Synthesis and characterization of bioplastic based on chitosan-urea-bentonite

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Abstract. Consumption of synthetic plastic made the level of plastic waste in the world become massive problem in environment. Biopolymer is an alternative which produced from renewable material with an abundant amount in the world. This study aimed to produce bioplastic materials based on chitosan and bentonite, with addition of urea. The method in this research consisted of bentonite preparation, synthesis bioplastics and characterization. Characterization in this research include FTIR, XRD, mechanical strength, and biodegradation. The result in this research showed that the addition of bentonite increased tensile strength of bioplastic. The more bentonite added in the bioplastic system, the higher tensile strength value. The addition of 0.1; 0.5; and 1 g bentonite made the tensile strength of bioplastic increased become 4.17; 4.28; and 4.90 MPa. Whereas the addition of 2 g bentonite decreased the tensile strength of bioplastic become 2.69 MPa, as the structure which formed in bioplastic was exfoliation which was strengthen from XRD pattern. Biodegradation test showed that bioplastic contained of 2 g bentonite has the fastest time to perfectly lose in the soil which only 12 days.

Keywords: bioplastic, chitosan, mechanical strength

1. Introduction
Recently, the pollution problem caused of sintetic plastic have become increasingly prominent [1]. Consumption of synthetic plastic made the level of plastic waste in the world become massive problem in environment and caused the concern of scientific research. Lately, Plastic which is commonly used, was produced from nonrenewable material such polietylena (PE) polypropylene (PP), polystyrene (PS), etc. [2]. Biopolymers was an alternative which produced from renewable material with an abundant amount in the world. The renewable resources such as Cellulose, Chitosan, Starch, etc. Chitosan is well known for its biocompatibility, chitosan also has many pharmacological properties which makes it be a strong candidates to replace synthetic plastics [3].

Chitosan is natural polysaccharide produced from deacetylation of chitin which firstly found by Hoppe Seyler in 1894. Chitin is main component of exoskeleton from crustacean such as crab, and shrimp. The application of Chitosan as matrix of bioplastic is huge fabricated. Bentonite is widely used as strong reinforcing material for polymer composite preparation [4]. Bentonite has the ability to increase mechanical properties up to 10 fold for the composites [5]. Biopolymer modified by bentonite can be used
to bioplastic for slow release nitrogen, then the addition of urea in this research was nitrogen resources agent.

This study was aimed at producing bioplastic materials based on chitosan and bentonite, with addition of urea, and the characterization of structure, functional group, biodegradable capacity, and mechanical properties.

2. Method
The raw materials used in the process of making bioplastic-based slow release fertilizers are chitosan from Chem Mix Yogyakarta, bentonite (clay) from Wonosegoro Boyolali, aquademineralization, other chemicals used are Merck production with purity analysis including urea \((\text{CO(NH}_2\text{)})_2\), ethanol 96%, NaOH, acetone, Glacial acetic acid, and the materials used for biodegradable bioplastic tests is compost soil. Equipment used include laboratory glass equipment, magnetic stirrer, porcelain cup, grinder (lumpang and mortar), alcohol thermometer, 200 MESH size, oven, hot plate, petri disc, centrifuge. Analytical tools include: FTIR, SEM, XRD, and universal testing machine.

2.1 Bentonite Preparation
The natural bentonite used in this study comes from Wonosegoro, Boyolali district of Central Java. Natural bentonite was dried. Dried bentonite was pounded with mortar and sifted with 200 mesh, then 50 grams bentonite put in a beker glass and added 1000 mL of aquademin. The mixture was stirred at room temperature for 24 hours then centrifuged at a speed of 5000 rpm. Clay deposits are dried at a temperature of 110-120 °C. The results were characterized with FTIR, and XRD.

2.2 Synthesis of Chitosan Bioplastic
1 g of chitosan mixed with 80 mL of acetic acid 2%. The mixture was stirred at room temperature with a magnetic stirrer for 1 hour. The formed gel was printed using a petry disc. The gel was dried at room temperature. Bioplastic then characterized with FTIR, XRD, mechanical strength tests and biodegradation tests.

2.3 Synthesis of chitosan-Urea Bioplastic
1 g of chitosan and 0.5 g of urea mixed with 80 mL of acetic acid 2%. The mixture was stirred at room temperature with a magnetic stirrer for 1 hour. The formed gel was printed. The gel was dried at room temperature and was characterized with FTIR, XRD, mechanical strength tests and biodegradation tests.

2.4 Synthesis of Chitosan- Urea-Bentonite Bioplastic
0.1; 0.5; 1 and 2 g of bentonite was mixed with 10 mL of aquademin and stirred with a magnetic stirrer at room temperature for 24 hours until a suspension was formed. 0.5 g of urea was dissolved in each bentonite suspension. The suspension was dissolved in chitosan gel which was formed from the mixing of 1 g of chitosan in 80 mL of acetic acid 2%. The mixture was stirred at room temperature for 1 hour. The formed gel was printed and dried at room temperature. The bioplastics were analyzed with FTIR, XRD, biodegradable tests, and mechanical strength tests.

2.5 Bioplastic Characterization
Analysis of the structure of natural bentonite crystals was performed by X-ray diffraction technique (XRD, brand Philips type X’Pert MPD) with Cu Kα radiation (\(\lambda = 1.5405 \text{ Å}\)) at 40 kV and 30 mA, 20 is (5–90°) with a scan speed of 0.02 °/s. To detect the functional group and active side of bentonite, chitosan, urea, and bioplastic chitosan-urea-bentonite using Fourier Transform Infrared Spectroscopy (FTIR, Bruker) at wavelengths 400–4000cm\(^{-1}\) with spectrum separation of 2 cm\(^{-1}\), at a temperature
20°C with the KBr pellet method. Bioplastic mechanical strength analysis was determined using a universal testing machine (Zwick/Z 0.5) at a speed of 10 mm/min so that it obtains percent of the mulch and tensile strength. Measurements were performed with two repetitions for a single sample. In addition, the thickness of bioplastics was also analyzed using micrometers.

3. Result and Discussion

3.1 Bentonite preparation

The results of preparation bentonite formed a powder which analyzed with infrared spectroscopy in the wave number from (400 to 4000) cm⁻¹. FTIR analysis determined the functional group of clay. The infrared spectra of bentonite presented in Figure 1. And the interpretation of infrared spectra from bentonite was presented in Table 1.

![Figure 1. Infra Red Spectra of bentonite](image)

| Functional Group                  | Wave Number (cm⁻¹) |
|-----------------------------------|-------------------|
| Si-O-Si bending                   | 462.19            |
| Si-O-Al bending                   | 524.64            |
| Si-O bending                      | 794.67            |
| OH bending from AlOH              | 918.12            |
| Si-O stretching                   | 1041.56           |
| OH bending from H-O-H             | 1635.64           |
| OH stretching from H-O-H          | 3448.72           |
| OH stretching from Si-OH          | 3626.17           |
Based on Figure 1, natural bentonite has major absorption peaks at wave number 1635.64 cm\(^{-1}\), 3448.72 cm\(^{-1}\) and 3626.17 cm\(^{-1}\). The absorption band at wave number 3626.17 cm\(^{-1}\) is O-H stretching which located in the octahedral layer bound of Al. The absorption band at 3448.72 cm\(^{-1}\) indicates O-H vibrations corresponding to the absorption band at 1635.64 cm\(^{-1}\) which is the vibration of H-O-H water molecules in the bentonite inter-layer structure [8]. The interpretation of the infrared spectra indicated that the characteristic absorption from Si-O-Al and Si-O-Si indicated the presence of SiO\(_2\) and Al\(_2\)O\(_3\) in bentonite. The main component of bentonite minerals was smectict. The interpretation of infrared spectra reinforced with XRD data to show the mineral type and crystallization of the natural bentonite. Analysis of crystal structure from X-ray diffraction was performed by determining the position and height of the diffraction peaks on the diffractogram. The position of the peak diffraction at a certain value of 2θ was used to determine the type of mineral constituents of natural bentonite and the high or low intensity of the peak indicated the crystallization level of the structure. The X-ray diffractogram of boyolali's natural bentonite was shown in Figure 2.

![XRD pattern of natural bentonite](image)

**Figure 2.** XRD pattern of natural bentonite

XRD pattern of natural bentonite in Figure 2 showed that there are three main peaks at the diffraction angle of 5.94°, 20.16° and 27.04°. The highest peak of boyolali natural bentonite was found at a diffraction angle of 5.94° with a basal spacing of 1.48 nm (d\(_{001}\)) was the characteristic peak of smectit mineral [6]. The diffraction which appeared at 20.16° (d\(_{020}\)) with basal spacing of 4.40 nm which was the peak of d\(_{020}\). This result reinforced that was monmorillonite mineral. The peak that appears at a diffraction angle of 27.04° (d\(_{101}\)) with a basal spacing of 3.29 nm was a characteristic peak for quartz minerals, another peak for quartz appeared at a diffraction angle of 35.82° with a basal spacing of 2.50 nm which was the peak of d\(_{110}\), that peak was related with JCPDS monmorillonit no. 1318-93-0. Based on the interpretation of the X-ray diffractogram, it can be said that boyolali natural bentonite contained the main mineral of monmorillonit and quartz with the presence of several other minerals such as feldspar that appear with low intensity at 20.91° with basal spacing 4.24 nm [9].

3.2 Synthesis and characterization of bioplastics

Bioplastics synthesized in this research consist of 5 type, they are bioplastics based chitosan-urea, chitosan-urea-bentonite 0.1g; 0.5 g; 1 g; and 2 g. The physical performance of bioplastics showed in Figure 3. Bioplastics were characterized using FTIR instruments. Spectra bioplastics based chitosan-urea, chitosan-urea-bentonite 0.1g; 0.5 g; 1 g; and 2 g was presented in Figure 4. Based on Figure 4, the
addition of bentonite in bioplastics Chit-urea-bent 0.1 g; 0.5 g; and 1 g made instenity of peak which occurred at 3500-3400 cm\(^{-1}\) indicating the N-H cluster of urea\([10]\). have been decreased, that was indicating that urea enters the space between bentonite layers so that the peak characteristics of urea decreased. Whereas the characteristic peaks of the Urea (N-H functional group) from bioplastics Chit-urea-bent 2 g begin sharp again at wave numbers 3500-3400 cm\(^{-1}\). This is due to the addition of too much bentonite causing the bioplastic structure was distributed evenly, which was indicated that the bioplastic has high homogeneity and the results of x-ray diffractograms of bioplastic indicating exfoliated patterns.

![Figure 3](image)

**Figure 3.** The physical performance of bioplastics (a) Chit-urea; (b) Chit-urea-bent 0.1 g; (c) Chit-urea-bent 0.5 g; (d) Chit-urea-bent 1 g; (e) Chit-urea-bent 2 g
Figure 4. Infrared Spectra of Bioplastics (a) Chit-urea; (b) Chit-urea-bent 0.1 g; (c) Chit-urea-bent 0.5 g; (d) Chit-urea-bent 1 g; (e) Chit-urea-bent 2 g

Bioplastics based Chit-urea, Chit-urea-bent 0.1 g; 0.5 g; 1 g; and 2 g was analyzed using XRD to find out NH$_4^+$ of urea interacting with bentonite forming exfoliated or intercalated structures. XRD pattern of those bioplastics was presented in Figure 5. Based on Figure 5, it can be seen that for bioplastics Chit-urea, and Chit-urea-bent 0.1 g, the characteristic peaks of constituent material still appeared at 2θ 44° which is the peak of d$_{hkl}$ (210) urea. While the addition of bentonite 0.1 g, characteristic peak of bentonite has not appeared. In bioplastics with the addition of bentonite 0.5 g, the characteristic peaks of bentonite and urea appeared at 2θ 5.03° which is d$_{hkl}$ (001) and at 2θ 20.25° appeared the characteristic peak of d$_{hkl}$ (020) which further strengthens that the mineral smectit of bentonite was contained in bioplastic. In addition, at 2θ 44.02° appears the peak of d$_{hkl}$ (210) which is the characteristic peak of urea.

Figure 5. X-ray diffraction of Bioplastics (a) Chit-urea; (b) Chit-urea-bent 0.1 g; (c) Chit-urea-bent 0.5 g; (d) Chit-urea-bent 1 g; (e) Chit-urea-bent 2 g
The appearance of the peak in the price of \(d_{hkl}\) (001) indicates that the bioplastic structure that was formed was intercalation [9]. \(\text{NH}_4^+\) from urea is absorbed in the bentonite inter-layer space. As for bioplastics Chit-urea-bent \(1\) g, \(2\) \(5.03^\circ\) did not appeared. This indicated that the structure formed was exfoliation [11]. The characteristic peaks of the constituent materials in Bioplastics with the addition of bentonite \(2\) g did not occur. This indicated that all of the constituent materials in bioplastics are evenly distributed, the bioplastics formed have a high homogeneity, and the structure was exfoliation.

Tensile strength and Tensile strain of bioplastics Chit-urea; Chit-urea-bent \(0.1; 0.5; 1\) and \(2\) g are presented in Figure 6 and 7. The mechanical strength of the Chit-urea-bent bioplastics depends on the resistance of bentonite and ratio aspect of the intersected silicate layer. The silicate coating acts as a mechanical amplifier of citosan and reduces polymer flexibility. The main reason for the increase in mechanical properties is the interaction of a stronger interface between the matrix and the overlaid silicate as a result from the large surface area of the bentonite layer. During the process of making bioplastics and drying, the original hydrogen bonds formed between molecules inside the chitosan (intra-molecular hydrogen bond) were replaced by the new hydrogen bonds formed between the chitosan hydroxyl group and the hydroxyl group of bentonite. The presence of new hydrogen bonds (hydrogen bonds between molecules) led to an increase in mechanical properties in bioplastics[12].

Tensile strength in bioplastics that do not contain bentonite (Bioplastic chit-urea) was 2.92 MPa. Tensile strength of bioplastic without the addition of bentonite is lower compared to bioplastics containing bentonite. The tensile strength of bioplastics increased as much as the addition of bentonite to the bioplastic system. The addition of bentonite in the bioplastic system which formed the intercalation structure can increase the mechanical strength of bioplastics which indicated by the increasing tensile strength in bioplastics containing more bentonite. Addition of bentonite \(0.1; 0.5; \) and \(1\) g caused increasing of tensile strength in the bioplastic system were \(4.17; 4.28;\); and \(4.90\) MPa. This is because bentonite contains a silicate layer that can strengthen the tensile strength of the original polymer (chitosan). The more bentonite added to the system leads to the formation of hydrogen bonds between molecules between bentonite and chiosan. Hydrogen bonding between molecules is able to increase mechanical strength in bioplastics [13].

![Figure 6. Histogram of Tensile strength Bioplastics](image)
Increasing of mechanical strength in bioplastic systems followed by decreasing of strain (elongation). Bioplastics chit-urea has the highest elongation of 7.02%. This is because urea is hygroscopic, so it is able to make chit-urea bioplastic become more outstretched than other bioplastics. The addition of bentonite in the bioplastic system was able to increase tensile strength but caused a decrease in the elongation. The addition of bentonite 0.1; 0.5; 1 and 2 g caused a decrease in the elongation of 2.48; 2.18; 2.20 and 2.22 %. This was because the addition of bentonite to the bioplastic system caused urea's ability to make bioplastics more flexible. The presence of bentonite caused the hygroscopicity of urea to decrease.

Biodegradation tests are carried out by planting a certain amount of bioplastics in the compost soil at a certain depth within a certain time interval. Bioplastic weight loss was observed daily and noted. The interaction between urea and bentonite caused the bonding of ammonium ions (NH$_4^+$) in the space between bentonite layers, so that urea became protected by the existence of a silicate layer in bentonite. This caused the time to hydrolyzed urea by urease enzymes to vary. The 23$^{th}$ day of bioplastic weight shrink table was presented in Table 2.

| Sample          | The weight shrink in 23 days (g) |
|-----------------|---------------------------------|
| Chit-urea       | 0.0099                          |
| Chit-urea-bent 0.1 | 0.0118                          |
| Chit-urea-bent 0.5 | 0.0076                          |
| Chit-urea-bent 1 | 0.0036                          |
| Chit-urea-bent 2 | 0                               |

The bioplastic biodegradation showed that Chit-urea bioplastic has longer biodegradation times compared to Chit-urea-bentonite. Chit-urea-bent bioplastics 2 g has the fastest biodegradation time compared to other bioplastics. This was because the bioplastic structure of Chit-urea-bentonite 2 g was an exfoliated structure. The exfoliated structure caused the hydrogen bonds between urea and Chitosan...
began weaker. Silicate layers with exfoliated structures cannot protect urea in inter-layer space while hydrogen bonds formed between urea and chitosan became weaker as new hydrogen bonds form between chitosan and bentonite so the bioplastic-bound urea tends to be easier to interact with urease enzymes in the soil [14]. This caused chit-urea-bentonite 2 g bioplastic has the fastest biodegradation time compared to all other bioplastic variations. It only takes 12 days for all of part from bioplastics to disappear perfectly in the soil. The exfoliated structure caused the hydrogen bonds formed between urea and chitosan became weaker. Silicate layers with exfoliated structures cannot protect urea in inter-layered space while hydrogen bonds formed between urea and chitosan become weaker as new hydrogen bonds was formed between chitosan and bentonite, so urea from bioplastic tends to be easier to interact with urease enzymes in the soil [15]. This causes the 2 g addition of bentonite in the bioplastic has the fastest biodegradation time compared to all other bioplastic variations. The exfoliated structure in bioplastics containing 2 g bentonite is reinforced from the XRD test results, where the diffractograms that appear on the bioplastics do not show any peaks which indicated that the characteristic peaks of each of the constituent materials was not occurred. FTIR data also reinforces that the bioplastic structure that was formed was exfoliation, due to the appearance of sharp N-H bending peaks in wave numbers of (3400-3500) cm⁻¹ indicating that urea was not protected in the space between bentonite. While in bioplastics with the addition of bentonite 0.1 g; 0.5 g; and 1 g of bentonite peaks has decreased in intensity.

4. Conclusion

Bioplastic Chit-urea; Chit-urea-bent 0.1 g; 0.5 g; 1 g; and 2 g were successfully synthesized in this research. The addition of bentonite increased tensile strength of bioplastic. The more bentonite added in the bioplastic system, the higher tensile strength value. Whereas the addition of 2 g bentonite decreased the tensile strength of bioplastic as the structure which formed in bioplastic was exfoliation which was strength from XRD pattern.

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