

Article

Synthesis and Modification of Nano-Precipitated Calcium Carbonate (PCC) with Addition of Ethylene Glycol

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Abstract

ZA fertilizer waste (Ammonium sulfate) is waste generated from the industrial process of producing ZA fertilizer. The waste contains very high calcium and has the potential to be used as a raw material in the manufacture of Precipitated Calcium Carbonate (PCC). PCC with certain qualities can be developed in the field of advanced materials, with size modification into nanoparticles. One method to produce nanoparticles is using the coprecipitation method, with the help of a polymer solution. This study aims to produce Nano-PCC by finding the best conditions of CaCl₂: Ethylene Glycol mole ratio and stirring speed. Nano-PCC is synthesized by reacting fertilizer waste with HCl to form a CaCl₂ solution. Then, the solution is mixed with ethylene glycol to prevent particle agglomeration so that the size obtained will be smaller. The mixture is then reacted with Na₂CO₃ to form precipitated calcium carbonate (PCC). In this study, the variables were the mole ratio of CaCl₂: ethylene glycol (1:12, 1:14, 1:18, 1:20) and stirring speed (350, 500, 650, 800, and 950 rpm). Based on PSA analysis, the Nano-PCC obtained at the smallest CaCl₂: ethylene glycol ratio 1:12, stirring speed 950 rpm was 51.83 nm. Based on Scherrer's calculations with XRD, the particle size obtained was 48.25 nm. SEM analysis showed that the crystals formed were dominated by vaterite crystals, with a size range of 55.71-607.79 nm.

Keywords: ZA fertilize waste, Nano Precipitated Calcium Carbonate (PCC), Coprecipitation, Ethylene Glycol

1. Introduction

ZA fertilizer waste (Ammonium Sulfate) is waste generated from the industrial process of producing ZA fertilizer. The amount of ZA fertilizer waste increases along with the increase in ZA fertilizer production in Indonesia. From several studies, ZA waste produced is known to contain high calcium, amounting to 92.52%. Therefore, ZA fertilizer waste has the potential as raw material for Precipitated Calcium Carbonate (PCC) manufacture.

Precipitated Calcium Carbonate (PCC) is a widely studied material. The versatility and design of CaCO₃ particles have aroused considerable

interest in both the scientist and the industrial community due to their wide field of applications and biocompatibility. PCC is widely used as filler in paints, pigments, plastics, fibres and cement, according to its characteristics, such as morphology and size [1].

PCC has been widely used in various fields of health, food, and industry. Generally, PCC has a particle size from 0.1 to 3 μm. PCC with certain qualities can be developed as an advanced material, by turning it into nanoparticles. The synthesis of nanoparticles can change the properties and functions of a material. The research of [2] stated that the addition of Nano PCC can increase the tensile strength and

resilience of a composite. Research by [3] states that the use of nano PCC in the manufacture of PVC is proven to increase hardness, density, tensile strength, resistance to heat, and temperature onset, but decrease elongation at break.

Synthesis of nanoparticles can be processed by the coprecipitation method. The coprecipitation method is a bottom-up synthesis method that can be used in the manufacture of nanoparticles.

Various ways to control the morphology, structure, and size of nano PCC have been developed, one of which is by using organic compounds, such as surfactants and polymers. Surfactants and polymers can control the size and morphology of PCC by preventing particle agglomeration [4]. One of the polymers that can be used is ethylene glycol. The ethylene glycol molecule is small and can form network hydrogen bonds similar in nature to water, but differ greatly in structural details. Ethylene glycol also has a fairly high cohesive energy and dielectric constant [5].

In the research of [6] have conducted research on the synthesis of Nano CaO using several polymer solutions such as water, PEG 400, ethylene glycol, diethylene glycol, and glycerol, the smallest size obtained using ethylene glycol is 67.59 nm. Based on the research of [7] on the synthesis of CaCO₃ with the addition of PEG 1:16 and stirring for 12 hours at room temperature was able to reduce the particle size to 15 nm. The study showed that the greater the polymer concentration, the smaller the particle size.

In shortening the synthesis time, it can be done by using a higher variation of stirring speed. [8] stated that the higher the stirring speed, the smaller the particle size. This is because collisions between particles will often occur so that the agglomeration process will be avoided. If the agglomeration process can be avoided or stopped, the particle size can be maintained at the nanometer scale.

This study aims to find the best polymer concentration and stirring speed that can produce nano PCC.

2. Material and Method

2.1. Material

In this research, the main raw material is ZA fertilizer waste obtained from PT. Petrokimia Gresik.

2.1.1. Equipment

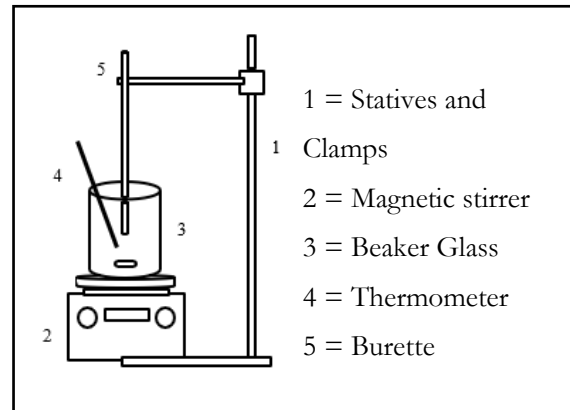


Fig. 1. The equipment of Nano-PCC synthesis

2.1.2. Nano-PCC Synthesis

ZA fertilizer waste was reacted with 2M HCl for 30 minutes. After filtering, the filtrate CaCl₂ was mixed with ethylene glycol with a mole ratio 1:12, 1:14, 1:16, 1:18, and 1:20 for 8 hours and stirring speed 350, 500, 650, 800, and 950 rpm. Subsequently, the pH was adjusted to 7.5 using NaOH. Then a precipitation process was carried out to obtain PCC by adding 1.5 M Na₂CO₃. The precipitate was allowed to stand for 12 hours and then dried in an oven to remove other substances and other solvents. The nano-PCC will be analyzed using Particle Size Analyzer (PSA), X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM).

3. Results and Discussion

PCC is a modern paper and plastic industry. [9] reports the effect of various organic and inorganic additives used in the synthesis of the different polymorph of calcium carbonate. The use of precipitated calcium carbonate fillers is the recommended choice in enhancing optical properties, durability, smoothness and ink adsorption in papermaking and improving the mechanical properties of plastic. PCC can best be synthesized using solid-liquid route or the gas-solid-liquid carbonation route, which consists of bubbling gaseous CO₂ through a concentrated calcium hydroxide (Ca(OH)₂) and/or calcium magnesium hydroxide (CaMg(OH)₂) slurry with suitable organic additives.

3.1 PSA Analysis (Particle Size Analyzer)

In the research of the synthesis and modification on nano-PCC particle size from ZA fertilizer industry waste using a polymer solution, with the variable mole ratio of CaCl_2 : ethylene glycol and stirring speed, the results of PSA (Particle Size Analyzer) analysis were obtained as shown in Figure 2.

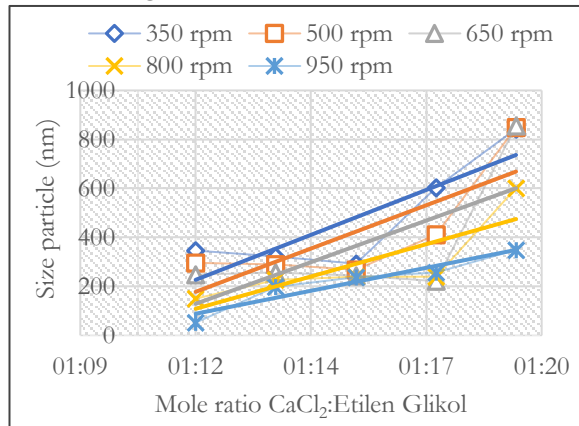


Fig. 2. Effect of CaCl_2 : ethylene glycol mole ratio on nanoparticle size at various stirring

Figure 2 shows that the higher the ethylene glycol concentration, the larger the particle size of the PCC produced will also tend to be. The higher the stirring speed, the smaller the PCC particle size. These results are not under the research of [6] which states that the higher the polymer concentration, obtained smaller the particle size.

In the study of [7] using PEG polymer with mole ratios of 1:4, 1:8, 1:12, and 1:16 the sizes were 39, 30, 21, and 15 nm. While in this study using ethylene glycol polymer at a stirring speed of 950 rpm, the smallest size was obtained with a mole ratio of CaCl_2 : ethylene glycol 1:12, 1:14, 1:16, 1:18, and 1:20, the sizes were 51.83, 198.4, 237.7, 256.4, and 348.7 nm. It can be seen that the use of different types of polymer can also affect particle size. PEG polymer requires a high concentration to get a small particle size, while ethylene glycol requires a concentration that is not too high or tends to be lower. According to the research of [10], stated that the formation of nanoparticles is only possible in certain ratios between polymers and crosslinkers (CaCl_2). Too high a polymer concentration maybe also not be good for forming nanoparticles. The higher the polymer concentration, the higher the particle viscosity. This can make the particles stick together, causing agglomeration and larger particle size [11]. In addition, ethylene glycol has a fairly high cohesive energy and dielectric constant [5], so

that with high cohesive energy and dielectric constant, the electrostatic force on the bound ions is greater, this causes aggregation of PCC particles which causes If the concentration is too high, the particle size obtained will be even greater.

Figure 2 shows that at a stirring speed of 350 to 950 rpm, the particle size decreased in all variables. It is because, with increasing stirring speed, the intensity of the molecules colliding with each other will occur more often to prevent particle agglomeration. The length of the stirring time also affects the particle size, because as the stirring time increases, the smaller the particle size obtained. This is due to the increasing number of particles that are split into nano-sized particles.

In this study, the best PCC nanoparticle size was obtained at a mole ratio of CaCl_2 : Ethylene glycol 1:12 and stirring speed 950 rpm is 51.83 nm, with a yield is 70.1117%. The result of the PSA analysis is shown in Figure 3.

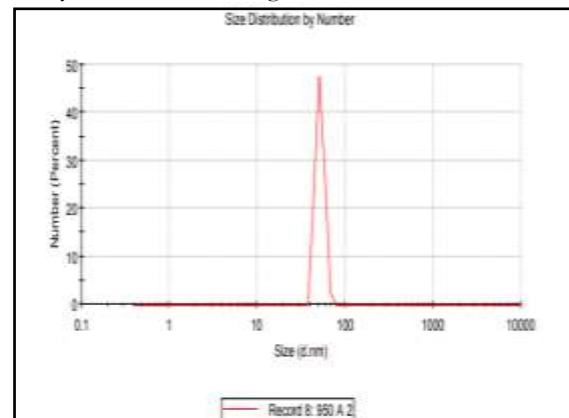


Fig. 3. PSA analysis of nano-PCC at the ratio of moles of CaCl_2 : ethylene glycol 1:12 and stirring speed 950 rpm

3.2 X-Ray Diffraction (XRD) Analysis

XRD analysis is used to determine the structure and size of the crystals contained in the product. XRD analysis on the best result of nano-PCC is at a size 51.83 nm. The result of the XRD analysis are shown in Figure 4

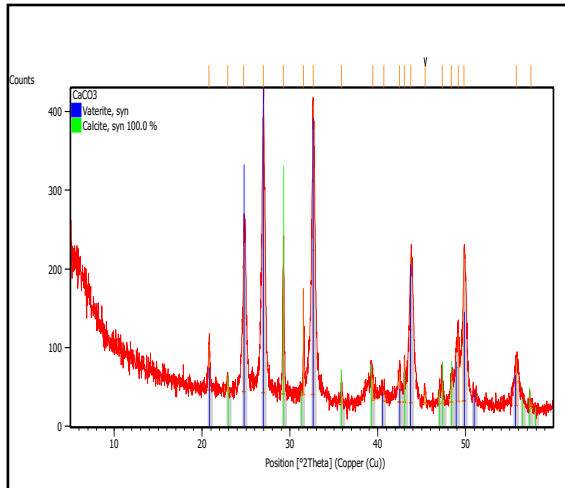


Fig. 4. XRD analysis of nano-PCC at the ratio of moles of CaCl_2 : ethylene glycol 1:12 and stirring speed 950 rpm

Based on Figure 4, it can be seen that the types of crystals formed are vaterite with a hexagonal morphology and calcite with a rhombohedral morphology. From Figure 4, it can be seen that the vaterite dominates about 93.7% and calcite by 6.3%. From the XRD characterization data, the crystal size can be estimated using the formula of the Scherrer equation.

$$D = \frac{K\lambda}{\beta \cos(\theta)} \quad (1)$$

Using equation (1), the crystal size can be calculated and obtained $D = 48.25$ nm. The results of calculations using the Scherrer method are not much different from the results of PSA analysis, which is around 51.83 nm. So, it can be concluded that the particle size obtained is appropriate in the nanoparticle size range of 1-100 nm.

3.3 Scanning Electron Microscopy (SEM) Analysis

SEM analysis aims to determine the shape and uniformity of the crystals of nano-PCC and their size. SEM analysis is shown in Figure 5.

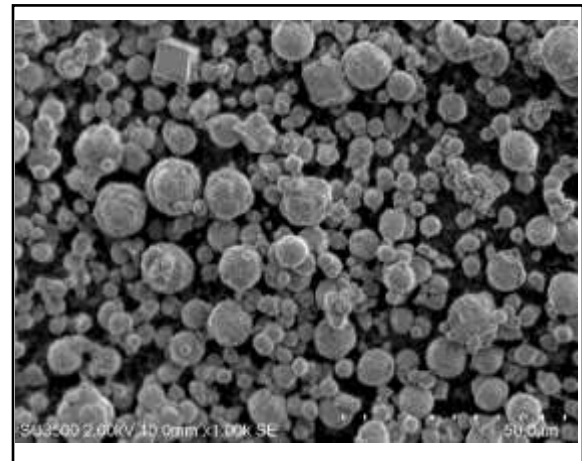


Fig. 5. SEM analysis of nano-PCC at the ratio of moles of CaCl_2 : ethylene glycol 1:12 and stirring speed 950 rpm

Based on the results of the SEM analysis in Figure 5, shows that the crystals formed are dominated by vaterite crystals because vaterite crystals have a hexagonal crystal system, where these crystals tend to be spherical. In addition to vaterite, there are small amounts of calcite crystals, this can happen because of the metasable nature of vaterite crystals where when vaterite crystals are exposed to water and at low temperatures, they can change shape into calcite crystals. Meanwhile, at high temperatures, vaterite crystals will turn into aragonite crystals.

In the research of [12], it was stated that the formation of the vaterite phase was influenced by many parameters, such as pH, temperature, and reactant concentration. It was also explained that vaterite forms calcite crystals for several hours and aragonite forms calcite forms several months at room temperature. Higher temperatures speed up the transformation. Vaterite can be transformed into calcite by solvent mediation [13]. The results of the SEM analysis are by the previous XRD results, vaterite crystals equally dominate in the product.

The results of the particle size range from the SEM analysis are shown in Figure 6.

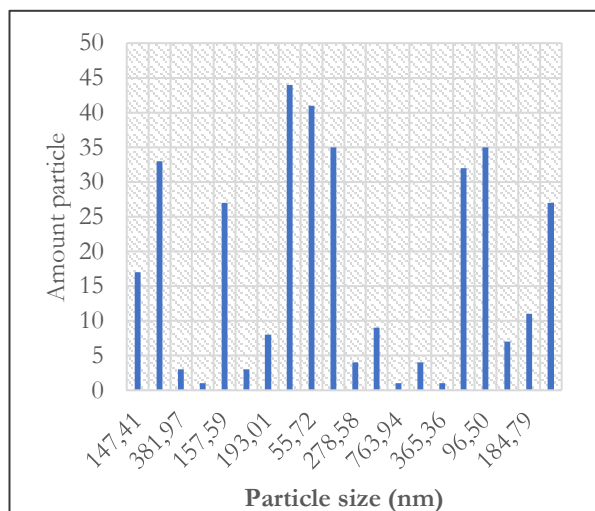


Fig. 6. Particle size Range of SEM analysis

Based on the analysis, the particle size ranged from 55.71 to 607.79 nm. From Figures 5 and 6, it is explained that the existence of non-uniformity of crystals shape and particle size is due to the crystal transformation that occurs and also the did not have pretreatment of raw materials such as milling and screening. So to get uniform results can not be achieved. It is known that the smallest size is 55.71 nm and the largest size is 78.79 nm. These results are almost the same as the previous two analyzes using PSA and XRD, wherewith PSA the particle size was 51.83 and with XRD was 48.25 nm.

In the [14] Carbonation was achieved by CO₂ bubbling and aqueous sodium carbonate addition. Precipitation was performed under different pH values of 7.5, 10.5 and 12.5 in the absence of an anionic surfactant and in the template of sodium dodecyl sulfate (SDS)/calcium-sucrate at pH 12.5. It was found that CO₂ bubbling slightly promotes smaller particles. The anionic surfactant enables particle size and agglomeration reduction while introducing some hydrophobicity. The smallest particles were achieved at a range of 40–55 nm in the presence of SDS/sucrose template and were of spherical morphology.

4. Conclusions

In this study, from the results obtained, it can be concluded that the larger the mole ratio of CaCl₂: ethylene glycol, the larger the PCC nanoparticle size will be. The higher the stirring speed, the smaller the particle size obtained. Nano-PCC synthesis can be carried out by adding ethylene glycol polymer. The best results were

obtained at a mole ratio of CaCl₂: ethylene glycol 1:12, with stirring speed 950 rpm to produce a nano-PCC size on PSA analysis of 51.83 nm and using Scherrer equation is 48.25 nm. The yield obtained is 70.1117%. For further research, it is recommended to do pretreatment on raw materials and use a smaller variable mole ratio of CaCl₂: ethylene glycol.

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