Optimum conditions for preparation of bio-calcium from blood cockle and golden apple snail shells and characterization

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ABSTRACT: Research on the utilization of calcium compounds from seashells has attracted much interest in diverse applications. However, the optimum temperature and time for preparation of calcium compounds from shells remains unknown. These factors have a direct effect on the purity of the obtained calcium phases. In this study, the influence of calcination temperature and holding time on the phase transformations of $CaCO_3$ from sea shells and freshwater shells, i.e., blood cockle and golden apple snail shells, was studied. High purity and crystalline $CaCO_3$ and CaO was produced from both types of shells by calcination at 600 °C and 800 °C, respectively. Overall both blood cockle and golden apple snail shells could be used to produce calcium compounds with 95–98% pure calcium with trace amounts of As, Cd, Hg, and Pb. Phase transformation of $CaCO_3$ depends on calcination temperature and holding time. The calcium content in $CaCO_3$ and CaO from golden apple snail shells was higher than that from blood cockle shells. This result also indicated that the calcium compounds from blood cockle shell were easier to grind than those from golden apple snail shells primarily due to an early transformation of the calcium phase of golden apple snail shells.

KEYWORDS: $CaCO_3$, CaO, phase transformations, calcination

INTRODUCTION

Blood cockles (*Anadara granosa*) are a type of bivalve mollusc, which are commonly found at muddy seashores. Blood cockle farming is quite extensive on the eastern and southern coasts of Thailand. The annual production of blood cockles in Thailand between 2009 and 2016 ranged from 40–81 thousand tonnes[1]. It is one of the most popular seafoods in Thailand and is a good protein source. Golden apple snails (*Pomacca canaliculata*) are very serious invasive freshwater pests. They cause damage to agricultural products, especially rice and aquatic plants, leading to huge economic losses[2]. It has been estimated that in Thailand, golden apple snails cause losses of at least 3000 million US dollars annually[3]. Nonetheless, they have been used as a

protein source in animal feeds and human foods[4–7]. The large consumption of blood cockle and golden apple snails results in a considerable amount of shell by-products that is now treated as waste.

The three common mineral forms found in various sea shells are the aragonite, calcite and vaterite phases of $CaCO_3$. These shells are composed of 97–99% of $CaCO_3$ with some minor compounds, viz., MgO, Al_2O_3, Fe_2O_3, SiO_2, $Ca_3P_2O_8$, $CaSO_4$, proteins and mucopolysaccharides. Additionally, trace amounts of Sn, Mo, Mn, Cd, Ti, B, Pb, Au, Ag, Ni, Co, Bi, Cu, Sr, Rb and As are present[8]. Another source of calcium, CaO, is obtained from the calcination of limestone or $CaCO_3$[9,10]. Normally, dolomite, limestone and magnesite from sedimentary rocks are the common natural sources for the production of $CaCO_3$ and CaO. Nevertheless, large scale mining

of raw materials, such as limestone, results in extensive deforestation and top soil loss. This contributes to environmental damage and the high costs for environmental compliance incurred.

Nowadays, research on the utilization of calcium compounds from seashells has attracted much interest. Numerous studies have been done with the aim of using alternative sources of $CaCO_3$ and CaO from various sea shells. This calcium has been widely used in diverse applications. It is notable that this approach uses shell by-products in an economically feasible manner and has the environmental benefits of waste recovery. For example, $CaCO_3$ from oyster, mussel, cockle, clam and bivalve shells has been applied as fillers in environmentally friendly thermoplastic composites [11–13], substitute materials in the production of plastering cement and construction materials [14–16], suitably used in plant fertilizer and as reagents for efficient phosphate removal from wastewater [17, 18] and in biomimetic designs of ceramic/polymer and ceramic/polymer/-fibre composites [19]. Additionally, $CaCO_3$ extracted from blood cockle shells has been used as a biomaterial for tissue engineering applications, drug delivery systems, bone tissue and bone grafts [20–22]. $CaCO_3$ can be prepared from shells with and without calcination. A temperature of 500 °C with various holding times from 15 min to 5 h was used to produce $CaCO_3$. CaO obtained from the calcination of shells has been used in various applications such as a renewable catalyst for biodiesel production [23–25], a material to absorb CO_2 for air cleaning applications [26, 27] and an initial substrate to produce hydroxyapatite ceramic biomaterials [28]. Various calcination temperatures from 600 °C to 1000 °C with holding times from 30 min to 4 h were applied to shells to obtain CaO. Insufficient information exists about the influence of calcination temperature and holding time on the phase transformations of $CaCO_3$ in shells that have a direct effect on the purity of the $CaCO_3$ and CaO phases.

In the present study, transformations of the calcium phase of seawater blood cockle and fresh water golden apple snail shells were studied. Calcination temperatures ranging from 600 °C to 900 °C with 1–4 h holding periods were used to investigate the effects of these parameters on their transformation and elemental composition. This information will be useful in understanding of the effects of calcination temperature and holding time. Effective calcination method to obtain the required calcium compounds from shells could thus be developed.

MATERIALS AND METHODS

Material preparation

The blood cockle (BC) shells used in this study were collected from seafood restaurants in Khon Kaen province. These restaurants are supplied by producers from the coastal areas of Eastern Thailand. Golden apple snail (GAS) shells were collected from paddy fields in Khon Kaen province, Thailand. First, the collected GAS shells were broken into pieces with sizes similar to those of BC shell, the average size of shell was 3×4 cm^2. The broken GAS and the BC shells were then cleaned with a brush in tap water to remove dirt and then boiled in hot water for 20 min. After cleaning, they were air-dried for 24 h and oven-dried at 60 °C for another 24 h. The prepared shells were stored in a desiccator at a room temperature of 25–29 °C.

Material characterization

To study the weight loss and thermal behaviour of these calcium products, the prepared shells were separately crushed into fine powders using a porcelain mortar and pestle. Thermogravimetric analysis at ambient temperature (25–29 °C) to 1100 °C at a heating rate of 5 °C/min under an O_2 atmosphere was done on the samples using a thermogravimetric analyser/differential scanning calorimeter (TGA/DSC1, Mettler).

To study the influence of calcination temperature and holding period on the transformation of the crystalline phases in BC and GAS shells, the prepared shells were separately calcined at four different temperatures, viz., 600, 700, 800, and 900 °C for 1, 2, 3, and 4 h using a heating rate of 5 °C/min. After calcination, they were crushed in a porcelain mortar into fine powders. The crystalline phase composition of these powders was investigated using X-ray diffraction (XRD, Bruker D8) at a scan rate of 2.4° 2θ/min in 0.02° 2θ increments with CuKα radiation. The elemental composition of raw shells and shells calcined at 600, 700, 800, and 900 °C for 1 h were determined using wavelength dispersive X-ray fluorescence (WDXRF, Axios mAX). Microstructural observations of shell samples were carried out using scanning electron microscopy (SEM, LEO 1450). 100 g of shell samples calcined for 1 h were ground and analysed for their particle size distributions using a particle size analyser (HORIBA, LA-950). The trace (heavy metal) elements (As, Cd, Hg, and Pb) in shell powders were also analysed using inductively coupled plasma/mass spectroscopy (ICP/MS, AGILENT 7500C).
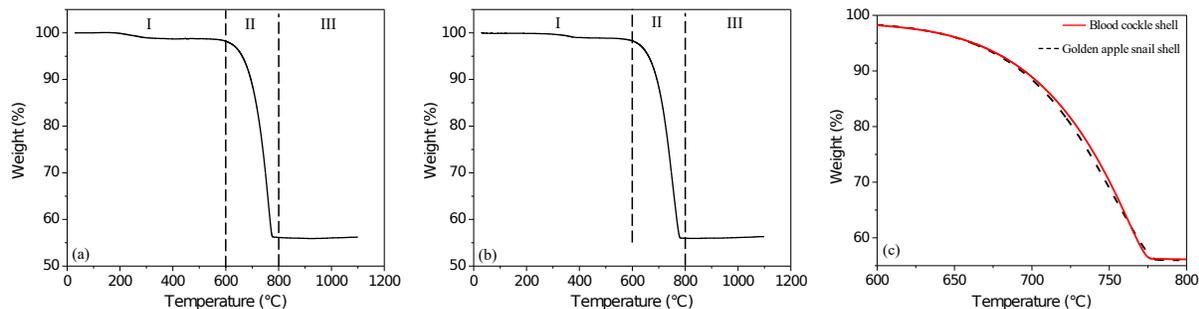
Fig. 1 TGA patterns of (a) blood cockle shell, (b) golden apple snail shell, and (c) blood cockle and golden apple snail shells between 600 and 800 °C.

RESULTS AND DISCUSSION

Thermogravimetric analysis of shells

Fig. 1 shows the results of thermogravimetric analysis (TGA) of shell samples. The TGA curves for both types of shells were similar to three distinct stages of weight loss, as shown in Fig. 1a,b. In the initial stage (I) at temperatures below 600 °C, the weight of both shell samples decreased slightly by 2–3%. In the second stage (II) at temperatures between 600 and 800 °C, the weights decreased rapidly until they had lost 44% of their weight. In the final stage (III) at temperatures above 800 °C, the weight of shell samples remained almost constant. Fig. 1c shows a comparison of shell weight losses in stage II. The weight loss of BC shell was slightly slower than that of GAS shell. From the results, calcination temperatures of 600, 700, 800, and 900 °C were selected to investigate the changes in elemental composition and transformation of the crystalline phases of shells. To study the influence of holding period on phase transformation, four different holding times, 1, 2, 3, and 4 h, were used.

Transformation of the crystalline phases during calcination

The XRD patterns of raw BC and GAS shells are shown in Fig. 2. The broad peak patterns of both shells corresponded to an amorphous (poorly crystallized) aragonite phase of $CaCO_3$. This is in agreement with previous reports of the presence of an aragonite phase in bivalve shells[29] and cockle shells[30].

Figs. 3 and 4 show XRD patterns of shells after calcination at temperatures of 600, 700, 800, and 900 °C and 1–4 h holding times. The XRD patterns of both shells calcined at 600 °C at all holding periods showed only the sharp characteristic peaks of a calcite phase, as shown in Figs. 3a and 4a.
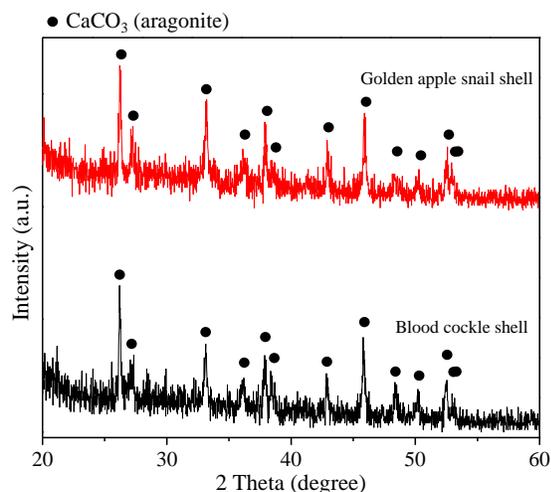
Fig. 2 XRD patterns of raw blood cockle and golden apple snail shells.

For the samples calcined at 700 °C, the single sharp characteristic peaks of a calcite phase was observed for BC shells after a holding period of 1–3 h and for GAS shells after a holding period of 1–2 h, as depicted in Figs. 3b and 4b. This finding is in good agreement with previous XRD results for patterns of aragonite and calcite of $CaCO_3$[31]. The initial stage of weight loss observed in TGA analysis was due to the removal of water from shells and phase transformation of amorphous aragonite into crystalline calcite. Bischoff[32] reported that this transformation occurred at low temperatures due to the instability of the aragonite phase. For the BC shells calcined at 700 °C for 4 h and 800 °C for 1 h, as well as the GAS shells calcined at 700 °C for 3 and 4 h, calcite co-existed with CaO as shown in Figs. 3b,c and 4b. This suggests that the phase transformation of $CaCO_3$ to CaO started at a temperature between 700
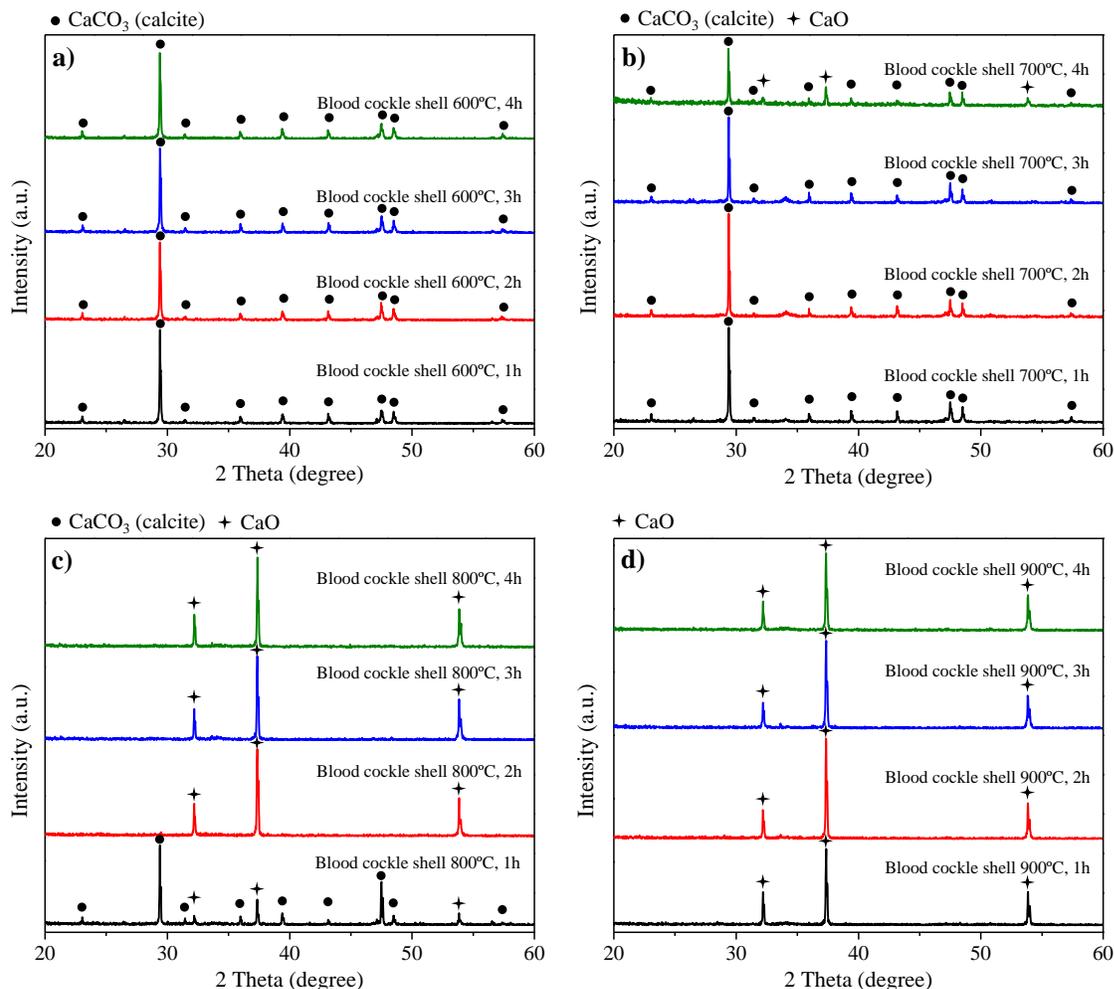
Fig. 3 XRD patterns of blood cockle shell after calcination at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C for various holding times.

and 800 °C. The characteristic peaks associated with complete disappearance of the $CaCO_3$ phase after calcination at 800 °C for 2 h for the BC shells and after all holding durations at 800 °C for GAS shells, are shown in Figs. 3c and 4c. The phase change in the BC shells was slower than for the GAS shells since the BC shells were thicker. This result is consistent with TGA analysis showing that the weight loss of the BC shells was slightly slower than for the GAS shells. When the calcination temperature was 900 °C for all holding periods, only the characteristic peaks associated with CaO phase were observed, as shown in Figs. 3d and 4d. This result indicated that amorphous $CaCO_3$ (aragonite) was completely transformed to crystalline $CaCO_3$ (calcite) and CaO at temperatures of 600 °C and 800 °C, respectively. The XRD results thus indicated that both calcination

temperature and holding time were important for the phase transformation of $CaCO_3$ in both shells.

Surface morphology observation during calcination

The surface morphologies of raw shells and calcined shells at 600, 700, 800, and 900 °C for 1 h were observed under SEM and the results are shown in Figs. 5–7. The surfaces of BC shells contained parallel cleavages (Fig. 5a) similar to a prismatic structure with prominent and uniformly distributed pores. The structure was well connected and composed of fine grains (approximately 2 μm) of calcium compounds, (Fig. 5b). Alternatively, the surface of GAS shells was relatively smooth (Fig. 5c) consisting of small compact and connected homogeneous fine grains (approximately 1 μm) of calcium
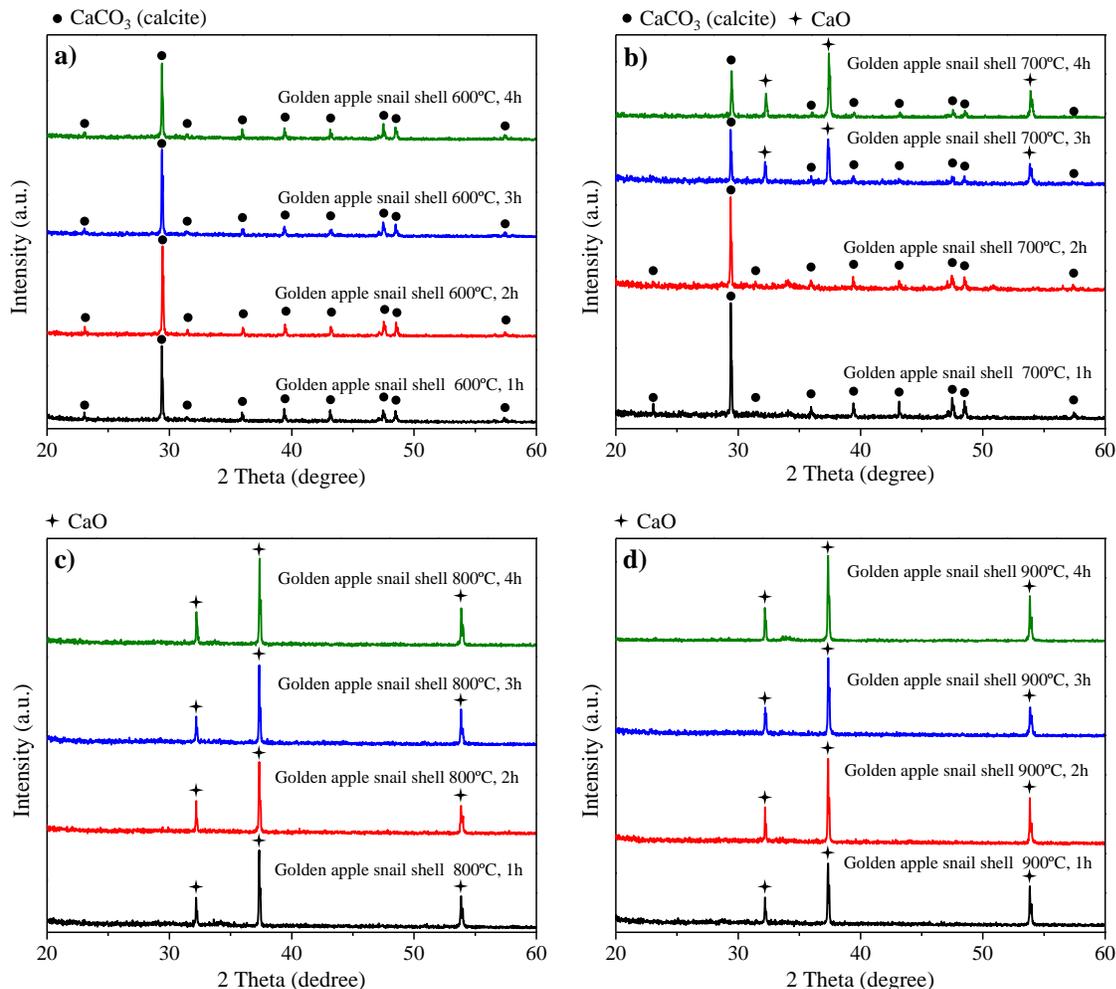
Fig. 4 XRD patterns of golden apple snail shell after calcination at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C for various holding times.

compounds (Fig. 5d).

Figs. 6 and 7 show scanning electron micrographs of shells that were calcined at 600, 700, 800, and 900 °C for 1 h. After calcination at 600 °C, the surface morphologies of both shell types changed quite noticeably. In the BC shell, the parallel cleavages were not present. Both shells showed non-uniform irregular surfaces consisting of units up to 10–15 µm, as shown in Figs. 6a and 7a. The surface showed an agglomerated phase of a sintered matrix that was due to the removal of water and organic material from the raw shells. The amorphous aragonite phase of $CaCO_3$ in raw shells was transformed into a crystalline calcite phase of $CaCO_3$ after calcination at 600 °C. This finding concurs with the results of XRD analysis. After calcination at 700 °C, the surfaces became more uniform with the

presence of many small units (approximately 3–5 µm) of a calcium compound, as shown in Figs. 6b and 7b. In these figures, the microstructure of both raw shells calcined at high temperatures of 800 and 900 °C were markedly different from the shells calcined at 600 and 700 °C. Increasing the temperature to 800 °C and 900 °C resulted in the formation of uniform micro-granules and fine grains (approximately 3–5 µm) of calcium compounds, as shown in Figs. 6c,d and 7c,d. This change in surface morphology resulted from a transformation of the calcite phase of $CaCO_3$ to CaO, releasing CO_2 during high temperature calcination. The surface densities of GAS shell were higher than those of BC shells at all calcination temperatures.
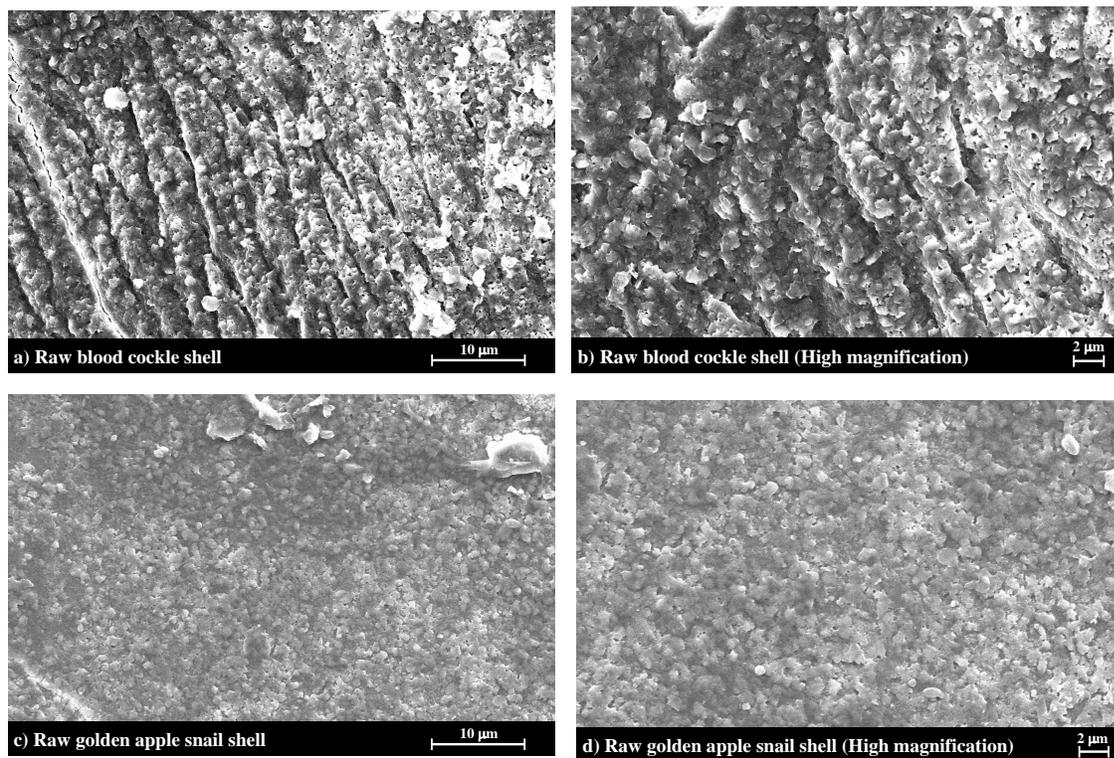
Fig. 5 SEM micrographs of surface morphology of (a) raw blood cockle shell, (b) high magnification of raw blood cockle shell, (c) raw golden apple snail shell, and (d) high magnification of raw golden apple snail shell.

Elemental composition in shells during calcination

The elemental composition of raw and calcined BC and GAS shell powders at all calcination temperatures for 1 h was determined using X-ray fluorescence. The results presented in Table 1 show that raw BC and GAS shells were comprised of 93% and 93% CaO by weight, respectively. These findings show that a high amount of calcium was present in both shells. Other minor elements, viz., Na, Sr, Cl, Si, Mg, S, Fe, Al, K, Mn, P, and Ba, were also present and their levels decreased with increasing calcination temperature. Awang-Hazmi[33] and Bharatham[34] studied the mineral and physiochemical properties of raw cockle and molluscan shells and their potential for use as a biomaterial for bone repair. They found that cockle shells contain more than 90% calcium. This finding is similar to reported literature values. Other elements present were Na, Mg, P, K, Fe, Cu, Ni, B, Zn, and Si. The proportion of CaO in BC and GAS shells calcined at 900 °C was 97% and 98%, respectively. This was higher than that of those shells calcined at 600 °C, 95%, and 96%, respectively. The calcium content of

GAS shells was higher than that of BC shells. This result is mainly due to a higher content of Na_2O in BC shells. The influence of environmental factors (seawater and freshwater) affects the composition of shells in surficial sediment[35]. The large amount of CaO is associated with the presence of calcium compounds, which was confirmed by the XRD results. The XRF and XRD analysis indicated that highly pure $CaCO_3$ and CaO can be produced from BC and GAS shells.

Grindability of $CaCO_3$ and CaO

$CaCO_3$ (calcite) was obtained after calcination of shells at 600 °C for 1 h, while CaO was obtained after calcination at 900 °C for same time. The shells calcined at 600 and 900 °C for 1 h were used to test material grindability. 100 g of each type of calcined shell was manually ground for 10 min in a porcelain mortar using a pestle. The particle size distribution of shell powders was characterized using a particle size analyser (HORIBA, LA 950). Fig. 8 presents the particle size distributions of these shells. The BC shells showed finer particles than the GAS shells. For shells calcined at 600 °C, the
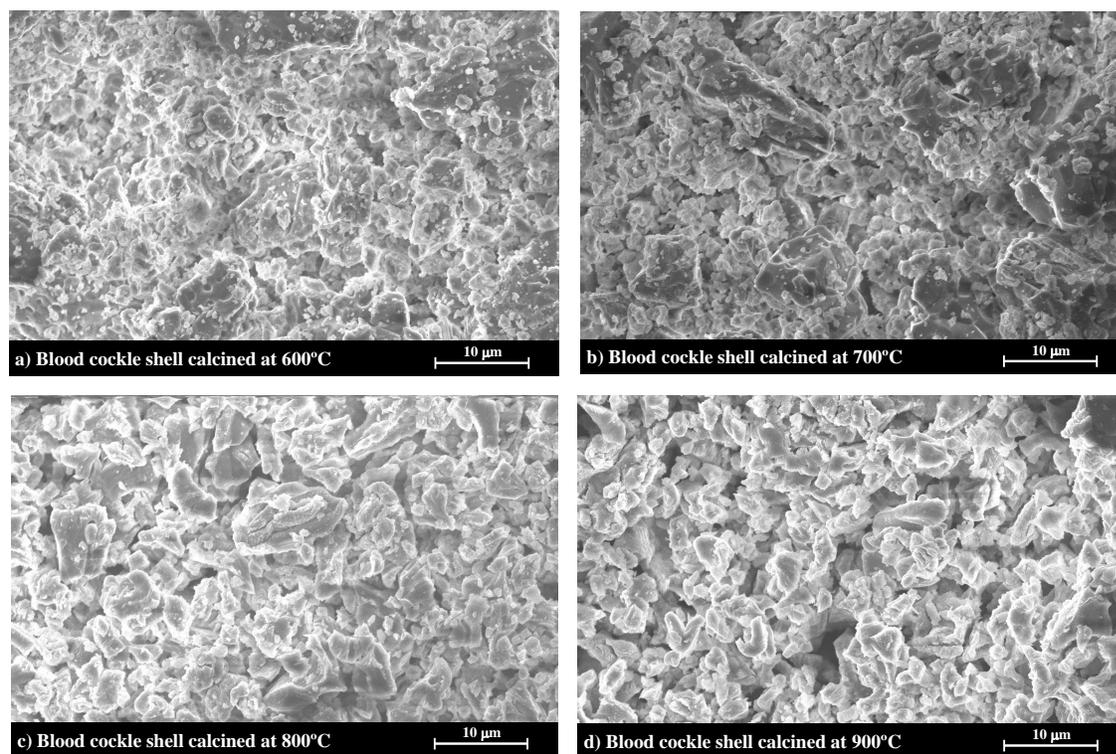
Fig. 6 SEM micrographs of surface morphology of blood cockle shell after calcination at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.

Table 1 Elemental composition of raw and calcined blood cockle and golden apple snail shells calcined for 1 h.

Element	Blood cockle shell (%w)					Golden apple snail shell (%w)				
	Raw	600 °C	700 °C	800 °C	900 °C	Raw	600 °C	700 °C	800 °C	900 °C
CaO	93.23	95.43	95.45	95.98	97.19	93.26	96.22	96.81	96.90	98.29
Na_2O	3.77	2.67	2.91	2.20	1.64	1.75	1.40	1.46	1.29	0.77
SrO	0.52	0.04	0.41	0.42	0.39	0.28	0.19	0.27	0.25	0.25
Cl	0.49	0.43	0.35	0.21	0.20	0.37	0.60	0.38	0.27	0.19
SiO_2	0.35	0.40	0.28	0.17	0.14	2.33	0.53	0.23	0.18	0.10
MgO	0.21	0.22	0.16	0.13	0.13	0.16	0.24	0.18	0.12	0.06
SO_3	0.13	0.12	0.11	0.08	0.08	0.22	0.09	0.07	0.06	0.04
Fe_2O_3	0.13	0.14	0.09	0.06	0.06	0.12	0.10	0.06	0.05	–
Al_2O_3	0.12	0.30	0.10	0.05	0.06	1.10	0.20	0.20	0.05	0.07
K_2O	0.79	0.05	0.06	0.59	0.08	0.05	0.06	0.03	0.52	–
MnO	0.05	0.04	0.05	–	–	0.07	0.08	0.08	0.08	0.08
P_2O_5	0.03	0.03	0.02	–	0.02	0.04	–	0.03	0.03	–
BaO	0.16	0.12	–	0.11	–	0.23	0.29	0.18	0.20	0.14

average particle sizes of BC and GAS shells were 7 and 10 µm, respectively. These values were 22 and 30 µm, respectively, for shells calcined at 900 °C. The particle size of shells calcined at 900 °C was greater than that of 600 °C due to the increased hardness of CaO obtained from a higher calcination temperature. This result indicates that the calcium compounds obtained from BC shells were easier to grind than those of GAS shells. The GAS shells were slightly more difficult to grind as a result of continue heating after the phase change was completed due to the early transformation of the calcium phase and the surface density of the calcined shells.

Scanning electron micrographs of $CaCO_3$ (cal-
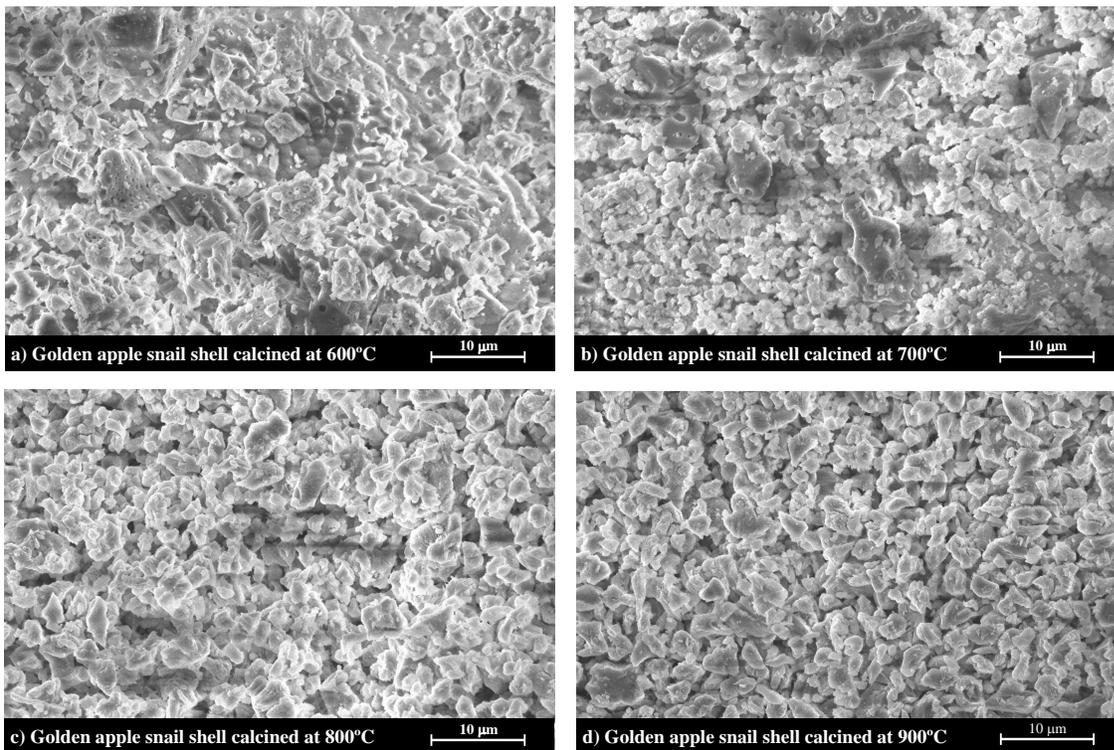
Fig. 7 SEM micrographs of surface morphology of golden apple snail shell after calcination at (a) 600 °C, (b) 700 °C, (c) 800 °C, and (d) 900 °C.
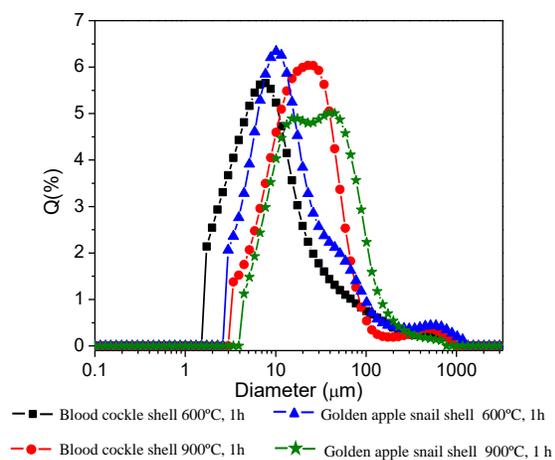
Fig. 8 Particle size distribution of blood cockle and golden apple snail shells after calcination at 600 °C and 900 °C.

cite) and CaO from shells are shown in Fig. 9. The SEM micrographs of $CaCO_3$ (calcite) (Fig. 9a,b) show highly crystallized particles with dense surfaces and irregular morphology. The morphology of CaO was different than $CaCO_3$. For CaO, small

round particles were agglomerated at the surfaces, as shown in Fig. 9c,d.

Trace (heavy metal) element in blood cockle and golden apple snail shells

Many products, especially pharmaceutical materials and those for surgical implants[36, 37] (e.g., hydroxyapatite and beta tricalcium phosphate) require materials that are relatively free of heavy metal elements. Further investigation of the amount of As, Cd, Hg, and Pb heavy metal elements was thus required. The presence of elements was quantitatively determined using inductively coupled plasma/mass spectroscopy on shell powders. The results, (Table 2), indicate that the amounts of these elements in both raw and calcined shells (600 and 900 °C) are very low. Neither BC nor GAS shells contained As, Cd, Hg, or Pb concentrations exceeding the levels established by ASTM F1185-03 and ASTM F1108-04a required for ceramic hydroxyapatite and beta tricalcium phosphate for surgical implants derived from natural sources. These results are in agreement with a study on cockle and three other shells for used as a material for bone implants[34]. The levels
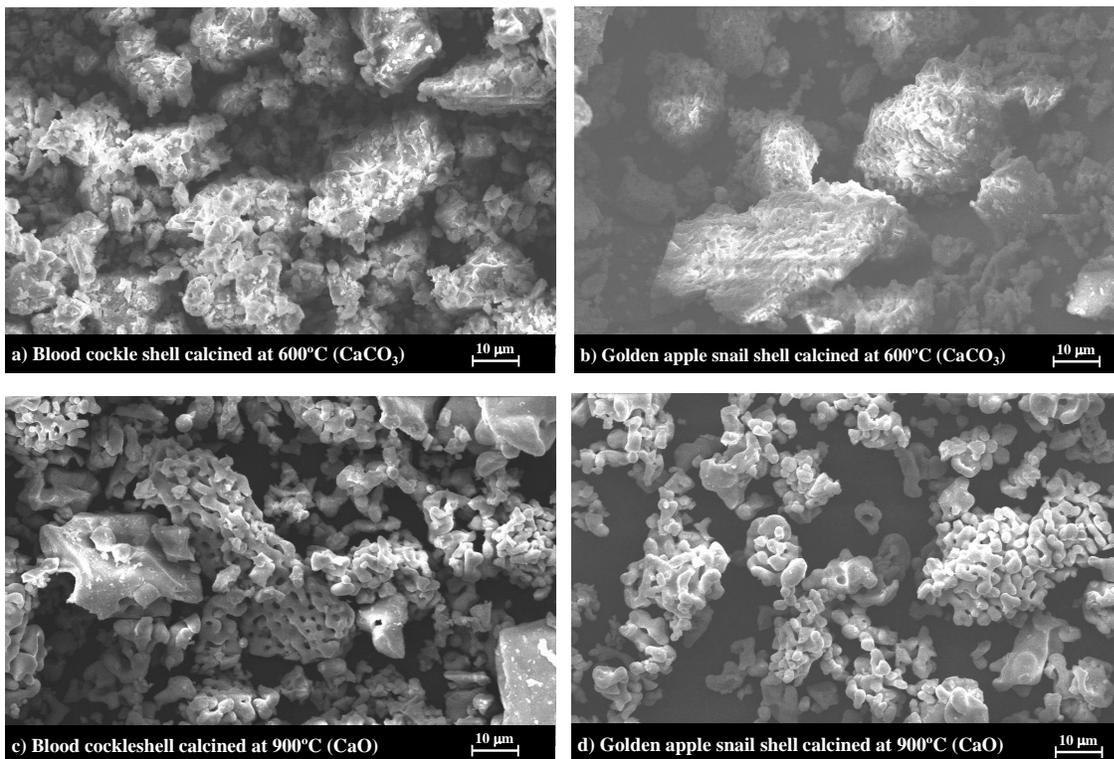
Fig. 9 SEM micrographs of $CaCO_3$ (calcite) powders from (a) blood cockle shell, (b) golden apple snail shell, and CaO powders from (c) blood cockle shell, and (d) golden apple snail shell.

Table 2 Concentrations of heavy metal element in raw and calcined blood cockle and golden apple snail shells at 600 and 900 °C for 1 h.

Element	Blood cockle shell (ppm)			Golden apple snail shell (ppm)			ASTM standard[†]
	Raw	600 °C	900 °C	Raw	600 °C	900 °C	(ppm)
Arsenic (As)	0.093	0.881	0.533	0.049	0.137	0.145	5
Cadmium (Cd)	ND[†]	0.032	0.051	ND	ND	ND	3
Lead (Pb)	0.219	0.633	0.399	0.065	0.056	0.051	30
Mercury (Hg)	ND	ND	ND	ND	ND	ND	5

[†] ASTM F1185-03 and ASTM F1108-04a; ND = Not Detected.

of heavy metal elements in BC shells were higher than those in GAS shells. This may result from the influence of environmental factors. Seawater can be highly polluted as a result of domestic and industrial wastewater discharge, sea traffic, accidents and wastewater from port services.

CONCLUSIONS

The influences of calcination temperature and holding time on the transformation of the crystalline phases in seawater blood cockle and fresh water golden apple snail shells were investigated. The elemental composition, heavy metal element content and physical characterization of both shells were determined. The main conclusions are as follows.

(1) Thermal gravimetric and XRD analyses showed three distinct stages of crystalline phase transformation in both shells. In Stage I, weight of shells slightly decreased during heating from ambient temperature to 600 °C. An amorphous aragonite phase of $CaCO_3$ was transformed into a crystalline calcite phase of $CaCO_3$. In Stage II, the weight of shells rapidly decreased in the temperature range of 600–800 °C. Here, the calcite phase of $CaCO_3$ was transformed into CaO. In Stage III, weight of shells was constant at temperatures higher than 800 °C. At

this point, $CaCO_3$ in shells were completely transformed into CaO. Both calcination temperature and holding time were important for the phase transformation of $CaCO_3$ in each of these shell types. The phase transformation in golden apple snail shells was faster than that of blood cockle shells due to the thickness of their shells.

(2) The elemental composition of blood cockle and golden apple snail shells can be altered by calcination. Fine particle and highly crystalline $CaCO_3$ (calcite) and CaO with some minor elements, Na, Sr, Cl, Si, Mg, S, Fe, Al, K, Mn, P, and Ba, can be produced from blood cockle and golden apple snail shells. The calcium content in the form of $CaCO_3$ and CaO from fresh water golden apple snail shells was higher than that of seawater blood cockle shells. The influence of environmental factors (seawater and freshwater) may have affected the chemical composition of the shell products.

(3) The average particle size of calcium compounds ($CaCO_3$ and CaO) obtained from blood cockle shells was finer than from golden apple snail shells by about 3–8 μm. This resulted from continued heating after the phase transformation of calcium in golden apple snail shells and the surface morphology of these shells.

(4) The content of heavy metal elements (As, Cd, Hg, and Pb) found in raw and calcined blood cockle and golden apple snail shells was much less than the requirements of ASTM standard specifications for producing ceramic hydroxyapatite and beta tricalcium phosphate for surgical implants.

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