Production of biodegradable plastics using aking rice starch and chitosan from crab shells as a substitute for conventional plastic

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Abstract. The aim of this research is to make biodegradable plastics using starch and chitosan from crab shells as a substitute for conventional plastic. Biodegradable plastic synthesis can utilize organic materials such as crab shell waste and Aking rice as the basic ingredients. Crab shells are used as basic ingredients because they contain chitosan which has several beneficial properties namely biocompatibility, biodegradability, hydrophilicity and antibacterial. Meanwhile, aking rice waste which is a household waste can also be used as a biodegradable plastic base material because it contains starch consisting of two types of polymers namely amylose and amylpectin which can form a thin layer. In the manufacture of bioplastics, a transparent and strong enough sample was obtained, namely 1 g of chitosan, 3% glycerol and bioplastic which had sufficient flexibility but had an uneven surface, namely 2 gr chitosan, 5% glycerol samples. Plastics with the highest percentage of biodegradation, 33.3%, were found in samples with 1 g of chitosan, 3% glycerol, while the lowest percentage of biodegradation was 2% which was obtained in samples with 2 gr chitosan, 5% glycerol.

1. Introduction
Plastic is a chemical polymer material that is widely used by humans in everyday life as packaging. This material is widely used because it is lightweight, practical and the price is affordable for all Indonesians. However, this plastic material also has properties that are difficult to decompose or completely degrade in the earth's environment, some even need decades to decompose. In addition, reducing plastic waste cannot be done by burning because it can release harmful gases that can damage the environment and health [1].

Based on this, a new type of plastic is needed, namely biodegradable plastic or plastic that can be recycled biologically because it is made from organic materials [2]. Biodegradable plastic is a type of plastic that can be used as a substitute for conventional plastic and is classified as a plastic material that is friendly to the environment because of its nature that can return to nature or can decompose in nature [3]. This biodegradable plastic can be recycled because it is made from starch, cellulose and lignin as well as those of animal origin such as chitosan, protein and lipids [4].

The addition of chitosan and amylose from starch is needed in making biodegradable plastics in order to obtain a plastic that is stronger, more plastic and slippery. Biodegradable plastic structures that use chitosan have many pores when compared to those that do not use chitosan. These pores cause the plastic to be hydrophilic because it easily absorbs water. In addition, it is also influenced by the amount of starch amylose content, because amylose contains a lot of hydroxyl groups which are hydrophilic. Meanwhile, the biodegradable plastic structure that does not add chitosan looks denser (dense), so it has a good percent elongation, but lacks water
absorption so it is more difficult to degrade. However, the chitosan material is hard and stiff, so the addition of glycerol plasticizer is required in order to produce a biodegradable plastic that is more flexible, slippery, and elastic. In addition, the mechanical properties of plastics are also transparent, elastic, hydrophilic, and easily degraded.

Thus, a research was conducted on the manufacture of environmentally friendly biodegradable plastics and then analyzed its mechanical and morphological properties using starch as a base ingredient from rice aking which has known starch content from carbohydrate extraction, namely \( \pm 83.19\% \) [5] and chitosan from shells crab, which has been known to have a chitosan content of 70\% [6]. Apart from their content, the ingredients are used to minimize the amount of waste aking rice and crab shell waste in the Karang Joang area, North Balikpapan. Although these materials are very popular as materials for making biodegradable plastics, the materials taken in the Karang Joang area, North Balikpapan have never been processed into biodegradable plastics.

Besides using these materials, glycerol plasticizers were also used because it can improve the biodegradable plastic properties [7]. While, the research variables in the form of a ratio of starch: chitosan (K1 = 2g: 2g, K2 = 2g: 1.5g, K3 = 2g: 1g), glycerol concentrations of 1\%, 1.5\% and 2\%, and the length of time biodegradation testing in soil media for 30 days. This biodegradable plastic is made so that it can be used as a substitute for conventional plastics to solve the problem of plastic waste buildup which is difficult to decompose in nature. While still being able to produce products that have the same mechanical or strength properties as synthetic plastics.

2. Experimental method
2.1. Materials
The materials used in this research are aking rice starch, chitosan from crab shells, 1 M NaOH, HCl, acetone, 0.315\% NaOCl, 2\% acetic acid (CH\(_3\)COOH), 99\% glycerol (C\(_3\)H\(_8\)O\(_3\)), 96\% alcohol and distilled water.

2.2. Synthesis of Aking Rice Starch
Taking rice waste from restaurants and cleaning it from food scraps. Aking rice is dried in an oven with a temperature of 70 °C for 20 hours. It is hoped that the water content in the rice is reduced or lost. After drying, then mashed in a blender to form flour and sieved with a mesh sieve so that the particles are 100 mesh in size.

2.3. Synthesis of Biodegradable Plastic
Aking rice flour is diluted with 15 ml of 2\% acetic acid under stirring at 65 °C. Furthermore, chitosan was dissolved with 30 ml of 2\% acetic acid under stirring for 30 minutes at a temperature of 65 °C. After all the solutions dissolved, the aking rice starch dissolved in distilled water was mixed into the chitosan solution with stirring for 15 minutes so that the mixture was expected to be homogeneous. Then added with glycerol and stirring and heating for 15 minutes and the temperature reached 65 °C. The mold was cleaned with 96\% alcohol and then poured the biodegradable plastic solution into a Teflon mold with a diameter of 20 cm. Then, put it in the oven with a temperature of 70 °C for 10 hours. After drying, the molds were removed from the oven and cooled to room temperature. The biodegradable plastic is ready for analysis.

In the manufacture of this plastic, two variables are used, the first is the composition (K) of a mixture of rice starch and chitosan which consists of K1 = 2g: 2g, K2 = 2g: 1.5g, K3 = 2g: 1g. The second variable is the concentration of glycerol (G) which consists of G1 = 1\%, G2 = 1.5\% and G3 = 2\%.
2.4. Characterization.

The chitosan and starch samples that had been made were analyzed for their functional groups using Fourier Transform Infrared (FTIR). The biodegradability test was carried out to determine the time it takes for plastic film samples to degrade. The biodegradability test is selected by using soil as an aid to the degradation process or what is called the soil burial test technique [8]. Observations of the samples were carried out within a span of 7 days for 30 days. Then the samples with the best mechanical properties and biodegradability were analyzed for their surface morphology using an optical microscope.

3. Result and Discussion

Before turning into plastic, aking rice starch and chitosan were tested using Fourier Transform Infrared (FTIR). The bioplastics that have been made were tested for their microstructure characteristics, as well as biodegradability in the soil for 30 days to monitor the mass reduction of the bioplastics, with the largest and smallest mass reductions.

3.1. FTIR of Aking Rice Starch

![FTIR spectrum of aking rice starch.](image)

Based on Figure 1 it can be seen that in the rice starch sample there are several functional groups. These groups are presented in Table 1 below.

| Functional groups | Functional group bonding | Wavelength (cm⁻¹) |
|-------------------|--------------------------|-------------------|
| Hydroxyl          | O-H                      | 3274              |

Table 1. Functional groups of aking rice starch
Table 1 and Figure 1 show the presence of several functional groups that appear in the rice starch sample, namely the O-H group at wave number 3274 cm$^{-1}$. This shows that the starch sample contains cellulose compounds which have a hydroxyl group. The -C-H alkane and -C-H alken functional groups show the formation of amylose and amyllopectin structures, while the C=O carbonyl groups are formed from the oxidation process of the alcohol groups present in the starch amyllopectin structure. In the amyllopectin structure there are also functional groups -OH and C=O [9]. The appearance of C=O carbonyl and C-O ester functional groups indicates that the plastic samples that have been made are capable of biodegradation. This is evidenced by the presence of functional groups O-H hydroxyl, C=O carbonyl and C-O ester which are hydrophilic so that the absorbed water molecules are able to encourage microorganisms around the plastic to enter the plastic structure [10] so that they are easily degraded. This shows that the starch samples have been made well so that they can be applied in making biodegradable plastics.

### 3.2. FTIR of Chitosan

![FTIR spectrum of chitosan.](image)

\[
A3410 = \log \left(\frac{102.1 - 88.3}{88.3 - 54}\right) = 0.742
\]
\[
A1655 = \log \left( \frac{95.9 - 87.1}{87.1 - 54} \right) = 0.4137
\]
\[
DD = \left[ 1 - \left( \frac{2.413}{8742} \times \frac{1}{133} \right) \right] \times 100\% = 58.16\%
\]

(1)

Figure 2 shows the FTIR results of crab shell chitosan material using the absorbance method and looking for the degree of deacetylation was carried out using the formula Moore [11] and Robert [12] where the results showed that the amine groups ranged from 82.5% transmission and the frequency of the wave number was 3292 cm\(^{-1}\). While the acetamide group ranged from 87.9% transmission with a wave number frequency of 2873 cm\(^{-1}\). Here the acetamide group wave number frequency is higher than the amine group wave number frequency because the amine group wave number frequency is medium intensity at 3500 – 3100 cm\(^{-1}\). There is a decrease in the graph in the frequency area 1300 – 1000 cm\(^{-1}\). This decrease in the graph area is often called the fingerprint area, this area the vibrational bands cannot be determined with certainty. In this chitosan product, the deacetylation degree was obtained by 58.16%. From chitin, chitosan can be produced by removing the acetyl group (CH\(_3\)-C=O) so that the molecule can dissolve in an acidic solution, this process is called deacetylation, which produces a free amine group (-NH) so that chitosan has characteristics as a cation. In general, the deacetylation degree for chitosan is around 60% [13].

3.2. Bioplastics Results

Figure 3 shows that 9 samples were made namely sample A-I with 2 variables. The first variable chitosan 1 gr, 1.5 gr and 2 gr. As for the second variable, namely the variation in glycerol 3%, 4%, 5%. Meanwhile for starch, a control variable is used 2 gr. Biodegradable plastics that have been made with variations of 1 g of chitosan and 3% glycerol produce starch powder which is very soluble but less elastic, while for variations of 2 gr chitosan and 5% glycerol it looks quite strong but a lot of starch powder and chitosan solution are visible on the surface of the plastic. The manufacture of biodegradable plastics for variations of 1 g chitosan and 3% glycerol looks very transparent because the starch and chitosan are quite soluble, while for the 2 gr chitosan and 5% glycerol variations it looks stronger and less brittle but there are still a lot of starch powder and chitosan that are not dissolved, because inhomogeneous. This is because the
composition of the plastic mixture is not balanced compared to the composition of the other samples. In plastics with the addition of 1 g chitosan and 3% glycerol variations, it looks almost transparent compared to other plastics, this may be due to the use of the lowest mass of chitosan and the lowest glycerol of 3% which makes plastic solutions easy to form. This shows that the difference in the percentage of starch and chitosan also affects the dissolution of plastic that can be made.

3.3. Biodegradation Analysis

Biodegradable plastics from aking rice starch and crab shell chitosan were tested to see their biodegradability. Where in this study to find out how long the sample was degraded using the method of planting the sample in the soil. The sample is planted in the soil. After that, cut samples with a size of 3 x 2 cm$^2$ were planted, then observed from week to week for up to 30 days. The weight of the sample was measured before and after degradation [14]. The percentage of weight loss can be calculated by the formula:

$$\text{% Loss Weight} = \frac{W_1 - W_2}{W_1} \times 100\%$$ (2)

Where:

$W_1$ = Plastic weight before degradation

$W_2$ = Plastic weight after degradation

| Biodegradation Analysis Sample | Initial Weight (gram) | Final Weight (gram) | Degradation Percentage (%) |
|-------------------------------|-----------------------|---------------------|----------------------------|
| Sample A (1 gr chitosan : 3% glycerol) | 0.30 | 0.20 | 33.3 |
| Sample B (1 gr chitosan : 4% glycerol) | 0.31 | 0.23 | 25.8 |
| Sample C (1 gr chitosan : 5% glycerol) | 0.32 | 0.27 | 15.6 |
| Sample D (1,5 gr chitosan : 3% glycerol) | 0.36 | 0.34 | 5.5 |
| Sample E (1,5 gr chitosan : 4% glycerol) | 0.39 | 0.37 | 5.1 |
| Sample F (1,5 gr chitosan : 5% glycerol) | 0.40 | 0.38 | 5 |
| Sample G (2 gr chitosan : 3% glycerol) | 0.50 | 0.48 | 4 |
| Sample H (2 gr chitosan : 4% glycerol) | 0.51 | 0.49 | 3.9 |
| Sample I (2 gr chitosan : 5% glycerol) | 0.52 | 0.51 | 2 |

In the Table 2, it can be seen that chitosan inhibits the absorption rate of water which makes it easier for bacteria to decompose plastic samples. The use of chitosan has water resistance, this is because chitosan is hydrophobic. This also applies to the addition of glycerol composition, where the percentage value of degradation will be smaller as the glycerol concentration increases.
In Figure 4 it can be seen visually the chitosan variable on biodegradation where the more the percentage of chitosan, the less biodegradation will occur. This is due to the slow absorption of water due to high levels of chitosan. Hydrophobic chitosan inhibits the absorption rate of water which makes it easier for bacteria to decompose plastic samples. This also applies to the addition of the glycerol composition, where the percentage value of degradation will be smaller as the glycerol concentration increases. It can be seen that sample I from its visual appearance is the one with the lowest biodegradation. This is also supported by the weight loss of sample I which is only 3.9%.

From the results of bioplastic analysis, the starch is not cleaned so that it can cause mixing of starch with other ingredients, this should be a concern so that the percent of starch mixed is actually starch from aking rice, so that when the biodegradation test is carried out, the microorganisms actually decompose the bioplastic from plastic.

3.4. Optical Microscope Analysis
After passing the FTIR chitosan material testing and also the biodegradation stage, an optical microscope test was carried out to determine the biodegradation results with the lowest degradation percentage and the highest degradation percentage. Optical Microscope is a tool that can be used to study or observe the details of the shape and microstructure of the surface of an object that cannot be seen with the eye. Optical microscopy is used to observe the microstructure characteristics of solid samples from metal, polymer or ceramic materials.
In Figure 5, for the microstructure of the sample with a variation of 2 gr chitosan and 5% glycerol, there is a surface indentation which indicates that the surface of this bioplastic sample is uneven and the starch and chitosan contained in the sample are not well dissolved. This is in accordance with the theory which says that the increasing the mass of starch and chitosan, the value will also increase. The greater the starch concentration, the greater the value due to the tendency of starch to have more hydroxyl (OH) groups so that it absorbs more water so that the low starch percentage and high chitosan make it difficult for chitosan to dissolve because the solution does not dissolve homogeneously [15].

Figure 5. Microstructure of Chitosan 2 gr, glycerol 5%.

Figure 6. Microstructure of Chitosan 1 gr, glycerol 3%.
So that for sample A with the lowest percentage of chitosan and starch which is only 2 grams, it is easy to dissolve and in Figure 5 it can also be seen that in Figure 6 there are air bubbles caused by heating from the oven causing air to be trapped in the solution mixture before the solution dries up and becomes bioplastic. This bad surface is due to an inhomogeneous mixture of materials. This is also supported by the worst physical appearance of plastic, namely the surface of the plastic is very rough compared to other samples and also the appearance of the rough surface indicating that chitosan and starch are not well dissolved but the plastic looks quite strong. This is due to the addition of percent glycerol and chitosan which is the most among other samples.

In Figure 6, for the microstructure of 1 g chitosan and 3% glycerol samples, it can be seen that the surface is flat and there are no visible curves, which means that the starch and chitosan are well dissolved, but there are also air bubbles due to heating. This good surface is due to a more homogeneous mixture of materials. This is also supported by the best physical appearance of plastic, namely the surface of the plastic is smoother than the other samples and also a more transparent appearance indicating that chitosan and starch are well dissolved.

Conclusion
Biodegradable plastic synthesis can utilize organic materials such as crab shell waste and aking rice as basic materials. In bioplastic testing, the sample with the highest percentage of biodegradation was 33.3% containing 1 g of chitosan and 3% glycerol, while the sample with the lowest percentage of biodegradation was 2% containing 2 g of chitosan and 5% glycerol. The sample with the lowest percentage of degradation has curvature and air bubbles which indicate that the surface of this bioplastic sample is uneven. Whereas the sample with the highest percentage of degradation only contained air bubbles on the surface. So, based on their degradation properties, this sample is better used as a substitute for conventional plastics.

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