraction peak at 26º and 30º. Previously Ishikawa et al. (2017) obtained the results of 2 phases of CaSO4 and CaCO3 but only after soaking for 3 days.

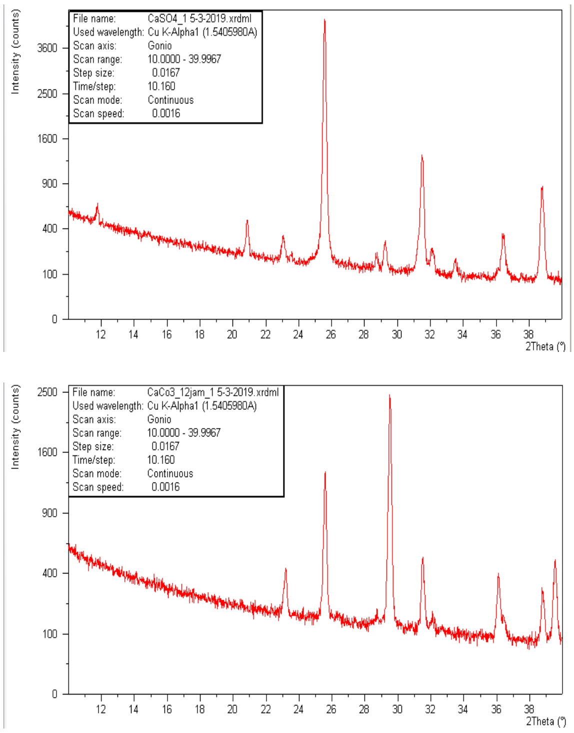

Figure 2. (A) XRD difraction of $CaSO_4$ before immersion. (B) XRD difraction of $CaSO_4$ after immersion for 12h at 100ºC.

XRD diffraction pattern (fig. 2, (A)) which is seen from specimens in the form of $CaSO_4$ granules obtained from $CaSO_4.2H_2O$ combustion at 700ºC for 5 hours, shows visible peaks that match with ICDD cards which indicate that the sample still has $CaSO_4.2H_2O$ phase (ICDD) database ref. code 96-901-5351) at peak 12º and 20.8º with very low intensity. Phase $CaSO_4$ (ICDD database ref. Code 96-500-0041) which is located at a peak of 23º, 26º, 32º, 36,2º and 38,7º. The characteristic peak of $CaSO_4$ is 26º, in the picture it appears to be the peak with the highest intensity compared to the other peaks. In figure (B) the XRD diffraction pattern shows that there are 2 phases namely $CaSO_4$ and $CaCO_3$, in the $CaSO_4$ granule treated with 12 hours immersion in a solution of 0.5 mol /L Na_2CO_3 indicating the existence of $CaSO_4$ phase (ICDD database ref. Code 96-500 -0041) which is located at 2 23º, 26º, 32º, 36.2º and 38.7º also has the phase of CaCO3 (ICDD ref. Code 96-450-2444) at 2θ, 23º, 30º, 32º, 36º, 39º. Diffraction pattern image 2 (B) shows the main characteristic peak of $CaCO_3$, which is at 30º.

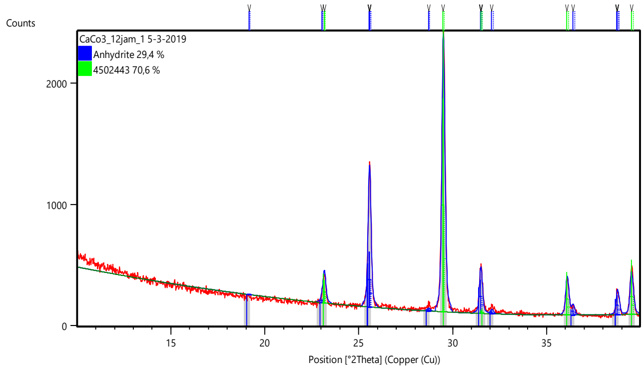

Figure 3. XRD data match of $CaSO_4$ after immersion for 12h with ICDD referrence, shown that $CaSO_4$ phase (blue) and $CaCO_3$ (green).

DISCUSSIONS

Phase transformations based on precipitation dissolution reactions, precipitation reaction occur only on the surface of the precursor (Ishikawa, 2010). In immersing the granule $CaSO_4$ in Na_2CO_3 solution as shown in the reactions below:

$$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-} \quad (1)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (2)$$

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4 \quad (3)$$

Solubility of $CaSO_4$ is very low, but it can be partially dissolved in aqueous solution. Granule $CaSO_4$ releases Ca^{2+} and SO_4^{2-} (reaction 1), Ca^{2+} reacts with CO_3^{2-} from a solution of Na_2CO_3 will be saturated to $CaCO_3$ because of calcite solubility is very small (Ksp = 10-8.4 at 20ºC). Calcite crystals are precipitated on the surface of the granule. The overall reaction can be seen in reaction 3, Na_2SO_4 formed is by product which is produced by high solubility and dissolved in water. .[5]

Immersion temperature and duration can have an effect on precipitation dissolution reactions (Noorzidah, 2016; Ishikawa et al., 2017) along with the results of 12-hour studies where pure $CaCO_3$ not formed (figure 2). Crystals of $CaCO_3$ can be formed by immersion treatment at 100ºC, seen in the XRD characterization results that match with the ICDD reference (no. 96-450-2444), 12-hour immersion produces crystals showing the presence of CaCO3 phase formed at 2θ 30º (figure 3).

This study has its shortcomings, because the resulting $CaCO_3$ granule still contains the $CaSO_4$ phase. Further studies are needed regarding the effect of the long immersion of $CaSO_4$ in Na_2CO_3 to produce pure $CaCO_3$. The use of $CaSO_4$ as a precursor is a potential material in producing $CaCO_3$ within a shorter time. From the results of this study it can be concluded that the use of $CaSO_4$ granules to produce $CaCO_3$ granules can be done by soaking for 12 hours in a solution of 0.5 mol /L Na_2CO_3 at 100ºC. Longer immersion is expected to totally convert $CaSO_4$ to $CaCO_3$.

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