Scylla Serrata Shells Calcination using Electric Furnace and Microwave Kiln

Vivien Yiik Mei Hii, Fethma M Nor, Denni Kurniawan

Abstract: To accommodate the rising demands for artificial bone substitutes, the possibilities of extracting calcium oxide (CaO) as precursor of hydroxyapatite (HAP) from Scylla serrata (crab) shells via electric furnace and microwave kiln heating (calcination) were investigated. The crab shells were obtained from food wastes from local restaurants in Miri, Malaysia. They were treated by calcination with temperatures of 600°C, 800°C, and 1000°C for 3 and 4 hours in electric furnace. The shells were also calcined in microwave kiln at power levels of 60%, 80% and 100% for 1 hour. Characterization on the calcined shell samples were done using Fourier Transform Infrared Spectroscopy (FTIR) and X-ray Diffractometer (XRD). Based on the FTIR and XRD spectra, it was found that calcium oxide was obtained through calcination at temperatures ≥ 800°C. The results also indicated that a higher calcination temperature and duration would yield CaO with larger crystallite size. Through calcination in microwave kiln, CaO was readily produced when calcination was done at 60% power.

Keywords: Calcination, calcium oxide, crab shell, furnace, microwave.

I. INTRODUCTION

To accommodate the growing demands for bone grafting, alloplastic grafts have been widely researched to minimize the reliance on allograft and autograft methods as the bone grafts obtained through these means are very limited. Alloplastic grafts can be made from synthetic or natural hydroxyapatite (HAP) combined with other biopolymers such as collagen, chitosan and silk for bone regeneration enhancement [1].

HAP is a type of calcium phosphate which is very similar to human hard tissues in terms of the morphology and composition. Recently, it is gaining a lot of interest as a biomaterial due to its excellent properties. HAP may be classified into synthetic or natural depending on the methods of preparation. For instance, synthetic HAP can be produced through sol-gel [2], hydrolysis [3], and solid-state [4] methods. HAP can be synthesized through calcination [5], [6] and precipitation [7], [8] methods by using natural resources such as animal bones and shells.

In Malaysia, there is an abundant supply of seafood with the wastes being ultimately disposed which in turn causes many environmental impacts. To address the environmental issues, this study aims at exploring the possibilities of extracting calcium oxide (CaO) which is a precursor for HAP from Scylla serrata (crab) shells by solely using calcination method with the consideration of various parameters. These include the particle size of the samples, type of equipment for calcination of the samples, temperature, and duration of the calcination process. In addition to calcination using common electric furnace, this study also explores the usage of microwave kiln for the calcination, considering its low energy consumption. Microwave kiln has been used in previous calcination of sea shells [9].

II. METHODOLOGY

A. Crab Shell Sample Preparation

The shells of Scylla serrata were obtained from food wastes produced by local restaurants in Miri, Malaysia. Different parts of the crab shells were roughly washed with water and then crushed into smaller pieces. Next, the shells were immersed in 2.5 litres of acetone contained in a basin for 2 hours. After that, the shells were again rinsed with water to remove the remaining meat and soft tissues. Following this, overnight air drying was done on the crab shells to remove the remaining moisture. Then, crushing using pestle and mortar and further grinding using a dry blender were done on the crab shells to make them into smaller pieces and into powder, respectively. Lastly, the shell powder was sieved into two groups with particles of x ≤ 45 μm and 45 ≤ x ≤ 63 μm using sieve shaker (Endecotts, UK).

B. Calcination Process

Prior to the calcination process, the electric furnace (Carbolite, UK) was calibrated by using an infrared thermometer (RayTemp 28, ETI, UK) to measure the interior temperature of the furnace. Besides calibrating the furnace, the heating curves of the kiln in microwave (Sharp, Japan) at power levels of 60%, 80% and 100% (output power 900W) were also determined by using the infrared thermometer.

Shell powder, of 4 – 5 grams, was weighed using a weighing scale and placed into the porcelain crucible using a spatula. For conventional heating, the shell powder was calcined using furnace with an average heating rate of 45°C/min (for the first ten minutes) with settings at 600°C, 800°C, and 1000°C for 3 and 4 hours. As for microwave heating, the shell powder was placed inside the microwave kiln and was subsequently heated at power levels of 60%, 80% and 100% for 1 hour. After that, the shell powder samples were taken out from the equipment to cool to ambient temperature.

C. Sample Characterization

The composition of phases and the size of crystallites within the shell samples were determined using X-ray Diffractometer (XRD) (XRD-7000, Shimadzu, Japan) with copper K-Alpha radiation. The XRD spectra were taken at 40 kV and 30 mA over a range of 20°-70°.
angles from 10° to 80°. From the XRD spectra, to calculate the crystallite size of the shell sample, Scherrer’s equation was used. The presence of the functional groups in the shell samples was detected by using Fourier Transform Infrared Spectroscopy (FTIR) (Agilent Technologies, USA). The probing was done over the range of 650 to 4000 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Visual Inspection

The furnace heated shell samples at various temperatures are depicted in Fig. 1. The colour of raw crab shell powder was light pinkish but upon calcination at temperatures of 600°C to 1000°C, the corresponding shell samples changed to dark grey, light grey and dark white. Similarly, for microwave heating, upon calcination at power levels of 60%, 80% and 100%, the respective shell samples changed to light grey, dark white and white (not shown).

This colour change is supported by [10][11][12] whereby upon being heat treated at high temperatures, bone samples turned lighter in colour due to the diminishing collagen, protein and other organic substances.

In this study, decomposition of the chitin-protein matrix could have occurred in the calcined crab shell samples [13]. It could be observed that the shell samples calcined at temperature of 1000°C and at power level of 100% were lighter than other samples which indicate a more complete removal of the organic substances. Furthermore, it is also worth mentioning that the influences of different particle size and various calcination duration had insignificant effect on the shell samples as compared to the calcination temperature [6].

![Fig. 1. Furnace heated shell samples at 600°C (A), 800°C (B) and 1000°C (C)](Image)

B. FTIR Results

FTIR spectra of untreated and furnace heated crab shell samples are depicted in Fig. 2. The FTIR spectrum of untreated shell sample is clearly different than those which were heat treated. This is because calcination caused changes in their chemical bonds due to high temperature exposure [10].

Upon heating the shell samples at 600°C, one broad absorption band at 3242.78 cm⁻¹ and another low absorption band at 1654.94 cm⁻¹ which were present in the raw shell samples were completely eliminated. The former band was the characteristic stretching vibration of hydrogen bonded O-H which was contributed by the absorbed water molecules in the samples [10], while the latter band was the characteristic stretching vibration of C=O corresponding to Amide I of collagen [5]. This clearly shows that the water molecules and organic substances such as collagen diminished during the calcination. Conversely, absorption peaks' intensities at 1401.48 cm⁻¹, 1043.65 cm⁻¹, 872.2 cm⁻¹ and 715.65 cm⁻¹ had increased due to an increase in the crystallinity of the compound formed [12]. The 1401.48 cm⁻¹ as well as 1043.65 cm⁻¹ peaks were attributed to the C-O bond stretching vibrations [7], [14]. Moreover, the FTIR peak at 872.2 cm⁻¹ indicated B-type carbonate groups presence [15] while the 715.65 cm⁻¹ peak was due to C-H bond bending vibration [16].

![Fig. 2. FTIR spectra of untreated and furnace heated shells](Image)
be achieved [20] which subsequently aids the rate of chemical change in the shell samples.

C. XRD Results

XRD spectra in Fig. 3 belongs to untreated and microwave heated crab shell samples at the power levels of 60% and 100%. Fig. 4 shows the comparison between the spectra from furnace versus microwave kiln calcined crab shell samples at temperatures of 800°C for 3 hours and power level 60% for 1 hour, respectively. The XRD spectra obtained for the calcined crab shell samples were subsequently analyzed using standard of JCPDS 017-0912 calcium oxide (CaO) file.

![XRD spectra of untreated and microwave kiln calcined crab shell samples](image)

**Fig. 3.** XRD spectra of untreated and microwave kiln calcined crab shell samples

![XRD spectra of furnace heated versus microwave kiln calcined crab shell samples](image)

**Fig. 4.** XRD spectra of furnace heated versus microwave kiln calcined crab shell samples at comparable calcination temperature

In relation to the raw crab shell sample, the XRD diffraction patterns mainly corresponded to CaCO$_3$ [21]. For calcined shell samples, it was found that the primary compound produced was CaO with some minor traces of calcium hydroxide (Ca(OH)$_2$). The CaO showed its presence at peaks labelled as (1), (2), (3), (4) and (5) corresponding to 20 angles of 32.4°, 37.6°, 54.1°, 64.5° and 67.7° respectively as supported by the presence of stretching vibration of Ca-O at the peak of 656.01 cm$^{-1}$ and C-O stretching modes at the peaks of 1401.48 cm$^{-1}$ and 1043.65 cm$^{-1}$ which were detected in the earlier FTIR testing. With respect to the C-O stretching modes, the bands were due to CaO surface which was absorbing CO$_2$ [7]. As for Ca(OH)$_2$, presence of hydroxyl group at FTIR peak of 3637.88 cm$^{-1}$ confirms 20 angles of 18.25°, 29.05°, 34.35°, 47° and 51.1°.

Reference [18] concluded that the formation of Ca(OH)$_2$ was due to the reaction between CaO and water molecules in the air during calcination process. The crystallite sizes of CaO at three main peaks labelled as (1), (2) and (3) corresponding to (111), (200) and (202) lattice planes respectively [22], were determined with Scherrer’s equation. Crystallite size of CaO produced under microwave heating was calculated to be approximately 41.5 nm on average. Sizes of CaO crystallites at different main peaks for shell samples calcined at power levels of 60% and 100% are stated in Table I.

| Peak Number | Lattice Plane | 2θ (°) | Crystallite Size (nm) |
|-------------|---------------|-------|----------------------|
|             |               | 60%   | 100%                 |
| 1           | 111           | 32.4  | 32.33                |
| 2           | 200           | 37.6  | 46.42                |
| 3           | 202           | 54.15 | 46.32                |

According to [23], the average crystallite sizes of CaO obtained from the calcination of mud creeper shells ranged from 41 to 42 nm, which reflects the accuracy of the results gained in this study. As observed in Fig. 3, the XRD diffraction patterns of CaO generally became sharper and narrower as the temperature of calcination increased. This denotes that the size of CaO crystallites increased as shown in Table I. As diffusion dictates the crystallization, this results in crystallite size increment as the calcination temperature increases [24], [25]. At microwave power level of 100%, the crystallite sizes of CaO corresponding to lattice planes of (111), (200) and (202) displayed crystallite size increments of 31 nm, 0.86 nm, and 1.31 nm respectively. When the temperature is past 800°C, the crystallite size increment of CaO becomes relatively small due to less chemical changes occurring in the crab shell samples.

Based on Fig. 4, as compared to furnace heating, the XRD spectra have verified that microwave heating would yield the same product amount of CaO and Ca(OH)$_2$ in a shorter time span due to its rapid heating which in turn accelerates the rate of chemical change in the shell samples.

Table II summarizes the crystallite size of CaO produced under furnace and microwave heating. Based on Table II, it is clear that the crystallite size of CaO obtained via furnace heating was larger as compared to CaO in the microwave heated shell samples due to a longer calcination duration. Reference [24] has reported that the crystallite size of the calcined eggshell sample increased from 37.07 nm to 59.97 nm as the duration of calcination increased from 1 hour to 10 hours. However, it is apparent that the calcination temperature has more impact on the crystallite size of the crab shell samples as confirmed by the FTIR testing. This could be further supported by [10] who studied the effect of different particle size of bovine bone samples and it was found that the size increment of the crystallites was comparatively minute for calcination at the same temperature for samples with different sizes of particle.

| Table II: Size of CaO crystallites under different microwave power levels |
|-----------------------------|-----------------------------|
| Peak Number | Lattice Plane | 2θ (°) | Crystallite Size (nm) |
| 60% | 100% |
| 1 | 111 | 32.4 | 32.33 |
| 2 | 200 | 37.6 | 46.42 |
| 3 | 202 | 54.15 | 46.32 |
### IV. CONCLUSION

**Scylla serrata** (crab) shells were prepared and calcined using conventional electric furnace set for 600°C to 1000°C for 3 and 4 hours and using microwave kiln at power levels of 60%, 80% and 100% for 1 hour. It was found that the compound formed were mainly CaO with minor traces of Ca(OH)₂. With increased temperature of up to 800°C, all the FTIR peaks attributed to the carbonate groups and organic substances decreased in intensity. It was also observed that further heating at temperatures ≥ 800°C would not result in any substantial decomposition or increment in crystallinity of the shell samples. Crab shells which were microwave heated at the power levels of 60%, 80% and 100% for 1 hour, showed similar characteristics as those which were furnace heated at 800°C and 1000°C for 3 and 4 hours. Higher calcination temperature and duration would result in a highly crystalline CaO. Under microwave heating, the average size of CaO crystallites produced was around 41.5 nm.

### ACKNOWLEDGMENT

The Authors appreciate Centre for Advanced Material and Energy Sciences, Universiti Brunei Darussalam in facilitating XRD tests in this study.

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