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Research Article

Effect of mixed water and methanol solvents ratio on the CaCO3 characteristics via fine bubble diffuser as a dental biomaterial

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ABSTRACT

Introduction: The application of calcium carbonate in dental biomaterial depends on the charcateristics after the synthesis process. This study aims to determine the effect of the ratio of methanol and water on the characteristics of the CaCo3 produced through the fine bubble diffuser method. **Methods:** Synthesis of calcium carbonate by CO2 carbonation method using fine bubble diffuser to produce fine CO2 bubbles (bubble size range 100-500 nm). The Ca(OH)2 precursor was dissolved in various ratios of water and methanol mixtures, namely: 25% water 75% methanol, 20% water 80% methanol, 15% water 85% methanol, 10% water 90% methanol, 5% water 95% methanol, and 100% methanol. The suspension was carbonated using CO2 fine bubbles for 2 hours to produce CaCO3 powder. The resulting calcium carbonate powder was tested with FTIR (Fourier Transform Infra Red), PSA (Particle Size Analyzer), and Zeta-Potential. **Results:** The FTIR test obtained the wave numbers of calcite (712 cm-1), vaterite (744, 873, 874, and 875 cm-1) and aragonite (848, 849, and 854 cm-1) phases in the six variations of the solvent used. The PSA test showed that the particle size produced was submicron with the smallest size being 191.1 nm and the largest being 576.2 nm. The Zeta-Potential test showed that the particles were relatively stable in solution with a Zeta-Potential value range of -15.1 mV to -20.8 mV and particles with moderate stability -21.2 mV to -25.1 mV. **Conclusion:** The addition of the organic solvent methanol to water increases the solubility of CaOH and increases the formation of the vaterite phase. Increasing the amount of water decreases the amount of vaterite phase, increasing the particle size and zeta potential value. but the addition of 15% water decreases the particle size of CaCO3

KEY WORDS: CaCO3, fine bubble diffuser, FTIR, PSA, zeta potential

Pengaruh perbandingan campuran pelarut air dan metanol terhadap karakteristik *CaCO3* melalui metode *fine bubble diffuser* sebagai biomaterial kedokteran gigi

ABSTRAK

Pendahuluan: *Kalsium karbonat (CaCO3) merupakan salah satu sumber kalsium yang umum digunakan di bidang biomaterial kedokteran gigi. Aplikasi kalsium karbonat tergantung dari fasa dan ukuran partikelnya. Penelitian ini bertujuan untuk mengetahui pengaruh perbandingan metanol dan air terhadap karakteristik CaCO3 yang dihasilkan melalui metode fine bubble diffuser.* ***Metode:*** *Prekursor Ca(OH)2 dilarutkan dengan berbagai variasi campuran pelarut air dan metanol, yaitu: 25% air 75% metanol, 20% air 80% metanol, 15% air 85% metanol, 10% air 90% metanol, 5% air 95% metanol, dan 100% metanol. Suspensi Ca(OH)2 dikarbonasi menggunakan gelembung halus CO2 selama 2 jam untuk menghasilkan bubuk CaCO3. Bubuk CaCO3 yang dihasilkan diuji dengan FTIR (Fourier Transform Infra Red), PSA (Particle Size Analyzer), dan Zeta-Potential.* ***Hasil:*** *Uji FTIR didapatkan bilangan gelombang fasa kalsit (712 cm-1), vaterit (744, 873, 874, dan 875 cm-1) dan aragonit (848, 849, dan 854 cm-1) pada keenam variasi pelarut yang digunakan. Uji PSA didapatkan ukuran partikel terkecil 191,1 nm dan terbesar 576,2 nm. Partikel relatif stabil dalam larutan berdasarkan Uji Zeta-Potential (-15,1 mV sampai -17,8 mV) dan stabilitas moderat (-20,8 mV sampai -25,1 mV).* ***Simpulan:*** *Penambahan pelarut organik methanol pada pelarut air meningkatkan kelarutan CaOH dan meningkatkan pembentukan fasa vaterite. peningkatan jumlah air menurunkan jumlah fasa vaterite, meningkatkan ukuran partikel dan nilai zeta potensial. namun pada penambahan 15% air dan seterusnya menurunkan ukuran partikel CaCO3.*

KATA KUNCI: CaCO3, fine bubble diffuser, FTIR, PSA, zeta potential

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INTRODUCTION

Calcium carbonate (CaCO3) is a source of calcium that is commonly used in the biomedical field.[1] This is owing to the calcium carbonate can supply the calcium ion for some purposes. Calcium carbonate is considered as a dental biomaterial to its non-toxic nature, and the ease of metabolism by all cells.[2] The function of calcium carbonate in the dental field is to initiate the regeneration of bone tissue, toothpaste filling material, and as a precursor in the manufacture of scaffolds for engineering bone and tooth tissue.[1,3] Calcium carbonate is often applied as drug delivery, source of antacids, calcium supplements, and tablet excipients in the pharmaceutical field.[3,4,5]

CaCO3 has three crystalline phases namely calcite, aragonite, and vaterite with different morphological structures. The calcite phase is the most stable phase at room temperature, while the vaterite and aragonite phases are metastable phases which can be transformed into stable phases.[2,6] Each of the calcium carbonate phases influences its application as a biomaterial, for example the calcite phase can be used as an ingredient in medicine. cancer cells therapy, and the toothpaste material.[1,2,7] Aragonite and vaterit phases are widely used as bone substitutes and drug delivery in the pharmaceutical field.[1,5,8,9]

One method to synthesize calcium carbonate is the CO2 bubbling/carbonation method. The carbonation method is the most widely used due to cost-effective, simple, and can produce abundant particles with high purity.[10,11,12] CO2 bubbles in the carbonation method can be micro bubbling or fine bubbling. In this study, the CO2 was fine bubbles which are produced by a fine bubble diffuser.

The formation of CaCo3 in aqueous solvents, by the carbonation method, is influenced by the addition of promoters such as organic solvents (alcohol). Synthesis of CaCo3 using a solvent ratio of ethanol and water, with ratio 90%: 10% can produce 75% vaterite phase. Increasing the amount of water is known to decrease the amount of vaterite produced.[13,14] Synthesis of CaCo3 using water and other alcohol solvents such as ethanol, propanol and isopropanol has been widely carried out. However, research on CaCo3 using water and methanol through the carbonation method is unknown. Therefore, the researcher aims to determine the effect of the ratio of methanol and water on the characteristics of the CaCo3 produced through the fine bubble diffuser method.

METHODS

he reaction temperature was set at 20 ± 1 °C to produce CaCO3 powder with particle sizes on the nanometer scale based on previous research, Boyjo Y. *et al.*[12] The stirring speed was set at 300 rpm based on previous research, Wardhani S, dkk15 and Muljani S, dkk16, who varied the stirring speed at 100, 300, 500 rpm. They stated that a stirring speed of 300 rpm was best stirring speed, because the suspension could be stirred evenly and the precipitation process was not disturbed. The flow rate CO2 of 1 L/minute is based on previous research which found that a lower flow rate can make the suspension react completely with CO2, whereas at very high flow rates it can reduce the quality of results because CO2 is flowed at a low flow rate. higher will be more wasted CO2.[15]

RESULTS

The reaction temperature was set at 20 ± 1 °C to produce CaCO3 powder with particle sizes on the nanometer scale based on previous research, Boyjo Y. et al.12 The stirring speed was set at 300 rpm based on previous research, Wardhani S. et al[15] and Muljani S. et al[16] who varied the stirring speed at 100, 300, 500 rpm. They stated that a stirring speed of 300 rpm was best stirring speed, because the suspension could be stirred evenly and the precipitation process was not disturbed.[15,16] The flow rate CO2 of 1 L/minute is based on previous research which found that a lower flow rate can make the suspension react completely with CO2, whereas at very high flow rates it can reduce the quality of results because CO2 is flowed at a low flow rate. higher will be more wasted CO2.[15]

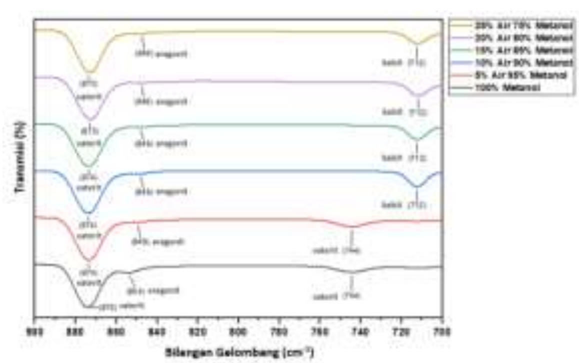


Figure 1. FTIR spectrum of $CaCO_3$ with various ratios of water and methanol mixtures.

Figure 1 shows the FTIR spectra of the $CaCO_3$ with varying ratios of water and methanol mixtures. Fourier Transform Infrared Spectroscopy (FTIR) was successfully used for simultaneous quantitative analysis of $CaCO_3$ phases (calcite, vaterite, aragonite). The spectrum showed wave numbers 712, 848, 873 cm-1 at 25% water 75% methanol and 20% water 80% methanol, wave number 712, 849, 874 cm-1 at 15% water 85% methanol and 10% water 90% methanol, wave numbers 744, 849, 874 cm-1 at 5% water 95% methanol, wave numbers 744, 854, 875 cm-1 at 100% methanol. The wave number of 712 cm-1 is the wave number of the calcite phase; 744, 873, 874, 875 cm-1 are the wavenumbers of the variable phase; and 848, 849, 854 cm-1 are the aragonite phase wave numbers. [17–20] The FTIR spectra show that all $CaCO_3$ wave numbers are found in each variation of the samples tested. The FTIR test uses wave numbers instead of wavelengths because the wave used is one unit per wavelength as seen from the peak, not the distance between one valley and one peak which is the meaning of the wavelength.

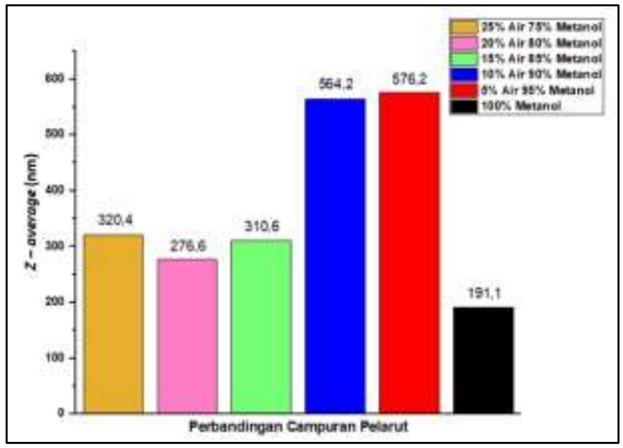
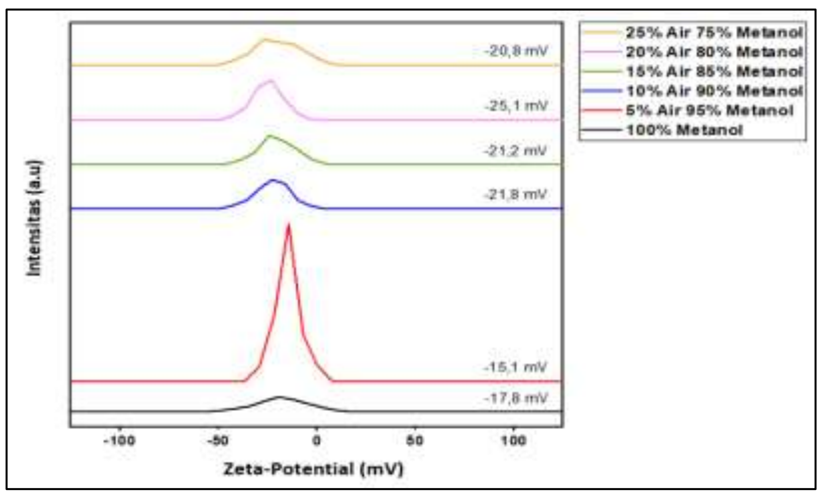


Figure 2. Particle size distribution of CaCO3 samples with varying ratios of water and methanol mixtures.



Graph 1. Zeta-Potential value of CaCO3 samples with varying ratios of water and methanolmixtures

Figure 3 shows the Zeta-Potential values of the samples with various solvent mixtures. The Zeta-Potential value indicates the stability of the sample dispersion. The Zeta-Potential value of CaCO3 samples with varying ratios of water and methanol mixtures (Figure 3) showed a range of -15.1 mV to -25.1 mV. The Zeta-Potential values of the samples are relatively stable (±10-20 mV) and moderately stable (±20 – 30 mV).[25]

DISCUSSION

Previous studies have shown that the addition of organic solvents can change the surface tension, density, viscosity, and dielectric constant. Organic solvents such as alcohol are known to affect the solubility of ionic substances on the surface of CaOH. The type and number of polar functional groups and the presence of hydrophobic and hydrophilic regions are thought to be important factors causing the process to occur. this is what causes the addition of alcohol solvents, in this study is methanol, can cause changes in the phase, size and distribution of $CaCO_3$ crystals. It is known that the more amount of methanol will result in higher surface solubility of CaOH so that the formation of the vaterite phase is much more (Figure 1). This research is in line with the research of Xiao et al, which is the higher the addition of alcohol to the water solvent CaOH, the more Vaterite $CaCO_3$

is produced.[20,24] Particle growth of $CaCO_3$ depends on the transfer of CO_2 from the gas phase to the liquid. CO_2 absorption is the slowest process of the $CaCO_3$ precipitation phenomenon in gas-liquid systems. The control of this process greatly influences the desired $CaCO_3$ phase characteristics. The addition of methanol solvent in this study promoted or inhibited the absorption process. Changes in the composition of the water phase result in changes in the solubility of CO_2 which affects the driving force of the absorption process.

The degree of absorption of CO_2 into the liquid affects the degree of chemical reaction between calcium and carbonate ions. when CO_2 absorption increases, the degree of precipitation also increases. in 100% methanol solvent (Figure 2) there is a process of CO_2 inhibition which causes inhibition of the absorption process and slows down precipitation. this causes the small particle size in the 100% methanol sample. Meanwhile, with the addition of 5% water, an accelerated process of CO_2 absorption occurs, thereby increasing precipitation and increasing particle size. this continues until the addition of 10%. while at the addition of 15% and so on the process of inhibition of CO_2 absorption occurs again and results in a smaller particle size. The submicron sized particles of calcium carbonate powder produced in the 6 variations of the solvent mixture that were carried out can be used as fillers for toothpaste, as precursors in the manufacture of scaffolds for bone and tooth tissue engineering,1 and as drug delivery.[13,14]

The Zeta-Potential test showed that the Zeta-Potential value in this study ranged from -15.1 mV to -25.1 mV. Based on the DLVO theory (colloidal stability in suspension) that the greater the Zeta-Potential value, the more stable a particle will be in suspension. Zeta-Potential adjustment allows to control the stability of the colloidal ceramic in suspension. The theory states that the Zeta-Potential values are grouped as follows: very unstable (±0-10 MV), relatively stable (±10-20 mV), moderate stability (±20-30 mV) and high stability (±30). 25 The results showed that the ratio of the solvent mixture 25% water 75% methanol, 20% water 80% methanol, 15 water 85% methanol, and 10 water 90% methanol was in the range of ±20 – 30 mV, which means the Zeta-Potential value is included in the category of moderate stability. The ratio of a solvent mixture of 5% water, 95% methanol and 100% methanol is in the range of ±10-20 mV, which means that the Zeta-Potential value is relatively stable.[23]

SIMPULAN

The addition of the organic solvent methanol to water increases the solubility of CaOH and increases the formation of the vaterite phase. Increasing the amount of water decreases the amount of vaterite phase, increasing the particle size and zeta potential value. but the addition of 15% water decreases the particle size of $CaCO_3$.

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Research contribution: "Conceptualization, F.R.; and F.M.; methodology, F.R.; software, F.M; validation, F.R.; K.E.; F.M.; A.N.S; formal analysis, F.M.; investigation, F.R.; resources, F.R.; F.M; data curation, F.M.; writing—preliminary drafting, F.R.; F.M.; K.E.; A.N.S writing-review and editing, F.R.; F.M.; visualization, F.M.; supervision, F.R.; project administration, F.M.; obtaining funding, F.R. All authors have read and agree to the published version of the manuscript."

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Ethical Approval: This research was conducted on research samples that did not involve humans or animals.

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