IOP Conf. Series: Materials Science and Engineering **333** (2018) 012043 doi:10.1088/1757-899X/333/1/012043

Synthesis of Calcite Nano Particles from Natural Limestone assisted with Ultrasonic Technique

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Abstract. This article represents a precipitation method assisted with ultrasonic process to synthesize precipitated calcium carbonate nano particles from natural limestone. The synthesis of nanoparticles material of precipitated calcium carbonate from commercial calcium carbonate was done for comparison. The process was performed using ultrasonic waves at optimum condition, that is, at temperature of 80oC for 10 minutes with various amplitudes. Synthesized precipitated calcium carbonate nanoparticles were characterized using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM) and Particle Size Analyzer (PSA). The result of PSA measurements showed that precipitated calcium carbonate nano particles was obtained with the average size of 109 nm.

1. Introduction

Calcium carbonate ($CaCO_3$) is an inorganic compound which has been widely studied owing to its abundance in nature as a mineral and biomineral. Calcium carbonate in the form of flour with particle size in nano-scale and a very high degree of purity is an indispensable material in the industrial field. In the industrial field, calcium carbonate is utilized as raw materials for filler on paper, rubber, paint and plastic [1]. Along with technological developments, the use of calcium carbonate is not only for fillers but also for biocompatible materials. The use of calcium carbonate as a biocompatible material is as a coating material because it has the advantage that is easily adaptable in the human body [2]. Calcium carbonate particles have three molecular crystal morphologies, which are Calcite, Aragonite and Vaterite, where calcium carbonate in aragonite crystal is the best form for the coating material [3].

Nano particle material of calcium carbonate for biocompatible coating materials can be made from shellfish material using chitosan as a precursor [3]. The experiments on synthesis of calcium carbonate from the shellfish material are capable to produce calcium carbonate with aragonite crystals, but the grain size is quite large around 5.000 nm [3]. Nanoparticle material of calcium carbonate can be prepared by precipitation process which capable to make calcite nanoparticles with a particle size of 140 nm [1]. The results of another study by precipitation process using sodium silicate with sol-gel system produced calcium carbonate in the form of calcite crystals with particle size of 40 nm [4].

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In addition to precipitation methods, synthesis of calcium carbonate could be performed with carbonatation system that is by blowing carbon dioxide gas in a solution of 5% $Ca(OH)_2$. This process used ultrasonic method to control the particle size. The result obtained was nanometer-sized calcium carbonate materials with a range of 45 nm to 72 nm [5]. The process of formation of calcium carbonate nanoparticles by ultrasonic process was also conducted by using surface particle modification with the used of Trioxy Vinyl Silane (TEVS). Through this surface modification process, precipitated calcium carbonate product with nano-size of 50-90 nm was obtained [6]. Ultrasonic process is a process of destruction of particles in a medium with ultrasonic waves that produce cavitation effects [7]. The cavitation effect produces energy propagation in the form of high and low pressure effects simultaneously and repeatedly resulting in a microbubble explosion emanated in a solution with very large quantities [7]. The microbubble, if collided with particles floating in liquid media, causes the particles to break into smaller particle sizes.

In this study, ultrasonic technique was employed to synthesis calcium carbonate nano particles from natural limestone. The synthesis of calcium carbonate nano particles from natural limestone is greatly promising process to be performed because limestone has extensive industrial application and the most common natural form of calcium carbonate. In addition, generally calcium carbonate nano particles were synthesized from commercial calcium carbonate materials, synthesis of calcium carbonate nano particles from natural resources was still very few. By mastering the synthesis technology of calcium carbonate nanoparticles, this will increase the added value of natural resources significantly.

2. Experimental

2.1. Ultrasonic technique

In this research, particle destruction process was performed using ultrasonic process that is sonication equipment Q-1357. The equipment has a maximum power of 1.375 watts by working at a frequency of 20.000 Hz and amplitude with a variation of 10% to 100%. The capacity of the equipment is capable of performing an ultrasonic process of up to 20 litres of fluid in every single process. The ultrasonic equipment is equipped with a temperature gauge to control temperature process. In this research, the variable used is the amplitude associated with ultrasonic power, while the frequency and temperature are fixed. The probe is suitable for the ultrasonic process capacity of 400 ml of fluid.

2.2. Experimental procedure

The natural limestone for experiment was obtained from Cibadak, Sukabumi. Calcium carbonate solution was prepared from dissolution process of limestone with chloride acid. In this research, ultrasonic process was performed on the optimum point of measurement result of precipitation rate in previous experiment. It was known that the optimum point of measurement result for precipitation rate on the concentration of calcium chloride at 0.16 molar for natural limestone and 0.12 molar for calcium carbonate commercially available (Merck). The sonication process and the addition of sodium carbonate solution were carried out for 10 minutes. At the sonication process, the temperature was maintained with maximum $80^{O}C$. The experimental variables used in the ultrasonic process were amplitude 20%, 30%, 40%, 50% and 60%. Characterization was performed using particle size analyser (PSA) equipment to observe the particle size distribution, scanning electron microscopy (SEM) to know grain size and particle shape and also X-ray Diffraction (XRD) to know the molecular structure of calcium carbonate produced.

3. Result and Discussion

3.1. Precipitation result of calcium carbonate of natural limestone using ultrasonic process

Precipitation result using ultrasonic process was conducted with experiment variables of amplitude of 20%, 30%, 40%, 50% and 60%, and obtained the result of a fine solid of calcium

carbonate. A fine solid of calcium carbonate was then washed and dissolved in aquadest to measure precipitation rate. From the experimental results, it can be seen that with the ultrasonic process, the particle precipitation rate slows down and particle size is getting smoother and smaller. The result of precipitation rate associated with the amplitude is shown in Figure 1.

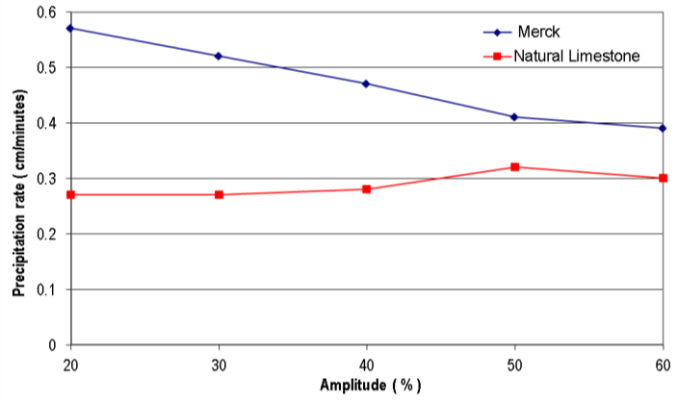


Figure 1. Graphic of correlation between amplitude of ultrasonic with the precipitation process for calcium carbonate.

It can be seen that the optimization point occurs in the ultrasonic process with 20% of amplitude for natural limestone. At amplitude above 20%, the rate of precipitation process decreases slightly, whereas the higher amplitude causes the power required to perform the ultrasonic process becomes greater. In the ultrasonic process of calcium carbonate from Merck, it is seen that the optimum point occurs at 50% of amplitude which is higher compared to the optimum point of natural limestone.

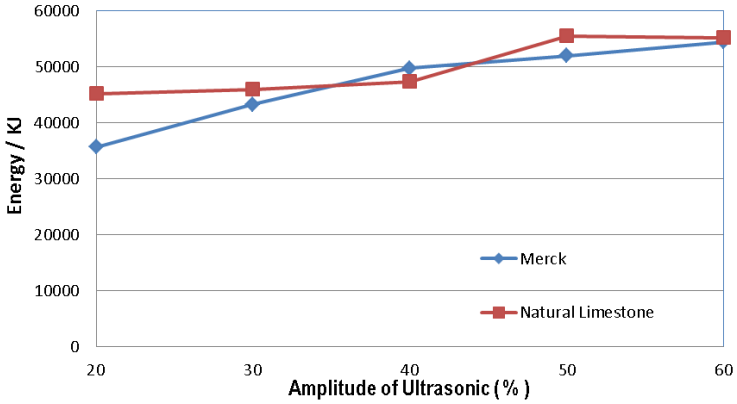
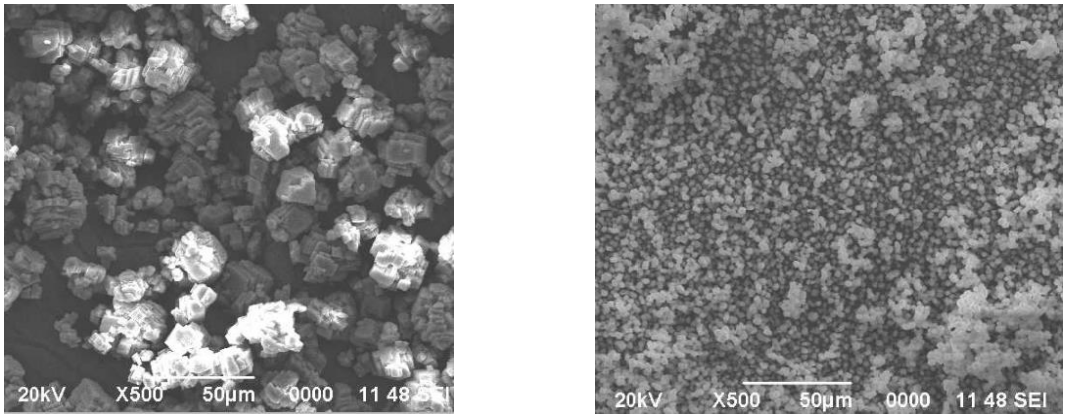


Figure 2. Graphic of correlation between amplitude with energy in ultrasonic process for calcium carbonate

Based on the calculation of energy requirements, it is seen that natural limestone need lower amplitude, this means that the energy for crushing calcium carbonate to make smaller particles is lower (Figure 2). At higher amplitude above 50%, the required energy requirement is greater for calcium carbonate from commercially available (Merck). Overall, the amount of energy required for the ultrasonic process is lower for natural limestone compared with calcium carbonate from Merck. From the calculation of precipitation rate, it is observed that optimum point of calcium carbonate is 0.16 molar with 20% of amplitude and 0.12 molar with 50% of amplitude for natural limestone and Merck, respectively.

3.2. Analysis of surface morphology of calcium carbonate using SEM

From the optimization point, the calcium carbonate solids are dried to get $CaCO_3$ powder and then the powder are filtered to separate the coagulated granules. Analysis of surface morphology of particles using SEM was conducted for calcium carbonate resulted from ultrasonic process compared with calcium carbonate without ultrasonic process. The result of SEM measurements is depicted in Figure 3 which shows that ultrasonic process produces smaller grain size.



Naturural Limestone Non Ultrasonic **Natural Limestone With Ultrasonic**

Figure 3. The result of SEM analysis comparing the grain size and surface morphology at the same magnification of 500 x .

3.3. Analysis of particle size using particle size analyzer(PSA)

Particle size distribution was measured using particle size analyser. Using this method, particle size could be measured quantitatively. We measured 4 samples for PSA analysis and then the averages were calculated. The result of the PSA measurement is depicted in Table 1

Table 1. Analysis of PSA (units are in nanomater)

Samples	**1st measurement**	**2nd measurement**	**3th measurement**	**Averages**
Natural Limestone Non Ultrasonic	989	26.049	811	9.283
Natural Limestone Ultrasonic	81	132	115	109

The result shows that $CaCO_3$ sample of natural limestone from Cibadak, Sukabumi is easier crushed into smaller particles with assisted by ultrasonic technique resulting significant decrease in particle size. It is observed that particle size $CaCO_3$ sample of natural limestone without ultrasonic showing particle size of 811 nm to 26,049 nm decreases to grain size of 81 nm to 132 nm when we employed ultrasonic process. The result of the analysis of particle distribution using PSA by taking the smallest measurement results on limestone from Cibadak, Sukabumi is shown as Figure 4.

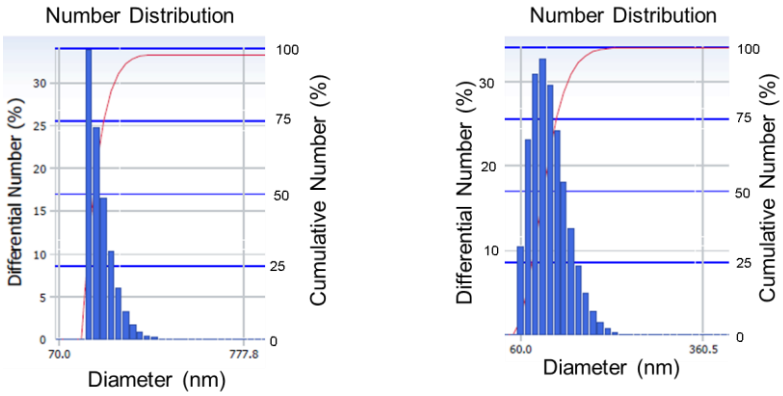


Figure 4. Analysis result of particle distribution by PSA Delsa Nano on $CaCO_3$ from Cibadak – Sukabumi without ultrasonic process (left) and with ultrasonic technique (right).

The results of the PSA analysis show that the particle distribution of precipitation process without ultrasonic method, the smallest particle size starts at 102 nm with a fraction of 33.9%, then continues with the number of fractions down to 270 nm. In the particle size with range 102 nm - 270 nm, there is a fraction count of 97.9%. There is a large grain of 2.2% with a size range between 24,933 nm to 48,933 nm. Iit can be concluded that without the ultrasonic process the resulting calcium carbonate has not qualified as a nano particle materials of $CaCO_3$.

In the precipitation process with ultrasonic technique, it is seen that the smallest fraction occurs at 60 nm with a fraction of 5.3%. Most fractions occur at 75 nm. The number of particles has reached 90.7% in a particle size range of 60 to 100 nm, and particles of a size above 100 nm are about 9.3%. Based on this PSA analysis, it is seen that the calcium carbonate particles after the ultrasonic process have particle size below 100 nm that reaches 90.7%, thus fulfilling the requirements as calcium carbonate nano particles.

3.4. Analysis of crystal structure of calcium carbonate using X-Ray diffraction (XRD)

Analysis of crystal structure using XRD of calcium carbonate nano particles obtained from HCl dissolution and precipitation process with sodium carbonate assisted by ultrasonic technique of natural limestone was conducted. Besides that, calcium carbonate from commercial was also analysed for comparison. The result of XRD analysis shows that the products of calcium carbonate gives the same result for the crystal structure as shown in Figure 5, where two compounds of $CaCO_3$ have identical peaks. This means that even though the raw materials are different but after HCl dissolution and precipitation process with sodium carbonate assisted by ultrasonic technique give the same crystal structure of $CaCO_3$.

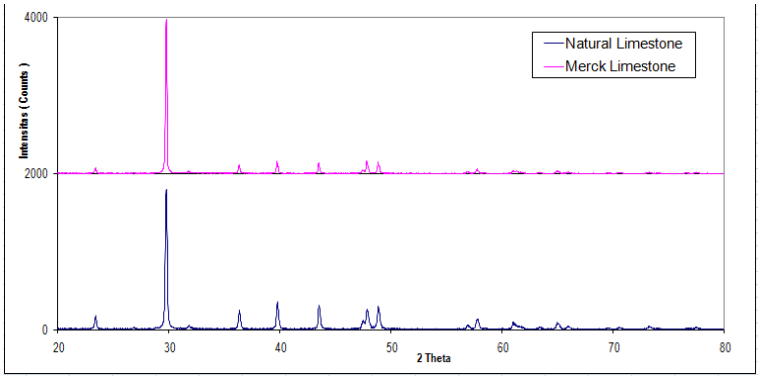


Figure 5. Comparison of XRD analysis of precipitated calcium carbonate resulted from ultrasonic process. Peak with pink color is crystal structure for $CaCO_3$ commercial (top) and peak with blue color is crystal structure for $CaCO_3$ nano particles obtained from natural limestone (down)

It is known that there are three types of crystal structure of calcium carbonate, those are calcite, aragonite and veterite. In order to observe the type of crystal structure of $CaCO_3$ nano particles obtained from natural limestone, the result in Figure 5 is compared with the standard of $CaCO_3$ using MATCH program as shown in Figure 6.

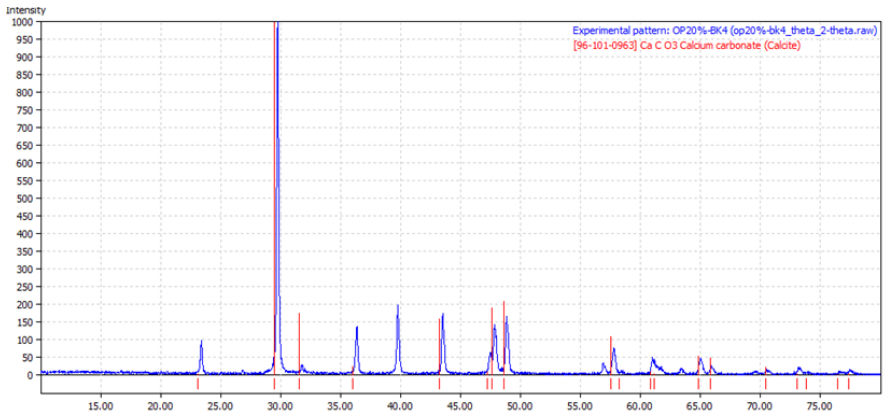


Figure 6. Analysis result of MATCH program on crystal structure of $CaCO_3$ nano particles obtained from natural limestone after ultrasonic process.

In this study, the standard of $CaCO_3$ which match with $CaCO_3$ nano particles obtained from natural limestone is Calcite. We can see that almost all of the peaks obtained in the XRD pattern of calcium carbonate nano particles from natural limestone match very well with the standard of calcite pattern. There are several unidentified peaks at 2Θ of 39.76^O, 57.72^O , 63.40^O and 70.08^O which is also observed in commercial calcium carbonate (see Figure 5). This illustrates that the result still contains impurities, even though the intensities of the impurities are small. The possibility of the impurities is because the compound is still wet or carbonization occurs.

4. Conclusion

Synthesis of calcium carbonate nano particles of natural limestone from Cibadak, Sukabumi was performed using ultrasonic process. 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.

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