

## Effect of CO<sub>2</sub> Flow Rate and Carbonation Temperature in the Synthesis of Crystalline Precipitated Calcium Carbonate (PCC) from Limestone

Sri Wardhani\*, Fanny Prasetya, Mohammad Misbah Khunur,  
Danar Purwonugroho, and Yuniar Ponco Prananto

Department Chemistry, Faculty of Mathematics and Natural Sciences, University of Brawijaya,  
Jl. Veteran, Malang 65145, Indonesia

Received July 17, 2017; Accepted March 19, 2018

### ABSTRACT

The effect of CO<sub>2</sub> flow rate and carbonation temperature were studied in the synthesis of PCC from limestone using carbonation method. The synthesis was started by dissolving CaO that was obtained from calcination of limestone into HNO<sub>3</sub> 6M. The solution was then added with ammonia solution and then streamed with CO<sub>2</sub> until pH 8 with flow rates of 0.5; 1.0; 1.5; and 2.0 L/min. The optimum flow rate obtained from this stage was then applied in the carbonation process with temperatures of 50, 80, 100, 150, 200, and 250 °C. The results showed that low flow rate give reasonably high yield but the yields obtained in every flow rate used in this work has insignificant difference based on F-test. The optimum flow rate used for the synthesis of PCC in the next stage was 0.5 L/min with a yield of 62.95%. Different carbonation temperature influences the polymorphs and crystallinity of the synthesized PCC. The synthesized PCC was analyzed by FT-IT, powder-XRD, SEM-EDX, and PSA. FT-IR analysis showed stretching vibrations of C–O at 1419, 1479, and 1384 cm<sup>-1</sup> which correspond to calcite, vaterite, and aragonite respectively. Powder-XRD and SEM-EDX confirms that at the carbonation temperature of 50 °C, calcite and vaterite were formed, while at the carbonation temperature of 80 °C, mixture of calcite-vaterite-aragonite were obtained. Higher carbonation temperature changes the vaterite and aragonite polymorphs into calcite, and the best crystallinity was obtained at 250 °C. PSA analysis showed that the particle diameter of the synthesized PCC was about 3.58 to 38.14 μm.

**Keywords:** PCC; limestone; carbonation; CO<sub>2</sub> gas flow rate; heating treatment

### ABSTRAK

Efek laju alir dan suhu kalsinasi pada sintesis PCC dari batu kapur menggunakan metode karbonasi telah dipelajari. Sintesis PCC diawali dengan melarutkan CaO yang merupakan hasil kalsinasi batu kapur ke dalam HNO<sub>3</sub> 6 M. Penambahan larutan ammonia dan aliran gas CO<sub>2</sub> dengan variasi laju alir, 0,5; 1,0; 1,5; and 2,0 L/min, dilakukan hingga pH mencapai 8. Proses karbonasi dilakukan pada laju alir optimum dengan variasi temperature 50, 80, 100, 150, 200, and 250 °C. Hasil yang cukup tinggi didapat ketika menggunakan laju alir yang rendah, namun hasilnya tidak berbeda signifikan ketika dilakukan uji-F. Oleh karena itu, laju alir optimal yang digunakan selanjutnya ialah 0,5 L/min yang mempunyai hasil sebesar 6,95%. Polymorphs dan kristalinitas PCC yang dihasilkan dipengaruhi oleh temperatur karbonasi. Spektra FT-IR menunjukkan bahwa terdapat vibrasi ulur C-O dari kalsit, vaterite dan aragonit secara berturut-turut pada bilangan gelombang 1419, 1479, and 1384 cm<sup>-1</sup>. Hasil analisis XRD dan SEM-EDX menunjukkan bahwa kalsit dan vaterite terbentuk pada temperature 50 °C, sedangkan campuran kalsit-vaterite-aragonit terbentuk pada suhu 80 °C. Temperatur karbonasi yang lebih tinggi akan mengubah vaterite dan aragonite menjadi kalsit dengan kristalinitas terbaik terbentuk pada suhu 250 °C. Analisis PSA menunjukkan bahwa PCC tersintesis mempunyai ukuran diameter partikel berkisar 3,58–38,14 μm.

**Kata Kunci:** PCC; batu kapur; karbonasi; laju alir gas CO<sub>2</sub>; pemanasan

### INTRODUCTION

Limestone is kind of raw materials which widespread interest due to its various advantages. It can be easily discovered in some regions in Indonesia. This material is extensively used in cement industry, manufacture of calcium oxide, road asphalt, steelmaking, and for

construction purposes [1-2]. The improvement of limestone is required to enhance the potencies of this material.

Precipitated calcium carbonate (PCC) is a kind of limestone that had been proceeding through some purification step to afford the pure material. The PCC crystal comprises three of crystal polymorphs namely

\* Corresponding author.  
Email address : wardhani@ub.ac.id

calcite, vaterite, and aragonite which have different properties, characteristics, and structures. Nowadays, PCC has many potentials not only as calcium source for livestock and fertilizers but also in several industrial processes, such as painting, paper, glue, pharmacy, cosmetics, food and beverages, nutrition supplement, and water treatment [3-8]. There are many methods to synthesize PCC were reported, such as solvay or ammonia-soda process, caustic soda, and carbonation method through calcination, hydration, and precipitation [3,7,9]. Solid-liquid route or gas-solid-liquid carbonation route for PCC synthesis were also reported [9].

Carbonation method has many advantages as compared to other methods, such as rapid process, easy handling, simple way, and the CO<sub>2</sub> gas as a by-product from calcination process can be reused therefore this method is low-cost [10]. However, this method afforded low yield due to the low solubility of CaO in water. To overcome the low yield, the reaction needs to add nitric acid to increase the soluble Ca<sup>2+</sup> ion in the filtrate and gave higher yield after precipitation with CO<sub>2</sub> [11].

There are some factors that give impact in the PCC synthesis via carbonation method such as CO<sub>2</sub> gas flow rate and carbonation temperature [4]. Lailiyah et al. has conducted PCC synthesis from limestone by carbonation methods employed CO<sub>2</sub> gas flow rate of 2 to 7 SCFH (0.94 to 3.29 L/min) and carbonation reaction temperature of 30, 50, and 70 °C. The product was characterized by XRD which indicate that aragonite polymorph was obtained at low flow rate. Moreover, calcite and vaterite polymorph was afforded at high flow rate. The temperature effect was shown in the formation of vaterite and calcite at 30 °C, three polymorphs have formed at 50 °C, and aragonite was found at 70 °C [12].

This paper reports the effect of low flow rate of CO<sub>2</sub> gas (2.0 L/min and below) and higher temperature of carbonation process (50 °C and above) toward the crystallization of PCC via carbonation method. These factors are influential and the parameter range value used in this work is an extension from previous work [12], thus this work builds up previous knowledge particularly on PCC crystallization via carbonation method. In this work, CO<sub>2</sub> gas flow rate used were 0.5; 1; 1.5; and 2 L/min, whereas carbonation temperature used were 50, 80, 100, 150, 200, and 250 °C. The PCC properties were analyzed using FT-IR spectrophotometer, X-Ray Diffraction, SEM-EDX, and Poly Surface Analyzer (PSA).

## EXPERIMENTAL SECTION

### Materials

The materials used in this work were white limestone (from Limestone Mountain area in Sumberarum village, Kerek District, Tuban, East Java), nitric acid 65%

(Merck), ammonia 25% (Merck), and calcium carbonate (Merck). Distilled water was also used in this work.

### Instrumentation

Analytical instrumentations and lab-wares used in this work were Ohaus analytical balance, 150 mesh sieve, Barnstead Thermolyne furnace, Fisher Scientific oven, and MN universal pH indicator. The synthesized PCC was characterized by FT-IR Spectrophotometer (Shimadzu FTIR-8400S) for investigating functional group with a range of 4000–400 cm<sup>-1</sup>. Crystallinity degree of the product was analyzed by X-Ray Diffraction (XRD Philips Diffractometer X'pert PRO PAnalytical at room temperature). Morphology, crystal size, and elemental analysis were measured by Scanning Electron Microscopy-Energy Dispersive X-ray Analyser (SEM-EDX Hitachi TM3000) whereas crystal size distribution was measured with Poly Surface Analyzer (PSA CILAS 1090 Liquid).

### Procedure

#### Preparation of CaO

Limestone, used as the starting material, was grinded by mortar and sieved using 150 mesh sieve. The limestone powder was then calcined at 1000 °C for 30 min, in which the limestone turned into white powder of CaO. The powder was characterized by FT-IR spectrophotometer to confirm this.

#### The effect of CO<sub>2</sub> gas flow rate in the carbonation process

A 5.6 g of CaO was dissolved in 20 mL of HNO<sub>3</sub> 6 M then added with 200 mL of water. The mixture was stirred at 65 °C and 700 rpm for 30 min. After standing the mixture for 30 min, the mixture was filtered off using filter paper to separate the filtrate and the suspension. The filtrate was added with 25 mL of NH<sub>3</sub> 25% and then flowed by CO<sub>2</sub> gas with flow rate of 0.5, 1.0, 1.5, and 2.0 L/min for 1 h in a closed container at room temperature (30 °C). Next, the mixture was filtrate off again using filter paper. The solid that obtained on the filter paper was dried at 100–105 °C in an oven for 12 h and finally cooled down to room temperature resulting in a white dry solid product. The yield was measured and the product was characterized by FT-IR spectrophotometer.

#### The effect of carbonation temperature

Another 5.6 g of CaO was dissolved in 20 mL of HNO<sub>3</sub> 6 M then added with 200 mL of water. The mixture was stirred at 65 °C and 700 rpm for 30 min. After standing the mixture for 30 min, the mixture was filtered off using filter paper to separate the filtrate and the suspension. The filtrate was added with 25 mL of NH<sub>3</sub>

25% and then flowed by CO<sub>2</sub> gas for 1 h using optimum flow rate that obtained from the previous step. During this stage, the temperatures were varied at 50, 80, 100, 150, 200, and 250 °C to investigate the effect of heating toward the carbonation process. Next, the mixture was filtrate off using filter paper. The solid that obtained on the filter paper was dried at 100–105 °C in an oven for 12 h and finally cooled down to room temperature resulting in a white dry solid product. The yield was measured and the product was characterized by FT-IR spectrophotometer XRD, SEM-EDX, and PSA.

## RESULT AND DISCUSSION

### Preparation of CaO

Limestone that was used as the starting material was calcined at 1000 °C for 30 min. The limestone decomposed into white powder CaO and gives 30% yield. FT-IR spectra of the CaO is presented in Fig. 1.

The FT-IR spectra shows that the CaO vibration was detected around 500 cm<sup>-1</sup>. However, several bands around 1800, 1500, and 850 cm<sup>-1</sup> were also observed, which are assigned to different vibration mode of CO from CO<sub>3</sub><sup>2-</sup>. This might be because the carbonate from limestone remain in the sample or atmospheric CO<sub>2</sub> was adsorbed by the sample during preparation and analysis. A sharp peak around 3600 cm<sup>-1</sup> which correspond to stretching mode of O–H also suggests that the sample was not fully dry or may absorb atmospheric vapor during preparation and analysis. Thus, the limestone was not completely decomposed from CaCO<sub>3</sub> to CaO as expected and may not fully dry. The powder can still be used as it is since in some cases the PCC that obtained from technical grade CaO gives high quality PCC. For future work, complete decomposition of limestone into high purity CaO can be optimized by increasing the temperature and/or calcination time.

### The Effect of CO<sub>2</sub> Gas Flow Rate in the Carbonation Process

Low CO<sub>2</sub> flow rates were chosen based on previous work [12] which suggests that flow rate (2.0 L/min) gave better yield than higher flow rate (above 2 L/min). Thus, flow rates below 2.0 L/min were explored in order get higher yield of PCC. The effect of CO<sub>2</sub> gas flow rate in the carbonation process toward the PCC yield is presented in Fig. 2. Fig. 2 showed that the highest PCC yield was obtained at CO<sub>2</sub> flow rate of 0.5 L/min, which is 62.95% yield. For the CO<sub>2</sub> flow rate of 1.0, 1.5, and 2.0 L/min, lower mass of PCC was yielded.

Each flow rate result was compared and statistically investigated by variant analysis in one way classification using F-test (5%). The F-test shows that the yield obtained

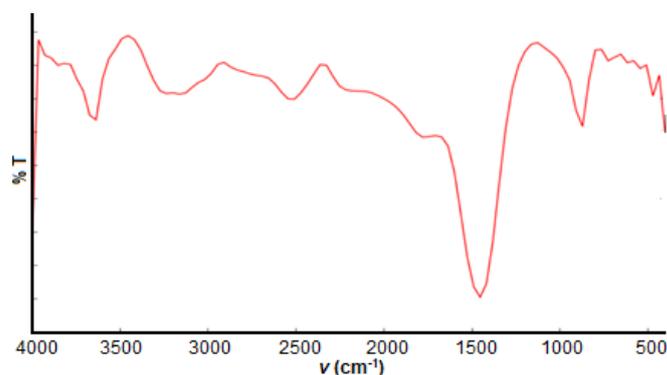


Fig 1. The FT-IR spectra of CaO used as the starting material for PCC synthesis

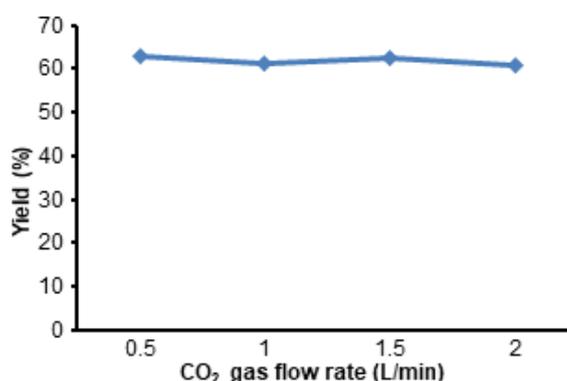


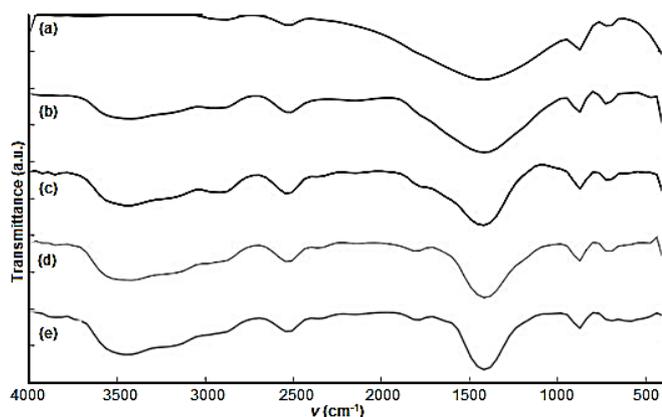
Fig 2. The effect of PCC yield by various CO<sub>2</sub> flow rate

in each flow rate has no significant difference (calculated F value (3.755) < F table (6.94)). Hence, at all flow rates used in this work, the yields were statistically equal. This result is in alignment with the fact that low flow rate gives more contact time to the mixture to fully reacted. On the other hand, very high flow rate may reduce the contact time and the yield, as well as may waste more CO<sub>2</sub> gas.

Synthesized PCC from all CO<sub>2</sub> low rates was characterized by FT-IR spectrophotometer and it is shown in Fig. 3 (top). The FT-IR spectra of all CO<sub>2</sub> flow rates are identical to that of pure CaCO<sub>3</sub> from the literature [13], with only small shift in some bands. Nevertheless, increasing of flow rate sharpen the bands around 1400 cm<sup>-1</sup> and may indicates the formation of vaterite polymorph. The closest similarity in the wavelengths with the pure CaCO<sub>3</sub> from literature was shown by the PCC obtained using 0.5 L/min flow rate (Fig. 3, bottom). Based on this reason, contact time, and CO<sub>2</sub> usage efficiency, 0.50 L/min was chosen as the optimum CO<sub>2</sub> flow rate and used in the next stage.

### The Effect of Carbonation Temperature

Temperature used during carbonation process may govern the formation of different polymorph (such as calcite, vaterite, or aragonite) in the crystallization of



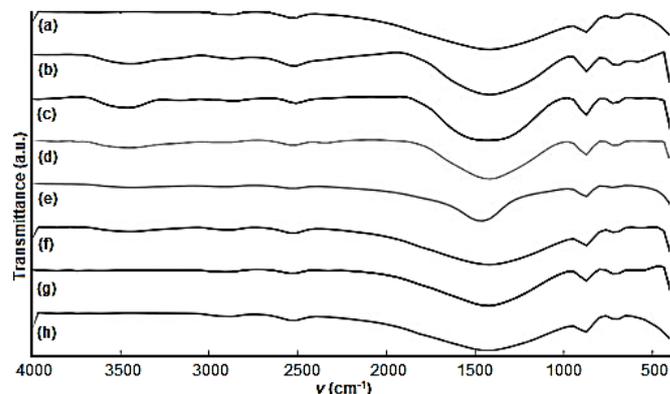
**Fig 3.** The FT-IR spectra of synthesized PCC in various CO<sub>2</sub> flow rates at 30 °C (a = CaCO<sub>3</sub>; b = PCC 0.5 L/min; c = PCC 1.0 L/min; d = PCC 1.5 L/min; e = PCC 2.0 L/min)

PCC. Therefore, wide range of temperature were explored from 50 to 250 °C. The FT-IR spectra of synthesized PCC without heating treatment and at several carbonation temperatures is presented in Fig. 4 (top).

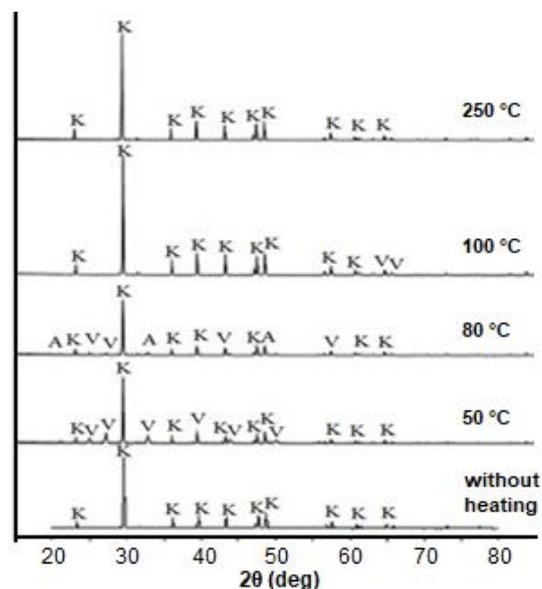
The FT-IR spectra confirmed the presence of trinary calcite–vaterite–aragonite from 50 and 80 °C treatment in the region of 2400, 1800, and 1400 cm<sup>-1</sup>, respectively. Vaterite polymorph was exclusively formed between 50–100 and 200 °C. The characteristic peak for vaterite was observed around 1400, 875, and 700 cm<sup>-1</sup> accordance with the Gopi and Subramanian's report [14]. Moreover, the aragonite polymorph was formed easily not only at ambient temperature but also at higher temperature i.e. 50, 80, and 150 °C. In addition, the synthesized PCC that was obtained at 250 °C treatment has the closest identical spectra with the pure CaCO<sub>3</sub> (Fig. 4, bottom). The high temperature also affect the hydration of the product as indicated from changing of a broad band around 3300–3500 cm<sup>-1</sup> which correspond to the O–H vibration. The band is getting smaller and then disappear as the temperature increased.

### Powder XRD Analysis

Synthesized PCC obtained without heating treatment and with heating treatment at 50, 80, 100, and 250 °C were analyzed using powder XRD to examine their crystalline phase in a bulk sample. Their powder pattern can be seen in Fig. 5. In general, synthesized PCC from the above treatment formed crystalline state which was confirmed by the sharp absorption in the 2θ angle. It also found that every diffraction peak was in agreement with the JCPDS standard 00-005-00586. The characteristic diffraction peaks (2θ) from sample without heating treatment were 23.20, 29.61, 39.61, 43.36, 47.70 and



**Fig 4.** The FT-IR spectra of synthesized PCC at 0.5 L/min in various carbonation temperature (a = CaCO<sub>3</sub>; b = PCC 30 °C; c = PCC 50 °C; d = PCC 80 °C; e = PCC 100 °C; f = PCC 150 °C; g = PCC 200 °C; h = PCC 100 °C)

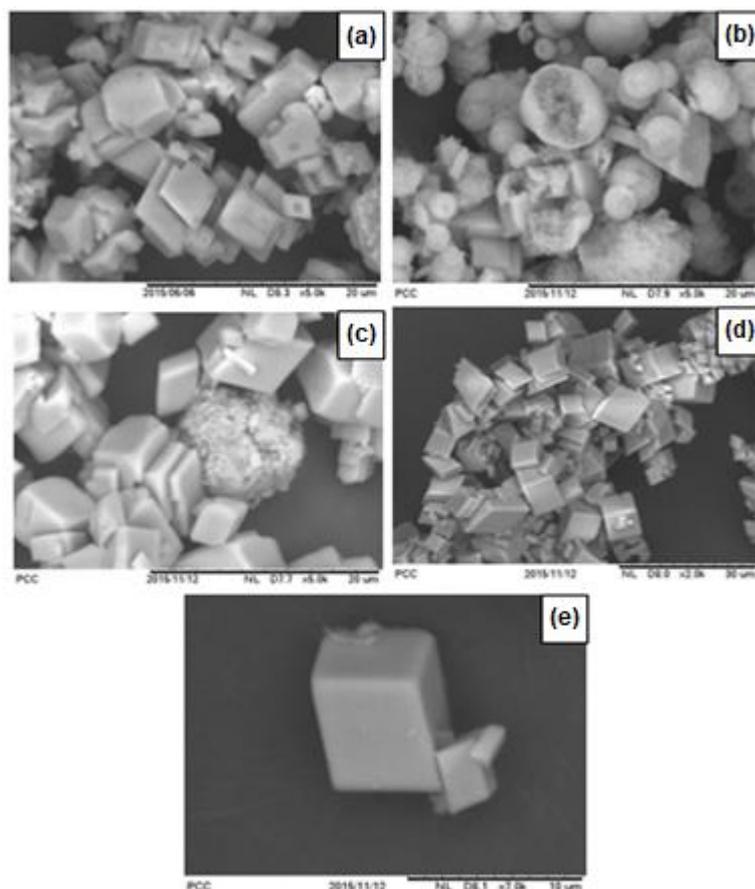


**Fig 5.** Powder pattern of the synthesized PCC in various carbonation temperatures (K = calcite; V = vaterite; A = aragonite)

48.70° which correspond to nucleation planes of calcite polymorph. This result is in line with earlier report which indicated that calcite polymorph could be formed at room temperature [13].

Both vaterite and calcite were formed at 50 °C which identified from 2θ of 20.97, 24.88, 27.09, 32.76, and 43.84° (JCPDS 01-074-1867). The calcite polymorph peaks were observed in 2θ of 23.07, 29.40, 39.41, 43.28, 47.63, and 48.5° (JCPDS 00-005-00586). This finding was in accordance to literature in which calcite could be formed at 10 to 45 °C while vaterite could be formed at 30 to 50 °C [12-13,16].

The formation of trinary calcite–vaterite–aragonite from 80 °C treatment was confirmed from 2θ of 21.00,



**Fig 6.** SEM images of PCC crystal: (a) without heating, (b) 50 °C, (c) 100 °C, (d) 250 °C, (e) 250 °C with magnification 7000x. Note: calcite forms cubic crystal and vaterite forms round crystal

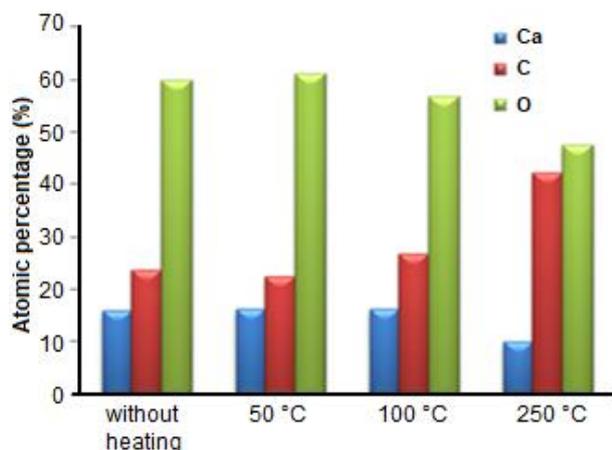
32.77, 48.44, and 77.09° for aragonite (JCPDS 01-076-0606),  $2\theta$  of 24.87, 27.00, 43.80, 47.06, and 56.51° for vaterite (JCPDS 01-074-1867), and  $2\theta$  of 23.01, 29.35, 39.47, 43.11, 47.44, and 48.59° for calcite (JCPDS 00-005-00586). This finding is also corresponding to Gopi and Subramanian's report [15] which stated that the formation of three polymorphs were obtained at 80 °C. Thriveni et al. [4] also suggest that aragonite can be formed at 80 °C.

For higher temperature, 100 and 250 °C causes phase changing of PCC from vaterite and aragonite into a more stable polymorph calcite. As expected, calcite was a major polymorph of PCC and only few  $2\theta$  peaks which belongs to vaterite was detected at 100°. Moreover, there is no aragonite polymorph obtained at high carbonation temperature. At 250 °C, only calcite polymorph was detected which was shown by the  $2\theta$  at 23.06, 29.49, 39.40, 43.15, 47.48, and 48.49° (JCPDS 00-005-00586). This finding was in-line with Gopi and Subramanian's report [15] which revealed that calcite and vaterite formed at 100–170 °C, while at above 170 °C, calcite is exclusively crystallized. The carbonation temperature is

likely governing the obtained polymorph during crystallization of PCC. From this work, the probability of obtaining good crystallinity PCC is getting higher as the carbonation temperature increased.

### SEM-EDX Analysis

SEM analyses of the synthesized PCC obtained without heating treatment and with heating treatment at 50, 100, and 250 °C are presented in Fig. 6. PCC obtained without heating treatment forms irregular shape and cubic form of rhombohedral calcite (Figure 6a). A round shape of vaterite started to crystallized as the temperature increases to 50 °C (Fig. 6(b)). This finding correlates to Pişkin dan Özdemir's report [16] in which the rhombohedral calcite has cubic shape while the vaterite has round shape. At higher temperature, the vaterite change again into more stable polymorph, which is calcite, as also mentioned in Gopi and Subramanian's paper [15]. At 100 °C, cubic shape solid was formed as major product than the round shape solid (Fig. 6(c)). Finally, better crystallinity and homogeneity of calcite is



**Fig 7.** EDX result (top: without heating, 100 °C, 250 °C, respectively) and atomic percentage of synthesized PCC crystals in various temperature (bottom)

**Table 1.** Particle diameter of PCC obtained without heating treatment and with heating treatment in some distribution percentage

No	PCC Sample	Diameter ( $\mu\text{m}$ )		
		10%	50%	90%
1.	Without heating	9.15	21.97	37.27
2.	50 °C	3.58	16.12	38.14
3.	80 °C	4.16	18.20	34.38
4.	100 °C	8.06	18.86	31.80
5.	250 °C	8.83	21.91	37.92

obtained at 250 °C. At this temperature, the PCC crystallizes in a cubic shape calcite only (Fig. 6(d) and 6(e)).

Combined analysis between SEM and EDX was also employed as elemental analysis of the synthesized PCC. According to the EDX analysis, the synthesized PCC has high purity with no other peaks that correspond to potential impurities such as Mg, Fe, etc. The synthesized PCC consist of calcium, carbon, and oxygen to produce  $\text{CaCO}_3$ . The EDX result of synthesized PCC obtained without heating treatment and with heating treatment at 100, and 250 °C are presented in Fig. 7. The increasing carbonation temperature leads to the reducing calcium and oxygen content in PCC (at 100 and 250 °C). Consequently, the carbon content raised significantly as the carbonation temperature increased. The increase of carbonation temperature affects the chemical equilibrium in the solution and thus the  $\text{CO}_2$  solvation during the process, although eventually this will increase the formation of  $\text{CaCO}_3$  [17].

### PSA Analysis

Particle size distribution analysis showed that the synthesized has diameter size about 3.58–38.14  $\mu\text{m}$  (Table 1). According to the highest distribution of 90%,

PCC obtained without heating treatment and with heating treatment at 50, 80, 100, and 250 °C has average diameter sizes of 37.27, 38.14, 34.38, 31.80, and 37.92  $\mu\text{m}$ , respectively. The diameter size of the synthesized PCC was not influenced by heating treatments. This result was also reported by Mihai et al. in which in their work, the PCC has diameter about 15 to 45  $\mu\text{m}$  [18].

### CONCLUSION

The  $\text{CO}_2$  gas flow rate and carbonation temperature are influencing the synthesis of PCC from limestones by carbonation process. At various  $\text{CO}_2$  flow rates of 0.5; 1; 1.5; and 2 L/min, the yields were higher than previous work [12] but the yield obtained in each flow rate has no significant difference to each other. The optimum  $\text{CO}_2$  flow rate was 0.5 L/min with yield of 62.95%. The heating treatment in carbonation process at 50, 80, 100, 150, 200, and 250 °C was affecting the formation of the synthesized PCC crystal polymorph, in which at 250 °C, only calcite polymorph was formed.

FT-IR spectra, XRD pattern and SEM-EDX confirmed that the product is high quality PCC. Moreover, at the carbonation temperature of 50 °C, calcite and vaterite were formed, while at the carbonation temperature of 80 °C, mixture of calcite-vaterite-aragonite were obtained. Higher carbonation changes the vaterite and aragonite polymorphs into calcite and the best crystallinity was obtained at 250 °C. PSA analysis showed that the particle diameter of the synthesized PCC was about 3.58 to 38.14  $\mu\text{m}$ .

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