The Properties of Eggshell Powders with the Variation of Sintering Duration

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Abstract. This study proposed to investigate the synthesis and characterization of eggshell nanopowders. The phase and morphological characterization of eggshell nanopowders for reducing their grain size from micro to nano involved ball milling with the variations of duration (1, 5, and 10 hours) and sintering temperature at 1100 °C for 1 hour. XRD test presented the phase characterization of eggshell nanopowder which ball-milled for 5 hours, obtained the smallest crystalite size at 46.37nm. The one subjected to 1-hour sintering and 1-hour ball milling had the highest degree of crystallinity. Based on the SEM analysis, the eggshell nanopowders experienced morphological changes in grain size and shape from chunks, triangular grains, and irregular grains in micro size to Nano-sized with spherical grains. The EDX test presented the highest and the lowest compound in eggshell which non-sintered and ball-milled for 5 hours, the result showed that C compound was the lowest level, and C and O level were the highest level.

Keywords: Hydroxyapatite, biocompatibility, bioactivity, eggshell nanopowder

1. Introduction

In general, eggshell waste is generated from not only households and food industries but also hatcheries [1]. Eggshell contains 1% magnesium carbonate, 1% calcium phosphate, 4% organic matter, and 94% calcium carbonate [2]. Based on previous work, it was found that the thickness of its outer and inner eggshell is 0.55 and 0.015 mm, respectively [2]. Interestingly, calcium, as the largest constituent of eggshell, affects the hardness of the eggshells [3]. To solve the eggshell waste problem can be conducted by turning eggshells into hydroxyapatite powders or calcium compounds served as materials for synthetic bone grafts [1].

Hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂) or H, kind of the primary mineral that contained in vertebrate bones and teeth, is the most recognized as crystalline phase of calcium phosphate (CaP) [4]. Hydroxyapatites is commonly utilized for repairing bone and augmentation because of its high osteoconductivity, biocompatibility, and bioactivity [5]. Also, all of apatite minerals exhibit superior properties as ion exchangers [3]. The previous study aimed to propose an inexpensive method for synthesizing HA powders or biphasic calcium phosphate with solid-state method using dicalcium phosphate dihydrate (CaHPO₄•2H₂O, DCPD) and eggshell powder used as initial material [3]. During characterization, initially, both of precursor powder were mixed by using ball milling machine and then...
heated at certain temperatures in various time duration, while materials were synthesized and characterized by using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM-EDX) [3]. Therefore, it is necessary to seek other viable material options that are extensible, inexpensive, and easily accessible [3]. To this end, the innovations in properties of eggshell powders in producing calcium carbonate using a ball milling process should be fostered to gain the usage of the organic source for dental and implant material.

2. Methods
The synthesis of eggshell was conducted to produce particles in nano-sized by mixing the micro-sized of eggshells powder in a ball milling machine; the mixture consisted of 300 g eggshells, 5 zirconia balls weighing 33.3 g each, and 30 ml acetone. The mixing was carried out with the variations of time, i.e., 1, 5, and 10 hours. The initial process was stirring for 1 hour at 570 rpm to produce a mixture of nanopowders/nanomaterials of which a single particle is sized between 1 to 100 nm [8]. The mixing process involved the dispersed phase in the form of a liquid, i.e., acetone. Acetone was used to provide lubrication in the milling process that can blend and bond eggshells. The eggshell powder was mixed with acetone in zirconia container, homogeneously. The mixture was milled in wet conditions in a planetary ball-mill machine (QM-3SP2) with the variations of ball milling duration at 570 rpm in the zirconia container. Next, the pulp was dried in microwave at 110 °C for 1 hour. The heating process in the oven was carried out for 1 hour to remove the moisture content, resulting in dry and well-developed eggshells powders. The dry eggshell powders were scraped out from the container and ready to be crushed for 1 hour. The crushing procedure was done to reduce the size of the eggshell powder. The crushed eggshell powders were put into a crushy-ball and sintered in the furnace at 1100 ºC for 1 hour to release water content in eggshell powders. Sintering process was performed at lower temperature than the other powder materials [9], making the eggshell powder was very dry.

Crystalline phase of powders milled using a zirconia ball was analyzed by utilized X-ray diffraction with Cu Kα radiation (XRD; X'pert Pro, PANalytical). The phase identification was conducted by comparing diffractogram of experimental X-ray with the standard that compiled by the Joint Committee on Powder Diffraction Standards (JCPDS). Scanning electron microscope (SEM; Phenom) was used to observe the microstructure of powder. This analysis was conducted into powder in condition after and before heat treatment process.

3. Results and Discussion

3.1. Phase identification
Identification of phase was conducted by utilizing XRD proposed to compare crystalline phases in materials and powders and to analyze the grain size, crystal orientation, phase structure, and crystal defect in every phase [10]. The Scherrer equation was used to calculate the crystallite size of eggshell powder as follows:

$$d = \frac{K \cdot \lambda}{\beta \cos \theta}$$

where $d$ is the diameter of crystallite, $\beta$ is Full-Width Half Maximum (FWHM), $K$ is the constant (0.89-0.9), and $\lambda$ is the wavelength (1.5406 Å). The results of the calculation for the X-ray diffraction data (see Figure 1) using the above formula are shown in Table 1.
Based on Figure 1, it can be seen visually that the XRD data have a similar pattern but different in intensity and FWHM. The results of data analysis showed that crystallite size of eggshell powders subjected to different ball-milling time and sintering was relatively smaller compared to those ball-milled for a different time and not sintered. However, the duration of sintering has not presented the trend of crystallite size. Based on Figure 1 and Table 1, the intensity of the sample has a correlation with the crystallite size. The higher the intensity, the bigger crystallite size originating from the increase of FWHM. It indicates that this work is in line with the mathematical formula for Scherer equation.
In this work, the crystalline phase was not observed significantly. It means that the duration and ball-milling process at those time and temperatures were not able to change the structure of the samples. Theoretically, the given energy from those processes was not able to overcome to break the structure.

In contrary with this work, a previous work reported that HA had trigonal and triclinic structures and then changed into hexagonal structures after the sintering process at 1100 °C for 1 hour [11]. In a sample of 10-hour ball milling with sintering at 1100 °C, the tricalcium phosphate compound lost and substituted completely into hydroxyapatite.

3.2. Morphological characterization

The morphology of eggshell material was observed by using SEM [12]. The morphological changes that occurred before and after synthesis with the variations of ball milling time as shown in Figure 2.

![Figure 2](image_url)

**Figure 2.** Morphology of eggshell nanopowders, (a) non-sintering + 1-hour ball milling, (b) non-sintering + 5-hour ball milling, (c) non-sintering + 10-hour ball milling, (d) sintering + 1-hour ball milling, (e) sintering + 5-hour ball milling, and (f) sintering + 10-hour ball milling

The sintering process that has been set up accurately explained that drying and shrinking were formed due to reaction of molecule that occurred at room temperature, powder formation and drying solutions [11]. In those conditions, the mixing ingredients had various characteristics and eggshells nanopowders in accordance with ball milling time from 1, 5, and 10 hours using sintering temperature at 1100 °C. Furthermore, Figure 2a is the result of SEM test, the morphology of non-sintered eggshells nanopowders with 1-hour ball milling was triangular with a few spheres, and it had the smallest and the largest size, i.e., for the smallest size was 33.23 nm and the largest size was 41.21 nm. The uniformity in the structure of grains on the surface showed that agglomeration was the sediment particles on the membrane of eggshells nanopowders grain [12]. Figure 2b shows the morphology of non-sintered nanopowder eggshells with 5 hours ball milling was small bunches with spheres and it had the smallest and largest size, i.e. for the smallest size was 18.66 nm and the largest size was 37.99 nm. The uniformity in the structure of grains on the surface showed that agglomeration was the sediment particles on the membrane of eggshells nanopowders grains [12]. Meanwhile, Figure 2c shows the morphology of non-sintered eggshells morphology with 10-hour ball milling was small irregular chunks with multiple
spheres, and it had the smallest and largest size, i.e. for the smallest size was 20.61 nm and the size largest size was 30.00 nm. The uniformity in the size and shape of grains on the surface showed that agglomeration occurred as particles deposited on the membrane of eggshells nanopowders grains [12].

In Figure 2d is a morphological image that still agglomerations and it is different from the previous work that the sample became spheres with no agglomeration [13]. The spheres had a uniform grain size that was not too significant to exceed above the size of eggshells nanopowders largest non-sintering with ball milling time. The grain size can be seen in the morphology of eggshells nanopowders with sintering and 1-hour ball milling variation, the smallest grain size was 20.61 nm, and the largest grain size was 47.44 nm. The differences in the morphology of eggshells nanopowders are also shown in Figure 2e; it shows no significant change in grain size occurring when compared with eggshells nanopowders sintering with 1-hour ball milling but the morphological differences began to show the number of round-shaped nanopowder eggshells grains and there was agglomeration at each its grain [14]. For the uniformity of the grain size of ball milling process for 5 hours had two sizes not seen much difference with the ball milling process for 1 hour, the smallest grain size was 21.01 nm, and the size of the biggest grain size was 27.65 nm. It was influenced by the room temperature in sintering at 1100 °C, 5-hour ball milling, 1-hour sintering time, and crushing time so that the changes in the form of micro eggshells nanopowders into nano-size had been successfully demonstrated on the morphology of nanopowders sintering eggshells with ball milling time of 5 hours, after the synthesis with a variety of ball milling and was performed sintering process. The difference begins in Figure 2f; the difference began to be seen from the morphology and the largest grain size. The size grains of eggshells nanopowders sintering with 10-hour ball milling had the smallest grain size was 18.66 nm and the largest grain size was 22.19 nm. For the morphological form that occurred in eggshells nanopowders sintering with a 10-hour ball milling, the spherical grain looked with large agglomeration. The large agglomerations can increase the size of crystals [14].

3.3. Characterization of Elemental Composition
The test using EDX aimed to analyze and compare the composition of calcium (Ca), carbon (C) and oxygen (O) which contained in eggshells. The purpose of analyzing the elements of C, O, and Ca in the eggshells powder was to know the element of the percentage content of C, O, and Ca with the variations of ball milling time of 1, 5, and 10 hours before and after the result of synthesis with sintering treatment with a long time of 1 hour on the eggshells powders material is shown in Figure 3.

As shown in Figure 3, the eggshell nanopowders ball-milled for 1 hour and without being sintered revealed consisted of 4.12% C, 39.5% O, and 56.39% Ca. The results showed the purity of non-sintered eggshell powders subjected to 1-hour ball milling, which formed a basis before sintering. Based on the EDX analysis, the non-sintered, 5-hour ball-milled eggshell nanopowder was composed of 4.71% C, 44.51% O, and 50.79% Ca. The results showed the purity of non-sintered eggshell powder subjected to 5-hour ball milling, which formed a basis before sintering. The non-sintered eggshell powders ball-milled for 10 hours was composed of 4.04% C, 39.42% O, and 56.54% Ca. This EDX result of the non-sintered eggshell powders formed the basis for observing the ones subjected to sintering [12].

The eggshell nanopowders sintered and ball-milled for 1 hour contained 3.38% C, 35.78% O, and 60.84% Ca, meaning that there was a decrease in 0.74% in C and 3.72% in O, and an increase in 4.45% in Ca. These changed might be influenced by the oxidation that occurred during the ball milling process, the sintering process, and acetone containing C, H, and O. The sintering and 5-hour ball milling resulted in eggshell powder with 2.66% C, 36.71%, and 60.64% Ca. In other words, there was a decrease in 2.25% in C, a decrease in 7.8% in O, and an increase in 9.85% in Ca. This was affected by impurities in the microwave and might also be affected by acetone that consisted of C, H, and O. Since acetone has the chemical formula of CH3COCH3, the level of Ca might increase during the sintering process and 5-hour ball milling. The elemental compositions of the eggshell powders sintered for 1 hour and ball-milled for 10 hours were 3.52% C, 37.59% O, and 58.89% Ca. Compared to those of the eggshell powder not subjected to sintering [12], the C level decreased by 0.52%, O decreased by 1.83% and Ca increased by 2.35%.
Figure 3. The difference between the composition of C, O, and Ca of eggshell nanopowder subjected to the variation of ball milling time (1, 5, and 10 hours) and synthesis with 1-hour sintering (before and after)

The eggshell powders sintered for 1 hour and ball-milled for 10 hours experienced 2.35% increase in Ca, a 0.52% decrease in C, 1.83% decrease in O if compared to the one sintered for 1 hour and ball milled for 5 hours. The sintering process and ball milling for 5 hours resulted in an increase in 9.85% in Ca but a decrease in 2.25% in C and 7.8% in O compared to the one subjected to sintering and 1-hour ball milling. The changes in the level of Ca, C, and O occurred because of the use of constant temperature of 1100 ºC for 1 hour resulting in a decrease in the C and O content of eggshells powder after sintering, resulting in a decrease for C and O while Ca increased [12].

4. Conclusion
In conclusion, the synthesis performed had successfully converted the eggshell powders from micro- into nano-sized powders due to ball milling and sintering process. The results of phase characterization obtained from XRD showed that the eggshell nanopowders ball-milled for 5 hours had the smallest crystallite size of 46.37 nm. The one subjected to sintering and 1-hour ball milling had the highest degree of crystallinity with the level of purity of 2126.27 counts and the crystallite size of 52.18 nm, hence the most favorable eggshell nanopowder. The changes in the morphology of eggshell powder took place due to the process of synthesis with the variations of ball milling time. The synthesis process with the variations of ball milling time caused the changes in the elemental composition of C, O and Ca. The non-sintered, 5-hour ball-milled eggshell powder exhibited the lowest Ca level and the highest level of C and O; it occurred due to the oxidation during the sintering process.
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