

Preparation and Characterization of Montmorillonite Particles under Calcination and Ball Milling Process

Martinus Heru Palmiyanto, Kaleb Priyanto

Abstract: This study aims to produce nano-sized montmorillonite particles which will be developed as polymer composites fillers. Montmorillonite particles were sieved and then calcined. Ball Milling process was applied to montmorillonite to achieve better particle size. Analyzing using Particle size analyzer (PSA) was carried out on montmorillonite powder without calcination process, calcined montmorillonite powder, and calcined montmorillonite which had ball milling treatment for 5,000 cycles and 10,000 cycles. Scanning Electron Microscope (SEM) used to find out the structure of particles due to the type of treatment that has been applied. As a result, the PSA shows that the calcination treatment produces smaller particle sizes. The smaller particle size was shown by the results of PSA testing of calcined montmorillonite powder and subjected to ball milling treatment for 10,000 cycles. The micrograph results confirm this phenomenon, where particles of 200nm appear on the powder that has undergone calcination and ball mill treatment.

Keywords: Ball Milling, Calcination, Montmorillonite, PSA.

I. INTRODUCTION

Many commercial applications are made of polymer composites. In the last 20 years, there has been an increase in the development of polymer composites, where at least one dimension of fillers is macro, micro, and nano. In material science, the size of nanopowder materials is generally used. It affects reinforcing efficiency because of their high aspect ratios. In addition to being profitable to reduce overall costs, combining fillers as driving force can change material properties. The incorporation of nanofillers such as nanoclay, nanoparticles, nanotubes, nanofibers into the polymer matrix produces better nanocomposite characteristics. The addition of nanofillers reduces the brittle properties of composite laminates. In addition, many of the experimental studies have been targeted to increase tensile strength, bending, compression, inter-intra laminar, impact strength, shear strength, stiffness, electricity, and thermal properties, chemical resistance and corrosion [1]. The incorporation of nano reinforcements into elastomers greatly improves their mechanical properties and thermal resistance in relation to real improvements in adhesion, rheology and processing

behavior. Furthermore, better dispersion of these fillers in the matrix provides high-performance nano composites and also the properties of the nanoscale filler are significantly higher than the base matrix [2]. Polymer nanocomposite is a new class of composite material that comprises of dispersion of nanometer size particles in a polymer matrix. The mechanical characteristics such as stiffness, tensile, and impact strength can be influenced by mineral particles' size and shape. When the filler is included, it affects the performance of a polymer in terms of tensile, flexural and its impact.

This study focuses on the mineral powders use in polymer composites. In this case, montmorillonite was the principle mineral for the development of polymer-clay nanocomposites. This particle occurs through natural processes and can be easily found in the earth. It is also easily mined and purified. The particle is a volcano material which has been exists since millions of years ago. The main components present in clay are SiO_2 and Al_2O_3 including clay originating from the plains of Wonosegoro, Boyolali, Central Java, Indonesia [3]. Few authors used Tunisian sample clays from different locations calcined at different temperatures and tested their potential use as pozzolanic materials [4]. These kinds of clays might be used as raw materials to synthesize geopolymers which is a novel class of materials. The structural evolution of two Tunisian clays on calcination is studied in detail to predict their behavior during geopolymerization. It was demonstrated that temperature calcination influenced the amorphous character of clays [5]. Appropriate and non-pollute techniques by involving High Energy Milling (HEM) can initiate varying degrees of size reduction, reduce crystallinity without chemicals, and also modifying filler morphology to improves compatibility with polymer mixtures [6]. HEM using ball mill is a non-equilibrium solid-state mixture technology for powder preparation that can be used to synthesize new materials that are not possible with conventional technology. It is well known that ball milling of powders can produce equilibrium and non-equilibrium structures, including saturated solid solutions, nanocrystalline powders, metastatic compounds, and amorphous solids. The size and agglomeration level of the mixed particles has a large influence on the final density which can improve particle properties and performance [7].

II. LITERATURE

Polymer matrix with the addition of nanoparticles is the common method that are used in polymer nanocomposites production.

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Titanium dioxide (TiO_2) has been investigated during the last decade as one of the candidates of nanoparticle for composites because of its scientific and technological importance [8]. For instance, Wang et al (2013) reported a double in situ approach for the preparation of PET/titanium dioxide (TiO_2) nanocomposites having flame retardant properties with improved mechanical strength. The appreciable flame retardation ability of the composite was shown by improved values for limiting oxygen index (LOI) and vertical burning test compared to bare PET [9]. Based on the number of dimensions of the nanometer size, nanoparticles that are used in polymeric nanocomposites have been categorized into three dimensions. One dimension (platelets), two dimensions (fibers and whiskers) and Three dimensions (nearly spherical particles). Layered nanoparticles can be exfoliated into a dispersion of individual platelets. Nanoclay/polymer composites are polymers reinforced with nanosized clay particles. The nanosized clay particles are achieved by either intercalating the polymer into the clay galleries or completely exfoliating the clay platelets to yield particles with average dimensions of 1nm in thickness and 70–150nm in width. Many review articles have been written describing the benefits that can be achieved from the nanoscale manipulation of fillers [10].

The platelet structures of clays make them interesting high aspect ratio fillers. Clays have aluminosilicate layers (i.e., platelets) interspersed with interlayer cations (i.e., the space between the parallel layers of clay platelets is the gallery. The gallery spacing changes depending on what cation occupies the space). Although the bulk clay particle is not nanosized, each platelet has an in-plane dimension of >100 nm and a thickness of 1–10 nm. To achieve nanoclay composites, the clay layers must be delaminated and dispersed in a polymer matrix. The smectic class of clays can be swollen, such that the gallery spacing is increased. Montmorillonite is the most common type of smectite clay. To fully disperse the clay, the particles are sheared apart, giving tactoids or polymer intercalated particles. The intercalated particles contain stacks of clay layers approximately 100–150nm high. These can be further exfoliated and dispersed when polymer enters the galleries of the clay, pushing the platelets apart Nanoclay/polymer composites were first utilized industrially by Toyota in 1990, where clays were incorporated into Nylon-6. It has been shown that incorporating nanoclays into polymers can increase the mechanical and thermal properties of the polymers [11].

The calcinations process is the main process that is considered as important for production high reactivity pozzolana from kaolin clay. The heating process drives off water from the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), the main constituent of kaolin clay, and collapses the material structure, resulting in an amorphous aluminosilicate ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), metakaolinite. The process is known as dehydroxylation. The thermal transformation of kaolinite, which has been the subject of a large number of investigations has shown that the heating parameters such as temperature, heating rate and time, as well as cooling parameters (cooling rate and ambient conditions), significantly influence the dehydroxylation process. Lecomte [12] reported that Vickers hardness values

of geopolymers are improved (from 191 ± 6 to 217 ± 5 MPa) with kaolin calcination temperatures (700 - 800°C). The geopolymers resulting from clays calcined at 700°C and 800°C have the highest compressive strengths because the disorder of the corresponding raw material induced by the thermal treatment is the most important. The compressive strength drops for higher calcination temperatures (850°C for Medenine clay and 900°C for Tabarka clay) because the clay structural reorganization proved previously limits the attack of the raw material by the basic solution. The feature of calcined (25°C, 700°C and 900°C) Medenine and Tabarka are evaluated using dilatometry measurements (Figure 1). Through the two types of clays, dimensional variations were appeared, which reflected phase transformations. Besides the sample, the peak which were observed at 572°C was because of the $\alpha \rightarrow \beta$ transition of quartz. In addition, the dilatometric curves show three different events at temperatures around 20°C, 450 - 600°C and 900°C in the case of any clay. The first event is because of the loss of free water molecules. The second event is due to the dehydroxylation of kaolinite phase. The third event is in relation with the mullite nuclei formation and the silica viscous flow's apparition. All of the calcined clays show at least 1 % in size at 800°C due to the reorganization of hydroxyl groups [13]. High Energy Milling using ball mill has advantages of being simple, relatively inexpensive to produce, applicable to any class of materials and can be easily scaled up to large quantities of nanosized particles. In ball milling process, the powder particles are subjected to a severe plastic deformation due to the repetitive compressive loads arising from the impacts between the ball and the powder. From it process, the nanometer size of crystalline and amorphous material produced. Zhen-Guo et al [14] investigated the in-situ synthesis of nanosized crystalline Silicon carbide powders at room temperature through high energy ball milling of elemental silicon and carbon mixtures. S. Raygan et al. [15] investigated the effect of 100 hours and 200 hours low energy ball milling on the carbothermic reduction of SiO_2 and C powder mixture. Morphology studies of the mixture by SEM revealed that the particle sizes have been decreased and the SiO_2 particles had been covered by carbon particles due to the milling.

III. EXPERIMENTAL PROCEDURE

The lumps of clay were dried, crushed, and filtered to obtain micro-sized particles. During four hours at 800 °C in a furnace, the calcination process has been applied. The calcined clay were sieved with a sieving machine to get 200 mesh pass particles. Calcined and sifted clay particles were ground through a ball mill process use a tumbler mill clamped to the lathe chuck. The volume of the tumbler was 300 cm^3 that filled by 50 cm^3 of powder and a steel ball with a volume of 50 cm^3 . The spindle speed of the lathe was 155 rpm. The milling cycle applied was 5,000 and 10,000 cycles which is equivalent to spindle rotation for 30 and 60 minutes.

The calcined clay microstructure before and after the ball mill process was observed using Scanning Electron Microscope (SEM, Hitachi SU 3500).



PSA Horiba SZ-100 was used to analyze particle size from calcined clay and milled clay.

IV. RESULT AND DISCUSSION

Figure 1 shows the results of PSA on raw montmorillonite clay material. Based on the graph, the particle size that appears to be very heterogeneous. This can be concluded because there are two frequency peaks that occur in the diameter of calcined montmorillonite clay particles. The average particle size was obtained at 1,663.1nm and the smallest particle size found at 579.1nm. Montmorillonite raw material has a very heterogeneous particle shape and size. These physical properties are less effective in forming polymer bonds. In addition before the calcination process occurs, montmorillonite particles are still quite moist and tend to be agglomerated.

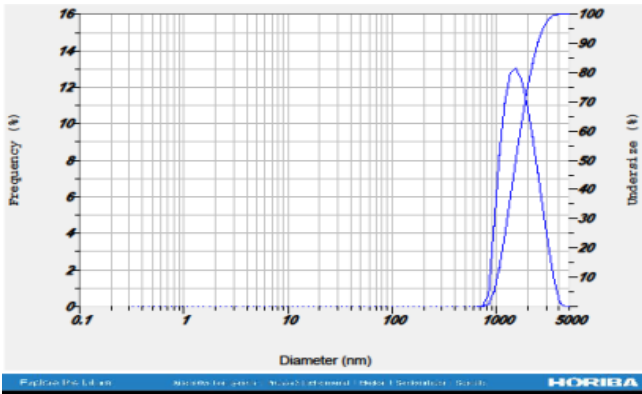


Fig 1. PSA graph of Clay Montmorillonite Raw Material

Different results were shown by calcined samples of montmorillonite clay. Where the average particle size decreases at 646nm. Figure 2 shows a significant percentage of particle frequency in a diameter range of 600nm to 700nm.

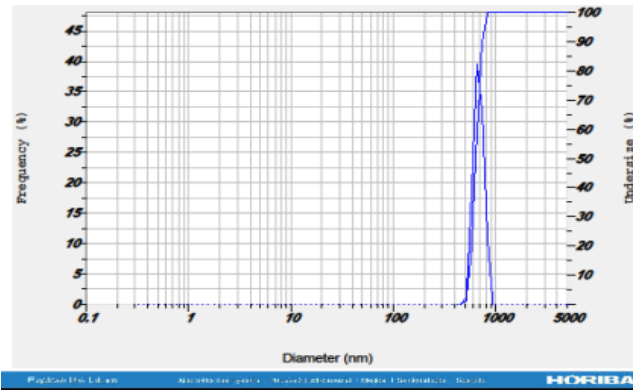


Fig 2. PSA graph of Calcined Clay Montmorillonite

The decrease in particle size occurred in the PSA results on montmorillonite clay samples processed by ball milling for 5,000 cycles and 10,000 cycles. The average particle size obtained were 418.6nm and 233.9nm respectively with the smallest particle size found in montmorillonite clay powder with 10,000 ball milling cycles at 20.8nm. Figure 3 shows a graph of PSA on the calcined Clay Montmorillonite Material and has been processed for 5,000 cycles of ball milling. While Figure 4 shows a graph of PSA on Clay Montmorillonite material that has been calcined and processed with ball milling for 10,000 cycles.

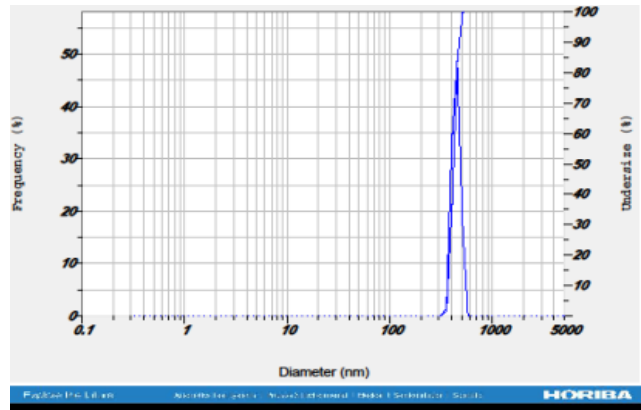


Fig 3. PSA graph of Calcined Clay Montmorillonite and processed by ball milling for 5,000 cycles.

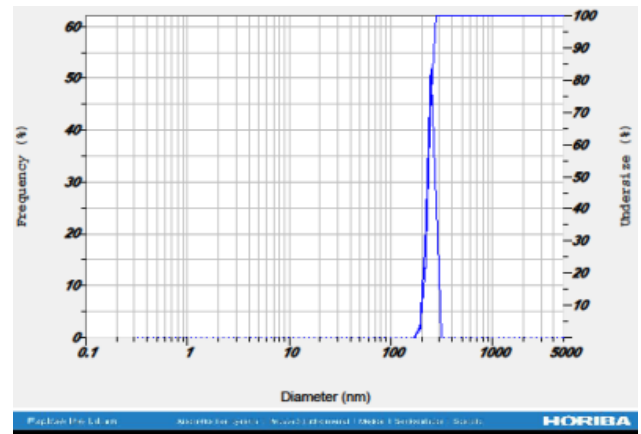
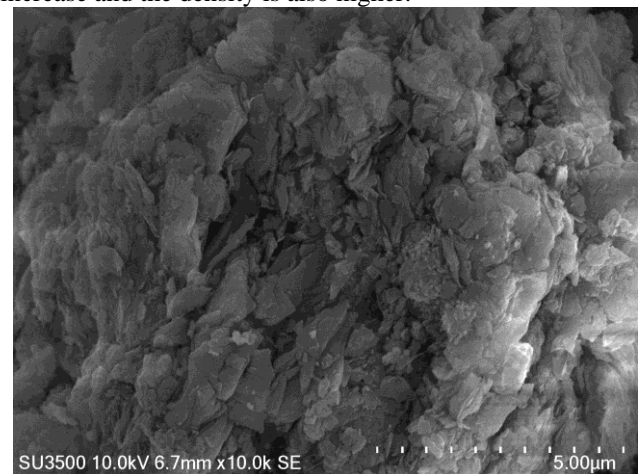


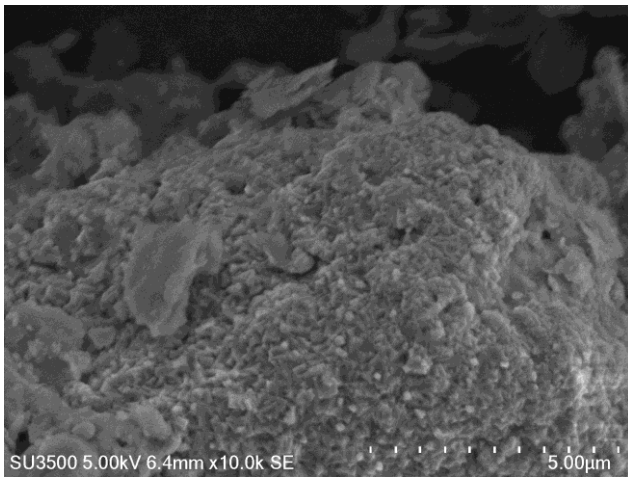
Fig 4. PSA graph of Calcined Clay Montmorillonite and processed by ball milling for 10,000 cycles.

The results of SEM micrography confirmed the physical changes in calcined clay montmorillonite particles. Increasing density can be indicated by the appearance of visible particles. But particle shape changes did not occur significantly. That was shown in Figure 5 (a). Figure 5 (b) shows the change in shape followed by the occurrence of dimensional changes seen in clay montmorillonite powder processed by milling. Fine particles with smaller dimensions increase and the density is also higher.



(a)





(b)

Fig 5. SEM Micrograph of (a) Calcined Clay Montmorillonite, (b) Calcined Clay Montmorillonite and Processed by Ball Milling for 10,000 Cycles.

V. CONCLUSION

There are several steps for preparing Montmorillonite clay to be used as a filler for polymer composites. It is crushed, sifted, calcined, then processed using ball milling. Based on the PSA results, the calcination process using an oven at 800C for four hours reduced the particle size of montmorillonite clay and made the particles more homogeneous. From the SEM Micrograph of the calcined clay montmorillonite and milled clay montmorillonite, the HEM process using ball milling not only decreases size but also changes the physical shape of particles and increases particle density.

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