Fabrication of Nano-Calcium Carbonate Precipitate by Ultrasonic Milling Technique using Ethylene Glycol Media

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Abstract, Calcium Carbonate Precipitate is one of the filler ingredients which have the advantage of being neutral to all materials, light and harmless. Along with the widespread use of composite materials, it is necessary to develop smaller size nano calcium carbonate materials having nano-size properties that are superior to ordinary calcium carbonate precipitates. The purpose of this study is to obtain nano-carbonate precipitate materials with the particle size below 100 nm. In this study, the method used is starting from the preparation of calcium carbonate precipitate through a carbonation process, and then an ultrasonic milling process with ethylene glycol media is carried out. The process step is calcination, then the slaking process with water and then the carbonation process using carbon dioxide gas. Variables in the process of making calcium carbonate precipitates were not carried out, whereas in the ultrasonic milling process the variables in the process were ultrasonic time and the use of amplitude. The results of the experiment are then analysed by testing the sediment rate to obtain optimal grain size results, then the PSA Nano analysis in wet conditions and SEM analysis after the product is dried. The experimental results showed that the optimum yield of calcium carbonate precipitate granules with a size of 64 nm at 20 minutes of the ultrasonic time and the use of waves with an amplitude of 30%.

1. Introduction
Ethylene Glycol is one of the alcohol compounds that has more than one branch chain, so that it can form more than one (OH) group. With a number of more than one chain, ethylene glycol is easier to bind tightly to suspended particles in it so that it is easier to be attacked using microbubble due to ultrasonic wave effect. This can be proven from the results of research on the manufacture of ZnO nanoparticles which are capable of producing particle sizes below 100 nm [1]. Besides that, the use of ethylene glycol is also effective for the manufacture of other oxide materials such as TiO₂ [1]. As ultrasonic media, ethylene glycol has the advantage of having a very high boiling point of 197.3 °C. The boiling point is very beneficial in terms of resistance to microbubble attack caused by ultrasonic waves, able to increase the solvent temperature by more than 100 °C. However, the use of ethylene glycol media has the disadvantage of not being suitable for particles that cannot bear at high temperatures during the process of separating particles with ethylene glycol after treatment with ultrasonic waves [2].
The material to be processed into nano-size particles in this experiment is calcium carbonate which results from the process of re-precipitation of calcium hydroxide with carbon dioxide gas. The result of this deposition process is an amorphous calcium carbonate known as Light Calcium Carbonate Precipitate, which has a lighter density than calcium carbonate in the form of Aragonite Crystals and calcite [3]. Calcite and Aragonite are the two main constituents of CaCO₃, which are known to be very easy to form in large quantities in nature both biologically and with technology. Interactions that occur between CaO-CO₂-H₂O systems have been studied in several researches. Several theories have succeeded in developing the core of carbonate and the complex model of the surface has been successfully applied to the dissolution and precipitation of CaCO₃ in solution with free of Magnesium [4]. Natural calcite rocks are minerals formed through crystallization in shallow sea areas. Calcite belong to the carbonate group with the same chemical composition, namely carbonate (CaCO₃), but sometimes these minerals also compose rocks that have different compositions [5]. Limestone (CaCO₃) is one of the many industrial minerals that are needed and used directly or indirectly. Direct use of limestone, for example, is in the industries of cement and sugar, ceramics, ingredients added to the smelter process and building materials, while the indirect use of limestone is still needs to be processed in advance into light calcium carbonate or quicklime (CaO). Light calcium carbonate and quicklime or burning lime are as much needed for the needs of the paint industries, toothpaste, paper bleach, cosmetics, soil neutralization, building materials and others [6]. In this study, the process of making Light Calcium Carbonate Precipitate from limestone originating from Klaten, Central Java was carried out. The raw material is then dissolved in ethylene Glycol as a media and given ultrasonic waves. In this experiment, the experimental variables used were ultrasonic time and ultrasonic wave amplitude in ethylene glycol media.

The calcium carbonate precipitated by mechanical stirring had a particle size of about 20 μm. By contrast, the particle size of vaterite formed under ultrasonic irradiation was about 2 μm, with a specific surface area of 25-30 m²/g. The major polymorph of calcium carbonate formed by ultrasonic irradiation was vaterite with some calcite present. For 40 kHz ultrasonic irradiation, the specific surface area of the calcium carbonate increased with increasing amplitude. The particle size of vaterite formed at this frequency was about 2 μm, and its distribution was sharper than that obtained at 20 kHz. The mode diameter of the synthesized vaterite was found to decrease with increasing amplitude at 40 kHz [7].

The de-agglomeration and charge nullification were achieved using surface modification of CaCO₃ nanoparticles using triethoxy vinyl silane (TEVS) under ultrasound environment. The size of unmodified and modified CaCO₃ was found to be ≈ 50-80 and 50-90 nm, respectively, with square crystal structure morphology [8].

The result shows that calcium carbonate nano particles fulfill the requirements of calcium carbonate nano material with averages of the particle size obtained from PSA analysis is 109 nm, with the number of particles has reached 90.7% in a particle size range of 60 to 100 nm. From XRD analysis, the crystal structure of calcium carbonate nano particles suits very well with calcite pattern [9]. The characterization using XRF showed that CaO content of precipitated calcium carbonate from natural limestone Sukabumi had high purity of 99.16%. The particle distribution using scanning electron microscope (SEM) showed that precipitated calcium carbonate from natural limestone Sukabumi revealed 1.79-11.46 μm, meanwhile the particle distribution of precipitated calcium carbonate Merck showed larger particles with the size of 3.22-10.68 μm [10].

2. Experimental
2.1. Materials used in the experiments
2.1.1. Natural Materials
The ultrasonic process in this study was to use calcium carbonate precipitates obtained from the calcination of limestone at a temperature of 900 °C for approximately six hours in a size of approximately 1 cm. In the calcination process, 5,000 g of limestone in the form of calcium carbonate in Calcite form experienced the release of carbon dioxide gas to form 2,600 g of calcium oxide. Furthermore, calcined limestone was ground and continued with the slaking process which is mixing
as much as 2,500 g of calcined limestone with 3,000 mL of distilled water and stirring for 4 hours. In this process, there is a reaction forming calcium hydroxide accompanied by heat which boils the remaining water of the reaction. The next process is carbonatization, by taking 200 g of the slaking process and added 500 mL of distilled water. This process can occur by adding CO$_2$ gas to Ca(OH)$_2$ solution. The carbonatization process is carried out with pH control until the pH becomes 6. Then proceed with filtration and drying of carbonatization results with an oven at 150 °C for 1 day. The end result of the process is a mild white calcium carbonate compound known as Light Calcium Carbonate precipitate. The form of raw materials during the process can be seen in the Figure 1.

![Figure 1](image_url)  
**Figure 1.** Results of the manufacturing stage of Light Calcium Carbonate Precipitate for experimental materials: (a) calcination results, (b) slaking results, (c) carbonatization results and (d) drying results.

The results in the form of calcium carbonate precipitates are then carried out by characterization process using XRF analysis. XRF analysis results showed that light Calcium Carbonate was obtained with a high purity level of 99.16%, and only a small amount of phosphorus and sulfur impurities.

| Component | Limestone (\%w) | Process result (\%w) | Comparison with Merck (\%w) |
|-----------|----------------|----------------------|-----------------------------|
| CaO       | 90.93          | 99.16                | 99.40                       |
| MgO       | 6.54           | Nd                   | Nd                          |
| SiO$_2$   | 0.74           | Nd                   | Nd                          |
| Al$_2$O$_3$ | 0.47        | Nd                   | Nd                          |
| P$_2$O$_5$ | 0.27          | 0.14                 | Nd                          |
| SO$_3$    | 0.05           | 0.14                 | 0.16                        |
| Fe$_2$O$_3$ | 0.71         | Nd                   | Nd                          |

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### 2.1.2. Commercial Materials

In this experiment in addition to materials derived from nature calcium carbonate as the row material for the process used materials derived from commercial purchases. These materials include Ethylene Glycol with Merck’s Pro Analysis specifications with catalog number: 1.09621.2500, aquadest form the ion exchange process and Filter paper Whatman Catalog number 42, 150 mm diameters.
2.2. Analysis Instrument
In this experiment, the analysis of the experimental results was carried out in stages where the first step was observed by sedimentation test by looking at the deposition velocity of calcium carbonate in ethylene glycol media before and after the ultrasonic process was carried out. The second stage is testing particle distribution using PSA Nano equipment from Beckman Coulter with Delsa Nano C 812 type. The results of PSA Nano analysis are then compared with visual testing with SEM using SEM equipment from JEOL with Type JSM-639OA.

2.3. Experiment
In this experiment the process of reducing the size of calcium carbonate precipitates was reduced from the carbonatation process of limestone from Bayat, Klaten Region, Central Java. So that the process of reducing the size of the grain is obtained nano-size calcium carbonate powder. In this experiment the grain size reduction process is carried out by using ultrasonic waves in ethylene glycol media. The experiment was carried out in a 500 ml beaker glass using 10 g of calcium carbonate precipitate and a 200 mL ethylene glycol media. The experiment was carried out 10 times with variables changing ultrasonic amplitude 20%, 25%, 30%, 35% and 40%, with an ultrasonic processing time of 10 minutes and 20 minutes. The ultrasonic process is carried out in a maximum temperature range of 90 °C and without heating from outside. After administration of calcium carbonate ultrasonic waves contained in ethylene glycol media the sedimentation rate was tested by the stokes method to see the longest sediment rate. The best results from the experiments with the longest sediment rate were analyzed by analysis of nano PSA and compared with before the ultrasonic process was carried out. Samples with the best results from measurements with nano PSA were then dried so that nano-size calcium carbonate dry solids were obtained. Dry solids are then analyzed visually the granular shape and size of the granules with SEM equipment.

3. Results and Discussion
3.1. Sedimentation Rate
The results of the analysis using the Stokes Method showed that the higher the amplitude process, the sedimentation rate decreases. However, at the point of amplitude 35% shows a different tendency, where the amplitude is added, the sedimentation rate of calcium carbonate granules is higher. The effect of ultrasonic time on the process of sedimentation rate of calcium carbonate granules was seen to have the same tendency between the ultrasonic time of 10 minutes and 20 minutes. In the ultrasonic process in 20 minutes results in a precipitation rate of calcium carbonate granules longer than the ultrasonic process in 10 minutes.

From the graph above, it can be seen that the optimal process occurs at the amplitude of 30% both for ultrasonic time 10 minutes and 20 minutes. For further analysis, the PSA Nano analysis will be carried out at 30% amplitude and ultrasonic time in 10 minutes and 20 minutes.
Figure 2. The results of measurements of sedimentation rate for amplitude during the ultrasonic process in 10 minutes and 20 minutes.

3.2. PSA Nano analysis
PSA Nano analysis has been carried out on three samples, namely a sample of calcium carbonate solids dissolved in ethylene glycol without ultrasonic waves, samples given ultrasonic waves in 10 minutes and 20 minutes at 30% amplitude.

Figure 3. Results of measurements of the distribution of calcium carbonate particles before ultrasonic process using PSA Nano. The analysis conditions is in a solution with a concentration of 10 g/200 mL of ethylene glycol.
The results of the PSA nano analysis showed the distribution of particles size in the range of 170 nm to 311 nm and the highest number of particles in the range 185 nm to 212 nm as depicted in figure 3. The results of the analysis illustrate that the results of carbonatization process of limestone from Bayat area, Klaten Regency, can produce very fine precipitate calcium carbonate granules, but the particle size has not reached the nanoparticle size. For this reason, it is necessary to do an ultrasonic process so that nano-size particles can be obtained.

The measurement of grain size was performed using the PSA Nano method on the optimum ultrasonic process. The results of the experiment using the Stokes Method obtained two optimum points: at the ultrasonic process in 10 minute with 30% amplitude and the ultrasonic process in 20 minutes with 30% amplitude.

The results of PSA Nano analysis showed that the particle size distribution resulted from the ultrasonic process in 10 minutes gave a particle size range of 57 nm to 193 nm. This result indicated that the cumulative particle size below 100 nm had reached 93.7%, this can be seen in the figure 4.

![Number Distribution](image)

**Figure 4.** Results of measurements of calcium carbonate particle distribution using PSA Nano analysis after ultrasonic processin 10 minutes. The condition is in a solution with a concentration of 10 g/200 mL of ethylene glycol.

The ultrasonic process in 20 minutes gave the particle size in the range of 56 nm to 104 nm, where the cumulative particle size below 100 nm reached 99.9% as shown in figure 5. The results of the ultrasonic process with a duration of 20 minutes has produced almost perfect calcium carbonate nanoparticles, so it can be concluded that the ultrasonic process with 30% amplitude and 20 minutes of ultrasonic time can convert calcium carbonate material into nano calcium carbonate precipitate.
Figure 5. Results of measurements of calcium carbonate particle distribution using PSA Nano analysis after ultrasonic process in 20 minutes. The condition is in a solution with a concentration of 10 g/200 mL of ethylene glycol.

3.3. The result of SEM analysis of nano-calcium carbonate precipitate
After analyzing using PSA Nano, the next step is to visually see calcium carbonate particles using the SEM method. Unlike the PSA analysis, where the PSA analysis the sample does not go through the drying process, it is immediately analyzed in the solution. While in the SEM analysis, sample must go through the drying process first. The results of SEM analysis on calcium carbonate samples without ultrasonic process are depicted in Figure 6.

Figure 6. SEM Analysis result of calcium carbonate precipitate before ultrasonic process where (left) magnification 20,000 times and (right) magnification 40,000 times.
From the results of SEM analysis, it can be seen that in the sample with a magnification of 20,000 times and a magnification of 40,000 times, there are several particles with sizes below 100 nm but they are mainly have the particles size above of 100 nm. It match with the result of the PSA analysis, that the size of the granules in the raw material is not nano-sized, where the particle size is in the range of 170 nm to 311 nm. By looking at the grain shape, it appears that the shape of the grain is irregular but shows a rectangular shape, which gives an indication of calcite compounds.

SEM analysis measurements with a magnification of 40,000 times for the samples with ultrasonic process at 30% amplitude in 10 minutes and 20 minutes show the results of the average grain size are smaller than without ultrasonic process as shown in figure 8.

![SEM Analysis result of calcium carbonate precipitate after ultrasonic process with magnification 40,000 times, (left) 10 minutes, and (right) 20 minutes.](image)

From figure 7, it shows that the ultrasonic process for 20 minutes give better result than the 10 minute ultrasonic process. Based on SEM images, it can be seen that the size of the granules in the ultrasonic process of 10 minutes is between 82 nm to 140 nm with an average size of 112 nm. Whereas in the ultrasound 20 minutes the grain size is between 79 and 114 with an average of 93 nm.

This is different from the PSA analysis which show the particle size of 57 nm to 193 nm and particles size below 100 nm has reached 93.7%. For the ultrasonic process in 20 minutes shows that there are 5 points of particles size below 100 nm and there are only 3 points above 100 nm. This is different from the PSA analysis which shows 99.9% nano-sized particles. The reason is that there is a coagulation process in drying process with ethylene glycol media. Another possibility is that there is also a little residual of ethylene glycol in the particle. This can be seen from the crystalline image which shows accumulate large grains. Qualitatively, the measurement of particle size by SEM analysis shows the tendency of reduction for the particle size of the samples when it is subjected to ultrasonic waves. Secondly there is a tendency to reduce grain size with the longer use of ultrasonic waves.

4. Conclusion

Qualitative measurement results with the Stoke method show that the optimum point of the ultrasonic process is at 30% amplitude, with a duration of 10 minutes and 20 minutes. The results of measurements with PSA nano at the optimum point show calcium carbonate precipitate in nano size as much as 93.7% for 10 minutes of ultrasonic process and 99.9% in 20 minutes of ultrasonic process. Analysis with SEM qualitatively showed that there is a tendency to reduce particle size by giving ultrasonic waves and in 20 minutes better than 10 minutes. During the drying process, the separation of ethylene glycol media with calcium carbonate precipitate results in a coagulation process which disrupts the observation process with SEM.
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