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PREPARATION OF PRECIPITATED CALCIUMCARBONATE USING ADDITIVE AND WITHOUT ADDITIVE

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Graphical abstract

Abstract

Precipitated calcium carbonate (PCC) chemically can be synthesized in the laboratory. In this study, hydrated lime or calcium hydroxide was used as raw material with sucrose as additive to produce PCC. The process was compared with the one without additive. PCC produced was observed based on morphology, mineral composition and size by using Fesem-Edx and LPSA, respectively. PCC products without additive demonstrated fine and more uniform size of calcite PCC as compared to the one with additive. Nevertheless, the process with additive produced more PCC product than without additive.

Keywords: Precipitated Calcium Carbonate (PCC), calcium sucrate, carbon dioxide gas, morphology

Abstrak

Kalsium karbonat termendak (PCC) boleh disintesis secara kimia di dalam makmal. Dalam kajian ini, kapur terhidrat telah digunakan sebagai bahan mentah dan sukros sebagai bahan tambahan dalam penghasilan PCC. Proses ini dibandingkan dengan proses tanpa menggunakan bahan tambahan. PCC terhasil diperhatikan berdasarkan morfologi, kandungan mineral dan saiz menggunakan Fesem-Edx and LPSA. Hasil PCC tanpa bahan tambahan mempunyai saiz lebih halus dan seragam berbanding dengan kalsium karbonat yang terhasil menggunakan bahan tambahan. Walau bagaimanapun kuantiti hasil PCC menggunakan bahan tambahan adalah lebih banyak berbanding dengan tanpa bahan tambahan

Kata kunci: Kalsium karbonat termendak (PCC), kalsium sukrat, gas karbon dioksida, morfologi

1.0 INTRODUCTION

Precipitated calcium carbonate (PCC) is one of the versatile materials that can be used in many fields such as in paper making, glass,rubber, plastic, paint, pharmacy, food, cosmetic, detergent and biomaterials[1-11]. PCC with different chemical and physical properties such as particle size, specific surface area, morphology and chemical purity are important for its application [1]. Precipitated calcium carbonate also known as synthetic calcium carbonate (SCC) [12, 13].

The term high grade calcium carbonatefrom industrial scope can be classified to in ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) [12].Ground calcium carbonate (GCC) can be produced by certain mechanical processes from carbonate ore. The process to produce ground calcium carbonate is exploitation, crushing and grinding. For precipitated calcium carbonate the process involved is chemical precipitation process [12].

Generally, precipitated calcium carbonate can be synthesized via the solution (gas-solution-solid) or the carbonation (solution-solution-solid) methods [1]. In this study the first method was used because it is commonly used and simple to investigate the effect of using additive in producing precipitated calcium carbonate.

Calcium carbonate presents in three different mineralssuch as calcite, aragonite and vaterite [14, 15]. These minerals have the same chemical formula but different crystal structure known as polymorph. The minerals can exist in natural or can be synthesized in laboratory. Calcite is the most stable as compared to aragonite and vaterite due to its thermodynamic stability. Aragonite and vaterite are thermodynamically unstable. They can be stabilized chemically or kinetically [14, 16]. Precipitated calcium carbonate can be synthesized with specific polymorph depending on the presence of additive at room temperature. The morphology of calcium carbonate phase formation depended on the process parameters [14, 17]. The use of additives especially polyelectrolytes can affect the selection of polymorph formation, growth mechanism, nucleation, size and shape crystal [14, 18].

Sucrose is known as table sugar or sugar and its obsolete name is saccharose. Sucrose is a disaccharide which is a combination between glucose molecule and fructose molecule. Chemical formula of sucrose is $C_{12}H_{22}O_{11}$ and it hydrate formula can be written as $C_{12}.H_2O$.The OH groups that exist in sucrose molecule are polar, this characteristic can increase the solubility of calcium ion in solution.

The objective of this research is to study the parameters that affect the morphologies, particle size and amount of PCC produced. The scope of the study is to assist the local industries to increase the value of calcium carbonate because the price of PCC is eight times as compared to ground calcium carbonate (GCC) or natural calcium carbonate.

2.0 EXPERIMENTAL

2.1 Materials

Hydrated lime wsw obtained locally, purified carbon dioxide gas 99% (Linde Malaysia Sdn.Bhd., Selangor) and sucrose ($C_6H_{14}O_6$) 98% (Merck, USA) were commercially obtained.

2.2 Preparation of Calcium Ion Solution

Four experiments were carried out to produce PCC products namely PCC1, PCC2, PCC3 and PCC4. In the first and second experiments, calcium ion solution was used. 111 g hydrated lime was added into 5 L beaker that contained 3 L ultrapure water, respectively. Magnetic stirrer was used to stir hydrated lime in water. The solution was stirred around 30 minutes at 700 rpm with magnetic stirrer at temperature around 12 to 15 °C. Then colloidal solutions were filtered by using Whatman No.1 filter paper. Calcium ion solutions were used as stock solution in producing PCC. Equation 1 shows the reaction between sucrose and water.

$$Ca(OH)_2(s) + H_2O(l) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq) \quad \text{(Eq. 1)}$$

2.3 Preparation of Sucrose Solution

In third and fourth experiments, sucrose solution was used. In the third experiment, 300 g sucrose was dissolved in 3 L ultrapure water and in the fourth experiment, 200 g sucrose was dissolved in 2 L ultrapure water. Both of the solutions had degree brix reading around 9.5°Bx. Magnetic stirrer was used to dissolve sucrose in water. The time used to dissolve sucrose was around 5 minutes at 700 rpm. A tago refractometer was used to determine degree brix reading of the sucrose solution. The sucrose solutions were used in producing calcium sucrate solution. Equation 2 shows the reaction between sucrose and water.

$$C_{12}H_{22}O_{11}(s) + H_2O(l) \longrightarrow C_{12}H_{22}O_{11}(aq) \quad \text{(Eq. 2)}$$

2.4 Preparation of Calcium Sucrate Solution

In the third experiment, 111 g hydrated lime hydroxide lime was added into 3 L sucrose solution and in the fourth experiment, 74 g hydrated lime was added into 2 L sucrose solution. These solutions were stirred at 700 rpm with magnetic stirrer for 10 to 15 minutes at room temperature. Then colloidal solutions were filtered by using Whatman No.1 filter paper. Calcium sucrate solutions were used as stock solution in producing PCC. The reaction occurs between sucrose solution and calcium hydroxide is shown in equation 3.

$$C_{12}H_{22}O_{11}(aq) + Ca(OH)_2(s) \longrightarrow C_{12}H_{22}O_{11}.CaO(aq) \quad \text{(Eq. 3)}$$

2.5 Preparation of Precipitated Calcium Carbonate

Two different volume rates of carbon dioxide gas were used in this study; 0.2 L/min and 1 L/min. In the first and second experiments, 0.2 L/min and 1 L/min CO_2 gas were flowed into 5 L beaker that contained 3 L calcium ion solution, respectively. The solutions were stirred at 900 rpm with magnetic stirrer at temperature around 12 to 15°C. In the third and fourth experiment experiments, 0.2 L/min and 1 L/min CO_2 gas were flowed into 5 L beaker that contained 3 L calcium sucrate, respectively. The solutions were stirred at 900 rpm with magnetic stirrer at temperature around 12 to 15°C. The equation occurs in the first and second experiments were shown in equation 4. Equation 5 shows the reaction occurred in third and fourth experiments.

$$Ca_2^{+}(aq) + 2OH^-(aq) + CO_2(g) \longrightarrow CaCO_3(s) + H_2O(l) \quad \text{(Eq. 4)}$$

$$C_{12}H_{22}O_{11}.CaO(aq) + CO_2(g) \longrightarrow CaCO_3(s) + C_{12}H_{22}O_{11}(aq) \quad \text{(Eq. 5)}$$

In these fourth experiments, the flow of carbon dioxide gas was terminated until the pH value reached around 7.5 to 8. The colloidal solutions were filtered by using

Whatman No.548 filter paper in first, second and third experiments. Then filtration residue (PCC) was rinsed by ultrapure water. In the fourth experiment the colloidal solution was centrifuged at 4000 rpm. After that the filtration and centrifuge residues were dried in the oven at 60°C for 6 hours.

3.0 RESULTS AND DISCUSSION

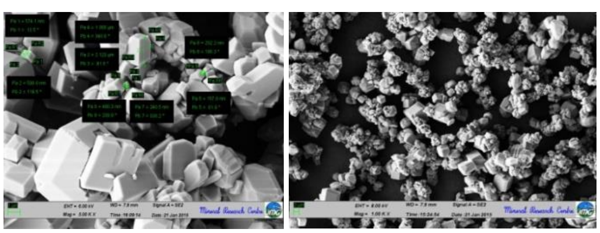
In this study, calcium ions were the main ion in synthesizing precipitated calcium carbonate (PCC). Table 1 shows the parameters and results of experiments that produce precipitated calcium carbonate. The PCC products were analysed by using Fesem-Edx and laser particle size analysis (LPSA).

3.1 Fesem-Edx Analysis

Fesem-Edx was used to analyse the four PCC samples (products). From Figure 1a, 1b, 1c and 1d, the smallest particle size produced in PCC1, PCC2, PCC3 and PCC4 were 157.9 nm, 1.194 μm, 2.374 μm and 2.534 μm, respectively. The morphologies in all PCC (products) were rhombohedral or cubic. Micrograph of PCC1 (Figure 1a) shows the distribution and size particles were more uniform and finer compared to others. The result indicated that without using additive the PCC size was more uniform and finer compared with PCC size produced using additive.Micrographs of the PCC products show that the particles had agglomerated so the dispersion agent such as stearic acid should be used to disperse the PCC particles.

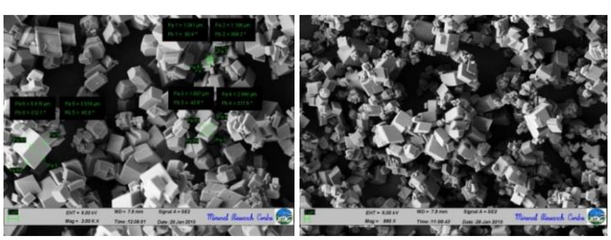
Table 1 Parameters and results of experiments in producing PCC

No. of sample	Volume of stock solution (L)	pH of stock solution	Brix readin g (°B)	Carbon dioxide gas flow rate (L/min)	Time for carbonation process completed (min)	Product weight (g)	Product size	Product morphology
PCC1	3.0	12.22	-	1.0	8.0	3.855	157.9 nm-2.123μm	cubic
PCC2	3.0	12.36	-	0.2	14.88	4.275	1.194 μm-5.416μm	cubic
PCC3	3.0	12.02	9.4	0.2	27.0	18.711	237.4 nm-1.875μm	cubic
PCC4	2.0	11.95	9.5	1.0	7.93	8.164	2.534 μm-3.397μm	cubic



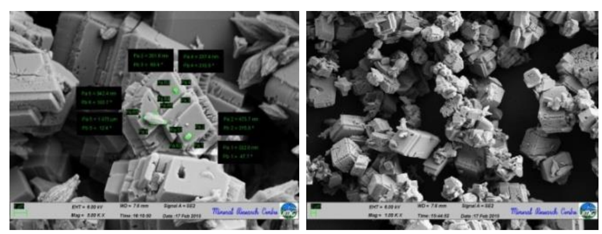
(a)

Figure 1a Fesem micrographs of PCC1 with magnifying 5000 times and 1000 times



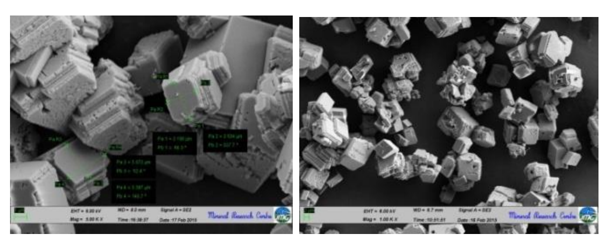
(b)

Figure 1b Fesem micrographs of PCC2 with magnifying 2000 times and 1000 times



(c)

Figure 1c Fesem micrographs of PCC3 with magnifying 5000 times and 1000 times



(d)

Figure 1d Fesem micrographs of PCC4 with magnifying 5000 times and 1000 times

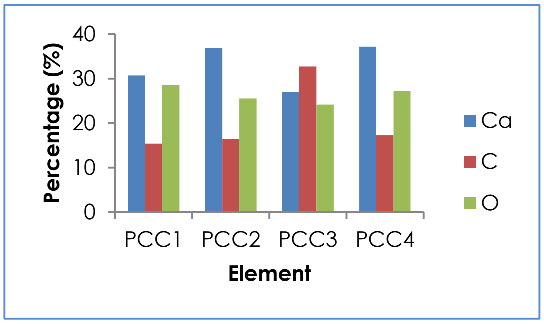


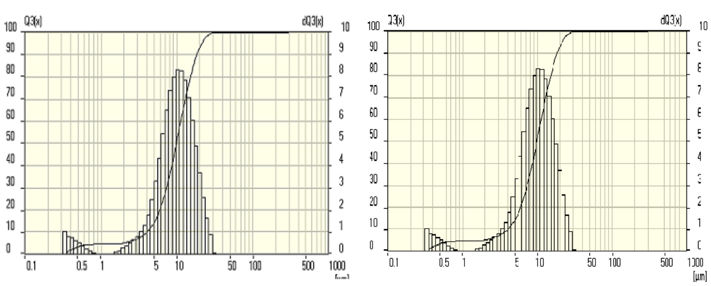
Figure 2 Percentage of elements in PCC

Figure 2 shows the percentage of elements in PCC based on Edx analysis. Calcium in PCC1, PCC2, PCC3 and PCC4 were 30.73%, 36.82%, 26.95% and 37.21%, respectively. Calcium ions play the main role to produce PCC when they react with carbon dioxide in the carbonation reaction as shown in Eq. 4.

3.2 Laser Particle Size Analysis (LPSA)

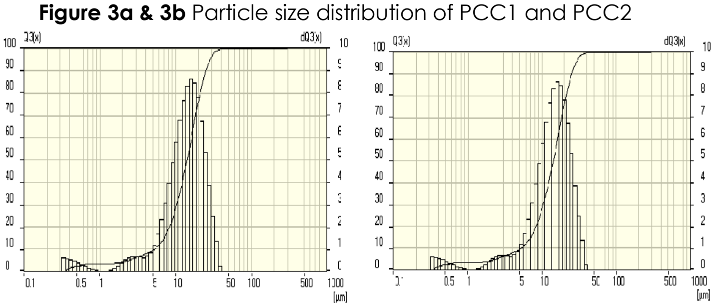
Figure 3a shows that 93.1% of size particles PPC1 was less or equal to 20 µm. The particles size at d90 and d50 were 18.4 µm and 9.9 µm, respectively. Figure 3b shows that 97.8% of size particles was less or equal to 20 µm. The particles size at d90 and d50 were 18.4 µm and 9.9 µm, respectively. Figure 3c shows that 96.4% of size particles was less or equal to 30 µm. The particles size at d90 and d50 were 25.2 µm and 14.157 µm, respectively. Figure 3d shows that 96.3% of size particles was less or equal to 30 µm. The particles size at d90 and d50 were 25.8 µm and 15.7 µm respectively.

The results indicate that PCC produced without additive has more fine size compared with PCC produced using additive.



(a) (b)

Figure 3a & 3b Particle size distribution of PCC1 and PCC2



(c) (d)

Figure 3c & 3d Particle size distribution of PCC3 and PCC4

4.0 CONCLUSION

Based on Fesem analysis, PCC products produced without additive had fine and uniform sizes as compared to PCC products produced by additive. Based on the result of laser particle size analysis PCC product without additive with flow rate of 1 L/min had fine size compared to the PCC product with flow rate of 0.2 L/min. However the amount of PCC produced with additive were more compared to PCC products produced without additive. The quantity of PCC product with additive and with flow rate 0.2 L/min is higher compared to the one without additive.

The increaseof CO_2 gas flowrate would decrease the size particle of the PCC produced as shown in PCC1 [8]. The use of additive such as sucrose can increase the PCC product as the solubility of hydrated lime in sucrose solution is higher compared to water [19]. The increase of the rate of CO_2 had insignificant effect on the morphology formation of the PCC.

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