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Physical properties and compressibility of quail eggshell nanopowder with heat treatment temperature variations

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Abstract

This research aimed to determine the effect of heat treatment temperature variations on the physical properties and the quail eggshell’s compressibility. The quail eggshells was obtained from the waste of restaurants and market traders and processed into powder form by ball milling method for 10 h and sintered at 900 °C, 1000 °C, and 1100 °C, a holding time of 1 h. The samples were characterized using x-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Pressure test for the compressibility result. The results showed that after the heat treatment process, the calcium carbonate phase (CaCO\textsubscript{3}) was transformed into calcium oxide (CaO). The crystal size on raw material was 52.18 nm and no more than 50 nm in all heat treatment samples. Morphology of eggshells showed variations in the size and shape of grains such as round, rod, and square. Whereas the compressibility test results showed that the addition of charging to the test conducted increased the compressibility value (density). The results also showed physical properties such as pore size and grain size affected quail eggshells’ compressibility value.

1. Introduction

Metal is a widely used material in various sectors of life that are useful for humans. The lightweight steel frame is one of the innovations and developments of metal material that makes it easy to construct multi-storey buildings and building warehouses [1]. However, metal will deplete over time; even if it can be recycled, its quality will decrease. Coral has been studied as an alternative material in medical applications by utilizing the main carbonate content, but coral is not available worldwide, and several coral species are endangered. Thus, the exploration of alternative renewable materials on low prices and easy process has been carried out, and eggshells were identified to have a mineral composition similar to coral [2].

Eggshell is a biomaterial from poultry, and the outer layer serves to protect the egg components from physical, chemical, and microbiological damage [3]. Eggshell production in Indonesia was estimated to reach 179,571 tons and currently still a waste with the potential to cause pollution due to the increased microbial activity in the environment [4]. Eggshell represents 9%–12% of the total egg weight, consisting of 94% calcium carbonate (CaCO\textsubscript{3}), 1% calcium phosphate (Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}), 1% magnesium carbonate (MgCO\textsubscript{3}), and 4% water and other organic matters [5, 6]. Recently, the need for calcium carbonate (CaCO\textsubscript{3}) has increased in the hydroxyapatite biomaterials development for medical applications such as teeth and bone tissue [7]. Calcium carbonate in eggshells has also been applied as an absorbent to remove the heavy metal content of Cadmium in aqueous solution [8]. Also, eggshells through the calcium content utilization have been processed as a supplement [9].

Eggshells with thermal treatment through heat treatment process can convert calcium carbonate (CaCO\textsubscript{3}) into various forms of calcium precursors such as calcium oxide (CaO) [10] and also calcium hydroxide (Ca(OH)\textsubscript{2}) [11]. In some cases, heat treatment helps increase the product’s crystallinity, making it higher than the samples without heat treatment process [12]. The heat treatment temperature influences decomposition because particles’ surface will interact with the surrounding environment [13]. Heat treatment can also increase...
2. Research methodology

Quail eggshells were obtained from traders and restaurants that use quail eggs as a food menu. The shells were washed with clean water to remove remaining impurities then were dried for 12 h. Before the milling process, quail eggshells have added a solution of solvent acetone as a solvent. The synthesis process used the Planetary Ball Mill (QM-3SP2 owned by Nano Materials and Advanced Materials Laboratory, State University of Malang) with a ratio of 100 ml acetone and 300 grams of eggshell mass. The milling process was carried out for 10 h; then the quail eggshell nanopowder was dried in an oven with a temperature of 110 °C for 60 min to get dry synthesis results. After, the crushing process was carried out for 60 min using Mortar and Crusher. The heat treatment process was carried out using a tubular furnace (RMF-Quartech 2800) with temperature variations of 900 °C, 1000 °C, and 1100 °C, a holding time of 1 h and a heating rate of 10 °C min⁻¹. Then the crushing process was performed 60 min for each sample.

The samples were then put in ziplock plastic with labelling and were prepared for the characterization process. Crystal phase identification in quail eggshell powder was analyzed using X-Ray Diffraction (XRD; Expert Pro, PANalytical). Phase identification was obtained by comparing the experimental diffraction with the Joint Committee on Powder Diffraction Standards (JCPDS) standard card. The morphological analysis used Scanning Electron Microscopy (SEM) (FEI-Inspect-S50), porosity was analyzed with SEM test results using Origin software, compressibility test used universal Testing Machine (ILE-IL 904) with a load of 1000 kgf and 2000 kgf and the dwelling time of 90 s [15].

3. Results and discussion

3.1. XRD characterization test

The crystallite size of quail eggshell powder was calculated using the Scherrer equation [15–17]. Table 1 shows quail eggshell nanopowder after being synthesized with a holding time of 1 h and temperature variations of
900 °C, 1000 °C, and 1100 °C. The results have smaller crystal sizes than raw material nanopowder, which was not more than 50 nm, conforming to similar studies [18].

Figure 1 presents the peaks in raw material quail eggshell nanopowder with the Miller index of [012], [104], [110], [113], [022], [108], and [116] which correspond to the shape of trigonal crystals (hexagonal axes) with the highest peak on the Miller’s index of [104] which has an intensity of 993.98 counts with the crystal size of 52.18 nm. The highest peak is at 2θ = 29.4° raw material, the calcite phase of calcium carbonate (CaCO3), indicating that the results followed the eggshell synthesis conducted by Kim, 2016 [19]. This result is also supported by Butcher’s research, in which eggshell raw material contained calcium carbonate with stable single-phase calcite with a rhombohedral structure [20] and a much higher percentage of calcite in raw material eggshell [21].

Figure 2 shows the XRD data on quail eggshell nanopowder with heat treatment temperature variations of 900 °C, 1000 °C, and 1100 °C which have almost the same pattern: the Miller index peaks of [012], [003], [020], [021], [105], [220] that corresponds to the cubic crystal form. The highest is peak 2θ = 34° with the Miller’s index of [200] which was the calcium oxide (CaO) phase with the intensity of each heat treatment sample with temperature variations of 900 °C, 1000 °C, and 1100 °C were 223.16; 254.97; and 259.29 counts, as well as 42.21; 19.20; and 30.16 nm for the crystal sizes. These results meant that the heat treatment process completely changed the calcium carbonate (CaCO3) phase to the calcium oxide (CaO) phase [22]. Research of Tangboriboon shows that the heat treatment time also affected the phase transition where heat treatment at 900 °C and the holding time of 3 and 5 h produced more calcium hydroxide (Ca(OH)2) due to reactive water-vapour adsorption [23]. Thus, the phase transformation depends on temperature and heat treatment time. Next, the phase changed from CaCO3 to CaO phase is due to the release of the CO2 compound [22], written as below:

\[ \text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g) \]  

(1)

3.2. SEM characterization test
The morphology of quail eggshell nanopowder in raw material and heat treatment samples with heat treatment temperature variations of 900 °C, 1000 °C, and 1100 °C was observed using SEM, and the results appear in figure 3 with 1000× magnification. Figure 3(a) shows that the morphology of raw material quail shell nanopowder has round and oval shapes with an average size of 94.21 nm. Figure 3(b) presents the sample sintered at 900 °C morphology with round, oval, and irregular shapes and an average size of 82.63 nm, meaning that particle agglomeration occurred so that the powder’s morphology was rounder and slightly smaller [2].

Figure 3(c) shows the morphology of sintered quail eggshell nanopowder with a temperature of 1000 °C that is round and oval with an average of 110.68 nm. Figure 3(d) presents the morphology of sintered quail eggshell nanopowder with a temperature of 1100 °C that is oval and rectangular with an average size of 182.5 nm. The increase in grain size from 900 °C to 1000 °C and 1100 °C heat treatment occurred because the higher the temperature gave higher energy and created greater atomic diffusion [24].

3.3. Thermal decomposition of quail eggshell
The TG graph (figure 4) shows the decrease in mass based on increasing temperature and time. The TG graph of quail eggshell powder shows a shift in the decomposition pattern to a higher temperature as the heating rate increases. The graph also shows that there was only a slight decrease in mass, namely less than 10%. A significant
A decrease in the mass of quail egg shell powder occurs at a temperature of 370 °C–425 °C. The decrease in temperature indicates the decomposition of Ca(OH)$_2$ which is formed from the reaction of CaO from quail egg shell powder with atmospheric air [25]. The slight decrease in mass that occurs at 580 °C–700 °C is related to the decomposition of the remaining CaCO$_3$ and other impurities [26, 27].
Figure 5 shows the mass loss rate continues to increase as the heating rate increases, at low heating rates the mass loss rate is less than at higher heating rates. The heating rate affects the pyrolysis temperature range where with increasing heating rate the thermal decomposition rate increases [28]. Specimens with a heating rate of 10 °C min$^{-1}$ have a maximum mass reduction rate of 0.021%/second, then samples with heating rates of 20, 30, and 40 °C min$^{-1}$ have a maximum mass reduction rate of 0.052, 0.073 and 0.095%/second, respectively.

### 3.4. Porosity and compressibility tests

Table 2 shows the porosity and compressibility values of each quail eggshell nanopowder. The raw material sample has higher porosity percentage than the sintered samples. Figure 4 observe that the 1100 °C heat treatment sample has a greater porosity percentage than other temperatures. This result might be due to the release or evaporation of gas during the heat treatment process of CO$_2$ [22], thus, creating pores in the sample of quail eggshell nanopowder. These results exhibited that higher heat treatment process temperature released more CO$_2$. The void space in the hollow spheres of CaO can buffer against the local large volume change during the calcination/heat treatment process. The porous CaCO$_3$ resulted the large surface reaction area for CO$_2$ adsorption, desorption, and also the aggregation. More importantly that CaCO$_3$ is usually act as a high performance CO$_2$ sorbent at high temperature [29].

Meanwhile, the difference between raw material and heat treatment samples percentages was due to the porosity and size reduction [30]. It was caused by an even distribution of particles and the particles size increase in quail eggshell nanopowder during heat treatment. The porosity increase in 1100 °C heat treatment sample was due to the trapped CO$_2$ gas. Previous work revealed that pore elimination in the powder could be hampered due to gas pressure trapped in the pores [31].

Table 2 states that the compression with a load of 2000 kgf has a greater compressibility value than compression with a load of 1000 kgf. The powder compressibility would be better when the compression loading is greater [32] because greater loading made particles have higher to be compact [15]. Figure 4 below is the correlation graph between porosity and compressibility. It shows that the raw material sample has the highest porosity value and the lowest compressibility value compared to other samples. Also, the suitability where higher porosity value of a sample decreases the compressibility value [31].

| Sample                | Porosity (%) | Compressibility 1000 kgf (g cm$^{-3}$) | Compressibility 2000 kgf (g cm$^{-3}$) |
|-----------------------|--------------|---------------------------------------|---------------------------------------|
| Raw material          | 74.51        | 1.52                                  | 1.62                                  |
| Heat treatment at 900 °C | 70.34           | 1.67                                  | 1.75                                  |
| Heat treatment at 1000 °C | 70.14           | 1.68                                  | 1.76                                  |
| Heat treatment at 1100 °C | 74.32           | 1.54                                  | 1.66                                  |
4. Conclusion

After the heat treatment process of quail eggshell powder, the phase changed from CaCO3 to CaO due to the release of CO2 compounds during the heat treatment process. The highest crystalline intensity of CaO was found in sintered quail eggshells at a temperature of 1100 °C. The SEM results showed morphology with grain shapes uniformity such as round, oval, and square shapes. The smallest grain size was found in the 900 °C sintered sample with an average grain size of 82.63 nm. Heat treatment helped reduce the porosity size because the grain size tends to increase during the heat treatment process. There was a significant increase in the porosity value at 1100 °C temperature due to trapped CO2 gas pressure. The grain size and powder porosity affected the density value. The amount of load given during the compressibility test affected the density value because higher the loading means higher particles’ ability to be compact.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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