Synthesis and characterization of $CaCO_3$/CaO from chicken eggshell with various calcination times

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This research aimed to examine the phase, morphology and elemental changes in calcium carbonate derived from chicken eggshell with variations in calcination times of 60, 90 and 120 min. Eggshell powder was comminuted through a ball mill process, operated for 10 h. Morphological testing was done using SEM-EDX and the phase identification using XRD. The results showed that the sample subjected to 90-min sintering had the highest degree of crystallinity. The 60-min sintered specimen had the smallest grain size of 14.6 nm, and the largest was 32.2 nm. The eggshell nanopowder sintered for 60 min had the lowest element content, while that sintered for 120 min had the highest. A simple route to produce $CaCO_3$ and CaO from chicken eggshells was successfully achieved using a ball mill process.

1. Introduction

An eggshell is the outermost part of the egg. It serves to protect its other components from physical, chemical and microbiological damage.[1] The eggshell is composed of 1.6% water and 98.4% dry matter. The dry matter consists of 95.1% minerals and 3.3% protein.[2] Calcium is the principal constituent of eggshell; it plays vital roles in bone and tooth formation, blood clotting, biological reaction catalysis, muscle contraction, balancing blood pH, maintaining fluid balance in the body, and osteoporosis prevention.[3]

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In Indonesia, the consumption of eggs is continuing to increase and resulting in an increase in eggshell waste. In fact, such waste is generated not only by households and food industries but also hatcheries.[4] Eggshells are often regarded only as waste by many, and thus only a few make use of them. Eggshells are resources that can be converted into useful materials: they can be used as an organic fertilizer that is essential for the growth of chilli plants; and turned into artwork like painted eggshells.[5] If not managed properly, eggshells become a medium for microbial growth and cause environmental pollution.[6] One way of dealing with the problem of eggshell waste is to transform eggshells into hydroxyapatite powder—a well-known material able to be used as a bone graft substitute.[3]

Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HA), one of the main mineral components of vertebrate bones and teeth, is the best-known crystalline phase of calcium phosphate (CaP).[7] HA is commonly used for bone repair and augmentation due to its high biocompatibility, osteoconductivity and bioactivity.[8] Also, all apatite minerals exhibit superior properties as ion exchangers;[6] HA-based materials are useful for removing heavy metals from wastewater and contaminated soil.[9]

The synthesis of HA requires eggshells as a precursor material.[6] The production of chicken eggs in Indonesia is quite high, reaching 1.5 million tonnes per year.[10] As a result, the amount of eggshell waste is high—and increasing rapidly. This abundant eggshell waste is useful for HA synthesis. HA is the most stable calcium phosphate under normal physiological conditions;[11] it is a compound consisting of calcium, phosphate, oxygen, and hydrogen. It can be produced from eggshells by taking their calcium via a heating process.[12,13] Hydroxyapatite has good bioactivity because its chemical composition is similar to the minerals contained in bones and teeth.[7] Eggshell-based hydroxyapatite is suitable for various medical applications. The

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treatments of bone fractures in surgery and grafting can involve the use of biomaterials. In Indonesia, the demand for biomaterials is fulfilled through imports, hence escalating costs.[7] Therefore, the production of synthetic HA is an effective solution to meet the needs of biomaterials since the raw material is cheap and easy to obtain. HA is, in fact, one of the most widely used biomaterials for the reconstruction of bones and teeth due to its nontoxic and biocompatible properties.[14] In addition, biologically derived apatite has a crystal structure similar to that of bone, and is thus compatible with physiological function after implantation.[14]

Wu et al.[6] proposed an inexpensive method for the synthesis of HA powder or biphasic calcium phosphate through a solid-state reaction using dicalcium phosphate dihydrate ($CaHPO_4 \bullet 2H_2O$, DCPD) and eggshell powder as the starting materials. The two precursor powders were initially mixed using ball milling and heated at various temperatures for different intervals. The materials were characterized using X-ray diffraction, infrared spectroscopy and scanning electron microscopy.

2. Methodology

To obtain single-phase $CaCO_3$/CaO particles, flakes of eggshell were placed in a zirconia container; the mixture consisted of 300 g eggshells, 5 zirconia balls weighing 33.3 g each, and 30 mL acetone. The mixture was milled with a planetary ball-mill machine (QM-3SP2) for 10 h at 570 rpm in the zirconia container. Next, the slurry was dried in an oven at 110 °C for 1 h to remove solvents. The dried eggshell powder was scraped out from the container and crushed for 1 h to eliminate agglomeration of the eggshell powder. It was then placed in a crucible and sintered in a furnace at 1100 °C for 60, 90 and 120 min. Note that sintering occurred at a lower temperature than that of conventional powder.[15]

The crystalline phase of the powder milled using zirconia balls before and after heat treatment was established using X-ray diffraction with Cu Kα radiation (XRD; X'pert Pro, PANalytical). The phase identification was made by comparing the experimental X-ray diffractograms with the standards compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). The microstructure of the powder was observed using a scanning electron microscope (SEM; Phenom).

3. Results

3.1 Phase identification

The XRD patterns (Fig. 1) showed that the non-sintered eggshell powder had the highest intensity of 1606 counts with full width at half maximum (FWHM) of 0.14 at $2\theta = 29.43^{\circ}$. The eggshell powder synthesized for 60 min had a peak of $2\theta = 37.38^{\circ}$ with an intensity of 884 counts and FWHM of 0.08. The 90-min synthesized eggshell powder had the highest intensity of 896 counts

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with FWHM of 0.08 at 2θ = 37.38º. The eggshell nanopowder synthesized for 120 min had the highest intensity of 668 counts with FWHM of 0.16 at 2θ = 29.40º.

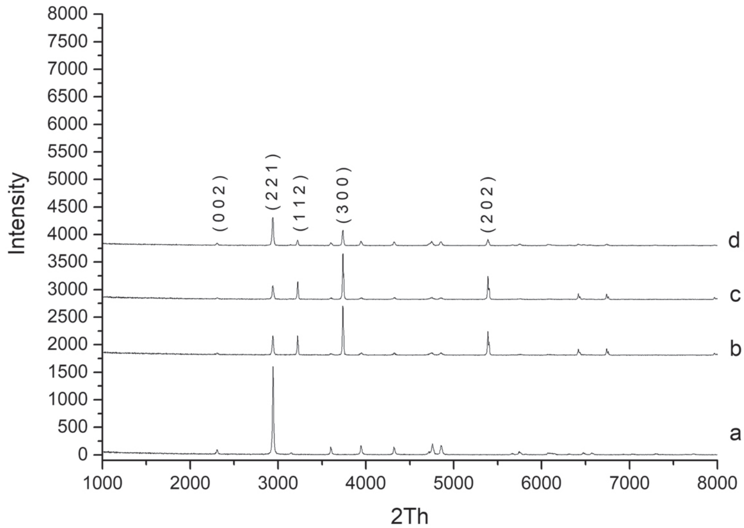

Figure. 1 Phase identification of eggshell nanopowders: (a), raw materials; (b), nanopowder eggshells with 60 min sintering time; (c), nanopowder eggshells with 90 min sintering time; (d), nanopowder eggshells with 120 min sintering time.

The crystallite size *D* of the eggshell nanopowder specimens was calculated using the Scherrer equation:[16,17]

$$D = \frac{K\lambda}{\beta \cos\theta}$$

where *K* is a constant with a value in the range 0.89–0.9, λ is wavelength (= 1.5406 Å) and β is full width at half maximum (FWHM).

The results (Table 1) showed that the eggshell nanopowder sintered for 120 min had the smallest crystallite size, i.e. 52 nm. It suggests that by solid state reaction, the eggshell powder is a single phase calcium oxide (CaO) at (211), (112), (300) and (202). This result is consistant with previous research that found that a sintering temperature above 900 °C produces calcium oxide.[18] The calcium oxide produced from calcium carbonate formed below this sintering temperature is white in colour. During the sintering time, the powder first becomes grey and then changes back to white, indicating calcium oxide.

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Table 1. Mean X-ray diffraction intensity, FWHM, D-spacing and crystallite size of eggshell nanopowders.

Sample	Intensity (counts)	FWHM /rad	Lattice spacing /Å	Crystallite size /nm
Raw eggshell nanopowder (211)	1606	0.1378	3.0354	60
60-min sintered eggshell nanopowder (300)	884	0.0787	2.4059	107
90-min sintered eggshell nanopowder (300)	896	0.0787	2.4056	107
120-min sintered eggshell nanopowder (211)	669	0.1574	3.0376	52

3.2 Morphological characterization

Figure 2 shows the morphologies of the eggshell nanopowders prior to synthesis with sintering. Each specimen underwent morphological changes due to the sintering treatment for various durations. Drying and shrinkage has been found to occur due to the sintering process.[19] The raw eggshell nanopowder appeared as nanorods with a few spheres; the smallest sphere was 20.61 nm, while the biggest was 30.00 nm in diameter. The nonuniformity of the grain size and shape indicates that agglomeration occurred in the eggshell nanopowder. Agglomeration also occurred in the eggshell nanopowder sintered for 60 min. The smallest grain size of this specimen was about 15 nm, whereas the biggest was 32 nm. The 90-min sintered specimen appeared as many spheres; agglomeration occurred; the smallest grain size was 25 nm and the largest was 36 nm. The specimen sintered for 120 min had a smallest grain size of 24 nm, while the largest was 40 nm. The nonuniformity of grain size and shape indicates that agglomeration occurred after undergoing synthesis. Prolonging the duration of sintering led to the recrystallization of eggshell nanopowder particles, in which they became denser than the nonsintered powder.

3.3 Elemental identification

The results of EDX testing showed that the raw eggshell nanopowder was composed of 57% Ca, 39% O, and 4% C. Eggshell nanopowder sintered for 60 min contained 55 wt% Ca, 42 wt% O, and 3 wt% C. The eggshell nanopowder sintered for 90 min contained Ca at 55 wt%, O at 42 wt% and C at 3 wt%. The 120-min sintering generated eggshell nanopowder with Ca contents of 56 wt%, O contents of 40 wt%, and C contents of 3 wt%.

These changes in elemental composition may have been influenced by impurities in the tubular furnace. The sintering process caused slight changes in the elemental composition of the nanopowder.

4. Discussion—comparison

According to our results, synthesis by ball milling was more efficient compared with the other methods. In this study, ball milling followed by 1 h calcination produced 600 g $CaCO_3$, while the other methods were more complicated. Previous studies demonstrated the synthesis of

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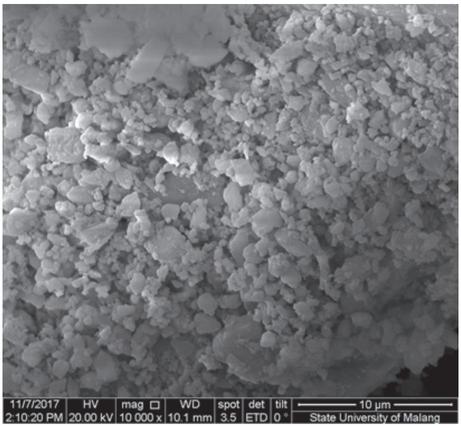

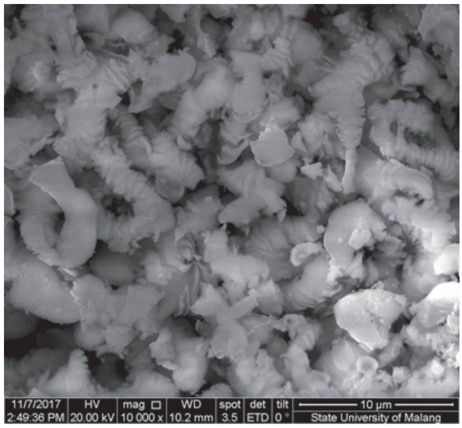

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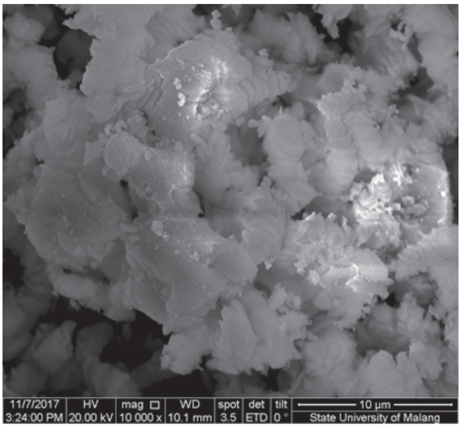

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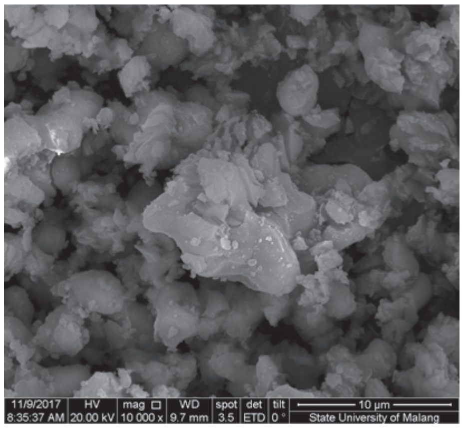

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Figure 2. Scann of eggshell nanopowders, for different durations of synthesis.

$CaCO_3$ by a wet chemical precipitation method.[20] The precursors for Ca and P were $Ca(OH)_2$ and H_3PO_4 (in laboratory quality). Both materials were dissolved in distilled water to obtain a concentration of 1 M $Ca(OH)_2$ (as a suspension) and 0.6 M H_3PO_4. Both solutions were mixed in a reactor, by titrating the H_3PO_4 solution into the $Ca(OH)_2$ at a rate of 1 mL/min while mixing with a magnetic stirrer. After all the phosphoric acid had been added, the mixture was held for 1 h at a temperature of 90 °C, then restirred for 1 h and reheld at 90 °C. After stirring, the pH of the mixture was adjusted to 10 by adding NaOH solution. Then the mixture was aged at room temperature for 24 h to allow the HA precipitate to form. The precipitate was then filtered, washed thrice using distilled water, and placed into a Petri dish for drying at 80 °C overnight. Finally, the $CaCO_3$ content in the sample was determined.

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The following study showed that $CaCO_3$ was produced by utilizing eggshell. The process of synthesis started with cleaning the eggshells in flowing water and separating the membrane. After that, the eggshell was dried at room temperature. Calcination was carried out at a temperature of 1000 °C for 5 h. After calcination, *in situ* precipitation was accomplished by dripping a solution of KH_2PO_4 (0.5 M) into the CaO solution–eggshell powder, and mixing with a magnetic stirrer for 30 min. The temperature during precipitation and stirring was at 37 °C. The result was stored for 12 h. The aged solution was filtered using filter paper to get a white precipitate. The filtered precipitate was heated in the furnace at 110 °C for 3 h, and then the $CaCO_3$ content was analysed.[21]

According to another study, $CaCO_3$ could be produced from eggshells.[22] The first step in that study was grinding the eggshell using ball milling. Then 10 g eggshell powder was taken and mixed with phosphoric acid and 1 g of gelatin. The gelatin functioned as a binder. The mass ratio of eggshell powder and phosphoric acid was 1:10. After grinding, the mixture was dried at 60 °C for 2 days. After the material was dry, an analysis of $CaCO_3$ content could be carried out. In yet another study,[23] eggshell powder was obtained by milling the eggshells; afterward the eggshell powder was sifted using an A325 mesh sieve. After that, the eggshell powder was mixed with dicalcium phosphate dehydrate (DCPD) at a ratio of 4:3 and then milled again. After the milling process, the mixture was dried at 150 °C for 24 h. After drying, the material could be analysed for $CaCO_3$ content.

5. Conclusions

According to several methods in synthesizing $CaCO_3$, it could be concluded that the synthesis method reported in this study was the simplest method to produce $CaCO_3$ in the shortest time for mass production. The synthesis successfully managed to transform eggshell powder to $CaCO_3$ and into calcium oxide. Evaluation of the various sintering times employed indicated that 120 min sintering generated the best calcium oxide, according to the criteria of phase, morphology and elemental composition.

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