

ORIGINAL ARTICLE

Preparation of micro-calcite powder using fine-bubble assisted carbonation as toothpaste material

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ABSTRACT

Introduction: Calcite (CaCO₃) is typically used in commercial toothpaste with particle size ranges from 1-12 µm. In the latest study, calcite was synthesized by using Ca(OH)₂ precursor from natural resources. However, the resulting particle size does not match the size of the toothpaste filler. This study aims to prepare micro-calcite via fine-bubble assisted carbonation as toothpaste material. **Methods:** The calcite powder was prepared from Ca(OH)₂ analytical grade powder utilizing the fine-bubble carbonation process with the Ca(OH)₂ concentration and initial pH variation. The study was started by making a Ca(OH)₂ suspension with a concentration of 0.25, 0.5, 0.75, 1 and 1.25 M using 2.000 ml methanol as a solvent. 0.5 M NaH₂PO₄ solutions were utilized to adjust the initial pH of 0.5 M Ca(OH)₂ suspension into 8, 9, and 10. The suspensions were aerated using CO₂ fine-bubble for two hours to produce CaCO₃ samples. All precipitated CaCO₃ particles were characterized by PSA, Zeta-Potential, and FTIR measurements. **Results:** The calcite phase was identified from the FTIR transmittance. Aragonite or vaterite phase was not observed in the samples. PSA result shows the size of CaCO₃ particles from samples 0.25 M to 1.25 M are as follows 3.03, 3.23, 2.79, 3.70, 0.99 µm respectively. Meanwhile, the particle sizes of CaCO₃ in samples with a pH of 8, 9 and 10 are 3.00, 2.03 and 2.50 µm respectively. The zeta potential shows the value ranges from -232 mV to -11.9 mV, indicating fair dispersion ability. **Conclusion:** The fine bubble assisted carbonation method in this study helps in producing calcite in micron size that could be used as alternative fillers for toothpaste.

KEYWORDS

calcite, fine-bubble, carbonation, particle size, toothpaste

INTRODUCTION

Calcium carbonate (CaCO₃) is one of the most abundant natural minerals. CaCO₃ is widely used for various applications in both industrial and biomedical fields. It was chosen because it has a large amount of availability, relatively cheap price, biocompatible, biodegradable, large surface area, and relatively easy synthesis method. Most importantly, CaCO₃ has been approved by the FDA as a food and pharmaceutical additive/ingredient.^{1,2}

In nature, CaCO₃ exists in three types of anhydrous crystals: calcite, aragonite, and vaterite.¹⁻⁷ Because of its shape, non-toxic properties, and ease of metabolism by all cells, calcite was regarded as an effective material in biomedical applications,⁶ such as toothpaste.⁸ Calcite, in toothpaste, plays role as the abrasive material to remove plaque and stains from the teeth. The size of calcite found in commercial toothpaste ranges from 1-12 µm.^{9,10} Previous studies have found that toothpaste containing calcite can enhance tooth remineralization, thereby preventing incipient enamel lesions.¹¹ Thanks to the calcite which can act as a source of calcium ions in a saturated state in enamel minerals.^{6,12}

Several methods for producing calcite have been reported. The carbonation method is the most widely used because it is simple, cost-effective, and produces abundant particles with high purity.^{1,2,13} However, the carbonation method is time-consuming due to water's low solubility of carbon dioxide gas (CO₂).¹ A previous study used a fine bubble generator to increase the solubility of CO₂. It shows faster precipitation of calcite and produces smaller particles than the ordinary carbonation method.¹⁴ Large bubbles have buoyant behavior in solution, making them difficult to dissolve and easily broken, whereas tiny bubbles can maintain their presence in solution, making them easier to dissolve.¹⁵

Synthesis of calcite via fine bubble carbonation has been applied.^{2-5,16} Research conducted by Adnyani et al succeeded in obtaining calcite using a fine bubble diffuser with different precursor concentration ratios.¹⁶ The synthesis of calcite is influenced by several parameters: precursor concentration, temperature, pH of the solution, CO₂ gas flow rate, and additives.^{1,2,4,13} The formation of calcite particles can be manipulated by modifying the parameters during the carbonation process.⁴

The previous study¹⁶, calcite was synthesized by using natural resources precursor (CaOH) via fine bubble carbonation. It produced 700 nm-sized calcite particles at the highest precursor concentration (0.05 M). However, the resulting particle size does not match the size of the filler that should be. The synthesis of calcite using analytical grade precursors and the effect of the parameters on the particle size of calcite has not been conducted. This study aims to prepare micro-calcite via fine-bubble assisted carbonation as toothpaste material

METHODS

Analytical grade calcium hydroxide (Ca(OH)₂, ACS, Reag.Ph Eur grade), with a multimodal distribution of size (2.7-3 μm), was used as a precursor. Methanol 98% was used as a solvent.¹⁷ Sodium dihydrogen phosphate (NaH₂PO₄, ACS, Reag.Ph Eur grade) was used to adjust the initial pH of the Ca(OH)₂ suspension. Whatman filter paper No.1 was purchased from Cytiva, Marlborough, MA, USA. Ethanol was purchased from Merck KGaA, Darmstadt, Germany.

The type of this research is qualitative descriptive. The study was started by making a Ca(OH)₂ suspension with a concentration of 0.25, 0.5, 0.75, 1 and 1.25 M using 2.000 ml methanol as a solvent. The mixtures were stirred using a magnetic stirrer for 60 minutes. 0.5 M NaH₂PO₄ solutions were utilized to adjust the initial pH of 0.5 M Ca(OH)₂ suspension into 8, 9, and 10. Subsequently, CO₂ was injected at 0.1 L/min into entire Ca(OH)₂ suspensions using a fine-bubble generator (Fig. 1). The reaction temperature was set at 20±1°C while the stirring speed was maintained at 200 rpm for 120 minutes. The temperature and pH of the suspension were monitored using a thermometer and digital pH meter during the reaction. Calcium carbonate suspension (CaCO₃) precipitated for 24 hours. The precipitate was filtered using a Whatman filter paper and a Buchner funnel, rinsed with ethanol solution, and dried in a desiccator for 48 hours to obtain powdered calcium carbonate (CaCO₃).

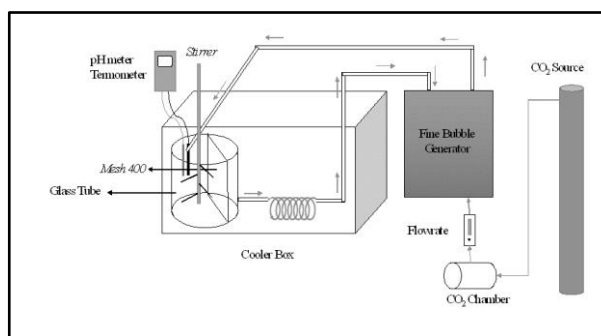


Figure 1. Fine-bubble generator illustration scheme. The machine made by Center of Excellence for Higher Education Institutions Functional Nano Powder University Center of Excellence, Universitas Padjadjaran, Jatinangor.

All precipitated CaCO₃ particles were characterized by PSA, Zeta-Potential, and FTIR measurements to identify the particle size distributions, the stability of particle dispersions, and the absorption bands of the CaCO₃ polymorph. The PSA and Zeta-Potential measurements were analyzed using Horiba Scientific SZ-100 Nanopartica. The FTIR measurement was analyzed using Thermo Scientific Nicolet iS5.

RESULTS

Characterization of CaCO₃ particles using PSA, Zeta-Potential, and FTIR were conducted to determine the characteristics of CaCO₃. The results of the characterization are shown in the figures below

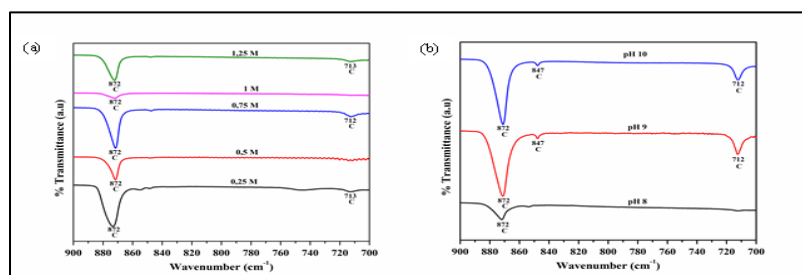


Figure 2. FTIR spectra of CaCO₃ samples with the variation of
a) Ca(OH)₂ concentration b) initial pH

Figure 2 shows the FTIR spectra of CaCO_3 samples with the variation of Ca(OH)_2 concentrations and initial pH. Fourier Transform Infrared Spectroscopy (FTIR) was used successfully for the identification of the CaCO_3 polymorph in the previous research.¹⁷ The Figure 2a shows the transmittance bands of the calcite structure at wavenumbers 712 and 872 cm^{-1} . The wavenumber of the calcite structure is visible in all samples. Meanwhile, all samples with various pH also showed absorption bands from the calcite structure at wave numbers 712 and 872 cm^{-1} .

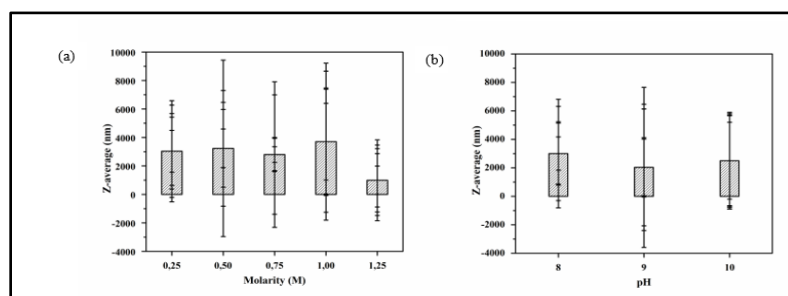


Figure 3. Particle size distribution of CaCO_3 samples with the variation of a) Ca(OH)_2 concentration b) initial pH

Fig. 3 shows the size distribution of the samples. Figure 3a shows the size of CaCO_3 particles from samples 0.25 M to 1.25 M are as follows 3.03, 3.23, 2.79, 3.70, 0.99 μm respectively. Meanwhile, Figure 3b shows the particle sizes of CaCO_3 in samples with a pH of 8, 9 and 10 are 3.00, 2.03 and 2.50 μm respectively. The results showed that there was no clear pattern of relationship between the concentration of the CaOH precursor and the pH of the solution on the size of the CaCO_3 particles.

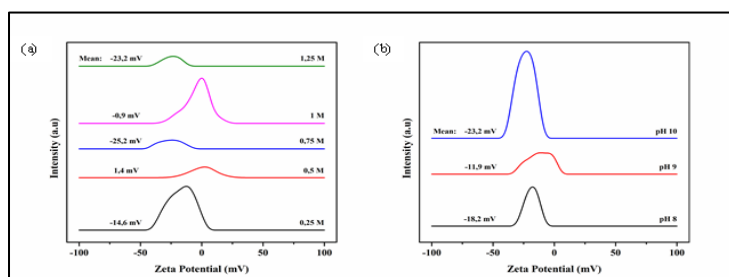


Figure 4. Zeta potential value of CaCO_3 samples with the variation of a) Ca(OH)_2 concentration b) initial pH.

Figure 4 shows the zeta potential value of the samples. Zeta potential values show the dispersion stability of the samples. The zeta potential value of the CaCO_3 samples with the variation of Ca(OH)_2 concentrations (Fig. 4a) shows the ranges from -25.2 mV to 1.4 mV, indicating the fair dispersion ability in the water. The samples with the variation of initial pH show the zeta potential value (Fig. 4b) ranges from -23.2 mV to -11.9 mV, indicating fair dispersion ability. Ca(OH)_2 concentration and initial pH variation showed no significant effect on the zeta potential value after two hours of carbonation.

DISCUSSION

The reaction during the CaCO_3 formation in the gas-slurry system has been briefly identified by an earlier study as follows: (1) CO_2 absorption, (2) hydration of dissolved CO_2 , (3) dissociation of calcium hydroxide, and (4) precipitation.¹⁸ The preparation involved the hydration of Ca(OH)_2 analytical grade powder using methanol (Eq. 1 and Eq. 2). The carbonation reaction starts from the hydration of CO_2 (Eq. 3) and the ionization of calcium methoxide (Eq. 4). Ionized calcium and carbon dioxide reacted together, and CaCO_3 was precipitated (Eq. 5). The following chemical reactions are identified during the CaCO_3 formation:

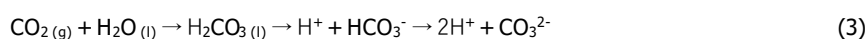
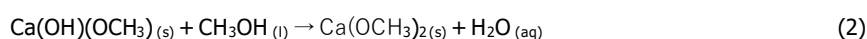
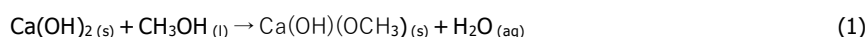


Figure 2 (2a and 2b) shows the calcite phase formed in samples with a concentration of 0.25 to 1.25 and at a solution pH of 8, 9 and 10. This can be explained by equation 2. The presence of methanol compounds initiates hydrolysis in CaOH which is then followed by a condensation process which is accelerated by the presence of H^+ from NaH_2PO_4 . Proton H^+ is also produced in the carbonation process of the fine bubble diffuser and can be seen in equation 3. FTIR results in Figure 2 show that the $CaCO_3$ particles have a calcite structure. The absorption band of aragonite and vaterite was not identified. The results of this study were slightly different from the Ishikawa study in which a combination of calcite and vaterite was produced using 90% methanol.¹⁹ The study revealed that the H_2O formed during the CaOH carbonation process (shown in equation 3) can accumulate during the CaOH solidification process so that it leads to the formation of a calcite phase.¹⁹

Calcite commonly used as an abrasive in toothpaste.¹⁶ Fine bubble generator used in this study is assumed to affect the resulting particle size of $CaCO_3$. This is due to the fine bubble generator producing bubbles in tiny size with a diameter of $< 50 \mu m$ and a higher surface tension compared to a normal bubble so that the bubble can be maintained in solution longer. Therefore, $Ca(OH)_2$ reacts with CO_2 slowly and influences the rate of precipitation of $CaCO_3$. This causes the size of the $CaCO_3$ particles formed to become smaller.

The variation of $Ca(OH)_2$ concentration and initial pH showed no significant effect on the particle size after two hours of carbonation (Figure 3 and 4). The range of particle sizes seems correlated with the size of the initial precursor, $Ca(OH)_2$ analytical grade powder (multimodal distribution, 2.7-3 μm). The results in this study are in line with the research of Liendo et al.²⁰ The study stated that the precursor concentration did not show any effect on the characteristics of the resulting $CaCO_3$ crystals. The parameter that affects the particle size of $CaCO_3$ is the reaction time.²¹

After two hours of carbonation, the Z-average data of particle size show that the samples have a consistent size (1-4 μm) that belongs to the medium size of $CaCO_3$ in commercial toothpaste (1-12 μm).^{10,21} The $CaCO_3$ particle size produced in this study is more suitable for the needs of toothpaste fillers than in Adnyani, et al¹⁶ study. This shows that the resulting $CaCO_3$ can be an alternative as a filler. Further research on morphology and calcium release tests needs to be carried out in the future to determine the effectiveness of $CaCO_3$ particles as toothpaste ingredients.

CONCLUSION

The fine bubble assisted carbonation method in this study helps in producing calcite in micron size that could be used as alternative fillers for toothpaste.

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