Regeneration of Spent Bleaching Earth for PLA Nanocomposite Filler

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Abstract. This paper concerns on regeneration of spent bleaching earth (SBE) as a filler in biodegradable nanocomposite. The nanocomposite were produced from two different production methods, solvent casting and extrusion. SBE can be used as filler after being regenerated by removing oil and impurities. A regeneration method for SBE was conducted using chemical treatment. Regeneration process was proved to be successful as shown in FTIR with the absence of peak at 2850 cm⁻¹–2930 cm⁻¹ and 1730 cm⁻¹ indicating the disappearance of free fatty acids and ester bonds from regenerated bleaching earth (RBE). The RBE was then applied as filler for PLA-Nanocomposite, biodegradable plastic, a suitable substitute for conventional plastic. The production of nanocomposite used two different surfactants, namely octadecyl amine (ODA) and trimethyl stearyl ammonium chloride (TSC) at two different concentration (20 mmol and 40 mmol). The mechanical property of PLA-Bentonite nanocomposite was then analyzed for tensile strength and permeability. The highest tensile strength and lowest gas permeability was obtained by nanocomposite that used 40 mmol TSC as surfactant, with 12.48 MPa and 0.017 g/day, respectively. Moreover, addition of regenerated bleaching earth to PLA-Nanocomposite during production using extrusion and solvent casting had slight different effect. XRD pattern of all extruded PLA-nanocomposite samples indicated the formation of exfoliated structure, as shown in XRD pattern with very low intensity peak around 2 nm at 2θ = 5, while only a few of samples of PLA-nanocomposite created by solvent casting indicating the same structure.

1. Introduction
PLA is an environmental-friendly polymer because it can easily degrade and can be produced from biomass material. Apart from that, PLA has the advantage of simple processing and biocompatible [1]. However, PLA has several weaknesses such as fast physical aging, sensitivity to water, limited impact resistance, and high rigidity [2]. Therefore, PLA modification really needs to be done to correct its weaknesses, such as modification with plasticization [3] or modification with addition of fillers. Commonly used fillers in PLA modification are nanoclay [4] and cellulosic fibers [5]. In Indonesia, bentonite is one of the most abundant clay.

Bentonite is used during the bleaching step of palm oil. After use, the bleaching earth loses its adsorption properties and becomes a waste dumped in landfills without any treatment. This waste, known as spent bleaching earth (SBE), contains up to 30%-wt residual oil that produces unpleasant odors and classified as hazardous waste [6]. Reactivation and reuse of SBE have been proposed as a
way to reduce the pollution arising from the inappropriate disposal of this waste. Some studies have examined the possibility of using reactivated SBE as a sorbent for different pollutants [7][8][9].

The activation process for SBE aims to create a distance between bentonite surfaces (distance between layers, so-called basal spacing), in order that regenerated bentonite can form a variety of nanocomposites shapes with PLA [10]. The basal spacing is then improved by surfactants [11], octadecylamine (ODA), and trimethyl stearylammonium chloride (TSC), in the activation process. A comparison of both surfactants need to be conducted.

Oil removal from SBE can be done by the extraction process. The main advantages of extraction methods are a short time and the use of minimum solvents. Extraction is carried out within a short time to minimize the potential degradation of the active components of bentonite. There are several methods of oil removal from SBE such as soxhlet extraction [12], membrane technology [13], subcritical water technology [14], and supercritical liquid extraction [15].

In this study, we used the soxhlet extraction method. Soxhlet extraction has traditionally been used for a solid sample with limited solubility in a solvent in the presence of insoluble impurities. A porous thimble loaded with a solid sample is placed inside the main chamber of the soxhlet extractor. By refluxing the solvent through the thimble using a condenser and a siphon sidearm, the extraction cycle is typically repeated many times. Soxhlet extraction is a rugged, well-established technique and permits unattended extraction [16].

Concerning nanocomposite, solvent casting is mostly used for the preparation of films containing nanocomposite scaffolds. This method is widely used because of low costs, shorter preparation time, and most importantly easy variation in reaction conditions [17]. On the other hand, the extrusion method can operate a continuous operation and can obtain high production volumes [18].

This study focuses on the use of regenerated SBE as fillers for producing PLA nanocomposite in order to improve the mechanical properties of PLA. Regenerated SBE as filler was compared with commercial bentonite and cloisite with regard to mechanical properties testing and water vapor permeability for PLA-Clay-Nanocomposite. In addition, the nanocomposite resulted from two methods are also compared with regards to intercalated and exfoliated structures.

2. SBR Regeneration Method and Nanocomposite Synthesis Method

2.1. Materials and Equipment

Bentonite, hexane and NaOCl was the main materials of SBE regeneration process. Used bentonite is obtained from the oil refining industry (Sinarmas Group) while hexane and NaOCl are obtained from Brataco Chemica, a local chemical company. To extract bentonite, soxhlet extractor was applied, equipped with heating mantle, two-neck round-bottom flask, timble, condensor, siphon tube and thermometer.

Previous research have been made to create a PLA-bentonite nanocomposite. In this study, PLA-nanocomposite that obtained from solvent casting method and extrusion method are analysed with several methods such as Universal Testing Machine (UTM), X-ray Powder Diffraction (XRD), Fourier-Transform Infraed Spectroscopy (FTIR), Water Vapor Permeability (WVP) methods.

XRD patterns were obtained from a Rigaku Smartlab diffractometer equipped with a Cu Ka generator (k = 1.5406 Å) operating at 45 kV, 30 mA, and at room temperature. On the XRD test, the basal spacing (d₀₀₁) of regenerated bleaching earth compared to the basal spacing of commercial bentonite.

The morphology of PLA-clay nanocomposites was characterized using scanning electron microscopy (SEM). Surfaces of nanocomposites were investigated in a Jeol, JSM-6510A (Japan) with the acceleration voltage was 5 kV. The specimens for the PLA-clay nanocomposites was carried out according to ASTM D683 type IV. The tensile test were performed using a universal testing machine RTF-1310, with a load cell of 10 kN and with crosshead speed of 2mm/min.
2.2. Working Procedure

SBE regeneration process started with soxhlet extraction. After the extraction, it was bleached using NaOCl before modified with surfactant to produce organobentonite. The resulting organobentonite is sized under 325 mesh or 0.044 mm. Organobentonite was then mixed with PLA by two different method, solvent casting and extrusion. Organobentonite was dispersed to PLA to create a nanoscale interlayer distance. The details for both methods can be found elsewhere [19, 26].

In brief, a solvent casting method, PLA and bentonite was mixed using chloroform as a solvent. The mixture then molded in a film shape. The extrusion method mixed PLA and bentonite. The mixture of PLA granule and bentonite was heated at high temperature in extrusion process until it reach its melting point. Extrusion result molded using compression molding to obtain a film shaped nanocomposite.

3. Results and Discussion

3.1. Characterization of Bentonite

Figure 1 shows XRD result of RBE. The addition of 20 mmol of ODA surfactant to regenerated bentonite increase the distance between layers. Increasing distance between layers of bentonite with surfactants was occured due to inorganic ions Na/Ca/Mg available between the bentonite layers swapped with positive ions possessed by organic surfactants [20]. The absorption of these ions resulted the surfactant entering the space between bentonite layers. The addition of surfactant by doubling concentration it also increased the distance between layers. Increasing amount of surfactant would increase the number of ions that can be exchanged, so that the repulsion force will be bigger and result in a greater distance [21].

Figure 1. XRD spectrum and space between bentonite layers before and after treatment [19].

Another type of surfactant TSC also gives similar result. The bentonite was treated with more surfactant portion showed a larger distance between layers. Therefore, it can be shown that the additional distance between layers is not only affected by the amount of surfactant but also influenced by the type of surfactant.

In general, bentonite contains montmorillonite and other minerals in the form of biedellite, nontronite, iron impurities, caolinite, feldspar, cristobalite, crystalline and amorf silica, and calcite. The mineral composition of bentonite can be analyzed using XRD to confirm the minerals.
XRD pattern of commercial bentonite, SBE and regenerated SBE showed that commercial bentonite mainly contains montmorillonite. Commercial bentonite, SBE and regenerated SBE have similar diffraction peak. Therefore, the removal of oil in SBE by adsorption process and regeneration of SBE do not affect the main structure of bentonite in RBE.

FTIR analysis was also conducted to find the effect of modification with surfactants on bentonite in RBE.

Figure 3 shows the regeneration process of spent bleaching earth with n-hexane and NaOCl solutions caused some of the absorption peaks at 2850-2930 cm\(^{-1}\) and 1730 cm\(^{-1}\) to disappear, indicating oil elimination.

3.2. Surface Structure of PLA-Bentonite Nanocomposite

The structures of the nanocomposites were analysed using X-ray diffraction (XRD). XRD was operated at 45 kV and 30 mA. The interlayer distance is calculated using Bragg’s equation [22]. This interlayer distance determines the structure of the nanocomposite whether it exfoliated or intercalated following Equation 1 below.

\[ n \times \lambda = 2 \times \sin \theta \]  

\( n \times \lambda \) is the interlayer distance, \( \lambda \) is the wavelength of the X-ray, and \( \theta \) is the diffraction angle.
Table 1 summarized the nanocomposites produced using solvent casting. Only TSC 40 mmol results in exfoliation structure compared with other concentration and surfactant, only intercalation.

Table 1. Surface structure of nanocomposite film with various surfactant by solvent casting [19].

| Variation | Concentration (mmol) | Morphology    |
|-----------|----------------------|---------------|
| ODA       | 20                   | Intercalated  |
|           | 40                   | Intercalated  |
| TSC       | 20                   | Intercalated  |
|           | 40                   | Exfoliated    |

![XRD Pattern](image)

Figure 4. XRD Pattern for PLA-Regenerated Organobentonite with various compositions of regenerated organobentonite without surfactant [23].

Nanocomposite structure from the extrusion method was estimated by XRD pattern of PLA-regenerated organobentonite that shown in Figure 4. XRD pattern for nanocomposites have a very low intensity peak at the same angle with that of regenerated organobentonite It indicates the formation of partially exfoliated structure of all nanocomposites.

3.3. Mechanical Strength of PLA-Bentonite Nanocomposite

In order to test the mechanical properties, pull test was held using Universal Testing Machine. Mechanical properties testing was carried out at all PLA-Bentonite film. The addition of bentonite which is used as filler in the PLA matrix nanocomposites decrease the elongation at break value, but it increases Young’s modulus. Use of activated bentonite has a different effect on film’s mechanical strength. For example, the use of bentonite that have been activated with TSC have a a higher tensile strength than film with ODA bentonite. The same can be done observed at the elongation at break of the film with TSC bentonite having a higher value than films with ODA bentonite.
Table 2. Mechanical properties of PLA-Bentonite nanocomposite film with various surfactant [19].

| Variation          | Concentration (mmol) | Tensile Strength (MPa) | Young’s Modulus (MPa) | Elongation at break (%) | PLA Molecular Weight (g/mol) |
|--------------------|----------------------|------------------------|-----------------------|------------------------|-----------------------------|
| Without bentonite  | -                    | 1.55                   | 59.72                 | 19.27                  | 111.174                     |
| Without surfactant | -                    | 1.59                   | 82.21                 | 5.03                   | 111.174                     |
| ODA                | 20                   | 7.87                   | 329.72                | 2.66                   | 111.174                     |
|                    | 40                   | 2.17                   | 194.62                | 3.00                   | 111.174                     |
| TSC                | 20                   | 10.31                  | 148.85                | 14.90                  | 111.174                     |
|                    | 40                   | 12.68                  | 194.58                | 8.02                   | 111.174                     |

To find the better surfactant type, we need to compare the result from both surfactant type. The highest tensile strength value obtained by activated bentonite with using 40 mmol of TSC, which also have the longest distance between layers. Longer distance between layers can increase the strength and stiffness of the nanocomposite film due to bentonite which has been activated can be intercalated inside the PLA matrix. Enhancement of mechanical properties are also affected by the increase of clay dispersion degree that can promote increased contact area and surface interaction between clay and PLA.

In general, it can be seen that bentonite activation using TSC surfactant result in higher tensile strength than the film activated using ODA surfactant. An increase in tensile strength can be affected by the presence of the evenly dispersed bentonite in the PLA matrix. This form of bentonite dispersion can be represented from the distance between the layers produced from the film. This large distance between layers can increase the area of contact and interaction between the surface of bentonite. The mechanical test results also showed that the film those using ODA surfactants have high value of Young’s modulus but low elongation at break value and TSC surfactant delivers the opposite result. However, because of bentonite use is intended to improve PLA brittleness, it can be concluded that the TSC 40 film produces the best tensile strength value.

In this study, there are also some relation between SBE composition and nanocomposite mechanical properties. Mechanical properties increase can be caused by stiffness, ratio and interaction area between filler and polymer matrix [24]. If filler composition exceed a certain value, it can create a local tension and decreased tensile strength [25]. Mechanical properties characterization of PLA-nanocomposites in various composition showed at Table 3.
Table 3. Mechanical properties of nanocomposite film (various filler composition).

| Filler                  | Composition (%) | Elongation at Break (%) | Tensile Strength (MPa) | Young’s Modulus (MPa) | PLA Molecular Weight (g/mol) | Reference |
|-------------------------|-----------------|-------------------------|------------------------|-----------------------|------------------------------|-----------|
|                         | -               | 3.02                    | 39.59                  | 1328.40               | 120000                       | [26]      |
| SBE                     | 5               | 1.69                    | 18.76                  | 1230.60               | 120000                       | [26]      |
| Modified regenerated SBE | 3               | 3.20                    | 41.10                  | 1327.00               | 120000                       | [26]      |
| Modified regenerated SBE | 5               | 3.26                    | 42.22                  | 1508.90               | 120000                       | [26]      |
|                         | 4               | 5.03                    | 1.59                   | 82.21                 | 120000                       | [26]      |
| Modified SBE            | 4               | 2.66                    | 7.87                   | 329.72                | 120000                       | [26]      |
| PLA/PBAT Cellulose      | 13.05           | 4.90                    | 27.00                  | 1328.00               | 155000                       | [27]      |
| Commercial Bentonite    | 0.5             | 5.03                    | 1.59                   | 82.21                 | 120000                       | [26]      |
| Cloisite 30B            | 0.5             | 5.03                    | 1.59                   | 82.21                 | 120000                       | [26]      |
| Commercial Bentonite    | 0.5             | 4.00                    | 52.00                  | 1400.00               | 120000                       | [23]      |
| Regenerated Bentonite   | 0.5             | 3.90                    | 51.00                  | 1420.00               | 120000                       | [23]      |
| Regenerated Bentonite   | 0.5             | 3.90                    | 51.00                  | 1420.00               | 120000                       | [23]      |

As showed above, 5 % addition of modified regenerated SBE have a better mechanical properties compared to both cellulose nanocomposite and PLA-cloisite nanocomposite. The highest tensile strength obtained from the PLA with filler addition. This result corresponds with another research about filler addition in HDPE [29]. However, addition of higher concentration of filler gives a drawback in elongation at break value as compared with no filler which have 19.27 % elongation at break value. The highest elongation at break was obtained at low clay compositions. The decrease in the elongation at break of nanocomposite can be caused by decreasing of PLA chain mobility due to the addition of clays [30].

Table 2 and table 3 are nanocomposites produced by solvent casting method and extrusion, respectively. By comparing the elongation at break value, tensile strength value and Young’s modulus value, it can be concluded that mechanical properties of nanocomposite from extrusion process are better than solvent casting method.

3.4. Water Vapor Permeability Test

In this study, the WVP of the samples was determined by calculating the change in mass of the silica gel which is covered by the sample. Mass data from silica gel was taken every 24 hours for 5 days. The largest mass change, at 1.1 g, was seen on films treated with 40 mmol ODA. Films formed in the 40 mmol ODA variation has a non-smooth surface structure as well as porous. This may contribute to higher water vapor absorption by silica gel compared to other samples. This may also contribute to higher water vapor absorption by silica gel compared to other samples. Lowest WVP is shown by the film with 40 mmol TSC with only 0.122 g after 7 days. The result confirms that films with bentonite TSC 40 has a better dispersion structure than other films. The presence of bentonite across the film can block water vapor to enter through the film that result in low value of WVP [30]. As distance between layers gets bigger, bentonite tends to form random structures in the film so that it blocks the entry of moisture. In addition, the presence of bentonite which contains a silicate coating can extends the path that water vapor has to travel water to penetrate the film [31].
Figure 5. Water vapor permeability curve at various PLA-bentonite nanocomposite film [19].

Water vapor permeability of nanocomposite using commercial Cloisite 30 B [32] and bentonite can be seen in Table 4.

Table 4. Water vapor transmission rates of PLA-Cloisite 30 B nanocomposites.

| Mass fraction (%) | WVTR (g/m².day) | Bentonite | Cloisite [32] |
|-------------------|-----------------|-----------|---------------|
| 0                 | -               | 177       |                |
| 1                 | 60              | 156       |                |
| 2                 | 25              | 139       |                |
| 3                 | 27              | 126       |                |
| 4                 | 39              | 114       |                |
| 5                 | 58              | 107       |                |
| 6                 | -               | 101       |                |

Table 4 showed WVTR comparison between PLA-Cloisite 30 B and PLA-Bentonite nanocomposite. PLA-bentonite nanocomposite showed better WVTR performance due to their low transmission rate. It indicated the ability to be a good food packaging materials especially in high humidity environment.

4. Conclusion

The regeneration method for SBE has been successfully conducted by soxhlet extraction method continued by modification using surfactants. Those method was proved to eliminate oil from bentonite indicated by the absence of hydrocarbon peaks at the FTIR result. The use of surfactants on various concentration increases the distance between layers of bentonite. Furthermore, activated bentonite TSC 40 has the largest distance between layers. The increase in the distance between layers may be caused by the entry of surfactant chains into the bentonite layers, as shown by the FTIR results.

When a mixture of PLA and bentonite was sonicated and molded, the distance between the layers of bentonite larger. This indicates that the incoming PLA chain between the layers of bentonite in forming nanocomposite film. Most of the samples produce an intercalation structure between the bentonite with PLA, except the PLA-Bentonite TSC 40 producing exfoliated structures. Hence, samples containing TSC 40 have the best mechanical properties with regards to tensile strength result.

The film containing TSC 40 is the best film to withstand the entry of moisture into the sample. Compared to Cloisite 30 B, bentonite as a filler resulted in a better water vapor permeability of nanocomposite. Mechanical properties characterization also showed that PLA that added with regenerated bentonite have a better mechanical properties compared to PLA that added with cellulose.
and cloisite. When nanocomposite production from solvent casting and extrusion compared, their mechanical strength showed that the extruded nanocomposite have a better properties. It may be caused by a better mixing condition which reaches its melting point. Therefore, it can be concluded that extrusion result in better nanocomposite quality.

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5. References
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