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Transformation of Calcium Carbonate Polymorph from Various Type of Shells by Carbonation Methods

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Abstract

*The utilization of shells can reduce the accumulation of shell wastes and increase the value of shells to achieve ecological and economic incentives. This study examines the transformation of calcium carbonate polymorph from several types of shells to understand the causes of their characteristics in order to suitable for their use. The types of shells used in this experiment are selected based on consumables and their habitats such as snail shells, crab shells, eggshells, batik mussels' shells, and golden conch shells. The prepared shells calcinate at 900 °C, the reaction with hydrochloric acid, and carbonation by flowing CO2 into a stirred reactor to produce precipitated CaCO3. The characteristics of polymorph CaCO3 in the sintering temperature of 30, 50, and 70 ℃ were identified by XRD, FTIR, and SEM morphological. The result is that the polymorphs formed from each shell are different in shape, size, and crystallinity. At the temperature of 70 ℃, the rhombohedral calcite was obtained from snail shells, the cubic calcite was obtained from batik mussel shells, while rhombohedral calcite multilayers obtained (100%) from golden conch shells. The aragonite was obtained from batik mussel shells at 30 and 70 ℃. The pure vaterite (100%) was obtained from snail shells and crab shells at 50 ℃. The characteristic of polymorph formed might be useful as information for more suitable applications, especially as nano-biomaterials, optical, or fille*r.

Keywords: *aragonite; biomaterials; calcium carbonate; calcite; carbonation; vaterite*

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INTRODUCTION

In recent years the process of natural bio-mineralization has stimulated significant interest because of its potential to be emulated and applied to form industrial products with certain particle shapes (Rodriguez-Blanco et al., 2011; Tsuboi & Koga, 2018,). The need for nano-micro calcium carbonate (Jin et al., 2020) as a biomaterial is increasing lately, make it one interesting topic for the research. Natural biomineral has a complex morphology because organisms use inorganic ions and macromolecules to regulate crystallization from amorphous precursors. The mechanisms by which modifiers enable these shape-preserving transformations are poorly understood (Liu et al., 2020). Kitamura (2002), argues that complicated precipitation behavior and morphological changes may be related to precursor formation. The selection of biomineral polymorphs based on biomacromolecular morphology is very important in the bionic and biometric fields. (Sarkar and Mahapatra, 2010). It was important to understand the causes of $CaCO_3$ characteristics in order to be useful in utilization (Abeywardena et al., 2020).

Calcium carbonate ($CaCO_3$) is generally in the form of amorphous calcium carbonate or one of three polymorphs such as calcite, vaterite, and aragonite (Chang et al., 2017). The complex crystallization behavior of these polymorphs is a challenging task to systematically control the physical properties of $CaCO_3$ particles for the desired application (Çağatay and Ercan, 2018). Each polymorph has different properties. Calcite is almost formed in every synthesis treatment while vaterite and aragonite require certain treatments (Onimisi et al., 2016). Calcite is a good and more suitable functional mineral filler for plastics and papers (Ramakrishna et al., 2017). The synthesis of vaterite has been used as a carrier of active compounds for medical treatment purposes, biodegradable polymer capsules (Choukrani et al., 2020), and supported the field of microrheology and microfluidics (Han et al., 2006). Aragonite is a potential biomaterial for the development of anticancer drugs (Abd Ghafar et al., 2017), sophisticated drug delivery systems, scaffolding for bone repair and tissue engineering (Muhammad Mailafiya et al., 2019).

Research on $CaCO_3$ has been widely reported to produced calcite (Ding et al., 2018), aragonite (Ramakrishna et al., 2017), vaterite (Konopacka-Łyskawa et al., 2020), and amorphous precipitated calcium carbonate (Dominique et al., 2016) using various methods. Precipitated calcium carbonate usually produced through several processes such as calcium chloride, lime-soda, and carbonation process (Chang et al., 2017). Carbonation has the advantage associated with the highest conversion, high purity, and eco-friendly process (Jimoh et al., 2017; Thriveni et al., 2016). The absorption of CO_2 becomes a controller during $CaCO_3$ precipitation stages (Feng et al., 2007).The studies on the effect of CO_2 flow rates reported on different ranges. The gas flow rate is of course related to the process of displacement or dissolution; therefore it was necessary to determine the flow rate considering sufficient contact time (Onimisi et al., 2016; Jimoh et al., 2017).

$CaCO_3$ was difficult in controlling its polymorphic character (Chong et al., 2014). Several factors affect the precipitation process and polymorph characteristics such as pH (Thriveni et al., 2016; Tobler et al., 2016), supersaturation (Ding et al., 2018), temperature (Chong et al., 2014), calcium source (Bang et al., 2015), precipitation method (Thriveni et al., 2016), mixing intensity (Ševčík, et al., 2015) and co-solvent type (Konopacka-Łyskawa et al., 2020). Organic additives affected the rate of precipitation and the morphology of the precipitated particles (Polat, 2020; Liu et al., 2012). On the other hand, the pH of the solution is one of the important factors that determine the $CaCO_3$ polymorph (Çağatay and Ercan, 2018; Abeywardena et al., 2020).

The effect of temperature was generally studied in almost the same range, from 20 to 80 ℃ (Song et al., 2020). Calcite is a dominant polymorph at low temperatures and decreases with increasing temperature (Trushina et al., 2014). It was reported that the change in polymorph from calcite to vaterite and aragonite formation occurred at 40 ℃. The different report stated by Song et al., (2020) that the vaterite phase changes to calcite with an increase in temperature from 20 to 80 ° C. The vaterite formation observed at 60 ℃ (Konopacka-Łyskawa et al., 2020). Polymorph aragonite is the dominant species at high temperatures (Ramakrishna et al., 2017) due to higher growth rates of aragonite as compared to the other polymorphs (Chong et al., 2014). Even though the calcium source was the same and also used the carbonation method, the product of polymorph was different. Other operating parameters also influence each other.

Usually, the calcium source used for the polymorph $CaCO_3$ synthesis was $CaOH_2$ or limestone. The types of shells have been studied for the synthesis of calcium carbonate, such as oyster shells (Ramakrishna et al., 2017), eggshells (Yoo et al., 2009), cockle shells (Abd Ghafar et al., 2017), and white mussel shells (Muljani et al., 2019), but those studied use different experimental methods and parameters. Thus, it is difficult to compare the results of available studies on the effects of calcium sources on the polymorph formation process. The structural characterization of $CaCO_3$ polymorphs formed by different calcium sources are of great importance for several research fields.

As previously described, studies have been carried out to obtained polymorphs of $CaCO_3$ by different mechanisms and different morphologies through various methods. Various types of additives were used in order to obtain specific types of polymorphs either calcite, vaterite, or aragonite. The CO_2 bubbling method is a widely used and highly efficient method for producing $CaCO_3$ micro-nanoparticles. However, in the CO_2 bubbling method, $CaCO_3$ particles were usually inhomogeneous and agglomerated, even in the presence of additives (Zhao et al., 2016). Stephen and Cree (2020) reported that in recent years, the use of eggshells and seashells waste resources has begun to develop for the production of new thermoplastic and thermoset polymer materials. There has been no study on the mechanism of polymorph transformation of several organic calcium sources through the same method and operating conditions. In fact, it was very possible to obtain the desired crystal polymorph by choosing the right calcium source without going through specific treatment which might increase the cost. This research aims to study the $CaCO_3$ polymorph transformation from various natural calcium sources. The types of calcium sources used in this study were snail shells (*Achatina fulica*), batik mussel shells (*Paphia undulata*), eggshells, golden conch shells (*Pomacea canaliculata*) and small crab shells (*Portunus pelagicus*). The precipitation of $CaCO_3$ in this experiment was carried out by passing CO_2 into a mixture of calcium chloride and ammonium hydroxide solution at temperatures of 30, 50, and 70 °C. The calcium carbonate polymorph was characterized by XRD, FTIR, and SEM image.

MATERIALS AND METHODS

Preparation of materials

Ammonium hydroxide and hydrochloric acid purchase at Indo Kimia store, Tidar 278, Surabaya. Pure CO_2 gas from distributor of chemicals Dunia Kimia. Snail shells, batik mussel shells, eggshells, golden conch shells, and crab shells are obtained from food processing and bakeries waste in Surabaya, East Java, Indonesia. The shells were washed, cleaned, and dried naturally with the sun's heat for three days. The dried shell was crushed, milling, and sieved through 80-100 mesh sieves, yielding a mean particle size of 160 µm. Shell powder was analyzed by an X-ray fluorescence spectrometer (Shimadzu XRF-1800) to find out the calcium content as shown in Table 1.

Table 1. Component of calcium in the shells

Type of Shells	Ca (%)	CaO (%)
Eggshell	99.27	99.14
Snail shells	99.02	99.18
Golden conchs	98.67	98.65
Batik mussels	97.95	98.30
Crab shells	92.13	91.20

Carbonation

The five types of shells powder were calcined in the furnace at 900 °C for 3 h to produced Calcium Oxide (CaO). The CaO of each shell was dissolved with 2M hydrochloric acid with a ratio of 17 g CaO to 300 ml of acid and stirred in a reactor for 30 minutes. After acidification, the solution was filtered by whatman filter paper. The solution was adjusted to pH 10 by adding 6.4M ammonium hydroxide solution. Gas is fed into the stirred reactor through a gas distributor at the bottom of tank. The reactor operates in a semi-batch manner, where during the carbonation process pure CO_2 gas was supplied to the reactor with a flow rate of 1 $Lmin^{-1}$ for 20 min at various temperatures of 30, 50 and 70 °C. Stirring was set at 300 rpm so that the gas was mixed evenly in liquid and the settling process was uninterrupted. CO_2 reacts with calcium ions which are presented in the liquid phase following the reaction (Jimoh et al., 2017):

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \qquad (1)$$

$$CaCl_2 + 2NH_4OH + CO_2 + H_2O \rightarrow CaCO_{3\downarrow} + 2\,NH_4Cl + 2H_2O \qquad (2)$$

The white precipitate was then filtered and dried in an oven (Memmert UN110) at 100 °C to remove any residual water from the precipitation process.

Characterization

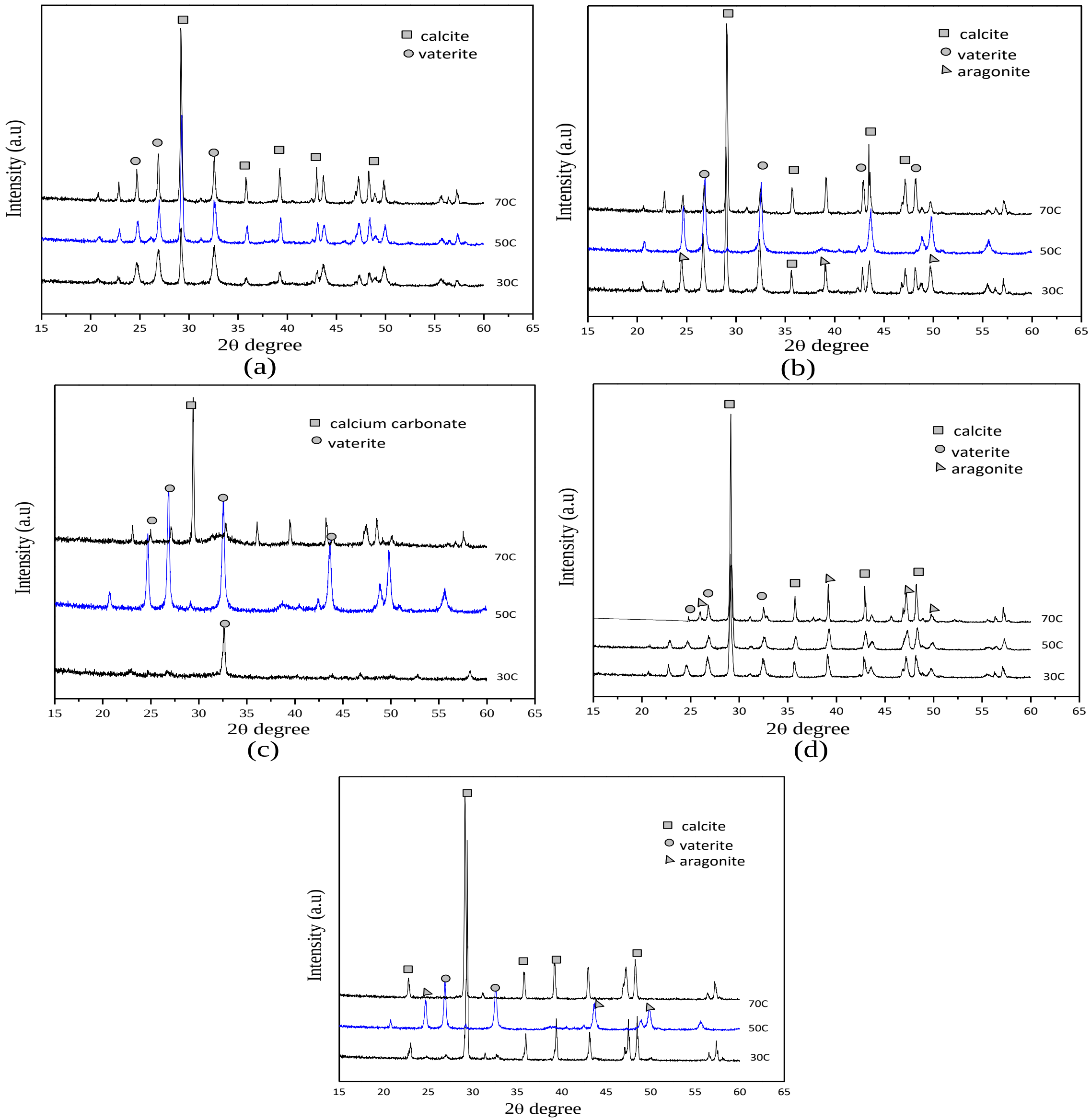
The Samples of precipitated $CaCO_3$ were characterized by X-ray diffraction, XPert-PRO and XPert-MPD diffractometer system, 30 mA, 40 kV with PANalytical measurement. Scan parameter for measurement was 10-60°. XRD pattern analysis to determine the polymorph phase using the Rietveld method with the X'PERT HIGHSCORE PLUS application. Matching XRD patterns from samples with XRD patterns from the JCPDS / ICDD database includes crystal system data, space groups, lattice parameters, atomic positions and the peaks of diffraction patterns. SEM images were obtained from the SU3500 which operates at low vacuum, 7nm SE Image resolution at 3 kV, 10 nm BSE image resolution at 5kV. IR spectra were measured with a Shimadzu 8400S FTIR, Beam Splitter: KBr plate and DTGS with IR solution sofware, wave numbers range of 400-4000 cm^{-1} at room temperature.

RESULTS AND DISCUSSION

Effect of Temperature on PCC Polymorph

Figure 1 showed the XRD pattern of precipitated $CaCO_3$ prepared from a) eggshells and b) snail shells c) golden conch shells d) batik mussel shells and e) crab shells at carbonation temperatures of 30, 50 and 70 °C. All samples showed peaks characteristic of calcium carbonate in comparison with their respective standard JCPDS. The peaks that assign to the calcite refers to JCPDS 010721937, vaterite refers to JCPDS 000330268 and aragonite refers to JCPDS 00030425. Observations on XRD result regarding the polymorph phase were confirmed by IR spectra and SEM images for the same samples of shells.

Table 2 corresponds to Figure 1 presented the composition of polymorph phase at a temperature of 30, 50 and 70 °C for each shell. XRD pattern (Figure 1a) confirmed the presence of vaterite at 2θ are 24.92, 26.99, and 32.78° and calcite at 2θ values of 29.4, 36.0, 39.4, 43.1, 47.4, and 48.5° in PCC from eggshells at 30 C. Calcite, vaterite, and aragonite peaks coexisted in PCC from snail shells (Figure 1b),



(a) (b) (c) (d) (e)

Figure 1. XRD pattern of $CaCO_3$ polymorph prepared from a) eggshells b) snail shells c) crab shells d) batik mussel shells, and e) golden conch shells at 30,50 and 70 °C

batik mussel shells (Figure 1d), and golden conch shells (Figure 1e). The XRD pattern of PCC from crab shells (Figure 1c) showed differences from other shells. At 30 °C the initial deposit appeared only one diffraction peak that differed in the XRD pattern, the rest only revealed a wide ridge derived from a combined scattering that had poorly ordered sediments.

At 50 °C, the polymorphs $CaCO_3$ from the five types of shells are almost dominated by vaterite, especially in the $CaCO_3$ from snail shells (Figure1b) and crab shells (Figure1c) which reached 100% vaterite at 300 rpm. Repetition of the samples test prepared from the two shell types showed consistency of 100% vaterite at 50 °C. Ševčík et al., (2015) reported that without additive the pure vaterite (≥ 99%) was obtained at 60 °C and 600 rpm.

At a temperature of 70 °C based on XRD pattern (Figure 1) corresponding with Table 2, the calcite polymorphs were dominant in $CaCO_3$ from eggshells (65%), snail shells (60.6%), golden conch shells (100%), and batik mussel shells (49%). Calcium carbonate was dominant in precipitated $CaCO_3$ from crab shells (75%) while aragonite was quite large in PCC from batik mussel shells (49%). As previously described, calcite is a dominant polymorph at low temperatures (around 20-30 °C) and decreases with increasing temperature to form aragonite (Chong et al., 2014; Trushina et al., 2014)).

The calcite phase transforms into aragonite phase at around 60 °C (Jimoh et al., 2017). The results of this study proved that the transformation process of the polymorph phase was not only influenced by temperature but also significantly by the calcium source.

Table 2. Observed composition of polymorph phase on precipitated $CaCO_3$ at 30,50 and 70 °C based on XRD analysis

T (°C)	$CaCO_3$ Polymorphs	Egg shells (%)	Snail shells (%)	Golden conch shells (%)	Batik shells (%)	Crab Shells (%)
30	Vaterite	55	64.4	3	23	64
	Calcite	45	14.9	55	30	7
	Aragonite		20.8	42	47	
	Calcium Carbonate					29
50	Vaterite	36	100	65.7	31	100
	Calcite	64		1	69	
	Aragonite			33.3		
70	Vaterite	35	37.4		11	25
	Calcite	65	60.6	100	49	
	Aragonite		2		40	
	Calcium carbonate					75

It was observed that aragonite appeared at low temperature (30 °C) and remained to exist at 70 °C when the calcium source was from batik mussel shells. On the other hand, there was no change from calcite to aragonite at an increase in temperature from 30 to 70 °C when the calcium source was from the eggshell.

Figure 2 corresponds to Table 3 showed the IR spectra of calcium carbonate prepared from five type of the shell at 70 °C. Carbonate absorption bands are usually divided into four regions of vibration (υ) such as: symmetrical sequence of carbonate ions around 1080 cm^1 (υ_1), flexural absorption outside the plane of about 870 cm(υ_2), an asymmetrical stretch of about 1400 cm^1(υ_3), and bending on the plane around 700 cm^1(υ_4) (Frost et al., 2002).

The observations on the IR spectra and SEM image for $CaCO_3$ prepared from each shell at 70 °C showed consistency with the XRD pattern. IR spectra of $CaCO_3$ prepared from eggshells at 70 °C (Table 3) showed the sharp absorption bands at 1083 (υ1), 876 (υ2) and 745 cm^{-1} identified of vaterite, while at 712 cm^{-1}(υ4) identified the polymorph phase of calcite. The asymmetrical stretches are splits in 1407 cm^{-1} and 1466 cm^{-1} (υ3) usually correspond with vaterite phase or monohydrate calcite. The same vibration pattern of the IR spectra was observed in the $CaCO_3$ polymorphs from the snail shells, batik mussel shells, and golden conch shells. The difference is the appearance of absorption bands at 710 and 1086 cm^{-1} corresponding to the aragonite in polymorph $CaCO_3$ from batik mussel shells.

Amorphous of this final phase (at 70 °C) were characterized by a broadband between 2800 and 3600 cm^{-1}(O–H stretching) and a shaper band at 1634 cm-1 as O–H bending. The observation of the difference in -O-H stretching is from the amorphous hydrated precursor to the non-hydrated crystalline calcium carbonate phases. The crystal calcium carbonate phases such as calcite from golden conch shells have absorption bands at 712 cm^{-1} (υ4), 874 cm^{-1} (υ2), 1083 cm^{-1} (υ1) and 1418 cm^{-1} (υ3).

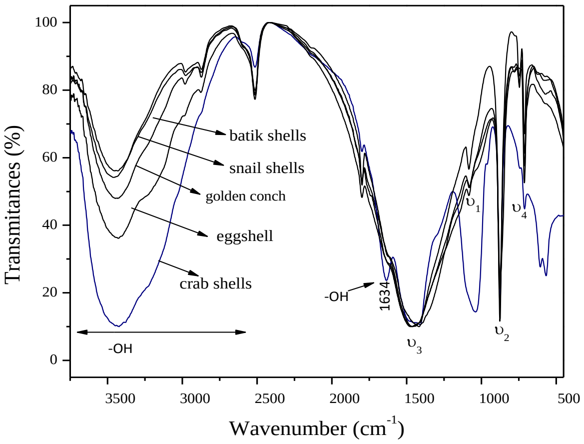


Figure 2. IR spectra of $CaCO_3$ prepared from a) eggshells b) snail shells c) crab shells d) batik mussel shells, and e) golden conch shells at 70 °C

Table 3. Observed vibration frequencies of the carbonate ion at 70°C

Sources of $CaCO_3$	υ_1 (cm^{-1})	υ_2 (cm^{-1})	υ_3 (cm^{-1})	υ_4 (cm^{-1})
Eggshells	1083	876	1407 1466	712
Snail shells	1081	874	1464 -	710
Crab shells	-	874	1409 1474	-
Batik mussel shells	1083	874	1451 1474	710
Golden conch shells	1079	874	1418 -	712

Amorphous calcium carbonate has no vibration band at 712 cm^{-1} (Hodson et al., 2016) and the asymmetric stretch peaks split into two parts at around 1420 and 1470 cm^{-1} (Chang et al.) This was observed in the PCC polymorph from the crab's shell (Figure 2) where the bend in the plane (υ4) at 712 cm^{-1} appeared to disappear (fragile vibration) and the peak of the asymmetrical stretch was divided into two parts in 1409 and 1474 cm^{-1} which identified the amorphous phase. This is consistent with XRD pattern (Figure 1c).

SEM Image characteristics

The SEM images of precipitated $CaCO_3$ from eggshells at 70°C (Figure5a) confirmed the existence of two polymorph phases which are spherical vaterite and calcite. Rhombohedral calcite diameter varies from 4 to 6.6 µm while the diameter of the spherical vaterite is greater, from 5.5 to 9.94 µm. In addition to the rhombohedral and spherical forms, oval particle shapes were also observed. This morphology is typical of vaterite as the metastable polymorph of calcium carbonate. It was reported that calcite has a trigonal crystal structure which was usually rhombohedral (Chang et al., 2017), and also exists as hexagonal, cubic, and prismatic prisms (Ding et al., 2018). Whereas vaterite has a round or hexagonal polycrystalline shape and has a metastable phase at

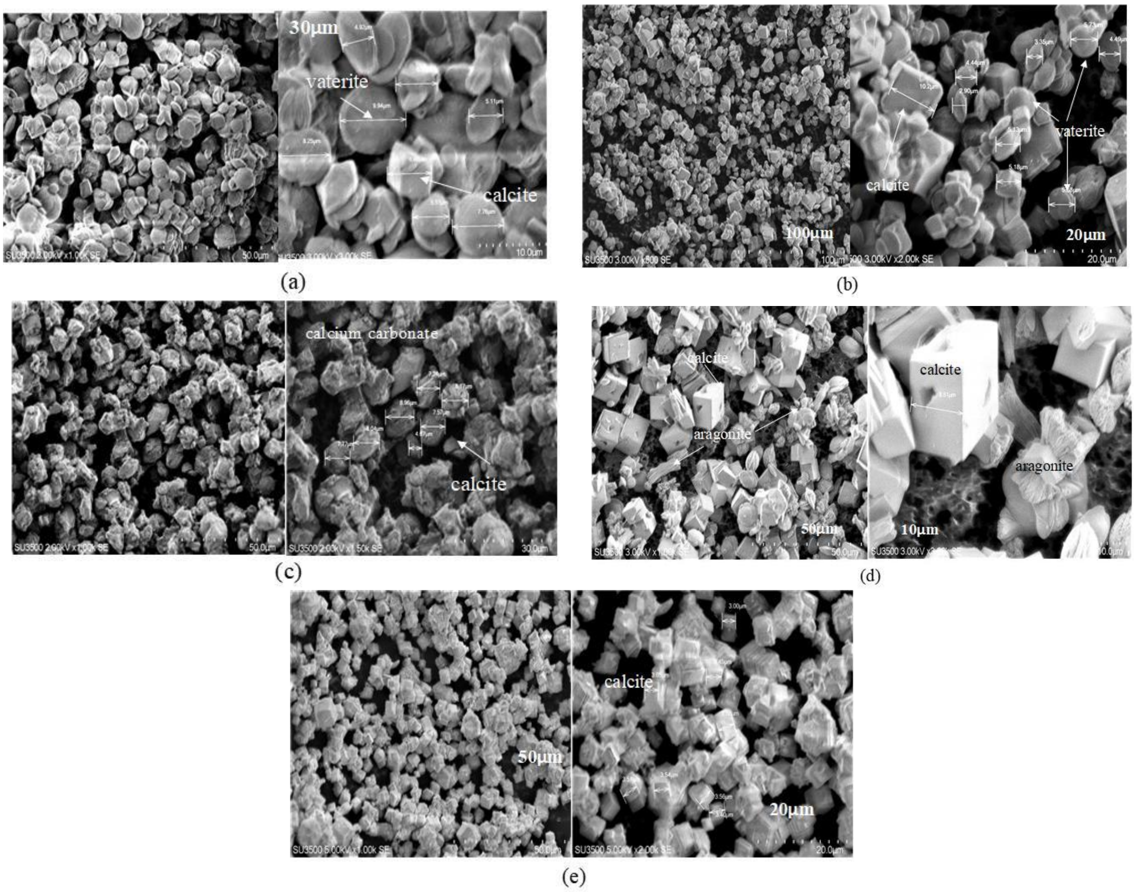


Figure 3. SEM Image of CaCO$_3$ polymorph prepared from a) eggshells b) snail shells c) crab shells d) batik mussel shells, and e) golden conch shells at 70 °C

room temperature (Jimoh et al., 2017). Figure 5b showed the SEM image of CaCO$_3$ prepared from snails shell at 70°C. The particle size of spherical vaterite varies from 3 μm to 5.5 μm while rhombohedral vaterite varies from 4.4 μm to 10.2 μm. The diameter of the calcite polymorph appears larger twice than the diameter of the vaterite. Without additives, the diameter of calcium carbonate formed is around 5-12 μm (Cheng et al., 2014). Observations in this condition (70 °C) the transformation process is still ongoing where some vaterites (metastable) are still oval in shape.

While the SEM image of CaCO3 from crab shells showed the presence of polymorph vaterite but most of the particles are still in an irregular shape (Figure 5c). This condition occurs may cause most likely at 70 °C was still in the process of transformation from polymorph vaterite to polymorph calcite or aragonite. Particle diameter in the range of 4 - 8 μm. The CaCO3 polymorphs prepared from batik mussel shells at 70°C consist of calcite and aragonite (Figure 1d). The SEM image (Figure 5d) showed the characteristic of calcite in a cubic shape with thickness reaching 8 μm and width 11 μm. While the aragonite features resemble needle-shaped. The aragonite has some characteristics, such as: the form is unstable at room temperatures and pressures, it has orthorhombic structure and needle-like shape (Ramakrishna et al., 2017). The SEM image of CaCO3 from golden conch shells (Figure 5e) showed the agreement that only calcite polymorphs exist. This is consistent with XRD pattern. Particle diameter approaches uniformly in the range of 3 - 3.56 μm. The layered rhombohedral shapes are characteristic of calcite polymorphs.

CONCLUSIONS

This study provides new insights into the mechanism for the calcium carbonate polymorphic transformation processes from various shells.

The observations showed the consistency of the results from XRD pattern, IR spectra, and SEM images on all of the samples of CaCO3 polymorph.

Due to the predominantly calcite polymorph produced at 70 °C from several shells, they have different shapes, sizes, and crystal types. The rhombohedral calcite was obtained from snail shells, the cubic calcite was obtained from batik mussel shells, while calcite multilayers obtained from golden conch shells. While calcite from eggshells was still largely oval, it is possible that a temperature increase of more than 70 °C can ensure a clearer polymorph shape. The pure vaterite (100%) was obtained from snail shells and crab shells at 50 °C. The difference in crystallinity between calcium carbonate from crab shells and snail shells even though the polymorph transformation process and polymorph products are almost the same from a temperature of 30 to 70 °C. The particles of CaCO3 obtained from eggshells and snail shells have the opposite size between calcite and vaterite polymorph.

Based on SEM images, IR spectra, and XRD patterns, the multilayer calcite polymorphs from the golden snail shells were obtained up to 100% at 70°C. This is interesting for further research because apart from its small diameter (3-3.5μm) the size is almost uniform. In addition, it is also a consideration to overcome the inhomogeneous and agglomerated conditions that often occur in calcite production in the industry using the carbonation method.

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