Improving the quality of biopolymer (poly lactic acid) with the addition of bentonite as filler

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Abstract. PLA (Poly Lactid Acid) - Bentonite polymer nanocomposite which is a combination of natural and nanometer-scale inorganic substances created through three processes, mixing using a melt blending, molding with a hot press using specimens Standard ASTM D 638 Type IV and drying. In this study, PLA combined with two types of natural bentonite obtained from different areas to find differences in the quality of the results of characterization. To optimize the performance of filler, before mixing, bentonite have to furificate first with (NaPO3)6 and also open the interlayer space with CTAB. D-spacing of bentonite interlayer were analyze by X-Ray difraction (XRD). Characterization bionanocomposite resulting morphologic structure was tested using a Transmission Electron Microscope (TEM). Mechanical analysis of PLA-bentonite nanocomposite in the form of tensile strength was tested using a tensile test specimens of standard American Standard for Testing Materials (ASTM) D 638 Type 4, and thermal resistance using Thermo Gravimetric Analysis (TGA).

1. Introduction
Some material polymer derived from environmentally friendly materials (biopolymers) has generated a lot of Poly Hydroxy alkanoic eg, PHA (PHA), poly hydroxy butyrate (PHB), and Poly Lactid Acid (PLA). However, one of the emerging biopolymers examined are PLA (Poly Lactid Acid) due biodegradation capabilities so high that classified as environmentally friendly polymers. Unlike synthetic polymers are generally derived from petroleum materials, PLA is derived from renewable sources, namely from a variety of plants that have a high starch content such as cassava, sweet potato, banana, corn and so on [1].
PLA can be formed through a process of esterification of lactic acid obtained by fermentation by bacteria using substrates starches or simple sugars. There are two optical isomers of lactic acid as the main carbon atom binds to different groups, namely poly (L (+) - laktid) (PLLA), poly (D (-) -laktid) (PDLA), and poly (DL- laktid ) (PDLLA). PLLA and PDLA usually crystalline because it has the isotactic optically active isomer, while the relative PDLLA amorphous shape because it has the inactive optical isomer atactic. Commercial products are usually in the form of DL-. The process in the synthesis of poly lactic acid according Averous (2008) can be through three methods, namely Polycondensation Direct (direct condensation polymerization), azeotropic dehydration condensation, and Methods Ring Opening Polymerization (ROP). Compared with other methods, the ROP method is a method that is extremely complex and produces PLA with good characteristics for various applications. Ring opening polymerization method that produces PLA with a molecular weight of 2 x 104 to 6.8 x 105 has been patented by Cargill (USA) in 1992 [2].

Another advantage of the PLA include Biodegradable, biocompatible, 100% recyclable and can be burned perfectly and produces CO2 gas and water. However, these biopolymers also has drawbacks one of which is a low melting point so that the heat resistance is not so good. Therefore, to overcome these weaknesses, PLA its properties can be improved by the addition of fillers (filler) to form nano-sized nanocomposite [3].

Bentonite is a mineral's where its use as a filler material economical to modify the creation and performance of the material. In mineralogy bentonite by Gilson in 1960 was defined as a clay that consists of 85% montmorillonite which has the chemical formula (Al2O3.4SiO2xH2O). Bentonite is a mineral resources are abundant in Indonesia. Minerals bentonite has a diameter of less than 2 micrometers are composed of various phyllosilicate containing silica, aluminum oxides and hydroxides which bind water. Bentonite structure consisting of two layers (three layers) composed of two layers of silica tetrahedral and octahedral central one. tetrahedral layers containing silicon atoms / silicate and octahedral layers made of aluminum or magnesium hydroxide. Generally, this layer has a thickness of about 1 nm and can be widened to 30 nm. Among the octahedral and tetrahedral layers are monovalent or bivalent cations, such as Na+, Ca+ and Mg 2+. The purpose of the addition of filler is to improve and enhance the material properties of the polymer to make it more stable, stronger mechanical and chemical as well as more resistant to heat in order to function optimally in the various sectors of human life such as household appliances, automotive, agriculture, healthcare and packaging [4].

In general, nanocomposite polymer formed by dispersing organic or inorganic nanoparticles in the polymer matrix. Nanobentonit have a very large surface area so that it can interact effectively with the polymer matrix at low concentrations (2-8%). Various process for forming a bentonite-polymer nanocomposite, ie in situ polymerization, exfoliation solution and melt intercalation. On learning this, the PLA-bentonite nanocomposite formed through melt intercalation bentonite is mixed directly into the polymer matrix in the molten state. Sodium hexametaphosphate (SHMP) or (NaPO3) 6 is used as defloculant to purify bentonite before mixed with polymers with the separation of montmorillonite with other substances that are impurities and disturbing keoptimalan interact with the filler in the polymer matrix. CTAB (cetyl trimethyl ammonium bromide) is used to unlock the layer (layer) in order to more bentonite expands so as to maximize the intercalation of bentonite in the polymer matrix. After purification, the content in the bentonite was investigated using X-ray apparatus Diffraction (XRD) while seeing an increasing number of montmorillonite contained [4].

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PLA-bentonite nanocomposite formed tested strength using a tensile test specimens of standard ASTM D 638 Type 4. Then morphologic structure was analyzed under the tool Transmission Electron Microscope (TEM). To determine the increase of the polymers to heat, PLA-bentonite nanocomposite analyzed using Thermo Gravimetric Analyzer (TGA).

2. Experimental

2.1. Material

PLA (Poly Lactid Acid) crystalline type used in the study came from Nature Works Co. (USA), while bentonite used in the study came from two different regions of the region, namely bentonite I Nisam, Aceh Utara (UA’s Bentonite) and Bentonite II of the District. Bener Meriah, Takengon, Central Aceh (Tkg’s Bentonite). Other additives that are used in the form of distilled water, cetyl trimethyl ammonium bromide (CTAB) and sodium hexametaphosphate (NaPO₃)₆ for the purification of bentonite.

2.2. Methods

2.2.1. Purification of bentonite top of form

Prepared two containers for purification of two types of natural bentonite. Each Bentonite weighed as much as 3 grams are weighed and then in grinding for 60 minutes. After sifting it done at a size of 230 mesh. Bentonite grinding results put into 250 ml of distilled water and dispersed by mixing for 2 hours on a magnetic mixer until it forms a suspension. Then added 1.86 grams of CTAB and also (NaPO₃)₆ as much as 0.06 grams and carried back in dispersing magnetic mixer for 6 hours at a speed of 50 rpm. Results disenstrifugasi dispersion for 2 minutes at a speed of 700 rpm and is separated from the liquid. Results centrifuging and then washed with distilled water to remove any remaining back (NaPO₃)₆ overproduction. Dried in an oven with a temperature of 60 °C for 1 day [5].

2.2.2. Nanocomposites preparation

Prepared 3 PLA samples each of 20 g. Bentonite is mixed filler PLA and is purified beforehand by comparison, namely: 20 g: 0.2 g (1% by weight polymer); 20 g: 0.6 g (3% by weight of polymer) and 20 g: 1.0 g (5% by weight of polymer). Melt blending the mixture melted at the temperature of 140 °C, then hardens by itself to form PLA-Bentonite Nanocomposite. PLA-bentonite nanocomposite further cut into granules and inserted into a mold specimens according to Standard ASTM D 638 Type IV, then compressed with a hot press at a temperature of 190 oC. PLA-bentonite nanocomposite that has been printed is then dried in a vacuum oven with a temperature of 60 °C for 24 hours or can be dried in ambient air [6].

2.3. Characterization

The extent of dispersion of the bentonit in the filled samples and also the nanobentonite interlayer spacing was examine by X-Ray Diffraction (XRD) which performed at room temperature using a Shimadzu XRD 600 X-Ray diffractometer (30 kV, 30 mA) with a nickel CuKα radiation source. The data was collected over a range of scattering angels (20) of (1-10°) [7].

In order to know the tensile properties, the tensile strength test were carried out with an Instron 4468 machine according to ASTM D 638 Type IV. Samples were cut to 165 x 19 x 0.5 mm in size and
straining was carried out at 50 mm/min crosshead speed. For each specimen, five samples were tested and average values of the tensile strength was calculated.

The morphology of the disk-shaped nanocomposites was investigated by Transmission Electron Microscope (TEM). The TEM samples were cut in thin section (50-80 nm thickness) at -100 °C using an ultramicrotome with a diamond knife.

Thermo Gravimetric Analyzer (TGA) used to determine the glass transition temperature (Tg) of PLA-bentonite nanocomposites which carried out using a Perkin-Elmer instrument TGA equipment at 1 Hz from -98 to 140 °C with a heating rate of 5 °C/min in tensile mode. The sample was cut into just a small size. The position of the maximum tan δ value was used to determine the glass transition temperature (Tg).

3. Result and Discussion

3.1 XRD analysis

XRD was used to examine the extent of dispersion of the bentonite in the filled samples (PLA) and also the nanobentonite interlayer spacing. In Figure 1a the pure AU’s bentonite-PLA shows a diffraction peak at 2θ = 3.870°, indicating that the d-spacing between the silicate layer was about 1.163 nm. Meanwhile, the broad diffraction peaks in 1%, 3% and 5% of AU’s bentonite were 2θ = 6.356° (d-spacing = 1.478 nm), 7.137° (d-spacing=1.953 nm), and 5.901° (d-spacing = 2.677 nm) respectively. This implies that after the cation exchange reaction in CTAB-montmorillonite was larger than that of the pure bentonite. This is turn indicates that in bentonite was succesfully intercalated in polymer matrix in increase of its content.

| Table 1. Summary of the d-spacing and 2θ values for pure bentonit, PLA-AU’s bentonite and PLA-Tkg’s bentonite |
|--------------------------------------------------|---------------------|
| 2θ (degree) | d-spacing   |
| Pure AU     | 2.0         | 1.163 nm     |
| Pure Tkg    | 2.0         | 1.105 nm     |
| 1% AU-PLA   | 2.0         | 1.478 nm     |
| 3% AU-PLA   | 2.0         | 1.953 nm     |
| 5% AU-PLA   | 2.0         | 2.677 nm     |
| 1% Tkg-PLA  | 2.0         | 1.372 nm     |
| 3% Tkg-PLA  | 2.0         | 1.731 nm     |
| 5% Tkg-PLA  | 2.0         | 2.071 nm     |

Figure 1b also present three series of XRD curves of PLA - Tkg’s bentonite nanocomposites. In the case of 1%, a very small basal spacing was observed, from 1.105 nm in pure-bentonite to 1.372 nm. In 3%, the d-spacing layer was 1.371 nm. With increasing bentonite content, the peak became stronger and exhibited a sharply increased peak toward the d-spacing of 2.077 nm for 5% Tkg’s bentonit-PLA. Meanwhile, these results suggest that intercalated PLA-Tkg’s bentonites nanocomposites was low than the AU’s bentonites. It caused the different swollen spacings in these two bentonites which are influenced of CTAB attributes and bentonites composition. Table 1 summaries the d-spacing and 2θ (degrees) for PLA-AU’s bentonite and PLA-Tkg’s bentonite.
3.2 Mechanical properties
The mechanical properties of PLA-bentonite nanocomposites are given in Figure 2. The pure bentonites had a remarkably beneficial effect on the tensile strength of the nanocomposites which increased with increasing bentonite content (1, 3, and 5%) having highest values in each of bentonite (AU’s and Tkg’s). Figure 2 explains the tensile strength of pure PLA and PLA-bentonite nanocomposites were usually higher than without.

In the result, PLA which used a mixture of Tkg’s bentonite has lower of tensile strength than PLA with AU’s bentonite on each % increase. This indicates that the quality of bentonite AU better in improving the tensile strength of polymer. This is due to the content of montmorillonite in the AU’s bentonite is much larger than the Tkg has.
3.3 Morphology analysis

Figure 3 shows the TEM micrographs of PLA-bentonite nanocomposites prepared by 5% of bentonite inserted in polymer matrix which is taken by the most excellent quality. Figure (a) and (b) shows the surface structure of the polymer with bentonite AU’s and Tkg’s where it can be seen that the surface is not much different.

![Figure 3. TEM Micrographs of PLA-bentonit nanocomposites with (a) 5% Aceh Utara’s bentonite (b) 5% Takengon’s bentonite](image)

3.4 Thermal stability

![Figure 4. (a). The TGA curves of Neat PLA and PLA – AU’s Bentonite 1, 3, 5 wt% ; (b) The TGA curves of Neat PLA and PLA – Tkg’s Bentonite 1, 3, 5 wt%](image)

The thermal properties were determined using thermogravimetric analysis (TGA). The TGA analysis of neat PLA, PLA – AU’s Bentonite 1, 3, 5 wt% and PLA – Tkg’s Bentonite 1, 3, 5 wt%, respectively, are shown in Figure 4 (a) and (b). With regard to neat PLA, the degradation at 200-450 °C is attributed to depolycondensation reaction. Then at higher temperature, the material degrades slowly, and it degrades completely at about 700°C. The results show that as compared to pure PLA, thermal resistance is enhanced in the presence of bentonite. This indicates an improvement in thermal stability of PLA because the organic material can prevent the heat from expanding quickly and limit further degradation. Onset degradation of PLA is at 250°C, and is lower than of the PLA – AU’s bentonite and PLA – Tkg’s bentonite takes place at about 350°C and 367°C, respectively. It means the thermal resistance of nanocomposites improved above 70% compared pure polymer.
4. Conclusion

The combination of PLA-bentonite as nanocomposite aims to improve the properties of PLA as a polymer. Bentonite was intercalated into the polymer matrix by melting intercalation. The raw bentonite used came from two different regions to look for differences in quality. The d-spacing of bentonite interlayer was the investigation and the result is bentonite from Aceh Utara more swell than bentonite from Takengon. In the analysis of tensile strength, the addition of Aceh Utara’s bentonite also shows the results of tensile strength better than Takengon’s bentonite, it caused of montmorillonite content and as the increasing of % of bentonite make it more strong. For morphology structure, PLA with the addition of bentonite of Aceh Utara and also Takengon shows the results that were not significantly different that was investigated under TEM.

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