Utilization of Blood Cockle Shell (Anadara Granosa) Waste and Silica Sand in Manufacturing Calcium Silicate as Fillers in Paper Making Industry

Abstract—This research aims to utilize blood cockle shell waste and silica sand as a new innovation in the manufacture of calcium silicate minerals which were used as fillers in paper making industry. In this study the manufacture of calcium silicate mineral fillers (CaSiO$_3$) used solid state reaction technique at a temperature of 1000°C. Some researchers have tested the use of blood cockle shells as the raw materials for making calcium silicate, so further research was needed to find out whether the calcium silicate produced can be used in paper making. Sample characterization was carried out with Fourier Transform Infrared (FTIR), Keyence microscopy and X-Ray Diffraction (XRD). The results showed that the calcium silicate phase contained the wollastonite-1A phase (CaSiO$_3$) with the highest intensity peak at an angle of 2θ = 26.8225. FTIR analysis also showed the structure of calcium silicate with the formation of Si-O-Si and O-Si-O functional groups at a wavelength of 460 cm$^{-1}$, Si-O-Ca at a wavelength of 962 cm$^{-1}$ and O-Si-O cm$^{-1}$ at a wavelength of 901 cm$^{-1}$. The microstructure analysis using Keyence microscope showed that the sample granules were globular in shape with a particle size of approximately 14 µm. From all the paper testing results consist of brightness, bulk density, tearing, bursting, tensile and folding endurance showed that calcium silicate filler has fulfill the TAPPI International standard.

Keywords—blood cockle shell, Calcium Silicate (CaSiO$_3$), Solid State, Filler, Paper

I. INTRODUCTION

Paper companies always innovate in creating quality products at relatively inexpensive costs. One of the market needs for paper quality is the high level of paper and bulky brightness. The most widely used fillers in the paper industry are the Ground Calcium Carbonate (GCC) and Precipitated Calcium Carbonate (PCC), but the largest consumption is GCC type. To meet market needs related to high quality, it is necessary to conduct laboratory-scale research, especially on supporting raw materials for paper making such as mineral fillers. Mineral filler is the second raw material after fiber is used for several grades of paper [1]. Mineral fillers are used on printing paper and writing paper to improve the optical properties and printing power of paper. Mineral filler can act as a cellulose fiber substitute at a low price which reduce the production costs. Mineral fillers can also increase opacity, brightness and sheet paper formation [2].

One of the innovations made toward fillers is gaining fillers with good quality, without utilizing additional chemicals and as much as possible from waste. From several studies that have been carried out by previous researchers, blood cockle shells can be used to manufacture calcium silicate filler minerals (CaSiO$_3$) which can be used as fillers in paper making [3].

Blood cockle shells are one of the mineral sources which generally come from marine animals in the form of shells that have been milled and have high carbonate. The main components of blood cockle are 66.7% CaO, 7.88% SiO$_2$, 0.03%, Fe$_2$O$_3$, 22.28% Al$_2$O$_3$ and 1.25% MgO [4]. The blood cockle shell (Anadara granosa) has the potential to produce calcium silicate (CaSiO$_3$) because it contains CaCO$_3$ which when calcined at a temperature of > 800°C produces CaO [5].

Synthesizd calcium silicate from the composition of natural silica with natural carbonates from quartz sand and limestone has been done by researcher [6]. The study used a solid reaction method with a calcination temperature of 1100°C. The study results indicated that calcium silicate appears at temperatures of 850°C and 1100°C. While another researcher [7] conducted a study of the synthesis and characterization of calcium silicate, the results of the study showed that the microstructure of natural calcium silicate after calcination at 850°C had different chemical phases and compositions. After 900°C calcination, the phase composition of the composting process and crystallization increases. Then the physical properties of calcium silicate studied showed that density, shrinkage and fracture strength increased with increasing temperature, while porosity and water absorption decreased. Based on research conducted by previous researchers, the authors are interested in making calcium silicate fillers from blood cockle shells with a solid reaction method. The manufacturing process is carried out by reacting calcium oxide extracted from the shells with silica sand. Furthermore, the calcium silicate produced will be characterized by its structure and morphology and applied in paper making.

II. MATERIALS AND METHODS

The materials used include blood cockle shells (Anadara granosa), distilled water, pure silica sand from brands, bayclin bleach liquid, PC-101 dispersants. Paper sheeting requires materials such as the pulp of short fiber type Leave Bleach Kraft Pulp (LBKP) with 4-5% consistency, paper
chemicals such as fillers of PCC, GCC and CaSiO₃ types with 68% consistency, Alkyl Ketene Dimer additives (AKD), OBA-type lightening chemicals with 3-4% consistency, positively charged tapioca with 2-3% consistency, detention chemicals and water.

The tools used have been calibrated including furnace, Excalibur UMA 600 type FTIR, Marvern Mastersizer 2000, Keyence microscope, oven, Hanna PH2211 pH meter, Elrepho 2000 brand brightness test, XRD Pert Powder Analytical, dispersion mill, press tools, desiccator, agitator, tensile strength testing equipment, folding endurance testing, tearing strength, bursting resistance and laboratory sheet paper making machines. Other tools were large glass beaker of plastic with a capacity of 8 liters, stirrer, tools glass commonly used in laboratories, analytical scales and paper thickness test kits, paper cutters, alumina balls, medium size porcelain cup, ring press, power press, sieve, mortar, analytic balance sheet, aluminum foil, heat-resistant gloves, gloves, magnetic stirrer, coating plates, blotting paper (standard 200 mm², weight 250 + 10 g / m² and thickness 0. 508 ± 0.013 mm as absorbent.

A. Sample preparation

The first process was the preparation of blood cockle shells and silica sand by cleaning the shells and silica sand with running water, then drying with an oven. After dried up, the shells then grounded with mortar, then sieved with a 60 mesh sieved for blood cockle shells and 100 mesh sieved for silica sand to obtain blood cockle and silica sand powder. After that the blood cockle powder was calcined at 800°C for 2 hours. The calcined blood cockle powder then mixed with a dispersant mill for 10 minutes and sieved with a 100 mesh sieved.

The calcined blood cockle powder was mixed with silica sand powder by composition 1:1 in an alumina ball for 1 hour. Then the mixture was calcined in a furnace with a temperature of 1000°C for 2 hours. The calcination results were then smoothed in a dispersant mill and sieved with a 100 mesh sieved to obtain calcium silicate powder.

B. Characterization of calcium silicate

Functional groups test was carried out based on the FTIR Instrument standard test method. A calcium silica mixture was mixed with 0.15 g potassium bromide to be printed on the mold (pellets). Measured with FTIR spectral resolution of 4 cm⁻¹, wavelength of 400-4000 cm⁻¹ and scanning process 32 times.

Morphology test was carried out based on the standard test method of the Keyence Microscope Instrument Manual. 1 g of calcium powder Silicate dissolved in 100 ml water. Stirred using a stirrer ± 15 minutes. Drop the solution on the test glass and observed with a Keyence microscope with magnification 400 times and 800 times.

Crystallinity analysis was carried out using CuKa radiation (1,506 Å), X-ray tubes operated at 45 kV and 30 mA. The measured diffraction range (2θ) was in the range of 10-90°, with a scan size of 0.05°/minute. The peaks in the diffractogram were then identified using the Search Match method with the standard data contained in the ICDD programmed.

C. pH measurements

The test was carried out based on the ASTM E70-97 standard test method and the pH meter manual Hanna PH2211 model. Make a 0.05% calcium silicate solution and measure it with a pH meter by dipping the pH meter electrode in the solution.

D. Particle size measurements

The test was carried out based on the Manual standard Instrument Mastersizer 2000 test method. Weighed 10 grams of calcium oxide powder and calcium silicate in 100 ml glass beaker and dissolved it by adding 100 ml of distilled water. Insert the sample into the Mastersizer 2000 to 20% container (seen on the monitor screen). Run the Mastersizer 2000 tool by pressing the run button on the monitor screen. Wait for the results to appear on the monitor screen about ± 10 seconds. Also did particle size measurements for GCC and PCC fillers with the same procedure.

E. Brightness measurements

The test was carried out based on the TAPPI standard test method 425 om-08 and the Elrepho color manual (L & W). Solid calcium silicate was pressed in a ring press with a pressure of 210 kPa for 5 seconds. Measure brightness on a flat surface using Elrepho 2000. Also did brightness measurements for GCC and PCC fillers with the same procedure.

F. Application of Calcium Silicate on Paper Sheets

Prepare paper chemicals with the following dosage: 7,000 ppm of OBA-type chemical, 100 ppm of coloring agent, 20% of filler, 0.8% of positively charged tapioca starch, 500 ppm of retention chemicals, 0.8% other additives Alkyl Ketene Dimer (AKD) and 600 gr LBKP pulp (paper making with 75 or 80 g/m²).

Mix LBKP pulp with water until the consistency was 3.5-4% and stirred at 1,200 rpm. Add filler, tapioca starch, OBA lightening chemicals, paper dye (blue and violet) and AKD then stirred for 2 minutes with an agitator at the same speed. Then diluted the mixture to a consistency of 0.8-1% while stirring and finally add the chemical retention. Print sheets of paper using a laboratory-scale paper sheet making machine. Perform this procedure to make paper sheets for PCC and GCC fillers.

III. RESULTS AND DISCUSSION

The initial characterization carried out after the manufacture of calcium silicate (CaSiO₃) from blood cockle shells and silica sand was the measurement of functional groups by FTIR, morphology by Keyence Microscopes and Crystallinity by XRD. The parameters of pH, particle size and brightness observed either. These three parameters were the initial stages to determine whether or not a mineral filler was suitable for making paper. After that, it was continued by observing the quality of paper sheets after adding calcium silicate filler compared with GCC and PCC filler.

The main reason of using calcium silicate (CaSiO₃) in paper making besides as a filler between cellulose fibers, also helps to reduce the use of fiber and improve the optical properties of paper in the papermaking process. In addition, the filler can increase the softness of the surface on printed paper and improve the quality of paper [8].
The making of calcium silicate (CaSiO$_3$) from blood cockle shells and silica sand was done by reacting calcium carbonate contained in the blood cockle shells and silica on the sand by the solid state method with a calcination process of 1000°C for 2 hours. The principle of solid reaction is based that the cations and/or anions of one structure must be moved or exchanged by several mechanisms to another structure to form new compounds [9]. The calcination process at a temperature of 1000°C was intended to cause a process of changes in microstructure such as changes in pore size, grain growth, increased density and mass shrinkage. Previous researchers [10] made calcium silicate using a mixture of shells and rice husks. The results of the study showed that calcium silicate appeared at 1000°C for 2 hours.

A. FTIR analysis

From the results of observations in Fig. 1, the formation of the Si-O-Si structure of the group formed on the wave number of 460 cm$^{-1}$, Si-O-Ca at wave number 962 cm$^{-1}$, O-Si-O at wave number 901 cm$^{-1}$. In addition, from the measurement results there was also -OH group at wave number 3426 cm$^{-1}$ and CO$_2$ group at wave number 1423 cm$^{-1}$, and possibility of existence of other organic groups at wave number 643 cm$^{-1}$, 683 cm$^{-1}$ and 2515 cm$^{-1}$.

In general, the crystal structure of calcium silicate consists of the bonds between the atoms of Ca (calcium), Si (silicon) and O (oxygen) obtained from the PCW (Powder Cell Wollastonite) program which has a space group value of 2 with an ionic radius of Ca$^{2+}$, Si$^{4+}$ and O$^{2-}$ respectively 2Å, 1.15Å, 0.73Å and perspective 1.00 and size factor 0.50, then with the composition value of atoms a = 7.9400Å, b = 7.3200Å, c = 7.0700Å and the value of the angle $\alpha = 90.0300^\circ$, $\beta = 95.3700^\circ$ and $\gamma = 103.4300^\circ$ [11].

B. Keyence Microscope analysis

As showed in Fig. 2, observations with Keyence microscopy were carried out for microstructure analysis of the resulting calcium silicate particles. The particle shape and particle size greatly affect the quality of the mineral filler. The PCC filler has a needle-like filler shape with a size of approximately 3.55 μm while the GCC filler has the form of rhombohedral (cubic) particles and a size of approximately 2.36 μm. Forms of fillers such as needles or stems were preferred as fillers in paper making. This is because the form of fillers such as needles or rods better adjust the shape of the cellulose fibres that were elongated. So that it can increase the smoothness of the surface and porosity of the paper made. However, the form of round filler, rhombohedral or granular did not mean that it cannot be used as a filler, as titanium TiO2 filler has a round filler shape but its quality was still good for paper making. In the observation with the Keyence microscope in Figure 2, the form of calcium silicate was obtained at a magnification of 400 times and 800 times, globular/spherical shape with a particle size of approximately 14 μm.

C. XRD Analysis

The resulting diffraction pattern was in the form of diffraction peaks with a relative intensity that varies along a value of 20. The peaks obtained from this measurement data were then matched with X-ray diffraction standards called the Joint Committee on Powder Diffraction Standards (JCPDS). Based on the results of matching diffraction peaks obtained from measurement data with the JCPDS standard, it showed that the calcium silicate X-ray diffraction pattern at a temperature of 1000°C contained the wollastonite-1A phase (CaSiO$_3$) with the similarity of rows of diffraction peaks at an angle of $20 = 11.4841- 63.7146$ and the highest intensity peak at an angle of $20 = 26.8225$. The Wollastonite-1A phase was a crystalline phase with a triclin shape.

| Functional groups | Waves number (cm$^{-1}$) CaSiO$_3$ | Waves number (cm$^{-1}$) Standards |
|-------------------|----------------------------------|-----------------------------------|
| Si-O-Si Bend      | 451                              | 400-600                            |
| Si-O-Si Symmetric Stretch | 901                          | 805-910                            |
| Si-O-Ca Stretch   | 962                              | 850-1000                           |
| Si-O-Si Asymmetric Stretch | 1064                      | 1000-1200                           |
| CO$_2$           | 1423                             | 1410-1490                          |
| OH               | 3426                             | 3200-3700                          |

Figure 1. FTIR Spectrum of Calcium Silicate

Figure 2. Calcium Silicate Filler (CaSiO$_3$), (a) Keyence Microscope 400x Magnification, (b) Keyence Microscope 800x Magnification

Figure 3. X-ray Diffraction Pattern of Calcium Silicate Diffractogram
The sharp peak indicates that the mineral filler calcium silicate has a crystalline solid structure. Crystalline solids have neat and regular arrangement of atoms and molecules, whereas amorphous solids are solid structures with random and irregular patterns of atoms and molecules. The sharper the peak diffraction, the more crystalline, the more amorphous solids in nature [13]. The difference in intensity values between the measurement results with the literature depends on the atom or the number of ions that exist and its distribution in the unit cell of the material [14]. The more Crystal fields contained in the sample, the gentler the diffraction peak ramps, the more uniform the distribution of solids in nature [13]. Each peak that appears in the XRD pattern, represents a Crystal field that has a certain orientation on the three-dimensional axis [15].

D. Comparison analysis of pH, Particle Size and Brightness of 3 fillers

Table 3 showed parameter analysis for 3 different fillers. These three parameters were the initial stages to determine whether or not a mineral filler was suitable for making paper. From the results of the 3 parameters measurement, calcium silicate has a measurement value of pH, particle size and brightness fulfilled the standard and the results were not much different from the GCC and PCC filler. The pH value of the filler has an effect on the paper making process [16]. The pH value must be alkaline, if the filler has an acid pH or out of the standard, foam will form in the paper making process. Likewise the particle size and brightness also affect the paper making process. Size of filler particles which were not uniform and low brightness will produce rough paper quality and low brightness.

Table 4 above showed the result of paper measurements parameter on the application of calcium silicate filler (CaSiO₃), GCC and PCC in the manufacture of paper sheets. The values listed in the table were the results of calculating the average of three measurements (triple) in each parameter. Each measurement parameter was carried out according to the appropriate test method. The paper measurement parameters results were used as a reference for filler comparison in the application of paper making sheets. The standard used in paper quality parameters test was the TAPPI International Standard.

The Gramature test was carried out to find out the uniformity of the paper samples that had been made. From the results of the paper strength test results showed that the three types of filler provide a nearly uniform Gramature value with an average of 75 g/m².

The brightness of the paper made with GCC and PCC fillers has a brightness of 79.34% ISO and 80.53% ISO respectively, while the brightness for calcium silicate was only 75.16% ISO. According to Wirawan [17], fillers can increase the brightness and optical properties of paper sheets. The low brightness of paper with calcium silicate filler was
caused by the basic ingredients of calcium silicate fillers, blood cockle shells and silica sand having low brightness, therefore the brightness of the resulting filler decreased. However, the brightness of paper made with calcium silicate fillers was still fulfill the TAPPI international standards so that it can be used in paper making.

Bulk density is the ratio of paper grams to its thickness in g/cm². In the paper industry, bulk density is associated with the thickness of the paper made. Paper companies are competing to make paper with the same dose but able to obtain high bulk density. One of the innovations made is to find a filler that has a high particle size in order to obtain paper with high bulk density. In Table 4 it was found that the bulk density for paper sheets made with calcium silicate filler 1.80 cm³/g is highest than the others.

Tearing strength is the force in grams (gf) or milli Newton (mN) required to tear a sheet of paper. There are three factors that affect tearing strength, namely the total number of fibers damaged by sheets, fiber length and the amount and strength of bonds between fibers [17]. If it is associated with a filler, it is known that the type of filler used in paper making greatly influences the tearing strength value of the paper. According to Kurniati [18] increasing the amount of filler will reduce the tearing strength of the paper. This is possible because the filler that fills the pores of the fiber prevents bonds between the fibers. In the tests that have been done, the dosage of filler used for the three types of filler has the same dose, so the dosage of filler cannot be used as a comparison in this discussion. Table 4 showed the paper sheets made with calcium silicate fillers having lower tearing strength than GCC and PCC fillers. This is probably caused by differences in interactions that occur between the fiber and the filler. However, the tearing strength value was still fulfill the TAPPI International standards.

Bursting resistance is influenced by the use of fillers, the composition of long fibers and short fibers and the use of positively charged starches [19]. From Table 4, it can be seen that the bursting resistance of paper sheets made with PCC fillers has a higher bursting resistance value than calcium silicate fillers and PCC. This is probably caused by differences in interactions that occur between the fiber and the filler.

Tensile strength of paper is influenced by the type of fiber used (long fibers or short fibers), the fiber grinding process and the use of positively charged starches [19]. The effect of using filler only slightly affects the paper's tensile strength. From Table 4 it can be seen that paper sheets made with calcium silicate fillers have lower tensile strength compared to GCC and PCC fillers. This may be due to differences in paper thickness (bulk), where paper sheets made with calcium silicate fillers have a greater thickness (bulk) of 1.80 cm³/g while paper sheets made with PCC and GCC fillers have thickness (bulk) 1.67 cm³/g and 1.68 cm³/g respectively. The thickness of the paper will affect the tensile strength of the paper sheet made.

The folding endurance is affected by the use of long fibers, positively charged starch and little influenced by the filler. The higher the dose of the long fibers used, the higher the folding endurance, as well as the use of the filler, the increase in the filler will reduce the paper folding endurance. This is possible because of the filler that fills the pores of the fiber prevents bonds between the fibers [19]. From Table 4 it can be seen that paper sheets made with calcium silicate fillers have almost the same folding endurance as GCC and PCC fillers.

IV. CONCLUSIONS

From the observation with FTIR and X-Ray Diffractometer (XRD), it showed that the calcium silicate sample contained wollastonite-1A (CaSiO₃) phase with similarities of Si-O-Si bend functional groups at wave numbers 460 cm⁻¹, Si-O-Ca at wave numbers 962 cm⁻¹, O-Si-O at wave number 901 cm⁻¹ in FTIR equipment, and similarity of diffraction peaks rows at 2θ = 11.4841-63.7146 angle on XRD devices. A sharp hill at the peak showed that calcium silicate filler minerals have a crystalline solid structure. Observation result with Keyence Microscope showed that calcium silicate microstructure was globular in shape with particle size of 14.55 μm. Calcium silicate made has pH, particle size and brightness respectively 10.3; 14.55 μm and 78.66% ISO which were fulfilled the TAPPI International standard. From all the test results that have been carried out, the brightness, tearing, bursting, tensile and folding endurance, it can be seen that calcium silicate filler has a lower value than GCC and PCC filler, but still fulfilled the TAPPI International standard. Therefore, calcium silicate will potentially be an alternative source of filler which cost effective.

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