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THE EFFECT OF PRECURSOR CONCENTRATION, pH OF THE SOLUTION AND CARBONATION DURATION ON $CACO_3$ PARTICLE SIZE VIA CARBONATION METHOD

Renny Febrida[*,,***], Yanwar Faza[*,**,***]**

[*]Departement of Dental Materials, FKG Universitas Padjadjaran
[**]Oral Biomaterials Study Center, FKG Universitas Padjadjaran
[**]Functional Nano Powder University Centre of Excellence, Universitas Padjadjaran
e-mail: (yanwar.faza@unpad.ac.id)

KEYWORDS

$CaCO_3$, concentration, carbonation duration, particle size, pH

ABSTRACT

Introduction: *There are multiple techniques for generating $CaCO_3$, one of which is the carbonation method. Currently, the particle size of $CaCO_3$ is primarily determined by the combined influence of various variables.* ***Aims:*** *This study investigates the effect of precursor concentrations, pH of the solution, and carbonation duration on the size of $CaCO_3$ particles.* ***Methods:*** *The type of research in this study is experimental laboratory with a descriptive presentation of data. This study is divided into two stages: first, synthesis of $CaCO_3$ with different concentration of precursors and carbonation duration. Second, the use of different pH value of the solution and carbonation duration. The particle size of $CaCO_3$ were characterized using the Particle Size Analyzer (PSA).* ***Result:*** *The smallest $CaCO_3$ at first stage, 548 nm, obtained at concentration of 0.75 M with carbonation duration of 30 minutes. The largest $CaCO_3$-size, 6194 nm, is seen at a 0.5 M concentration with a carbonation duration of 10 minutes. The second stage show the smallest particle size, 1165 nm, obtained at a pH value of 8 with a carbonation duration of 60 minutes. Meanwhile, the largest size, 5621 nm, is obtaining at a pH value of 9 with a carbonation duration of 90 minutes* ***Conclusion:*** *The concentration of precursors and the duration of carbonation have no effect on the size of $CaCO_3$ particles, however the pH value of the solution may affect the particle size of $CaCO_3$. It is directly proportional to the pH value of the solution.*

INTRODUCTION

Calcium carbonate is a biomineral that can be synthesized by living organisms.[1–3] It is a crucial constituent of mineralized tissues, such as bone and teeth. Because of its biocompatibility, non-toxic qualities, and other functional features, it was commonly employed in the medical industry for purposes such as drug delivery and tissue engineering.[4–6]

Calcium carbonate ($CaCO_3$) generates solid deposits from a liquid solution, resulting in three forms (calcite, aragonite, and vaterite), two forms with water molecules attached (hexahydrate and monohydrate), and a form without a defined structure.[7–9] Vaterite particles, which are a type of polymorph, are widely utilized in various applications because they have a higher solubility in water and possess unique mechanical,

physical, and chemical properties. Additionally, they have minimal toxicity and are biologically inert.[4,10,11]

The utilization of $CaCO_3$ particles primarily relies on a multitude of precisely determined factors, including average particle size, particle size distribution, shape, polymorphism, and chemical purity. The precise fabrication of $CaCO_3$ with desired size, shape, and crystallographic structure has attracted significant interest due to its potential utilization in dentistry.[4,12]

Particle size is a crucial element. The technique, which involves investigating the concentration of precursor, pH of the solution, reaction temperature and the addition of certain additives to regulate the formation, development, and arrangement of inorganic crystals, has been extensively utilized for the production of $CaCO_3$ with adjustable crystallographic structure.[12–14]

There are multiple techniques for generating $CaCO_3$, one of which is the carbonation method. $CaCO_3$ has been effectively produced by researchers using the carbonation method. The carbonation process is mostly utilized due to its affordability, straightforward methodology, increased productivity, and enhanced purity. The carbonation process progresses through the stages of solid, liquid, and gas.[15,16] Nevertheless, there is a limited availability of studies examining the effect of carbonation duration on the formation of $CaCO_3$.

We propose that the size of $CaCO_3$ particles is primarily determined by the combined influence of various variables. The study investigates the effect of precursor concentrations, pH of the solution, and carbonation duration on the size of $CaCO_3$ particles.

METHODS

The type of research in this study is experimental laboratory with a descriptive presentation of data. The research was conducted in January – February 2024 at the Nano Technology Laboratory Finder-U CoE, Universitas Padjadjaran. Materials used in this study include calcium hydroxide ($Ca(OH)_2$) as a precursor obtained from Merck with CAS Number: 1305-62-0, Aquadest as a solvent obtaining from a local chemical store, and pure carbon dioxide (CO_2) as the source of carbonate ions from Samator Indo Gas, Ciroyom, Indonesia. The particle size and distribution of the $Ca(OH)_2$ are shown in table 1.

Table 1. size and particle distribution characteristics of $Ca(OH)_2$

Sample	Mean Size (nm)	Standard Deviation (nm)	Distribution form
$Ca(OH)_2$	2616.7	892.7	Polydisperse

Calcium carbonate particles are synthesized via carbonation methods using three variables: precursor concentration, pH of the solution and carbonation duration. The study is divided into two stages: first, synthesis of $CaCO_3$ with different concentration of

precursors and the duration of carbonation. Second, it used the different pH value of the solution and the duration of carbonation.

The first stage research procedure begins with dissolving $Ca(OH)_2$ powder at a concentration of 0.25, 0.50, 0.75, 1.25 M in 2000 ml of aquades solvent. The solution is then mixed with a magnetic stirrer for 60 minutes. Then, adjust the temperature to 20 ± 3 °C by placing ice around the chemical glass. Subsequently, the carbonation process is carried out using a fine bubble diffuser (300 rpm; 1 L/min; 20± 3°) with a carbonation duration of 5, 10, 30, 60, 90 and 120 minutes. After the carbonization process is completed, the suspension is then aged for 24 hours. The result is filtered and dried in the oven at 40 °C until calcium carbonate powder is obtained.

The second stage research procedure is performed by dissolving $Ca(OH)_2$ powder at a concentration of 0.25 M into 2000 ml of aquadest solvent. At this stage the pH is adjusted until the pH values of 8, 9 and 10 are obtained by adding NaOH. The next procedure at the second stage is similar to the first stage. The particle size of the calcium carbonate powder obtained in the first and second stages were characterized using the Particle Size Analyzer (PSA) (Horiba Scientific SZ-100 Nanopartica).

RESULTS

Particle size results, at first stage, are shown in Figure 1. It shows the smallest $CaCO_3$ size, 548 nm, obtained at a concentration of 0.75 M with a carbonation duration of 30 minutes. The largest CaCO3-size, 6194 nm, is seen at a 0.5 M concentration with a carbonation time of 10 minutes.

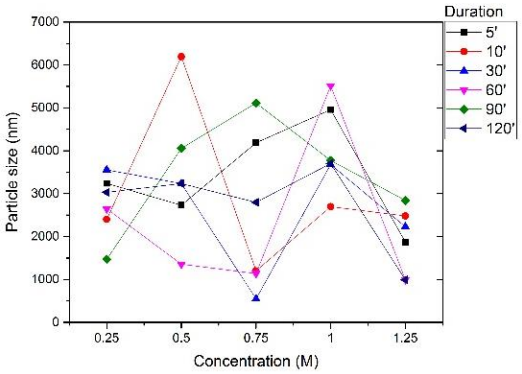

Figure 1. $CaCO_3$ particle size at first stage with $Ca(OH)_2$ precursor concentration and CO_2 carbonation duration variables

The $CaCO_3$ particle size of the second stage is shown in Figure 2. It shows the smallest particle size of $CaCO_3$, 1165 nm, obtained at a pH value of 8 with a carbonation duration of 60 minutes. Meanwhile, the greatest size of $CaCO_3$, 5621 nm, is obtaining at a pH value of 9 with a carbonation duration of 90 minutes.

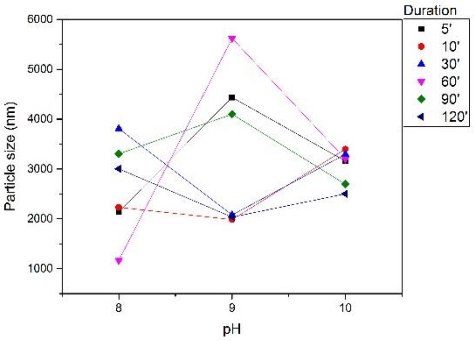

Figure 2. $CaCO_3$ particle measurement in the second stage with variables of pH values and carbonation duration

DISCUSSION

The synthesis of $CaCO_3$ starts with the hydrolysis of the $Ca(OH)_2$ precursor by water, resulting in the formation of Ca^{2+} and OH^- ions, as shown in Equation 1. During the carbonation process, when CO^2 is used, the OH^- ion will undergo a reaction with CO^{2-} to generate the HCO^{3-} compound (Equation 2). A sufficient quantity of OH- ions will persistently react with the HCO_3 molecule, resulting in the formation of the CO_3^{2-} ion (Equation 3). During the last phase, the Ca^{2+} ion will undergo a chemical reaction with the CO_3^{2-} ion, resulting in the formation of the molecule $CaCO_3$ (Equation 4).[1,5,17,18]

$$Ca(OH)_2 \rightarrow Ca^{2+} + OH^- \quad (1)$$

$$CO_2 + OH^- \leftrightarrow HCO^{3-} \quad (2)$$

$$HCO^{3-} + OH^- \leftrightarrow CO_3^{2-} \quad (3)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \quad (4)$$

Figure 1, first stage, demonstrates that the size of $CaCO_3$ is more uniform at concentrations of 0.25 and 1.25 M, regardless of the duration of carbonation. At this particular concentration, the particle size of $CaCO_3$ is generally homogen. However, at concentrations of 0.5, 0.75, and 1 M, it results in an uneven or inconsistent particle size. The smallest size is achieved at a concentration of 0.75 M with a carbonation duration of 30 minutes. However, when the concentration remains the same but the carbonation duration is increased to 90 minutes, the particle size increases to 5111 nm. The maximum particle size was achieved when the concentration was 0.5 M and the carbonation duration lasted for 10 minutes.

Currently, there is no clear pattern observed in the relationship between the change in concentration and duration of carbonation and the size of the $CaCO_3$ particle. However, the authors hypothesize that this lack of pattern may be attributed to the varying saturation values of the OH^- and CO_2 ions, which serve as the nucleus for the growth of $CaCO_3$.[1] These saturation values change each time the concentration and carbonation duration are changed.

Figure 2 shows the size of the $CaCO_3$ particle (second stage) increasing as the pH value increases. This is supposed to be due to an increase in the amount of OH^- ions that become the nucleus of the particle growth so that it tends to increase the Particle size of $CaCO_3$.[1,4] When compared to the first phase particle size (neutral pH: 7), the second phase is larger. It can be stated that the size of the $CaCO_3$ particle increases as the pH value and the amount of OH^- ions increase.

CONCLUSION

The concentration of precursors and the duration of carbonation have no effect on the size of $CaCO_3$ particles, however the pH value of the solution can affect the particle size of $CaCO_3$. This effect is directly proportional to the pH value of the solution.

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