Processing and characterization of natural Bentonite from Aceh, Indonesia as filler of Poly-Caprolactone/Poly-Lactic Acid/Chitosan, (PCL/PLA/Chitosan) nanocomposites

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Abstract. The formation of composite from polymer mixture PCL / PLA / Chitosan bentonite was carried out through the melt intercalation method using an extruder at 180 °C with a holding time of 20 minutes. Bentonite is obtained from Kab. North Aceh which has been modified with CTAB surfactant. The sample formulations used were single PCL and PCL polymers each given 3, 5 and 8 % chitosan fillers. A mixture of PCL / PLA (50: 50) was given 3, 5 and 8 % chitosan / bentonite fillers. The sample is a white plastic rod (bone) material which is tested for its nature through several types of characterization. Modified bentonite and chitosan have an effect on increasing the mechanical and thermal properties of PCL, PLA and mixture polymers both based on the results of tensile test, TGA test (thermal) and bacterial test. PCL / PLA 50:50 with the addition of 8 % bentonite-chitosan filler is the most perfect composition which provides the best test value.

Keywords. PCL; PLA; Chitosan; Bentonite; Composite; Filler.

1. Introduction
Synthetic polymers have caused significant environmental problems [1]. Biopolymers can be used to replace non-biodegradable plastics with other more natural and environmentally friendly biodegradable materials, for example, Polycaprolactone (PCL) and Poly Acid Lactic (PLA) [2].

The use of PCL biodegradable polymers has attracted much attention in recent years, PCL is a linear, hydrophobic, semicrystalline (50%), and biocompatible aliphatic polyester that has been widely used in the biomedical world over the past few decades [3]. However, PCL is relatively brittle and rigid with low deformation when broken [4].

Polylactic acid (PLA) is a linear aliphatic thermoplastic polyester derived from lactic acid, which is obtained from 100% fermentation of renewable and biodegradable plant sources, such as corn or rice flour and sugar supply stocks. PLA has good mechanical properties, plasticity, and biocompatibility [5].

Polycaprolactone (PCL) and polylactic acid (PLA) have the same properties which can be degraded but also have very clear differences from their physical properties, namely in polycaprolactone (PCL) polymers having physical properties that are very fragile and stiff so they are easily broken [6], while polylactid acid (PLA) has physical properties that are flexible and strong...
enough. If these two compounds are combined, the resulting polymer can improve the mechanical properties possessed by the original polymer.

Chern et al. have explained that chitosan can be added to PCL so that it can improve the degradation properties of polymers in addition to the addition of chitosan the properties possessed by chitosan will be transferred to materials mixed like anti-bacterial properties [7]. Rihayat et al. have added bentonite to polymers aims to improve and improve the properties of polymer materials to be more stable, mechanically and chemically stronger so that they function optimally in various sectors of life such as household, automotive, agriculture, health and packaging [8]. From the results of previous studies it was reported that the surface and interlayer space of bentonite can be modified [9]. In particular, the interlayer space of montmorillonite can be inserted with cations through ion exchange reactions or other physical and chemical interactions. This explains that cationic, anionic and non-ionic species of organic surfactants can be sequentially included in the interlayer space of montmorillonite [10].

This study focuses on processing natural bentonite into modified bentonite in an effort to improve the properties of PCL / PLA biodegradable polymers and to study the effects of variations in the composition of polymer mixtures and mixtures of chitosan-bentonite fillers. Thus polycaprolactone (PCL) polymers, polyactic acid (PLA), bentonite and chitosan if combined will produce different materials if combined together and produce a different compound. With the addition of fillers the material will have different mechanical, thermal and anti-microbial properties than the polymer before added filler.

2. Materials

2.1. Material
The materials used in this study were Polycaprolactone (Sigma Aldrich), Poly Lactic Acid (Nature Work Co), bentonite originating from the local area (North Aceh), chitosan, Lactobacillus bacteria, Cetyl Trimethyl Ammonium Bromide / CTAB (Sigma Aldrich), and (NaPO3)6 (Merck). The equipment used in this study are diffraction X-Ray (X-RD), Thermogrametric Analysis (TGA), Tensile test and Scan Electron Microscopy (SEM).

3. Methodology

3.1 Bentonite processing to montmorillonite
Bentonite was taken from North Aceh Regency. Bentonite is then dried at 105 °C and stored in a desiccator, then partially separated as a pure bentonite sample. Then purification of the sample was done to get montmorillonite. The bentonite purification method was carried out following the method carried out by Gong et al [11]. The process of purification through 3 stages, grinding, dispersion and centrifugation. Raw materials of bentonite were smoothed using a grinder for 60 minutes, then sifted with a 230 mesh sieve. 3 grams of fine bentonite and dissolved in 36 grams of free water mixed with 0.03 gr (NaPO3)6 or 1% of the weight of bentonite. The mixture is then stirred using a magnetic stirrer for 24 hours. After stirring, then centrifuging at a speed of 700 rpm for 2 minutes. The precipitate obtained is then heated with an oven at a temperature of 60 °C to a constant weight. Furthermore, the bentonite sample was reprocessed with the addition of CTAB (Cethyl Trimethyl Ammonium Bromide) as surfactant to modify bentonite to form organo bentonite [8].

3.2 Sample preparation
PCL and PLA were dried in a vacuum oven at ± 40 °C for 24 hours. After drying, the composite sample was printed using an extruder which was operated at 180 °C with a combination process carried out specifically as many as 12 sample formulations with different concentrations in each sample. Each PCL and PLA polymer is mixed with chitosan at a ratio of 3%, 5% and 8% chitosan. Then PCL-PLA was mixed with a ratio of 50:50 where the total mass of PLA + PCL was 10 g, then
given chitosan filling material with a ratio of 3%, 5% and 8%. The last sample is PCL and PLA mixed with a ratio of 50:50 with a total mass of PLA + PCL is 10 g, then given a mixture of modified chitosan and bentonite with a ratio of 3%, 5% and 8%.

3.3 Characterization technique

3.3.1 X-Ray diffraction (XRD). X-RD is one of the material testing tools to test the expansion of sample layers. The XRD graph is obtained through a detector called V theta-2 theta goniometer and Si (Li) Peltier detector, and using radiation Cu on wavelength \( \lambda = 1.540562 \text{ angstrom} \ [3] \).

3.3.2 Scanning electron microscopy (SEM). SEM technique is surface analysis. The surface image obtained is topography with all bumps, curves and holes on the surface. Electron beam interactions with specimens will produce electron diffraction patterns that can provide information about crystallography, element type, distribution and morphology of the material surface [12].

3.3.3 Tensile test. Tensile testing is carried out using the UTM Universal Tensile Machine, where the sample is sized according to the standard ASTM D638 specimen and tensile testing is carried out with a coaxial force until it reaches a certain mechanical resistance until it breaks.

3.3.4 Thermogravimetric analysis (TGA). TGA is defined as a tool for studying changes in mass as a function: temperature, time and atmosphere. In principle this method measures the reduction in mass of material when heated from room temperature to high temperatures which is usually around 900 °C.

3.3.5 Bacterial test. Microbial testing was carried out using the compost soil media method. All samples are placed directly on nature and then left until the degradation rate obtained reaches two months until it is completely degraded and changes in new samples can be seen changing for one month.

4. Results and discussion

4.1 Results of analysis of bentonite X-ray diffraction (XRD)
Changes in diffracted intensity were measured and plotted against diffraction angles (20). The results of XRD analysis are shown in figure 1, it can be seen that the diffraction peak of natural bentonite is at 5.8° (d-spacing 0.74 nm). After modification using CTAB the diffraction peak of the modified bentonite was at 4.54° (d-spacing 1.9 nm). From the results of the XRD test it can be concluded that bentonite modified using CTAB will result in the formation of an increasingly large d-spacing layer. Modified bentonite is very well used for polymer-silicate nanocomposite processes, because of the widening of the distance between fields in CTAB modified bentonite where the distance obtained is greater [8].

Figure 1. Diffractogram of natural bentonite and modified bentonite.
4.2. Bentonite SEM analysis

The results of SEM analysis showed that there were morphological differences between natural bentonite and bentonite which had been modified using cationic surfactants. The results of SEM analysis can be seen in figure 2.

![SEM images of natural bentonite and CTAB modified bentonite.](image)

**Figure 2.** Results of SEM analysis (a) natural bentonite and (b) CTAB modified bentonite.

SEM images of natural bentonite and CTAB modified bentonite were taken at 1,000 X magnification. Based on the results of surface morphology characterization seen from SEM results, the surface structure of natural bentonite and CTAB modified bentonite has a different surface, the surface of bentonite after purification is more homogeneous and looks very well dispersed than bentonite before purification. shows a large particle surface size that indicates a good quality of combination with the polymer. These results are in accordance with previous studies reported by Priyal Pandey [10].

4.3. Test results of pull strength

Tensile strength of PCL / chitosan, PLA / chitosan, PCL / PLA / chitosan and PCL / PLA / chitosan / bentonite was illustrated in figure 3. Based on the tests carried out it shows the variations in the polymer and its fillers. Yun et al have added chitosan to bentonite filler concentrations of 5% to 10% [13]. But the results obtained contradict the observed results.

![Graph of tensile test results for sample formulations.](image)

**Figure 3.** Graph of tensile test results for sample formulations.

The addition of chitosan especially 5% in each sample resulted in an increase in the tensile strength of PCL, PLA and a mixture of both. However, when the composition of chitosan is added more to a
single polymer, the value of tensile strength obtained decreases. On the other hand when PCL and PLA polymers are mixed and bentonite and chitosan fillers are combined the interaction that occurs is an increase in the value of tensile strength that is significant and getting better from variations of 3%, 5% and 8%, the acquisition of tensile strength increases three times. The value of the biggest tensile strength obtained is in the F12 sample of 63.75 MPa. This increased value of tensile strength is obtained because of the better bonding power provided by the combination of polymer and filler mixtures, especially the effect of adding bentonite (montmorillonite).

4.4. Thermal resistance tests with thermo gravimetric analysis (TGA) tools

The process of mass loss in the thermal test occurs because of the decomposition process, namely the termination of the chemical bond. Figure 4 is a graph of the TGA test results for 4 samples with the highest value in the previous test, namely PCL / PLA / Chitosan without bentonite, and PCL / PLA / Chitosan / Bentonite varies.

![Figure 4. TGA graph of each sample to temperature.](image)

The graph shows that all samples experienced a single decomposition. The degradation temperature ranges in the temperature range 300-460 °C, at a temperature of 100-200 °C the sample loses mass, which is the evaporation of water content in the sample. Composite blend of PCL / PLA / Chitosan with bentonite addition has better thermal stability ability than without degraded bentonite at 317.61 °C. While PCL / PLA with the addition of 3 %, 5 % and 8 % Chitosan-Bentonite fillers began to be degraded at temperatures of 362.65 °C, 430.99 °C and 460 °C respectively. These results indicate that the addition of this filler mixture has succeeded in increasing thermal stability which is characterized by increasing degradation temperatures. The increase in the temperature of the degradation is caused by the bonding of the polymer and filler which fuses more strongly so that it is difficult to break and the decomposition of the material becomes slower. It also proves that bentonite can be combined with chitosan in this comparison as the newest double filler innovation in the world of biocomposite to improve the thermal properties of PCL / PLA materials.

4.5. Bacterial test

Bacterial testing was carried out through two different types of testing, using the ALT (Total Plate Number) method and biodegradation testing with compost technique. The time interval of the examination carried out on testing the sample lasted for 0; 3; 6; 9; and 12 days by observing its development in the stained cup which had been placed so that PDA (Potato Dextrose Agar) as a growth medium. The development of bacteria in 4 types of samples is shown in figure 5.
Figure 5. Average growth rate of daily bacteria from 0 to 12 days.

From figure 5 it can be seen that microbial development during the testing process that occurred in samples not coated with chitosan (F9) showed the highest colony growth rate of 130 colonies / gram during the 12 day testing period. This is because the composite material is directly contaminated with air which contains various types of microbes that can affect both physical and chemical ingredients. The results showed that the lowest colony growth rate of 65 colonies / gram was found in sample F12 with matrix composition PCL / PLA with the addition of 8% bentonite / chitosan filler, followed by F11 sample namely PCL / PLA with the addition of 5% samples with 80 colonies / gram and finally F10 sample where PCL / PLA with the addition of 3% bentonite / chitosan filler has a colony growth rate of 90 colonies / gram. From the test results there is a microbial reduction with the addition of chitosan compounds which have been shown to inhibit microbial growth and activity in the sample.

Meanwhile, the results of bacterial analysis using the compost method can be seen in figure 6. Obtained through direct observations for a month which showed little by little the changes experienced by polymers, but not yet clearly seen natural changes, obvious changes only in the color changes of the polymer tested. The single polymer PCL / Chitosan and PLA / Chitosan in all filler variations, the average structure changes tend to be porous and the color is darker as more and more fillers are added. While the combination of PCL / PLA polymer with bentonite and chitosan filler mixtures has a structure that tends to crack and has a slightly brownish color as more fillers increase. This proves that there is a collaboration of polymer alloy and filler alloys, especially the effects of chitosan providing degradation resistance by microbes.

Figure 6. Observations of biodegradation for 4 weeks.
5. Conclusion
Modified bentonite has an effect on improving the mechanical and thermal properties of PCL, PLA polymers as well as a mixture of both. The combination of PCL / PLA polymer with the addition of filler mixture of bentonite and chitosan can provide much better mechanical, thermal and material degradation properties. PCL / PLA 50:50 with the addition of 8% bentonite-chitosan filler is the most perfect composition which provides the best test value.

The addition of bentonite from Aceh, Indonesia as a filler contributed to the improvement of mechanical and thermal properties of the composite. The characteristics of PCL/PLA / bentonite/chitosan tensile strength test 8% composite material produced optimum tensile strength compared to pure PCL/PLA and PCL/PLA / bentonite/chitosan 3% and 5%. The mechanical properties of polymer materials increase with increasing filler number in the PCL/PLA matrix. Chitosan was antibacterial on its surface to both Gram-positive and Gram-negative bacteria. Blending chitosan with PCL/PLA/Bentonite minimized the antibacterial property.

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