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Characterization of Calcium Carbonate Extracted from Eggshell Waste at Various Calcination Temperature

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ABSTRACT

An efficient method to waste utilization is to successfully transform it into high value products. Chicken eggshell contain potential useful minerals of calcium carbonate in which can be processed into biomaterials used in biomedical application. The objective of this study is to derived calcium carbonate from eggshell and analyze the effect of various calcination temperatures on the properties of calcium carbonate. Fourier transform infrared (FTIR) spectroscopy indicates that all calcined samples reveals calcium carbonate is no longer present after calcination as it is already converted to calcium oxide. This also supported by x-ray diffraction (XRD) graphs notably on 900°C. Scanning electron microscopy (SEM) and particle size analysis are applied to determine morphological properties and mean sizes of particles for both raw and calcined samples.

Key words: Calcined, calcium carbonate, eggshell, extraction.

1. INTRODUCTION

The conversion of waste specifically from daily use and food industry into some useful product seems to be impossible and almost no value. Considering sustainable development, wastes should be recycled, reused and channeled towards the production of value added products. Normally at home, eggshells can easily be composted or sprinkled on flower beds as a snail and slug deterrent or soil enhancer. However, for poultry and egg production companies, shells have to be disposed in landfills because the waste egg attached to them rots quickly thus, lead to a smelly by-product. According to a report [1], regulation requires the disposal of eggshells to be heat treated to prevent it to become a source of disease towards humans, animals and vegetation. Hence, the industrial egg producers have developed a way in which eggshells and trays are incinerated together at a temperature around 1000 □ (the trays forming the fuel to burn the shells) resulting burnt limestone. Rather than worthless ash from incineration, burnt limestone turn out have potential as pozzolan served in production of high strength and high performance of building materials [2]-[4]. The process turns waste products into a valuable material, while the process energy is exploited in the production [5].

Eggshell is made of calcium carbonate like chalk, with a hard-wearing, crystalline structure. In addition, other studies revealed that eggshell to be in rich source for calcium from calcium carbonate which potentially can be served as useful raw materials for hydroxyapatite production in biomedical engineering. Besides, it is also found to be crucial as a biomaterial due to its osteophilic nature and its incorporation into bone tissues [6]-[9]. The advancement of biomaterials is carried out as a result of growing in the number of patients that requires medical and dental therapy. The production of this novel practice is expected to have successfully improved conventional clinical treatments and healing process. Natural bone is made up from inorganic and organic composite mainly nanostructure hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) or known as HAp and collagen fibers. Hydroxyapatite have similar chemical composition and biological affinity to the mineral component of bone. Bone mineral is a salt where the ratio of calcium to phosphate (C/P) is 1.5-1.7 whereas hydroxyapatite C/P ratio is generally assumed to be 1.67 which is within the range [10]-[12]. Hydroxyapatite is among of the few materials that are classified as bioactive, implies that it will support bone ingrowth along with osseointegration when used in orthopaedic [13].

Calcium carbonate ($CaCO_3$) from eggshell can be converted into calcium oxide (CaO) by way of calcination process. CaO has proved to be the active phase in the eggshells and the adequate temperature for calcination process must be above 800□ [14]. Obtaining CaO is essential as it is a raw material for producing calcium phosphate or hydroxyapatite that will be further synthesized by means of various synthesis method such as precipitation, sol gel, etc. in manufacturing of scaffolds or any other biomedical needs [15]-[18]. Up to date, eggshell can serve as a promising biomaterials source because of its continuous resource compare to other natural sources of hydroxyapatite like bovine bones and corals.

This research work focused on the calcification chicken eggshells as the main source of calcium carbonate. The chemical and physical properties of the materials (uncalcined and calcined) as well as morphological were studied.

2. MATERIALS & METHOD

2.1 Sample preparation

Eggshell waste (EW) is collected from restaurants close proximity within Universiti Tun Hussein Onn main campus, Parit Raja, Johor, Malaysia. Later, the eggshells were cleaned and immersed in boiling water for 30 minutes to remove interference material and impurity on EW. Next, it being dry for 4 hours at temperature 100°C in oven and being crush to small size of flakes. The dry EW were calcined at four different temperature (600, 700, 800 and 900°C) for 4 hours with normal increment and decrement of calcification temperature profile. Next, all calcined sample and uncalcined sample were crush to size <40 µm using mortar and sieve. All sample were kept in drying box to avoid any reaction from air humidity and carbon dioxide (CO_2).

2.2 Characterization

Uncalcined EW along with all calcined samples were analyzed by Particle Size Analyzer (PSA), Fourier - transformed Infrared Spectroscopy (FTIR), X–Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) with combination of Energy Dispersive X – Ray (EDX). All samples with size <40µm were analyzed using PSA to obtain mean size distribution for every samples. For FTIR, IR spectra of every samples were recorded using ATR technique (range 4000 – 600 cm^{-1}) to find it functional group. For phase analysis by XRD, the range of diffraction angle 2Θ is 10° - 90° using radiation source of Cu Kα radiation (λ = 1.5406 Å). Morphology of all samples were characterized using SEM with magnification 50X (low magnification) and 3000X (high magnification). To find the percentage composition of sample, EDX was combine with SEM. For SEM characterization, all samples were double coated by gold using sputter coater to creating conductive layer.

3. RESULTS & DISCUSSIONS

3.1 Visual observation

The appearance of compound as the results of calcification on EW is one of the first qualitative analysis were analyzed. Heating a compound can cause liquid inside the samples to condensed. When strongly heated, calcium carbonate from eggshells undergoes thermal decomposition to yield calcium oxide and carbon dioxide gas via the reaction (1) below:

$$CaCO_3 \rightarrow CaO + CO_2 \quad (1)$$

In addition to that, eggshell waste experienced changes in color as calcination temperature rises up to 900□. Figure 1 shows color transition from uncalcined eggshell to calcined eggshell from 600□ to 900□. Color transition is due to a change in crystalline phase and structure [19], [20]. By enforcing heat to some substances, it can causes chemical changes or chemical reactions wherein one or more new substances are formed (with distinct properties from the original).

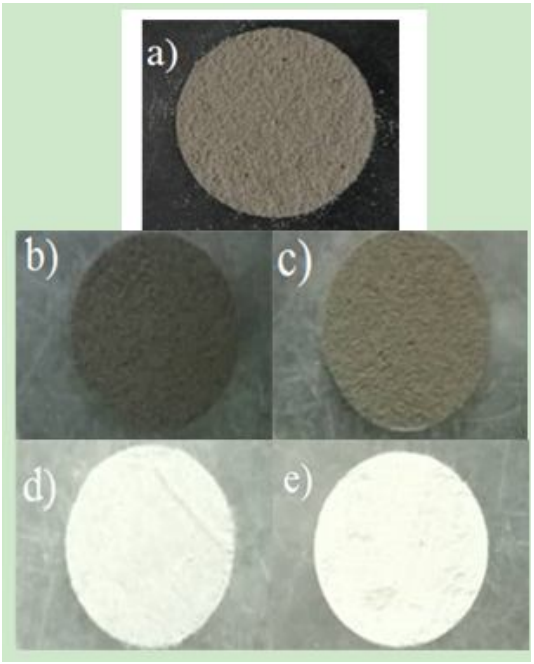


Figure 1: Calcined samples of EW from (a) Uncalcined (reference sample), (b) 600□, (c) 700□,(d) 800□, (e) 900□

It can be observed that from temperature of 600□, the samples color was darker and eventually turns white at the highest calcination temperature of 900□. The thermal decompositon of eggshell carried out by means of two mass-loss processes: first, the primary thermal degradation of the outer shell membrane and second, the subsequent thermal decomposition of calcite in the shell matrix [21]. In addition to that, a higher calcination temperature produced odorless and more softest powder compare to uncalcined eggshell that

give off stinky smell and more of hard and flakes powder. Table 1 below summarized the physical characterization of all samples.

Table 1: Physical observation of uncalcined and calcined EW

Temperature (℃)	Physical characterization		
	Color	Odor	Softness
0	White to light brown	Stench	Hard, flakes
600	Black	Stink	Hard, powder
700	Black mixed gray	Taint	Softer, powder
800	Solid gray	Taint	Softer, powder
900	White	Odorless	Softest, powder

3.2 Particle Size Analysis

The particle size analysis (PSA) of the uncalcined and calcined EW were characterized by using Fritsch particle sizer model 'analysette 22'. In this part, PSA provided us with information of mean sizes in which similar to the concept of average. Figure 2 shows graph of calcination temperature versus particle size of uncalcined and calcined EW samples.

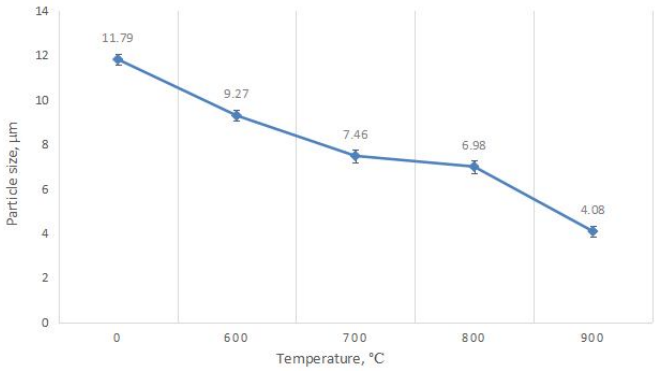


Figure 2: Mean sizes of uncalcined and calcined eggshell versus various calcination temperature

In accordance to the plotted PSA graph above, it can be considered that increasing of calcination temperature resulting considerable decreasing of the particle size of samples. Mean size of uncalcined EW displays to be on 11.79µm and continue to climbing down slowly at first calcination temperature of 600□ with mean size of 9.27µm, then continue to mean particle size of 7.46µm, 6.98µm then eventually to 4.08µm at the highest calcination temperature of 900□. Calcification to turn calcium carbonate to calcium oxide is considered as physical method where calcium oxide nanoparticles were obtained owing to the evaporation of the gaseous CO_2. Researcher [22] also claimed that the diameter of calcined particles will drastically decreased with increasing in temperature.

3.3 Chemical Bonding Analysis

Fourier transform infrared (FTIR) spectrometry was analyzed to determine the functional group of both simultaneously raw and calcined EW. According to the results in Figure 3, it shows the IR spectra of both raw and calcined EW. The IR spectra before calcination, that represent uncalcined EW displays that the sharp band at around 710 cm^{-1}. In common with IR spectra of EW calcined at 600□, 700□, 800□ and blunt peak at 900□ this can be representing to a Ca — O bond with which supported by [23]-[26] who observed similar band ranges for calcium carbonate, $CaCO_3$ study in eggshells. Next, IR spectra of uncalcined EW displays sharp band at around 875 cm^{-1} and a wide stretching peak at around 1415 cm^{-1} represent the C — O stretching and bending of $CaCO_3$. A broad transmission band around 1700 cm^{-1} can be referred to OH stretching vibration or carbonate mineral vibrations modes from residual waste.

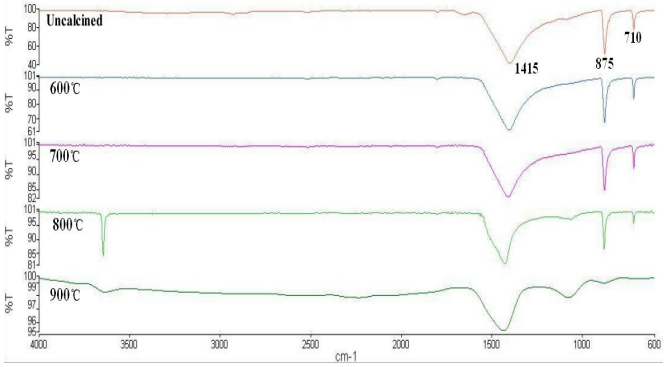


Figure 3: FTIR spectra of raw (uncalcined) and calcined EW

IR spectra after calcination, displays there is presence of OH in $Ca(OH)_2$ at the peak around 3600cm^{-1}. This matches to OH stretching during adsorption of water by CaO. Next, another band existence at around 875cm^{-1} as regards to identified vibration of the Ca — O bond. Lastly, there is sharp absorption region at around 1600 cm^{-1}, 1415 cm^{-1} and 1398 cm^{-1} which signifies functional groups present in eggshell where CO_2^{2-} vibrates. It also indicates that $CaCO_3$ was no longer present as it already converted to CaO. [24] added that, general reduction in intensity of the IR spectra peaks in the raw eggshells signified that most of the functional groups were destroyed during heat treatment.

3.4 Phase Analysis

Figure 4 shows XRD pattern of uncalcined and calcined EW at different temperature. From the pattern of graph, it shows that every graph have different diffraction pattern due to temperature change in calcination process.

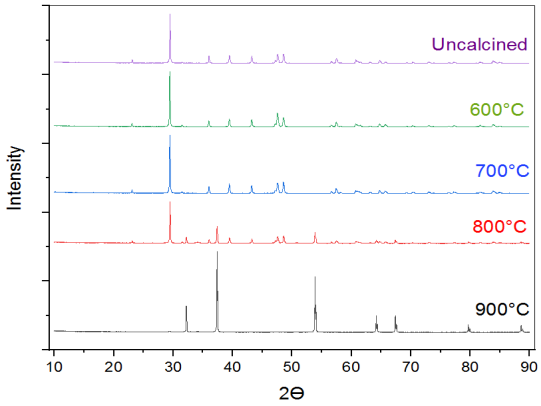


Figure 4: XRD pattern of uncalcined EW and calcined EW at 600,700,800 and 900°C

Uncalcined EW and other calcination temperature of EW diffraction pattern shows small change in it pattern. This occur due to the presence of $CaCO_3$ in other sample except 900°C [27]. $CaCO_3$ is appear at all diffraction peak of uncalcined EW while no CaO peak detected at uncalcined sample as major compound in pure eggshell is $CaCO_3$ [28]. For 600 and 700°C calcination of EW, all peak still shows $CaCO_3$ phase. So, both this temperature is not suitable to use in CaO production. At 800°C, CaO peak starting to appear. However, $CaCO_3$ peak still shows high intensity rather than CaO peak. This temperature still cannot be considering as suitable temperature to use in CaO processing as it still has high $CaCO_3$ compound in it sample. But from this temperature, it can be concluding that 800°C is the starting temperature for $CaCO_3$ transform to CaO. Diffraction pattern of 900°C shows major different when no phase of $CaCO_3$ detected. All peak in in this temperature successfully transform to CaO completely. So, this temperature is suitable to use for CaO production as it successfully turns to CaO without leaving any peak of $CaCO_3$.

The peaks existence was referred to the Joint Committee on Powder Diffraction Standards (JCPDS) data of CaO (PDF Card No. 99-0070) and $CaCO_3$ (PDF Card No. 00-081 2027) [27], [29]. The phase existence is summarizing in Table 2.

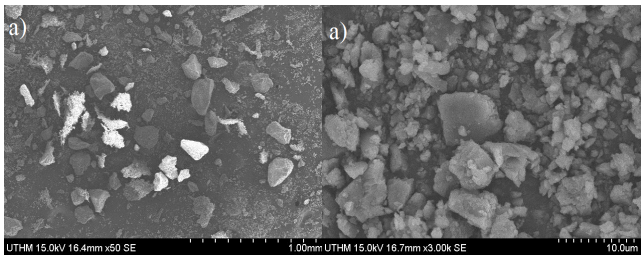
Table 2: XRD data of CaO and $CaCO_3$ from JCPDS, uncalcined and calcined EW at various temperature

Sample	Compound	2Θ				
JCPDS	CaO	32.2°	37.3°	58.3°	64.1°	67.3°
	$CaCO_3$	29.4°	39.4°	43.2°	47.4°	48.5°
Uncalcined	CaO	-	-	-	-	-
	$CaCO_3$	29.5°	39.4°	43.2°	47.5°	48.8°
600□	CaO	-	-	-	-	-
	$CaCO_3$	29.5°	39.5°	43.1°	47.7°	48.7°
700□	CaO	-	-	-	-	-
	$CaCO_3$	29.5	39.5	43.1	47.4	48.5
		°	°	°	°	°
800□	CaO	32.3°	37.4°	54.1°	64.4°	67.4°
	$CaCO_3$	29.5°	39.6°	43.2°	47.3°	48.8°
900□	CaO	32.2°	37.4°	53.8°	64.1°	67.3°
	$CaCO_3$	-	-	-	-	-

Based on the comparison in Table 2, all the diffraction peak that achieve from the sample is nearly similar to JCPDS data. This shows that the result of this experiment is valid due to the diffraction value that in range of JCPDS data. From this table, the statement from XRD pattern above is supported with this data where uncalcined and calcined EW at 600 and 700°C only have $CaCO_3$ while at temperature 800°C $CaCO_3$ and CaO peak both present. Lastly, 900°C temperature of calcination is proved contain only CaO in diffraction angle that suit JCPD data [27], [29]. So, 900°C is confirmed to be used for CaO processing temperature without any impurities.

3.5 Morphological Analysis

The apparent morphologies of uncalcined and calcined EW at different temperature examined by SEM are shown in Figure 5. Based on the image, it shows that when temperature increase, the size of particle decrease. This trend can be seen from Figure 5 (a) to Figure 5 (e) where uncalcined EW have large particle size and start to decrease when temperature increase. This trend follows PSA result where uncalcined EW have highest mean particle size while calcined EW at 900°C have smallest size of particle. At magnification 50X, uncalcined EW, 600°C and 700°C shows shape of particles with edges or like irregular flakes shape. At high magnification, this three sample look like concrete stone shape. For sample 800°C at low magnification, it changes to shape without edges. At high magnification, it starts to create different shape from temperature before. At temperature 900°C, the EW powder become finer at low magnification as can see at Figure 5 (e). At high magnification, shape of sample changed to interconnect like skeleton shape from irregular flakes shaped [23]. Increasing of heat caused the structure of EW change it shape.



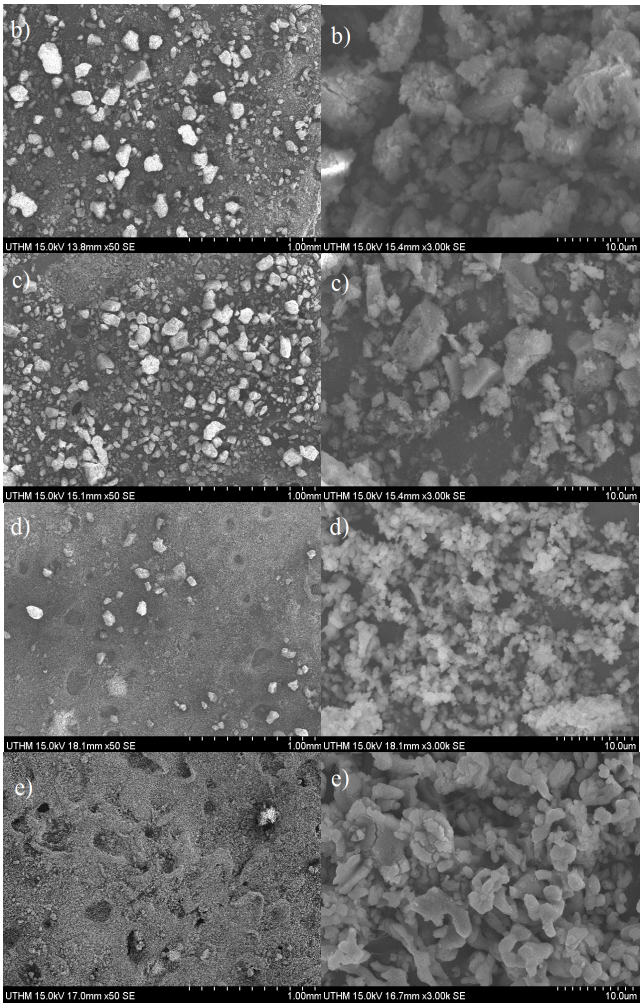


Figure 5: SEM image of (a) uncalcined EW and calcined EW at temperature (b) 600, (c) 700, (d) 800 and (e) 900°C (left) 50X and (right) 3000X

For EDX result, all sample were testing and it result shown in Table 3 below.

Table 3: EDX data of C.O, and Ca for uncalcined and calcined sample at different temperature.

Sample	Element	Weight %	Atomic %
Uncalcined	Carbon, C	29.76	41.55
	Oxygen, O	46.12	48.35
	Calcium, Ca	24.12	10.09
600°C	Carbon, C	24.28	35.36
	Oxygen, O	48.11	52.59
	Calcium, Ca	27.61	12.05
700°C	Carbon, C	16.86	25.93
	Oxygen, O	51.56	59.52
	Calcium, Ca	31.58	14.55
800°C	Carbon, C	16.67	26.71
	Oxygen, O	46.03	55.38
	Calcium, Ca	37.29	17.91
900°C	Carbon, C	16.28	26.89
	Oxygen, O	42.52	52.72
	Calcium, Ca	41.21	20.40

Based on the result, oxygen has highest weight% and atomic% in all sample. This is due to the oxygen content in $CaCO_3$ for uncalcined, 600°C and 700°C sample, CaO and $CaCO_3$ in 800°C sample and CaO in 900°C sample. For C element, uncalcined sample have highest weight% and atomic% of C. While at 900°C, Ca element appeared it highest value at both weight% and atomic% at this sample. Based on this result, increasing of temperature caused atomic% of Ca element increase and caused weight% of C element decrease.

5. CONCLUSION

From this study, it can be concluding that the physical and observation shows eggshell discoloration from black to white as increasing in calcination temperature. Apart from that, calcined eggshell at 900°C has the softest powder and less odor compare to other samples. IR spectra before calcinations shows wide stretching peaks attributing to OH vibrations from waste of residual in comparison to calcined IR spectra displays sharp absorption region of converted CaO. In addition to that, the diameter of calcined particles will drastically have decreased with increasing in temperature. The calcination of EW that consist high $CaCO_3$ produce CaO at temperature 900°C with XRD data of 2θ at: 32.2°, 37.4°, 53.8°, 64.1° and 67.3°. Lastly, SEM images showed the morphology of EW structure have transformed from irregular flakes shaped to skeleton liked structure with confirmation of EDX that EW at 900°C consist of CaO with decreasing of C weight %.

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