Synthesis and innovation of PLA/clay nanocomposite characterization against mechanical and thermal properties

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Abstract. Plastic polymer is one of the most dominant materials of daily human activities because of its multifunctional nature, light and strong and anti-corrosion so it is easy to apply in various equipment. Plastic is generally derived from petroleum material so it is nonbiodegradable. Therefore, this study aims to create a breakthrough of natural and biodegradable plastic materials from plant starch (pisok kepok starch) with the help of 3 types of acid (HNO₃, HCl and H₂SO₄) called Poly Lactid Acid (PLA). PLA is enhanced by mixing with a clay material with a variation of 1, 3 and 5% composition to form a PLA / Clay Nanocomposite material which is expected to have superior properties and resemble conventional plastics in general. Several types of characterization were performed to see the quality of the resulting material including tensile strength test with UTM tool, thermal endurance test with TGA tool, morphological structure test using SEM tool and additional test to see filler clay quality through X-RD tool. Based on the characterization of tensile and thermal test, 5B nanocomposite with addition of 5% clay and HCl acid aid showed the best tensile strength of 36 Mpa and the highest stability was 446,63 oC. Based on the results of morphological analysis of the best samples (5B) showed good interface ties. Meanwhile, based on the results of filler analysis, the opening of clay layer d-spacing occurred at 0.355 nm.

1. Introduction
Currently research on environmentally friendly products is of great concern by many researchers and industry players especially in the field of polymers [1]. One of the interesting biopolymers studied is PLA (Poly Lactid Acid) due to its biodegradable, biocompatible, recycleable and flammable properties that are safe for the environment [2]. Unlike typical synthetic polymers derived from petroleum materials, PLA comes from renewable sources from a variety of plants that have high starch content such as bananas, cassava, sweet potatoes, potatoes, corn and so on that help support the movement of go green and Reduce environmental waste.

PLA can be formed by esterification process of lactic acid obtained by fermentation by bacteria by using starch substrate or simple sugar [3]. These polymers may be amorphous and may also be

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crystalline. The PLA is applied usually to plastic bags, plastic packaging, drink bottles, plastic cups, hard plastic materials, tableware, car components, shelves, buckets and so on. The latest applications from the PLA, one of them in the medical field, among others, is used as artificial leather, sewing thread surgery, drug capsules and also for tissue engineering because it can be adsorbed by the body. However, this biopolymer also has a weakness that is lower melting point than other plastic polymers so that heat stability is not as good as other polymers [4]. In addition, PLA has mechanical properties that are also lower than synthetic polymers. Therefore, to overcome these weaknesses, PLA can be improved its properties by the addition of nano-sized filler material to form nanocomposite.

Based on some of the most prominent references, clay is a subject of considerable attention based on its ability to spread between layers and its ability to expand. Therefore, the clay can be processed into a composite with a polymer. Clay is a mineral decomposition of volcanic ash where its use as an economical filler to modify the creation and performance of the material. The mineralogy of bentonite is defined as clay consisting of 80% montmorillonite having a chemical formula (Al₂O₃·4SiO₂·xH₂O) [3].

There are many types of materials used as fillers, but clay (bentonite / clay) has a long record as the most inorganic material added as a filler into the polymer as a matrix [5]. This is potentially very large when compared to the original material without mixing. The purpose of adding fillers is to improve and improve the properties of polymeric materials to be mechanically stronger and more heat resistant.

Interest in research on nanocomposite polymers among researchers now shows an increasing trend. In addition, the material is also easy to find and economical. Plants rich in starch content are available in large quantities in Indonesia. Moreover, banana crops in the local area, especially in the North Aceh region are available in large quantities have great potential to be utilized as a natural raw material for the manufacture of plastic products (PLA). So far the utilization of these fruits is limited only as fruits and other processed foods. However, by doing this research is expected to be able to increase the value of use and also the selling value of banana with end product in the form of biodegradable plastic. Clay as a filler that is abundant in Indonesia especially in North Aceh region is also expected can be utilized to increase the superiority of plastic polymer product (PLA) in terms of strength and resistance to heat so it has value more than other conventional plastics.

Based on these reasons, this study aims to produce PLA (Poly Lactic Acid) as an environmentally-friendly biopolymer made from banana kepok starch. Additionally clay as a filler used is modified to improve biopolymer performance. The effect of acid variables (HNO₃, HCl and H₂SO₄) and the effect of adding clay amounts to the PLA polymer on the resultant characterization of the resulting PLA / Clay Nanocomposite was also identified. The final product is tested by performing some of the main characterization including tensile and thermal tests to determine its quality. In addition, morphological testing is also performed to support the results of the main characterization, as well as special tests on the quality of filler through d-spacing clay test also became one of the targets in this study.

2. Methodology/Experimental

2.1 Samples
The material used in this study is banana kepok originating from local area of North Aceh, aquades, glycerol, acidic substance (HNO₃, HCl, H₂SO₄), ethanol, reactant benedict, Lactobacillus Plantarum bacteria, zinc oxide catalyst, TBAB surfactant, dispersant (NaPO₃)₆ and clay from Aceh Utara as filler.

2.2 PLA Preparation
2.2.1 Starch Extraction. Banana kepok peeled, cut into pieces then mixed with aquades at a ratio of 1:3 and ground to form a slurry. Then the slurry was filtered and the filter result was precipitated for 8 hours. Furthermore, the precipitate is dried in an oven with a temperature of 60 °C and saturated into starch flour.
2.2.2 Hydrolysis Starch Becomes Glucose. The amount of starch flour was dissolved in aquades, adjusting the pH to ± 2 with various acid catalysts (5% HNO₃, 5% HCl, 2% H₂SO₄) for each sample. Further hydrolysis is done by heating the solution in the two neck flask and stirring done for 3 hours with a temperature of 100 °C. The resulting glucose was then tested using a Benedict test.

2.2.3 Glucose Fermentation Becomes Lactic Acid. Fermentation of glucose into lactic acid using Lactobacillus plantarum bacteria. Fermentation was carried out for 4 days on three hydrolyzed glucose samples with acid variation.

2.2.4 Polymerization of Lactic Acid forms the PLA. Acid produced by fermentation is then polymerized by ROP (Ring Opening Polymerization) method. This process consists of three stages: prepolymerization, depolymerization, and ring opening polymerization. In general the process is heating lactic acid as much as 100 ml under vacuum under pressure of 300 mmHg with a temperature of 100 °C for 6 hours and with the help of ZnO (Zinc Oxide) catalyst at 0.25 gr in the first 4 hours, and 0.75 gr at 6 Hour and added 1.75 ml glycerol as plasticizer.

2.3 Modifying of Filler
Each 100 grams of bentonite is weighed and then pounded with pestle. Performed sizing on 250 mesh. The sieved bentonite was introduced into 1200 ml of aquades and added (NaPO₃)₆ by 1 g and then dispersed by stirring for 6 hours using a medium-spin magnetic stirrer. The dispersion results are then allowed to form bentonite precipitate and separated by water containing impurities. The precipitate is washed with aquades to remove excess residue (NaPO₃)₆ and filtered using filter paper. Bentonite is dried in an oven with a temperature of ± 105 °C to dry. Furthermore, an interlayer opening analysis was used X-Ray Diffraction (XRD) tool for raw bentonite and purified bentonite.

2.4 Preparation of Nanocomposite
The formation of nanocomposite was done by mixing the PLA of the synthesized product with 3 kinds of acid catalyst variations of ± 100 ml and the modified filler clay with variations of 1, 3 and 5 % wt, then heated over hot plate at 65 °C for 20 min. The thickened solution is formed and then poured into a plastic pan and soaked in the oven to dry up to form a nanocomposite sheet of clear plastic. PLA / clay nanocomposites formed are expected to have mechanical and thermal properties that resemble conventional plastics in general.

2.5 Characterization Techniques

2.5.1 X-Ray Diffraction. The nanoclay interlayer spacing was determined by X-ray Diffraction (XRD) measurements using Cu Ka radiation (k = 0.1542 nm), while the generator was set up at 50 kV and 40 mA. The data was collected over a range of scattering angles (2θ) of 1–10.

2.5.2 Universal Tensile Machine (UTM). Dog-bone-shaped specimens for nanocomposite of 150 mm in total length, with a gage section of 12 mm wide by 4 mm thick and 80 mm long, type I based on standard ASTM D638, were prepared by compression molding at 150 °C and a pressure of 25 MPa and subsequent cooling down to 5 °C to avoid sample shrinkage. An Universal Tensile Machine was used to measure the tensile strength of pure PLA adn PLA/Bentonite nanocomposite, according to standard ASTM D638. All tests were carried out under ambient conditions using a cross-head speed of 5 mm/min.
2.5.3 Thermogravimetric Analyzer (TGA). A Thermogravimetric analyzer (TGA) Seiker Extar 6300, Japan) was used to measure the thermal weight loss of pure PLA, and PLA/Bentonite nanocomposite in the temperature range between 30 °C and 900 °C with a heating rate of 10 °C/min under nitrogen steam.

2.5.4 Scanning Electron Microscope (SEM). The morphology of the disk-shaped nanocomposites was investigated by Electron Microscopy (SEM) at room temperature. A high resolution Hitachi S-4700 microscope operated at 2 kV accelerating voltage was employed for SEM to observe surface of nanocomposite such nanofiller agglomeration and distribution. The SEM samples surfaces were cut using an ultramicrotome equipped with a diamond knife at 100 °C, and then coated with platinum vapor.

3. Result and Discussion

3.1. Characteristic of Filler

The process of clay modification as an initial stage before mixing with the PLA polymer in this study consists of the cleaning and opening stage of the d-spacing layer. The crushed clay filler is cleansed using Sodium Hexametafosphate (NaPO₃)₆ which acts as a dispersant. The dispersant time spent for 6 hours and the dispersant quantity of 1% of the treated clay weight is the best value [3]. The purge stage aims to eliminate the impurity content of the clay so as to produce pure montmorillonite. Montmorillonite has the ability to experience swelling to allow the polymer to be intercalated into the mineral gallery and to form a nanocomposite. This swelling power will affect whether or not the quality of nanocomposite produced at the time of mixing. Tetra n-Butyl Ammonium Bromide (TBAB) of 1.24 g as a surfactant used in the opening stage of clay-spacing layer aims to increase the distance between layers of the clay so as to maximize the filler interaction with the polymer to form the nanocomposite. The following table shows the results of the clay layer opening test (d-spacing) to compare the swelling clay power before and after the modification stage.

| Clay            | 2θ (degree) | d-spacing layer |
|-----------------|-------------|-----------------|
| Raw Clay        | 7.2         | 1,142 nm        |
| Modified Clay   | 4.52        | 1,511 nm        |

Based on Figure 1, d-spacing layer clay before and after modification yields values that are not too significantly different. The X-RD graph plots data between the angle of reflection on the x-axis and
the intensity on the y-axis to automatically generate the clay d-spacing layer size. Using the peak 20 setting which yields data at the reflection angle from 2° to 10° indicates that, clay North Aceh prior to modification has a maximum reflection angle peak at 7.2° with a d-spacing value of 1.142 nm, and an increase in the size of its d-spacing After being modified to 1.511 nm at the maximum reflection angle of 4.52°. If the calculated opening of the d-spacing layer on the clay is 0.355 nm. The increased d-spacing layer is caused by the Na + ion composition that affects the swelling properties. This proves that the use of Tetra n-Butyl Ammonium Bromide (TBAB) as a surfactant has succeeded in opening the d-spacing layer in bentonite in the presence of an organic compound exchanging between the two cations (ammonium) of surfactants with ions in montmorillonite (Na+). The opening of d-spacing is also due to the use of (NaPO₃)₆ as a cleansing agent which has worked effectively because it is capable of removing impurities that can block the interaction between surfactant and montmorillonite causing clay modification not to occur.

3.2 Mechanical Properties

PLA / Clay nanocomposites which have been mixed according to the variation of the composition are tested for their mechanical properties of the level of tensile strength through the axial forces provided by the tensile test apparatus until it reaches the maximum limit until interrupted. Here is a graph of tensile test results from nine nanocomposite samples and pure PLA samples without mixing with filler clay as a comparison.

![Graph of Tensile Test Results](image)

Figure 2. Graph of Tensile Test Results.

Figure 2. above shows the magnitude of the tensile strength value of each sample on the different compositions of PLA and filler and the different acid types. Based on the graph, it can be seen that the addition of a filler showed improved tensile strength to the polymer when compared to the original polymer without mixing. The tensile strength value of the nine samples is 17 to 36 Mpa, while the pure PLA tensile strength value is only 14 MPa. The graph shows that the tensile strength value of the 5B sample is PLA with the addition of 5% filler clay and the hydrolysis result using HCL acid is the maximum value of 36 MPa. Meanwhile, the 1A sample which is an PLA with 3% clay addition and hydrolysis result with 5% HNO₃ acid has the minimum tensile strength value of nanocomposite formed at 17 MPa. Based on the graph, it can be seen that the value of tensile strength of nanocomposite is directly proportional to the amount of filler. The more the amount of clay that is mixed into the PLA matrix, the greater the value of the resulting tensile test. That is, the amount of montmorillonite content as an amplifier causes the polymer and filler to bind well so that it has a higher stretch resistance to its peak. In retrospect, the best average tensile test results are shown by the hydrolysis resultant hydrolysis with 5% HCL acid at each filler concentration. This is because this type of acid has a better level of effectiveness where the rate of hydrolysis reaction of starch more quickly occurs so that the resulting glucose is more optimal than using other types of acids.
3.3 Thermal Stability
Thermal degradation test using TGA (Thermo Gravimetric Analysis) tool is aimed to know qualitatively the thermal stability of the nanocomposite based on the change of sample weight due to heating from room temperature to high temperature is usually hundreds of degrees Celsius, so the sample will be degradation as it burns at a certain temperature. This happens because of the decomposition of chemical bond termination. Here is a table of TGA test results of nine samples of nanocomposites that are formed.

| Sample | 1A | 3A | 5A | 1B | 3B | 5B | 1C | 3C | 5C |
|--------|----|----|----|----|----|----|----|----|----|
| Onset Temperature | 317.61 | 328.45 | 348.09 | 398.62 | 442.59 | 446.63 | 325.15 | 351.12 | 365.04 |

Table 2 above presents the thermal stability test results in terms of the temperature value on set ie the temperature at which the sample is degraded (thermally decreased) thermally by the increase in temperature. The degradation temperature of nanocomposite samples ranges from 300-450 oC. According to Table 3, PLA / Clay nanocomposites formed from hydrolysis results with three types of acid catalysts (5% HNO₃, 5% HCl and 2% H₂SO₄) have different onset values. Three nanocomposite samples with the best values of these test results (1B, 3B, 5B) began to degrade at a temperature of 398.62 °C; 442.59 °C; And 446.63 °C. The highest degradation temperature was shown by the 5B nanocomposite hydrolysis with HCl acid and the addition of 5% filler clay. As has been reported in the previous carrarization results that this type of acid is the best to be used as a catalyst because the resulting glucose product is more leverage. The results also show that the concentration of clay added in the PLA polymer affects the thermal stability of the nanocomposite. The higher the filler concentration is added, the better the defensive material is characterized by increased degradation temperature. This increase in degradation temperature is caused by bonding on the polymer and the fused filler is stronger so it is difficult to break and the material decomposition becomes slower[8].

3.4 Morphology
The SEM test as an additional test aims to support the main test results of tensile test and thermal degradation test. The samples tested were samples with maximum results (5B) and terminimum (1A) from previous test results. Here is a picture of the results under an electron microscope (SEM).

![Figure 3. SEM Test Result of 5B.](image1)

![Figure 4. SEM Test Result of 1A.](image2)

Figure 3 is the result of SEM test to the 5B sample which is the best resultant nanocomposite and Figure 4 is the result of SEM test to sample 1A which is the nanocomposite with the least result from the result of the previous characterization. When compared, with x50 magnification the two structures
look almost identical but the surface of the 5B sample tends to be smoother and forms a good interfacial bond between the matrix and the filler than the sample 1A which shows some aggregate shapes that clump and the cracked surface. This is due to the amount of filler added. Clay fillers as fillers function to bind polymers by the nature of swelling that allows the intercalation of polymers into the clay mineral gallery so as to experience exfoliation or good unification. When correlated with tensile and thermal tests, these SEM test results are correlated where the best nanocomposite surface structure has resulted in good tensile strength and thermal stability[9].

4. Conclusion
This research has generally obtained results in the form of PLA / Clay nanocomposite shaped clear plastic sheet with a thin, flexible and smooth texture that almost resembles conventional plastic in general from the physical aspect. The natural clay has been successfully modified so that it becomes compatible as a PLA filler based on the results of the d-spacing layer test. Based on tensile and thermal test results, tensile strength and thermal stability of nanocomposites increased with increasing amount of added filler and starch hydrolysis using HCL acid showed the best result on final product formation compared to other acids. Samples with maximum values were in 5B nanocomposite Hydrolysis with HCL acid and addition of 5% filler clay with value of tensile strength equal to 36 Mpa and degradation temperature equal to 446,63 °C. The SEM analysis results show that the best sample nanocomposite surface structure of 5B shows a uniform and supportive surface structure over the main test results.

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