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Natural Zeolite Modification With A Surfactant Cetyl Trimethyl Ammonium Bromide (Ctab) As Material To Filler In Polypropylene

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Abstract
Research purposes to determine the characteristics of the modification of natural zeolite (synthesis CTAB) and particle size, microstructure, as well as determine the effect of modification of natural zeolite as filler on the properties of thermoplastic polypropylene thermal and mechanical properties. Composite manufacture begins with a filler material synthesis of natural zeolite with CTAB. Results of modified zeolite is used as filler in polypropylene matrix mixed in an internal mixer with a temperature of 180 ^{0}C for 9 minutes at a mixing rate of 50 rpm. Results of the internal mixer is done printing the sample with hot and cold press and the result is a sample of the resulting sheet characterized the mechanical and thermal properties. Results obtained before the modification of natural zeolite particle size 74 µm, after modification with CTAB particle size to 1 µm. Morphology seen the cavities according to the characteristics of natural zeolite. By increasing CTAB zeolite composition on the polypropylene matrix resulted in decreased tensile strength and elongation at break, but Young's modulus increases. From the thermal analysis that the composite lost more than 3 % of its mass under heating to 447.17°C which is considered enough to deduce that it can absorb significant amounts of water. An increase in the decomposition temperature after the addition of modified zeolite with CTAB.

Keywords: Zeolite, CTAB, PP, Analysis, mechanical, thermal

1. Introduction

Polymer composites have become an important phenomenon in recent years. Many of researchers who studied polymer composites. Composite applications are widely used in automotive, electronics, construction industry, mechanical industry, transportation, marine, and so on.

In the manufacture of composite polymer material selected should have better properties than other similar class. One type of polymer composite that is mixing between the polymer-clay. Polymer-clay is a mixture between the polymer and composite materials as reinforcement, such as silica, zeolite, and others. Problems often arise in the manufacture of polymer composites is reduced due to the physical properties of high temperature so that the use of non-durable material. Therefore we need a proper selection of the type of polymer. Polypropylene is a type of polymer that has several advantages, including ease of production, high tensile strength, resistance to chemicals, and product price cheap [1]. To support the thermal properties and mechanical properties of polymer composites needed filler. Giving filler in polymers will provide a varied nature in order to obtain material properties of the thermal properties and excellent mechanical properties [2]. Zeolite as filler to improve and enhance the performance characteristics of the membrane [3]. Zeolites represent an attractive native material for removing heavy metal ions from industrial and processing effluent water. Their advantages are the following: low cost, stability and abrasion resistance, low swelling capacity, their exchangeable ions are relatively harmless Na, Ca and K; no secondary pollution can be caused during zeolites preparation and use, and relatively easy regeneration of spent zeolites.[4] In addition it has a surface area of zeolite is easily modified and acidity[5]. Zeolite mineral containing aluminum silicate compounds that have three-dimensional framework structure formed by tetrahedral $Al0_4{}^{5-}$ and $SiO_4{}^{4-}$ with a cavity in it filled metal ions usually alkaline earth metals (Na, K, Mg, Ca and Fe) and a water molecule tend to move freely in space intermilar cavity structure [6]. Zeolites can be modified in various ways such as by the addition of surfactant cetyl trimethyl ammonium bromide (CTAB).

Between polymer and zeolite have different properties. To combine the two materials is polypropylene which is nonpolar and polar clay that needed a unifying substance commonly called compatibilizer. The compatibilizer commonly used is identical to substances that can bind to the polymer matrix and filler itself. Compatibilizer material that is often used in the manufacture of polymer-composite is PP-g-MA. Compatibilizer plays an important role in the process of compounding. Compatibilizer same role as the role of emulsifiers in emulsion technology. Most compatibilizer widely used either type block copolymers or graft [7]. Modification of natural zeolite which aims to transform the negatively charged zeolite surface becomes positively charged with propylamine and N-cetyl-N, N, N-trimethyl ammonium bromide (CTAB) and its application to absorb Cr_2O_{72} and $-2[Fe(CN)_6]_3$ the results showed that the modified natural zeolite with CTAB (SMZ-CTAB) has a higher absorption [8].

Synthesis of natural zeolite is done by entering the 5 g of zeolite powder into the reactor already containing 90 ml solution of NaOH and sodium aluminate ($NaAlO_2$) solid 5.2 g [9]. According to[10] the addition of clay (monmorillonite) to the pure polypropylene become a key point of research to change the characteristics of the properties of polypropylene in general, especially the thermal properties of the results of this study indicate that the addition of bentonite ≥ 5 percent by weight of polypropylene clay nanocomposite, resulting in resistance to heat greater than 74 % when compared to use pure polypropylene sample without the addition of bentonite .

Modified polypropylene with montmorillonite clay containing 50-80 %. montmorillonite has a layer of nano-sized so it can be used as a nanofiller in polypropylene-nanocomposite production [1]. This study is conducted to determine the effect on the composition of polypropylene-montmorillonite nanocomposite mechanical properties into production. Mechanical tests in this study is the tensile strength and hardness. Nanocomposite compounds produced by the method using injection molding equipment.

In studies [11] Optimization of natural zeolite is as filler in polypropylene composite. The effect of the addition of zeolite and surface treatment performed in this study. Theoretically, produce a tensile modulus of greater value than the experimental values. The purpose of this study was to determine the effect of CTAB modified zeolite to zeolite particle size and mechanical and thermal properties composites PP/PP-g-MA with zeolite modified CTAB as filler

2. Experimentals

2.1 Materials.

Materials used in the study of natural zeolite comes from North Tapanuli Pahae District, North Sumatera Indonesia, Copolimer Polypropylene Production of Singapore, a melting temperature of 176° C, density 0.896 g /cm3, filter paper, PP-g-MA Japanese production, (Cetyl Trimethyl Ammonium Bromide, Hexadecyl Trimethyl Ammonium Bromide, CTAB) Merck Germany, $AgNO_3$, distilled water, Aquabides.

2.2 Instrumentation.

Internal Mixer Laboplastomil Model 30 R150, Hydraulic Hot Press, Cold Press of 37 ton from Genno Japan, Particle Size Analyzer Desla^{TM} nano, SEM, Universal Testing Mechanic, for simultaneous thermal analysis (DTA-TGA) Setaram TAG24.

2.3 The processing of zeolite with CTAB Surfactant.

Zeolites are still in the form of chunks of destroyed first, then crushed using a rolling pin. The zeolite is crushed sieved using a 200 mesh sieve (74 μm) 0.2 mol (approximately 21.88 g of Cetyl Trimethyl Ammonium Bromide-CTAB) is dissolved into 300 ml of water and then heated to 80 ^{0}C temperature for one hour stirring a solution of zeolite A. Furthermore, as much as 50 g of zeolite was added 1000 ml of water and heated and stirred at 100^{0}C for two hours as the solution B. After heating and stirring, solution A and solution B are mixed. The mixture is added with distilled water to a volume of 1500 ml. then heated to 100^{0}C temperature for one hour the mixture is filtered with a vacuum filter 2 g $AgNO_3$ is added with 100 ml of distilled water using a glass beaker. The purpose of the addition of $AgNO_3$ solution to eliminate bromide. The mixture is filtered using filter paper until it changes color to dark when using $AgNO_3$. If it still turns back mixed with distilled water and filtered again. Subsequently the mixture was dried in a microwave at a temperature of 100^{0}C for 24 hour [20].

Table 1. The Formula Used for Preparation Composite

Materials	The quantity (wt%)				
PP	100	95	92	90	88
Zeolite Synthesis CTAB	0	0	3	5	7
PP-g-MA	0	5	5	5	5

2.4 Preparation of thermoplastic PP blend.

To prepare thermoplastic PP blend, the zeolite CTAB was mixed with PP, PP-g-MA, According to the composition as presented in Table 1. The mixture was blended using Laboplastomil Model 30 R150 internal mixer with a volume of 60 cc. The blending was carried out at temperature of 180 °C with rotor speed of 50 rpm for 9 minutes.

2.5 Mechanical properties measurement.

Tensile strength measurement was performed according to JIS K 6781 standard using Universal Testing Machine, at crosshead speed of 50 mm min^{-1}. Young's modulus (E), ultimate tensile strength(σ_{max}), and fracture elogation (ε_b) were determined from the stress-strain curves.

2.6Thermal analysis.

Simultaneous thermal analysis (STA) was performed on TGA-DTA Setaram TAG 24, by scanning the sample over the temperature range of 50 – 600 °C using nitrogen gas with the flow rate of 50 mL/min and a heating rate of 20 °C/min.

3. Result and Discussion

3.1 Testing Results With Particle Size analyzer (PSA).

To find out how much exactly the particle size is measured with a gauge Particle Size Analyzer (PSA), obtained from this tool percent of the number distribution is shown in Figure 1.

Figure 1 shows the average size of modification of natural zeolite particles with a size of approximately 1μm particle. In this case the particle size of modified natural zeolite before about 74 μm, with such a small particle size increases with zeolite modification with CTAB surfactant. It is due to CTAB is a surfactant stabilized emulsion particle formation and control.

3.2 Analysis Microstucture.

Form of natural zeolite particles are observed with a Scanning Electron Microscope (SEM) is shown in Figure 2. Figure 3 Modification of Natural Zeolite with CTAB, from the SEM photograph shows that the dark color is a pore or cavity that size < 5 microns, and the bright colors are modifications of natural zeolite particles, when seen from the particle size of the zeolite is the kind of macropore because particle size > 50 nm, from the visible image aglomert or clumping occurs it is because zeolites are hydrophilic (readily absorbs water) due to the OH group around the pore. This is according to the results of research [12], as well as uneven distribution of particles with particle size of about 1μm.

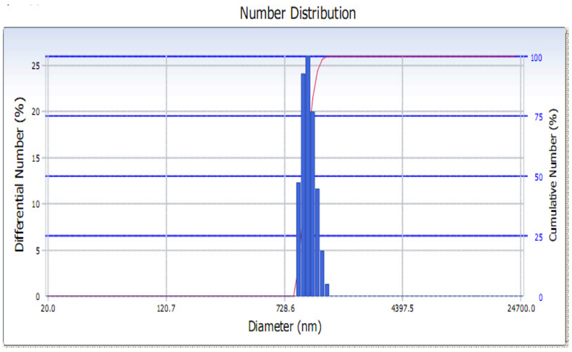


Figure 1. Particle Size Zeolite Modification

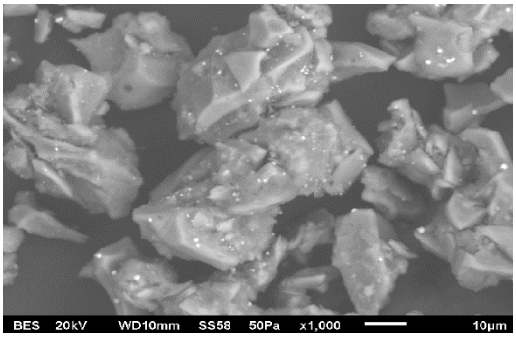


Figure 2. Particle Morphology of Natural Zeolite

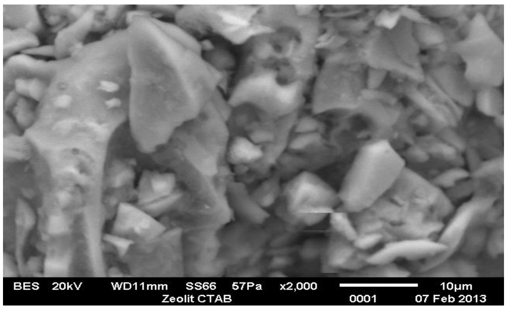


Figure 3. Particle Morphology Modification of Natural Zeolite with CTAB

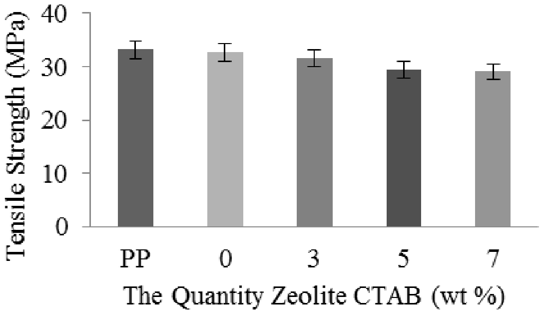


Figure 4. Tensile Strength of the Samples Filler with Zeolite CTAB

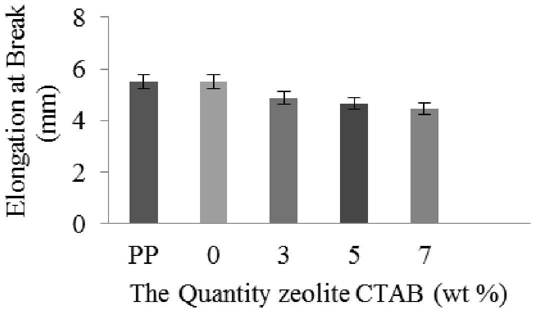


Figure 5. Elongation at Break of the Samples Filler with Zeolite CTAB

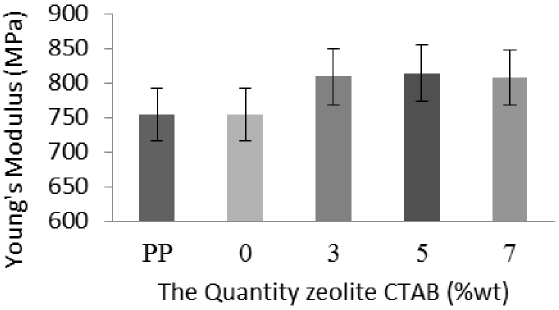


Figure 6. Young's Modulus of the Samples Filler with Zeolite CTAB

On the characterization results done with tensile strength testing machine mechanical data obtained are shown in Table 2, the tensile strength, elongation at break, modulus of elasticity. From these results it can be analyzed properties of thermoplastic composites for mixture properties and compatibilizer polypropylene PP-g-MA with variations in the composition of natural zeolite particles modified with CTAB.

3.3 Tensile Strength.

Figure 4. shows the graph of tensile strength on the composition of natural zeolite CTAB, from the figure shows that the addition of modified zeolite with CTAB, can decrease the tensile strength of the composite. This is likely due to a decrease in the degree of spread of exfoliation of silicate layers in the composite with a natural zeolite content of high natural zeolite particles (< 7 wt%). Moreover, the agglomeration natural zeolite particles also cause a decrease in tensile strength. The agglomeration natural zeolite is believed to be the place of stress concentration and the beginning of the crack so that the tensile strength decreases. According to research [13]. immiscible blend has a physical attraction between a weak component at the phase boundary, which can cause phase separation in certain conditions and cause the mechanical properties of the mixture becomes less good [14].

In a mixture of natural zeolite modified CTAB ,PP/PP-g-MA, incorporation of 3 wt% to 7 wt% polypropylene has caused the value of the tensile strength of polypropylene decreased. This means that the presence of a small amount of natural zeolite particles in the nucleation of PP polypropylene increases. This result is similar to the results of the study [15] who studied the crystallization behavior and morphology of pure polypropylene/clay nano composites. Found that clay particles act as a nucleating agent for crystallization of PP matrix and improve the content of crystallinity polypropylene matrix. On the other hand, the incorporation of natural zeolite with polypropylene particles also showed a similar effect, where cristality polypropylene increases with increasing CTAB content of natural zeolite particles.

3.4 Elongation at Break.

Figure 5 shows a graph of elongation at break of the composite composition of natural zeolite modified with CTAB. Figure 4 in lower elongation at break strain or a mixture of tenacity PP/PP-g-MA on the composition of 3 %wt. Decrease in ductility is due to the limited movement of the molecular chains of the polymer as a result of natural zeolite particles are rigid. Presence of agglomerates subtracting the surface area so weaken the interaction between the filler and matrix and the resulting decline in the physical properties of polymer materials. The results [16] reported the addition of compatibilizer PP-g-MA or the esterification reaction to form hydrogen bonds with the hydroxyl group interface that exist in the natural filler particles on the one hand and the carboxylic group compatibelizer PP-g-MA is diffuses into the polymer matrix on the other. Dewetting is one of the processes that can occur at a solid–liquid or liquid–liquid interface, is predominant around the zeolite particle, there by zeolite seems to be acting as non adhering filler. Thus enlargement,of the air holes upon stretching and merging between the neighboring air holes and the reduce cristallinity is responsible for poor mechanical properties. This is in accordance with studies [17].

3.5 Young's modulus.

Increasing natural zeolite particles in the mixture PP-g-MA/PP can cause an increase in Young's Modulus. Effect of the addition of natural zeolite particles modified with CTAB on Young 's modulus of composite PP-g-MA/PP/natural zeolite particles. It appears that the addition of natural zeolite particle composition of the mixture of CTAB PP-g-MA/PP increasing Young's Modulus. This means that the natural zeolite particles have added stiffness PP-g-MA/PP mix. Stiffness due to the addition of natural zeolite particles is possible due to the nature of its own natural zeolite which is a material that has a high stiffness which then limits the movement of the polymer molecule which is in line with research [12].

Figure 6 seen an increase in Young's modulus with zeolite additive CTAB, this is because when the hard chargers that are added to the soft polymer matrix, can cause most of the load on the polymer matrix in a state of stress, if the interfacial interaction between the filler and matrix adequate rigid structure of the silicate layers are very influential in increasing modulus and stiffness of the polymer can be dispersed evenly. It appears that the addition of modified natural zeolite particle composition of the mixture with CTAB PP-g-MA/PP increasing Young's Modulus. This means that the natural zeolite particles have added stiffness PP-g-MA/PP mix. Stiffness due to the addition of natural zeolite particles is possible due to the nature of its own natural zeolite which is a material that has a high stiffness which then limits the movement of the polymer molecule. This is in accordance with studies [11].

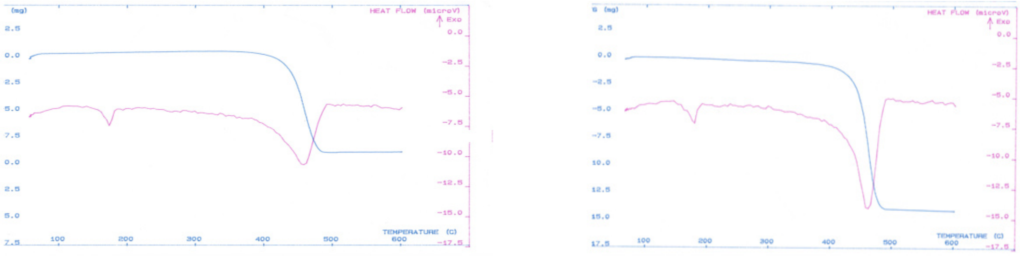
Table 2. Mechanical Characteristic

The Quantity Zeolite CTAB (% wt)	Tensile Strength (MPa)	Elongation at Break (mm)	Young’s Modulus (MPa)
0	33.235	5.511	754.350
0	32.718	5.494	753.580
3	31.531	4.875	809.080
5	29.441	4.671	813.440
7	29.141	4.444	807.360

Table 3. Properties Zeolite CTAB Composites Polypropylene

Quantity Zeolit CTAB (wt%)	Melt Point (^{0}C)	Mass Variation I (mg)	Enthalpy I (mJ/mg)	*Temperature Decomposition (^{o}C)*	Mass Variation II (mg)	Enthalpy II (mJ/mg)
PP	164.03-177.83	-0.06	-1.484	430.27 - 459.17	-13.31	-28.743
0	162.77-173.93	0.04	-2.122	427.53 - 455.70	-9.34	-20.041
3	157.10-173.93	-0.07	-2.810	432.10 - 455.30	-15.25	-27.490
5	157.10-171.57	0.11	-3.411	434.17- 455.70	-17.66	-32.180
7	162.77-169.03	0.57	-2.870	428.20 - 447.17	-19.69	-33.564

3.6 Analysis Thermal.



(a) **(b)**

Figure 7.Thermogram TGA-DTA (a) PP (b) Blend PP/PP-g-MA

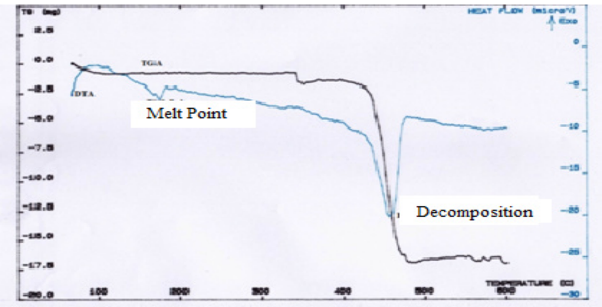


Figure 8.Thermogram TGA-DTA Blend PP/PP-g-MA/Zeolite 3 wt%

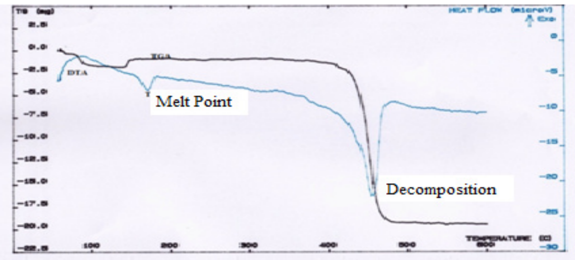


Figure 9.Thermogram TGA-DTA Blend PP/PP-g-MA/Zeolite 5 wt %

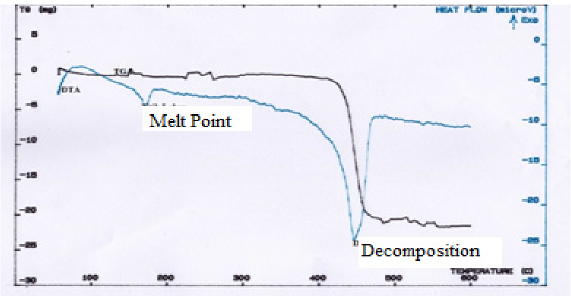


Figure 10.Thermogram TGA-DTA Blend PP/PP-g-MA/Zeolite 7 wt%

From Figure (8 – 10) shows thermogram TGA-DTA Blend PP/PP-g-MA/Zeolite , Table 3 has shown the decomposition of the PP started at a temperature of 430.27 ^{o}C, whereas the decomposition of the composite PP / PP-g-MA Figure 7(b) , with the addition of filler zeolite modified with CTAB occurs at a temperature of 432.10 ^{o}C. This is due to the compatibilizer addition of the PP and zeolite will increase the thermal stability. In accordance with [13].

As can be seen from Table 3, enthalpy experienced no significant reduction with the addition of natural zeolite particles compatibilizer CTAB well with PP-g-MA. However, the composite is slightly lower temperature than pure polypropylene after combined with a certain amount of natural zeolite particles. In contrast, the incorporation of the copolymer, the melting endothermic region is calculated and reported as the heat of fusion enthalpy. Where enthalpy is an important parameter because it is directly proportional to the magnitude of the overall level of which is owned by the polymer. So, from enthalpy, can be estimated enthalpy [18].

Table 3 shows the results from the DTA/TGA studies of Zeolite modified CTAB composite polypropylene. It can be seen from the thermal that the composite lost more than 3 % of its mass under heating to 447.17°C which is considered enough to deduce that it can absorb significant amounts of water. This is an important property for a zeolite which is to be used as a sorbent and for catalysis. This is in accordance with studies [19]

4. Conclusion

For the modification of natural zeolite before particle size 74 µm, after modification with CTAB particle size to 1 µm. From the results of morphological seen the cavities according to the characteristics of natural zeolite. There are significant variations in the composition of natural zeolite particles to the mixture of CTAB, PP/PP-g-MA on the mechanical properties with a decrease in tensile strength and elongation at break, but the Young's modulus increases. Results of thermal analysis of the composition variation CTAB concentration of natural zeolite particles to a mixture of PP/PP-g-MA with thermal analysis (TGA-DTA), obtained no drop in temperature melting point, the process of decomposition and weight reduction with the addition of natural zeolite particles.

5. References

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