Synthesis and Characterization of Polylactic Acid / Local Clay Nanocomposite for Packaging Applications

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Abstract. Plastic has become one of the most influential material in human lives due to it being light and strong enough. However, because plastic is non-degradable, it will cause other environmental problem and it is not renewable. Therefore a material that can produce plastic, where it could easily be degradable and the source is renewable. One of these materials is Polylactid acid (PLA) which is derived from starchy plants, such as cassava. However the physical and mechanical of pure PLA still has its downsides, such as low attraction and limited thermal degradation. This research is focused on synthesis PLA from local cassava and addition local clay into PLA in order to improve the two characteristics mentioned previously. The results that the highest was obtain 1,9 kg for 6 hours of disposition and the highest lactic acid obtained 35 % for 5 days fermentation. Polymerization PLA from a lactic acid has been determined by FTIR results. Based on the data show PLA/clay 0,05 M with 2 hours has better tensile strength is 36 MPa and thermal stability compared to pure PLA to be applied as the raw material for packaging.

Keywords: *PLA, clay, X-RD, FTIR, SEM, tensile strength, thermal, packaging*

1 Introduction

Data Plastic packaging is a container that is commonly used in people's daily activities. In this modern era, plastic packaging has its own advantages, some of them are flexibility, cheap, light, easily shaped and strong [1]. The consumption of plastic packaging in Indonesia is quite large, based on Aromatic Industry Association, Olefin and Plastic (Inaplas) on the year 2014, the number of usages reached 4,3 million tonnes or increased to 5-6% from the previous year [2]. In general, the current source of plastic material is from fossil raw materials which are non-renewable and not easily degradable, therefore its waste gave an enormous impact on the environment.

To cope with the limited raw materials issue and the environmental impact that arises with the usage of plastic consumption, there should be more usage of raw materials that are environmentally-friendly, which is commonly known as biodegradable plastic. One of the materials is Polyactic Acid (PLA), which is a polymer from lactate acid esterification that was produced from fermented starch substrate or simple sugar [3]–[5]. PLA can be made with three main methods, they are direct polycondensation, azeotropic dehydration condensation and ring-opening polymerization [6]–[8]. Ring-opening polymerization is a method that is mostly used to produce high molecules PLA; above 100,000 Da. Some catalysts are used in order to increase the PLA yield, such as Al, Zn, Ti dan Zr, the usage of catalyst is dependent on the mechanism used [9], [10]. Some researchers also compared the usage of the mentioned catalysts above with commonly used catalyst which is Sn(II)Ot with the result that particular catalyst produced a

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lower poisonous characteristics compared to Sn(II)Ot. Catalyst Zn and Zr produce 70-90% PLA with the purity of 90-97% [11].

The success of lactate acid polymerization becoming PLA depends on the monomer purity that is used [12] so the production of lactate acid can be an important parameter in the production of PLA. The process of lactate acid production can be done through a biological or chemical process, almost 90% of lactate acid current production is through biological process or fermentation. This method is used because of its advantages, they are a low operational condition, cheaper energy consumption, and low cost as well as non-toxic [13]. Bacteria that is used in the fermentation process of glucose turning to lactate acid are *Lactobacillus*, *Leuconostoc*, *Pediococcus* and *Streptococcus* which are grouped into homofermentative and heterofermentative groups. Currently, the *Lactobacillus* bacteria are grouped as homofermentative is mostly used because the side-effects that it produces is lower compared to heterofermentative bacteria. [13]–[16].

Glucose as a source of lactate acid can be derived from starch conversion; a method that is commonly used to convert starch into glucose through acidic hydrolysis or enzyme hydrolysis. Acidic hydrolysis is commonly used compared to enzyme hydrolysis. Acidic hydrolysis needs catalyzer, such as nitrate acid, hydrochloric acid, and sulphuric acid and it reacts in an acidic environment with pH 1,5 – 2,0 with the temperature of 140-160 °C. These supporting conditions have an important part in which the starch will hydrolyze into glucose [17].

The source of starch can be derived from plants such as corns, cassavas, bananas, sago, sweet potatoes and sorghum [18]. These plants are common in Indonesia, especially bananas, cassavas, and rice are plentiful in Aceh, therefore there is a potential in producing PLA.

PLA has the advantage of being the source of plastic material because its characteristics id almost the same with a plastic material that is sourced from fossil-based materials, such as polyethylene and polypropylene [19]. there are still disadvantages of the material, which are, brittles easily, low elongation and sensitive to water because it is hydrophobic, low tolerance to heat which leads to a modification to increase performance from PLA [6]. A number of scientists have made a filler to increase the physics and the mechanics of PLA.

The addition of filler can widen the area and increase the thermal stability of PLA. The addition of filler can also change the characteristics of the material, so it is possible to derive the material with the desired characteristics. Some fillers that can be used are carbon black, silica, clay, talc, and titanium oxide [7], [20]. Clay is used because of its abundance in Nisam Sub-district. This will also give an impact on the improvement of PLA characteristics.

Clay that is added in PLA sized under 100nm is commonly known as nanocomposite material that has new characteristics. The structure of nanocomposite that is produced depends on the level of dispersion into the polymer. In general, there is 3 nanocomposite structure formation, which is a conventional composite, intercalary and exfoliation. Each of the nanocomposite makings is hoped to be more structured by exfoliation so there will be a smoother later between the surfaces. In general, there are 4 methods of synthesizing nanocomposite to reach exfoliation structure; in-situ synthesis, intercalary solution, in-situ polymerization and melting intercalary.

Clay is hydrophobic just like PLA, so it is hard to interact. Therefore before the clay is mixed with PLA, it needs to be purified first, then modified with the addition of surfactant to make organophilic which will be suitable with the hydrophobic nature of PLA. A surfactant that is mostly used is *alkylammonium* or *alkyl phosphonium* to cation hydrate in between the layers of clay [21].

This research aims to make PLA qualitatively from cassava starch that is available in Aceh as well as to identify the influence of adding nano clay that is available in North Aceh towards the physics and mechanics from the formation of the nanocomposite material.

2 Material And Methodology

2.1 Material

The materials used in this research is cassava from the markets of North Aceh, Clay from Nisam Sub-district and other chemical materials which are: Chloride Acid, Phenol, Sodium Hydroxide, Cetyl Trimethyl Ammonium Bromide (CTAB), Iron (II) Oxide, agar Na as well as Lactobacillus bacteria.

2.2 Procedure

Generally, there are two stages that are conducted parallelly, they are the production of PLA and preparation of organoclay, then mixed in between PLA and organoclay.

The production of PLA is started with the extraction of starch from cassava using the wet method, where 10 kg of cassava is peeled, cleaned using water then grated. The grated cassava is dissolved in water with 1:3 ratio then soak for an hour. Then, strain and let it sit to deposit. In this stage the variable of deposition is as long as 4, 6, and 8 hours, then the starch is dried for 24 hours. The starch that has hydrolyzed into glucose through the acidic hydrolysis process where about 25 grams of the starch is dissolved into 100 ml of distilled water then added with 1% HCl until the pH reached 2,0. Then it is heated to the temperature of 120 ºC for 10 minutes and stirred with a speed of 300 rpm. The glucose produced is separated with water by distilling it with the temperature of 80-120 ºC. The deposit that was produced is then neutralized using NaOH, then dried.

Glucose that is produced is fermented into lactate acid. This stage is started by preparing Na nutrients, then followed by planting the bacteria and incubating for 18 hours. 25 grams of glucose that is dissolved in 100 ml distilled water is then planted into Petri dishes that have the bacteria. In this stage, a variation of fermenting time of 4, 5, 6 days is used while the bubbles formed are observed. After the fermenting time is reached, therefore the deposition that has been produced is separated from water then added with 5% HCI and then rinsed, dried and weighed for the production of lactate acid.

Lactate acid that was formed then is polymerized into PLA with the method of ring-opening polymerization, where lactate acid is inserted into a reactor and then being kept within the reaction temperature 160-200 ºC, on atm pressure and supplied with nitrogen. Lactate that was formed is then cooled to the temperature of 90 ºC until there is solidification. Then the ZnO catalyst is added into the reactor with reaction temperatures of 230-240 ºC. The formation of PLA is then observed. To prove the formation of PLA, characterization is conducted using FTIR.

Apart from that, the process of clay preparation is started with cleaned clay using Na, then it is mashed into powder with the size of 100 mesh, next the powder is centrifuged with the speed of 700 rpm. After that it is heated to the temperature of 60 ºC. Pure clay that is formed is added surfactant 0,04 M and 0,05 M with the stirring time variation 1 to 2 hours of stirring then it is followed with 12-hour suspension. The results of the suspension that was produced and free from chlorine and bromide is then dried in an oven on then temperature of 90 ºC for 24 hours until organoclay is present.

3 Result and Discussion

3.1 Starch Extraction

Extraction of starch from cassava with the deposition time variation of 4, 6, and 8 hours can be seen in figure 1

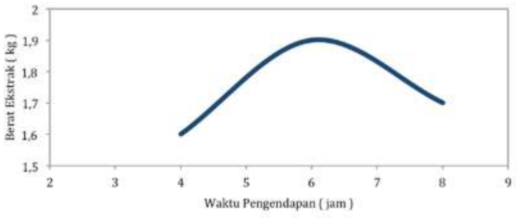

Figure 1. The Effects of Deposition Time against Starch Extraction

From Figure 1 it can be seen that the highest starch extraction is gained from the deposition time of 6 hours with 1,9 kg of the starch extract, the formation of starch starts to decrease after 6 hours, as seen in the deposition time of 8 hours where the starch extract formulated is 1,7 kg. Then there was also fungus present that is why the best deposition time is 6 hours.

3.2 Glucose Fermentation

The determination of fermented glucose is done by testing the concentrates of lactate acid formation. The concentrates of lactate acid formed can be seen in Figure 2

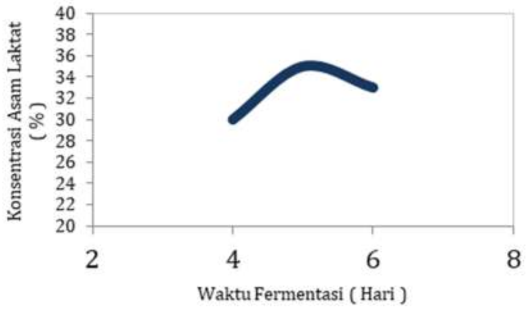

Figure 2. The Effects of Fermentation Time Towards Lactate Acid Concentrates

From Figure 2 it can be seen that the highest lactate acid concentrates is gained during the fermenting time of 5 (five) days as high as 35%, while for the sample fermenting time of 6 (six) days there was lactate acid concentrate as much as 33 %, which is lower compared to the 5-day fermenting time. It was also higher during the 4-day fermenting time which is 30%. According to the research conducted by [22]; the more fermenting time conducted, therefore, the amount of bacteria increases, so it is predicted that the lactate acid concentrates formed become higher, however in this research it was also shown that a different thing, which is a decrease after a 5-day fermenting time. This may be caused by the lactobacillus bacteria had a decrease inbreeding which is caused by the substrate condition that made it impossible for a continuous metabolism.

3.3 Synthesis of PLA

The synthesis of PLA is conducted qualitatively proven through analyzing using FTIR, where the analysis results can be seen in Image 3.3 below. The infrared spectrum for lactate acid is clearly showing some stretch on the O-H hydroxyl groups with a strong indication that hydrogen bonds were formed. This can be seen in the wide tip in the area with the waves of 3502,72 cm^{-1}. Carbonyl groups as C=O stretch are shown in the waves of 1759,08 cm^{-1}. Methylene groups as stretches in C-H groups are seen in the waves of 3000 cm^{-1}. The three spectrums prove that what was formed from lactate acid polymerization is PLA. This is in accordance to the research that was conducted by [23] with the results of absorption bands that was close to 3605,57 cm^{-1}, this shows that the absorption bands that are closer to 3605,57 cm^{-1} have OH groups. The absorption bands closing into 2930 cm^{-1} shows that there are C-H groups.

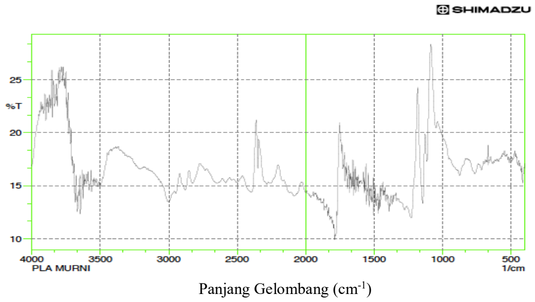

Figure 3. PLA Spectra Graph

3.4 Synthesis of Clay

Before clay was mixed with PLA, the local clay that was obtained must be prepared by adding CTAB surfactant. This is to prove that the clay has become organoclay, therefore, it will be analyzed by identifying the d-spacing layer from that particular material. Figure 4 shows the obtained measurements of the d-spacing layer from that material.

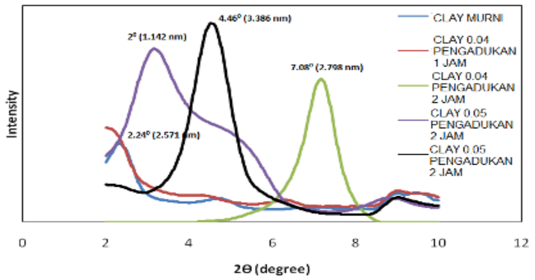

Figure 4. Clay Diffractogram clay

Figure 4 shows clay d-spacing layer of 0,04 m for 1 hour of stirring (*d-spacing* 2.571 nm), clay 0,04 m for 2 hour stirring 7.08° (d-spacing 2.798 nm), clay 0,05 for 1 hour stirring 3.06° (3.055 nm), clay 0,05m for 2 hour stirring 4.46° (3.386 nm) while layer from pure clay is 2.24° (1.142 = nm).

With the results from X-RD test, it can be concluded that the bigger concentration that was used, the longer the stirring time used, therefore the d-spacing layer that is formed will also be bigger. However pure clay that was not synthesized with CTAB surfactant has the smaller d-spacing layer. From the results above therefore, it is sure that CTAB surfactant has successfully enlarged the d-spacing layer from clay.

3.5 Tensile Strength Characterization

The nanocomposite material that was formed can be shaped according to ASTM D 638, then a tensile strength test was conducted and the results can be seen in Figure 5

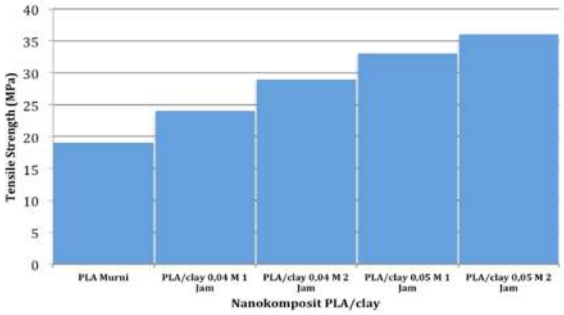

Figure 5. Tensile Strength Characterization

Figure 5 shows that by adding clay, it can increase the tensile strength, where for PLA/clay 0,04 M 1 hour, has the tensile strength of 24 MPa. However the highest tensile strength is obtained from PLA/clay 0,05 2 hours stirring. From the image above it can be concluded that by adding clay, the tensile strength can be increased.

3.6 Thermal Characterization

The thermal characterization is conducted on all samples to identify the stability of the thermal material produced by using the thermal degradation testing technique, with TGA tools. The test results are obtained as seen in Figure 6.

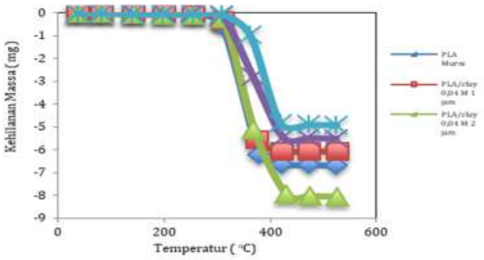

Figure 6. Nanocomposite Thermal Characterization

Figure 6 shows the pure PLA thermal stability is lower which is decomposing at the temperature of 317,61 ºC. For sample PLA/clay 0.04 M 1 hour and 0.04 M 2 hour was decomposing at the temperature of 328.45 ºC and 351.12 ºC. This suggests that the thermal stability is better than pure PLA. For samples, PLA/clay 0.05 M 1 hour and 0.05 M 2 hour were decomposing at the temperature of 353.79 ºC dan 365.04 ºC, which are higher compared to the PLA PLA 0,04 M 1 hour and 0,04 M 2 hour samples.

CTAB concentration within the clay can influence the thermal stability from the nanocomposites that were produced. This is seen from the decomposition of PLA/clay 0,05 M 2 hour stirring sample on a higher temperature compared to the temperature sample of PLA/clay 0,04 M 2 hours stirring. Thus, it is shown that adding clay to PLA can increase the thermal stability for the nanocomposites that were produced. The opening of the d-spacing layer in the clay is directly proportional to the number of surfactants concentrates within the clay.

4 Conclusion

Based on the research conducted, it can be concluded that:

1. The most optimal starch extract is 1,9 kg produced from 6 hours of deposition.
2. The highest formation of lactate acid is 35% produced from 5 (five) days deposition time.
3. Based on FTIR testing, there were: hydroxyl groups present in the wave of 3502,72 cm^{-1}, carbonyl groups present in the wave of 1759,08 cm^{-1} as well as methylene on the wave 3000 cm^{-1}, these have proven that PLA was successfully made from Northern Aceh's cassava.
4. The tensile strength test data showed that the tensile strength of pure PLA is 19 MPa, PLA/clay 0,04 M 1 hour is 24 MPa, PLA/clay 0,04 M 2 hour is 29 MPa, PLA/clay 0,05 M 1 hour is 33 MPa dan PLA/clay 0,05 M 2 hour is 36 MPa,. Their results show that increasing clay within PLA will increase the tensile strength compared to pure PLA as well as the CTAB concentration within the clay can increase the tensile strength of that material.
5. The thermal test data were pure PLA decomposition temperatures on 317,16 ºf, PLA/clay 0,04 M 1 hour, on 328,45 ºC, PLA/clay 0,04 M 2 hour, on 351,12 ºC, PLA/clay 0,05 M 1 hour, on 353,79 ºf and PLA/clay 0,05 M 2 hour, om 365,04 ºC. These results shown that increasing clay can increase the stability of the nanocomposite of that material, and the amount of CTAB surfactant concentrate also influenced the stability of thermal nanocomposite PLA/clay.

   The structure of PLA/clay 0,05 M 2 hour looked smoother compared to pure PLA.

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