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Blood Cockle Shells Waste as Renewable Source for the Production of Biogenic CaCO3 and Its Characterisation

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Abstract. The prowess to reuse and recycle of blood cockle shells for raw material in bio-ceramics applications is an attractive component of integrated waste management program. In this paper an attempt is made to introduce a simple process to manufacture biogenic $CaCO_3$ powder from blood cockle shells waste. The biogenic $CaCO_3$ powder was produced from rinsing of blood cockle shells waste using deionised water and oxalic acid for cleaning the dirt and stain on the shells, then drying and grinding followed by heat treatment at 500 and 800 ^oC for 5 h. The powder obtained was characterised by XRF, DTA/TG, SEM, FTIR, and XRD analysis. The amount of 97.1 % CaO was obtained from XRF result. The thermal decomposition of $CaCO_3$ become CaO due to mass loss was observed in the TG curve. The SEM result shows the needle-like aragonite morphology of blood cockle shells powder transformed to cubic-like calcite after heat treated at 500 ^oC. These results were consistent with FTIR and XRD results.

1. Introduction
Recently, blood cockle shells waste as one of the cheaper source of aragonite $CaCO_3$ was received a great attention from many researchers in the fields of science, engineering and medicine. $CaCO_3$ derived from blood cockle shells have been used in many applications such as in the preparation of bio-ceramics [1,2], in the production of biodiesel [3,4], and in the therapeutic and hormonal delivery vehicle for osteoporosis management [5]. There are many studies have been conducted to synthesis and evaluate the chemical composition, thermal properties and microstructural of $CaCO_3$ derived from bloods cockle shells [1,6-11], however, there are still have different opinion in the several point such as the presence of calcium carbonate and other constituents in this material. Therefore, the effort to study the characteristic of blood cockle shells waste from different region especially in Indonesia is challenge. In this paper, the simple technique to prepare and evaluate chemical composition and the microstructure characteristic of biogenic $CaCO_3$ powder obtained from blood cockle shells waste in order to add the currently existing data's on cockle shell materials was presented.

2. Experimental Method
Blood cockle shells waste used for preparation of biogenic $CaCO_3$ powder were collected from sea food restaurants around city of Bandar Lampung, Indonesia. The shells samples washed thoroughly in running tap water followed by boiling in pressure cooker for 10 h and dried in oven at 100 ^oC for 24 h.

The dried shells then brushed using oxalic acid to cleaning the dirt and stain on the shells continued washing using warm deionised water then drying and grinding. The dried blood cockles shell (BCS) powder were then heat treated in furnace at different temperature of 500 ºC and 800 ºC for 3 h then ground with mortar and pestle and screened through a 35 m sieved. Thermogravimetric analysis (DTA/TG) of the dried biogenic BCS powder was conducted using Thermal Analyzer (Netzsch, STA 409) in the temperature range of 20-1000 ºC with heating rate of 5 ºC/min. The chemical composition of cockle shells was analysed using X-ray Flourescence (XRF- PAN analytical). The crystal structure analysis of dried and heat treated samples phase was monitored by using x-ray diffractometer (PW3040/60 X'pert Pro) using CuK radiation, 40 kV and 30 mA in 2 theta range of 5-80 degrees. The compositional of functional group in the sample was monitored by using FTIR spectrophotometer (Perkin Elmer Optima 100), and the surface morphology observed by Scanning Electron Microscopy (JEOL JSM-5610LV).

3. Results and Discussion

The result of DTA/TG analyses of dried biogenic blood cockles shells (BCS) powder is shown in Figure 1. There are typically two successive steps of weight loss in the TG graph. The first step of small weight loss is at temperature below 200 ºC (2.7%), it can be ascribed to the moisture content of BCS sample and related to a broad endothermic peak in the DTA result. Small endothermic behaviour also observed at range temperature of 334 ºC – 344 ºC, it can be caused by dehydration of water from the carbonate lattice and transformation of aragonite to calcite phases [8,9,11]. The second step of large weight loss observed at temperature between 558 ºC – 755 ºC (41.25 %) and it is associated with sharp endothermic peak in the DTA results at 735.2 ºC, this result is due to the release of carbon dioxide (CO_2) as a result of calcium carbonate decomposition. The DTA/TG result of BCS obtained from this study is also in a good agreement with the results has been found by previous researcher [9].

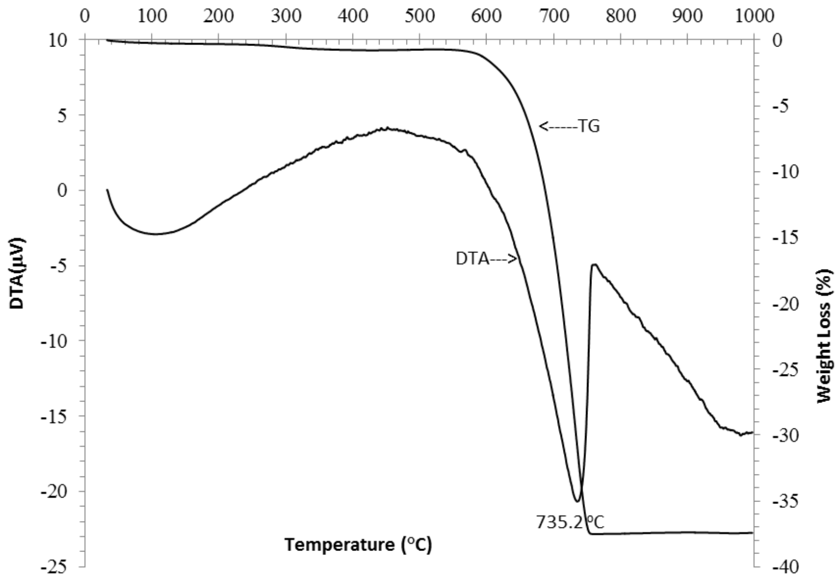


Figure 1. DTA/TG graph of dried biogenic blood cockle shells (BCS) powder.

XRF analysis was conducted to estimate the chemical composition of heat treated blood cockle shell at 800 ºC. The chemical composition obtained from XRF results at 800 ºC are 97.21 % of CaO, 0.29 % of MgO, 0.34 of Al_2O_3, 0.15 of Na_2O, 0.51 % of FeO and 1.50 % of SrO. This result was in a good agreement with the results found by Mohamed *et al* [9]. The high amount of CaO is correlated with the presence of calcium carbonate in the blood cockle shells waste.

Figure 2 shows x-ray diffraction (XRD) patterns of dried (a), heat treated at 500 ºC (b), and 800 ºC

(c) BCS samples, respectively. The diffraction pattern analysis of dried BSC sample shows aragonite phase, this phase matched with the characteristic peaks of the aragonite phase based Joint Committee of Powder Diffraction Society (JCPDS) file number of 00-041-1475. This result is in a good agreement with the results found by Islam *et al* [10]. The diffraction patterns of the heat treated sample at 500 ºC revealed that the phase form is calcite (JCPDS number 00-047-1743), whereas increasing heat treatment at 800 ºC, calcite phase decompose to CaO and some peaks belong to $Ca(OH)_2$ were present in the sample due to absorbing moisture or water from surrounding atmosphere [12].

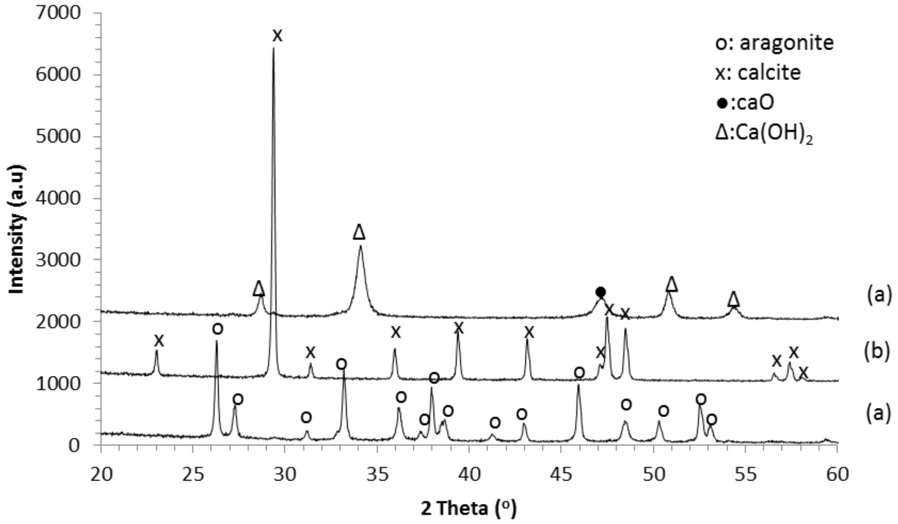


Figure 2. X-ray diffraction patterns of dried (a), and heat treated of blood cockle shells (BCS) powder at 500 ºC (b) and at 800 ºC.

Figure 3 shows the FTIR spectra of dried and heat treated of blood cockle shells at 500 ºC and 800 ºC in the range of 4000 – 400 cm^{-1}. The small frequency band centered at 3784 cm^{-1} as shown in Fig. 3a and 3b are associated with the stretching vibration of hydroxyl group. The characteristic peak band for CO_3^{2-} for BCS sample appear at 713 cm^{-1}, 861 cm^{-1}, 1083 cm^{-1}, 1476 cm^{-1}, 1786 cm^{-1}, and 2346 cm^{-1} which attributed to the common characteristic feature of the carbonate ions in calcium carbonate whereas for heat treated BCS sample at 500 ºC the characteristic band for CO_3^{2-} occur at 712 cm^{-1}, 876 cm^{-1}, 1439 cm^{-1}, 1798 cm^{-1}, and 2512 cm^{-1} [1,10,12]. The observed band at 1083 cm^{-1} was only appear in the spectrum of dried aragonite BCS sample (Fig.3a) but not in heat treated sample (Fig.3b and 3c), this results is due to symmetric stretching vibration of CO_3^{2-} [1,10-12]. The FTIR of BCS sample heat treated at 800 ºC is shown in Fig. 3c. There are two small frequency bands that related to the structure of CaO, i.e. at 876 cm^{-1} and 1482 cm^{-1}, these peaks are smaller compare with dried BCS sample, this result can be attributed to the decomposition of $CaCO_3$ become CaO by releasing CO_2. The sharp peak at 3646 cm^{-1} is related to -OH bond group present in CaO [13]. This sharp peak is due to the presence of $Ca(OH)_2$ in the sample as revealed in the XRD result.

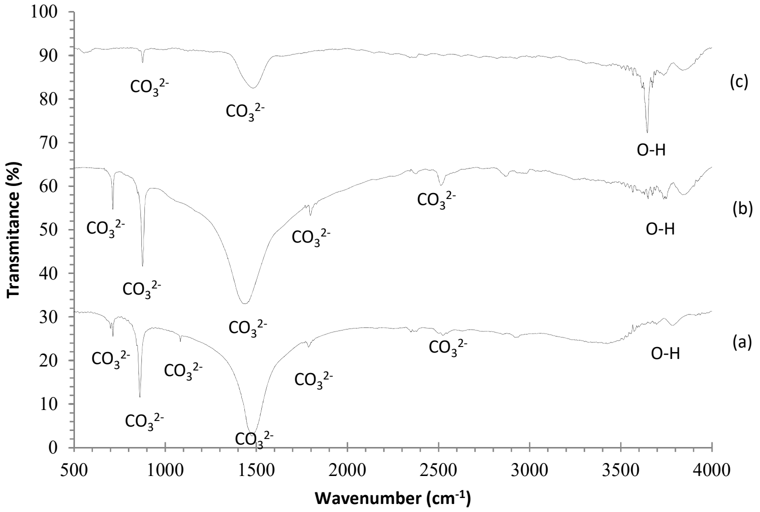
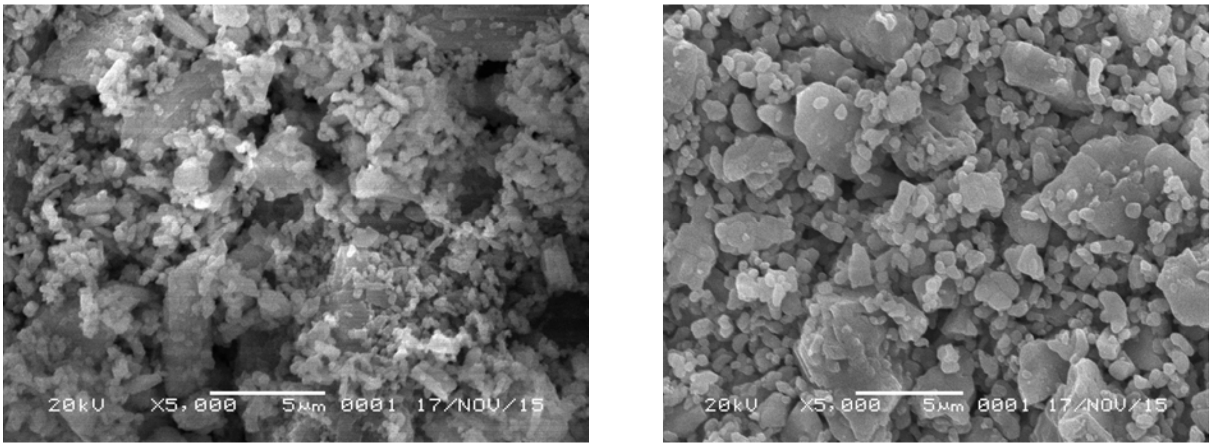


Figure 3. FTIR spectra of of dried (a), and heat treated of blood cockle shells at 500 ºC (b) and at 800 ºC.

Figure 4 shows the SEM morphology of dried BCS and heat treated BCS powders at 500 ºC. The dried BCS sample had *rod-like* morphology with average grains size of 1.85 m, whereas the heat treated BCS had *cubic-like* morphology with the average grains size of 1.48 m. This results is in a good agreement with the previous study have been conducted by Chenyu *et al* [14] and Chen and Xiang [15], where the *rod-like* aragonite and *cubic-like* calcite were observed.



(a) (b)

Figure 4. SEM of dried (a) and heat treated blood cockle shell powder at 500 ºC (b).

4. Conclusion

Biogenic $CaCO_3$ powder has been successfully synthesised by using blood cockle shells waste material. The results found that blood cockle shells have high content of CaO (97.1 %). This high content of CaO obtained from processed blood cockle shell is very useful for bioceramics and many industries applications. Therefore, recycle waste material into valued added material is promising challenge in development of functional material and also solution to the problems of disposal especially for the shell by-products.

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