Biodegradation Bioplastic Based on Arrowroot Starch with Glycerol Plasticizer and ZnO Fillers

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Abstract. Petroleum-based plastic packaging is very often found in everyday life. It is necessary to develop plastics made from polymers that can be decomposed naturally due to plastic waste problem. One of this polymer is starch. ZnO compounds are used as reinforcing bioplastics because bioplastics derived from starch are still brittle. This study aims to understand the biodegradability of arrowroot starch-based bioplastics with additional ZnO on soil media. This research was carried out in three stages: the production of arrowroot bioplastics with ZnO variations of 0%, 1%, 2%, 3%, 4%, and 5%, bioplastic characterization testing, and bioplastic biodegradation testing. Bioplastic’s characterization includes mechanical test (tensile strength, elongation, and young modulus), FTIR (Fourier Transform Infra-Red), and biodegradation testing of bioplastics carried out on soil pH 5 and pH 6. The result showed with variation 3% of ZnO produce are good mechanical and physical properties. Bioplastics produced tensile strength of 5,9966 MPa, elongation of 5,00045%, and young modulus of 118,1268 MPa. The biodegradation test results in soil pH 5 and pH 6, respectively, showed a decrease in the bioplastic mass up to 70% and 72% for 15 days.

1. Introduction

Petroleum-based plastic packaging, which is often found in everyday life, causes many pollutions and environmental damage [1]. Therefore it is necessary to develop plastics made from other polymers that can biodegrade naturally. One solution to solving this problem is to replace conventional plastic base materials with materials that are easily broken down by decomposers, which are called biodegradable plastics (bioplastics). The advantages of this bioplastic are obvious. Namely, it is cheap, easy to decompose and reduces plastic waste, which is increasing in number over time [2,3]

Bioplastics are designed to facilitate the degradation process of the enzymatic reactions of microorganisms, such as bacteria and fungi [4]. One of the promising bioplastic materials is starch. This is because starch is easy to decompose, universal, renewable, and affordable. [5] The production of bioplastics from starch requires plasticizer addition so that the resulting bioplastics are not brittle. Bioplastic additives are usually hydrophobic and anti-microbial [6]. The presence of this reinforcing material will influence the properties of the formed [7].

The reinforcement will increase the mechanical strength and barrier properties of the starch. ZnO is a piezoelectric, bio-safe, and bio-compatible material with starch [8]. ZnO has also been widely used as a reinforcement for starch, such as in the manufacture of sago starch-based plastics with glycerol coupled with ZnO filler variations [9,10,11]. Where ZnO can act as a filler and also as an attacking agent for microorganisms [12,13].
ZnO is an inorganic compound. It has a white color, is a powder and is hydrophobic [14]. Blended and wurtzite are these crystal structures. The wurtzite structure is a structure of ZnO, which is formed from Zn giving a cation and O giving anion, resulting in a tetrahedral coordination number. ZnO's function is as an antimicrobial and as a reinforcement of the bioplastics produced [15]. Therefore ZnO is used to improve the weaknesses of the resulting mechanical properties of bioplastics in terms of mechanical properties and water absorption properties.

In this study, a plastic biodegradation study was carried out from materials that can be degraded by microorganisms, namely arrowroot tuber starch and the effect of adding ZnO filler variations to the rate of biodegradation [16]. This study was also conducted to determine the ability of plastic degradation by soil microorganisms with a pH factor [17]. This study needs to be investigated so that it is expected to help efforts to manage plastic waste optimally and utilize natural resources [18]. The biodegradation level test of plastic is then linked to the analysis of functional groups contained in plastic using Fourier Transform Infra-Red (FTIR). Plastic mechanical tests, including tensile strength, elongation, thickness and water resistance tests are also carried out to help understand the biodegradation properties of the plastic produced [19].

2. Materials and Methods
Garut tubers used were obtained from the village of Kalijurang, Tonjong, Brebes, Central Java. This research was started by extracting arrowroot starch, and then proceed with making arrowroot starch with the addition of ZnO filler variations [20].

2.1. Manufacture of biodegradable plastic
This research carried out variations of ZnO filler, namely ZnO 0%, 1%, 2%, 3%, 4%, and 5% by weight of starch. The starch that has been weighed as much as 5 grams is put into a beaker glass then 100 ml distilled water is added while stirring. After that, 30% glycerol w / starch was added, and the ZnO variation was then heated on a hotplate at 90˚C while stirring for 40 minutes until gelatinization [21]. After that, bioplastic molding is done and dried in an oven at 50˚C for 4 hours. After drying, the plastic is allowed to stand at room temperature for 24 hours.

2.2. Bioplastic characterization test
The bioplastic films obtained were then characterized by mechanical testing and functional group testing with FTIR.

2.2.1. Thickness test. The film thickness test was measured using a micrometer scrap to the accuracy of 0.01 mm. Thickness values are measured at five points to obtain an average measurement result. This measurement is carried out three times. Plastic thickness values are obtained using the formula:

\[
\text{Average thickness} = \frac{\text{point 1 + point 2 + point 3 + point 4 + point 5}}{5} \quad (1)
\]

2.2.2. Tensile strength test. Tensile strength testing uses universal tensile strength using both ends of the film sheet clamped to the testing machine. The measurement results in the form of force (F) and sample extension are included in the formula:

\[
\text{Tensile strength} \left( \frac{\text{kgf}}{\text{mm}^2} \right) = \frac{\text{Force (F)}}{\text{Surface area (A)}} \quad (2)
\]

2.2.3. Elongation test. The sample is tested for elongation and measured by the formula:

\[
\text{Elongation} = \frac{\text{Final gage length} - \text{Initial gage length}}{\text{Initial gage length}} \times 100% \quad (3)
\]

2.2.4. Modulus young test. The relationship between tensile strength and elongation results in the Modulus Young value in the formula:
\[
\text{Modulus young} = \frac{\text{Tensile strength (MPa)}}{\text{Elongation}}
\]  

(4)

2. 2. 5. FTIR test. FTIR test was carried out on arrowroot tuber starch samples, arrowroot bioplastic (without ZnO addition) and arrowroot-ZnO bioplastic. Each sample is in the form of a thin and transparent layer measuring 1.5 x 1.5 cm.

2. 3. Biodegradation Test
Biodegradation test is done by mixing the soil with a variation of acetic acid concentration of 1% and 3% [22]. With a ratio of 1000 grams of soil : 100 ml of the acetic acid solution, then measured with a soil pH meter resulting in variations in soil pH of 5 and 6, according to soil pH in Indonesia. The plastic film that has been made is measured 3 x 3 cm buried in the ground for 15 days and then cleaned and weighed. Checking is done two days one time.

3. Results and Discussion

3.1. Physical properties of bioplastics.
The results showed that the arrowroot starch bioplastic results with variations of ZnO showed changes in different physical appearances. Bioplastic colors with a variation of 0% ZnO, which initially looks colorless and transparent, become whiter as ZnO fillers increase and are not too transparent. This is because ZnO will give a white effect according to the original color of ZnO in the form of white powder.

The surface texture of the arrowroot bioplastic tuber with ZnO filler produces a rough surface texture.

3. 2. Bioplastic characterization

3. 2. 1. Thickness. Increasing the concentration of the material can cause an increase in solids in the film-forming solution [23]. The more solids, the thicker the film produced, so that the permeability to water is smaller, and the packaged product is more protected. The value of the bioplastic thickness of arrowroot tubers with ZnO filler is presented in Figure 1.

| Variations | Thickness (mm) |
|------------|---------------|
| 0          | 0.068         |
| 1          | 0.071         |
| 2          | 0.063         |
| 3          | 0.063         |
| 4          | 0.063         |
| 5          | 0.063         |
| 6          | 0.071         |

Figure 1 shows that the thickness of the plastic film obtained ranged from 0.055-0.0945 mm according to the plastic criteria, which is equal to <0.25 mm. This result shows that it has reached the criteria so that it can be categorized as plastic. Irregularities in the thickness value of bioplastic samples may be caused by differences on each side of the glass plate when printing bioplastics manually before drying.
3.2.2. Tensile strength. The bioplastic tensile strength measurements results presented in Figure 2 show that the bioplastics without the addition of ZnO filler have the highest tensile strength of 11,1779 MPa. The tensile strength of bioplastics increases with the addition of ZnO fillers 1%-3% while the bioplastics with the addition of 4%-5% fillers decrease. This shows that the addition of ZnO filler affects the tensile strength of the bioplastics produced [24].

![Figure 2. Bioplastic Tensile Strength.](image)

Irregularities in values can be caused during the stirring process, where the ZnO filler, when added to the starch solution, cannot wholly spread, resulting in agglomerated ZnO. The bioplastic inhomogeneity can cause a decrease in tensile strength.

3.2.3. Elongation. The elongation value of bioplastics with the effect of ZnO filler addition can be seen in Figure 3, showing that the measurement results of elongation/percent bioplastic elongation with ZnO variations obtained the highest elongation value at 1% ZnO variation of 13.7491% while the smallest bioplastic elongation value at 0% variation amounted to 3.932%. The percent elongation produced has decreased in various variations of ZnO filler concentration due to ZnO as a filler or filler not evenly distributed [25,26].

![Figure 3. Bioplastic Elongation.](image)
The inequality of ZnO may be caused during the mixing process that is not quite right, so that bioplastic and filler solutions are not evenly dispersed but agglomerated.

3.2.4. Modulus Young. The value of the bioplastic modulus young with the effect of ZnO filler addition in Figure 4. shows that the modulus young value of the highest bioplastics produced was achieved on bioplastics with 0% ZnO that is equal to 291.3837 MPa. Bioplastics with 1%-3% variation have increased, whereas in 4-5% variation has decreased.

Figure 4. Modulus Young Bioplastics.

The amount of ZnO filler concentration in bioplastics significantly produced influences the mechanical properties of bioplastics [27,28]. If the number of fillers is too small, the polymer matrix cavities are increasing. As a result, the bonding matrix and filler are more easily separated, causing mechanical properties to decrease. Whereas if too many additions are added, the agglomerated fillers and their distribution in the matrix become less evenly distributed.

3.2.5. Spearman correlation test. Spearman correlation test was performed to determine whether there is a relationship between variations in the addition of ZnO fillers with thickness, tensile strength, elongation, and young modulus [22]. Spearman correlation test results in Table 1. show that the variation of ZnO to thickness has a spearman correlation coefficient of -0.365 with a significance value of 0.248 where shows a weak negative correlation between variations in the addition of ZnO to the thickness value. The addition of ZnO tends to reduce the thickness of the bioplastics produced, but the decrease that occurs is not significant.

| Spearman's Rho | Variation | Thickness | Tensile strength | Elongation | Modulus young |
|----------------|-----------|-----------|------------------|------------|---------------|
| Correlation coefficient | 1,000 | -0,365 | -0,608 | 0,042 | -0,184 |
| Sgl. (2-tailed) | 0,248 | 0,036 | 0,896 | 0,568 |
| N | 12 | 12 | 12 | 12 | 12 |

In Table 1., the spearman correlation coefficient between variations ZnO with the tensile strength is -0.608, with a significance value of 0.036. This shows that the variation of addition with tensile strength
has a strong negative correlation, where the addition of ZnO variations tends to reduce the tensile strength produced significantly.

The variation of the addition of ZnO by elongation has a spearman correlation coefficient of 0.042, with a significance of 0.896. From these data in Table 1, it can be concluded that the addition of variations has a very weak positive correlation related to the value of bioplastic elongation obtained.

In Table 1., the modulus young value with the addition of ZnO has the Spearman correlation coefficient value of -0.184 with a significance of 0.568. These data can be seen that the addition of ZnO variations has a very weak negative correlation relationship with the bioplastics produced.

3. 2. 6. Analysis of bioplastic functional groups. Bioplastics that have been formed are then characterized using FTIR. FTIR analysis of bioplastics is used to identify the interaction of glycerol and ZnO as plasticizers and fillers against arrowroot tuber starch as the matrix. The results of FTIR characterization on arrowroot starch, bioplastic arrowroot non-ZnO and bioplastic arrowroot starch-ZnO are presented in Figure 5.

![Figure 5. FTIR spectra (a) arrowroot starch, (b) bioplastic arrowroot non-ZnO (ZnO 0%), (c) bioplastic arrowroot starch-ZnO (ZnO 3%).](image)

FTIR results in Figure 5. showed that the arrowroot starch bioplastic with the addition of ZnO filler experienced a shift in the OH function group, the wavenumber shift occurred from 3410.15 cm\(^{-1}\) in the arrowroot bioplastic to 3425.58 cm\(^{-1}\) in the arrowroot starch bioplastic with the addition of arrowroot starch bioplastics with the addition of ZnO filler starch. Wavenumber shifting also occurs in the CH functional group, the wave number in the arrowroot tuber bioplastic is at 2931.80 cm\(^{-1}\), while the arrowroot tuber bioplastic with the addition of ZnO filler is at 2924.08 cm\(^{-1}\). Shifting of wave numbers occurs at CO in arrowroot bioplastic at 1026.13 cm\(^{-1}\), while in the arrowroot, bioplastic ZnO is at 1026.13 cm\(^{-1}\). This wavenumber shift is accompanied by changes in the intensity and widening of the OH wave number band.

The spectrum results in Figure 5. show that bioplastics based on arrowroot starch, glycerol and ZnO starches produce a spectrum with wavelengths similar to the constituent raw materials. Based on the interpretation of bioplastic FTIR spectra produced, there is no change in new functional groups, shifting of several wavenumbers and changes in absorption band intensity, which indicate that the interactions that occur between starch polymers and ZnO fillers are physical interaction.
3. 3. Biodegradation

3. 3. 1. Soil pH 5. Bioplastics produced in this study are biodegradable, evidenced by a decrease in bioplastic weight loss in each ZnO variation within 15 days of observation. Based on Table 6., as ZnO is added, the rate of biodegradation tends to slow down, because ZnO acts as the rate of diffusion of water against the polymer. ZnO particles act as attacking agents of microorganisms so that ZnO levels are large enough, and the frequency of attacking decomposing microorganisms becomes high [26].

Percent decrease in bioplastic weight loss in this study was further analyzed by Kruskal-Wallis variance to determine whether there were significant differences produced by biodegradation testing every day in Table 2. [29].

Table 2. The Kruskal-Wallis analysis on soil media pH 5.

| Day 1 | Day 3 | Day 5 | Day 8 | Day 10 | 12th day | Day 15 |
|-------|-------|-------|-------|--------|----------|-------|
| Chi-Square | 15,000 | 15,600 | 16,750 | 17,420 | 17,520 | 18,830 | 20,10 |
| Df     | 5   | 5   | 5     | 5      | 5      | 5       | 5     |
| Asymp. Sig. | 1,000 | 0,008 | 0,005 | 0,004 | 0,004 | 0,002 | 0,001 |

The analysis showed that there was a significant decrease in bioplastic weight loss on every biodegradation testing day. From the results of the analysis of variance, it can be seen that the influence of the addition of ZnO filler to the decrease in bioplastic weight loss in the biodegradation of soil media at pH 5 is seen significantly.

3. 3. 2. Soil pH 6. In Figure 7., the decrease in bioplastic weight loss at 0% variation of ZnO at pH 6 has a much faster decline in the biodegradation rate compared to bioplastics with the addition of ZnO. Where the rate of bioplastic biodegradation with the addition of ZnO tends to be slower. Based on this study, it can be concluded that bioplastics from arrowroot tubers using ZnO fillers are environmentally friendly.
The significance of the biodegradation test is then analyzed by Kruskal-Wallis variance to determine whether there is a significant difference produced by each day of biodegradation testing in Table 3. [29].

Table 3. The Kruskal-Wallis analysis on soil media pH 6.

|                      | 6 days 1 | 6 days 3 | 6 days 5 | 6 days 8 | 6 days 10 | 6 days 12 | 6 days 15 |
|----------------------|----------|----------|----------|----------|-----------|-----------|-----------|
| Chi-Square           | 15,000   | 15,500   | 15,530   | 15,750   | 17,230    | 15,940    | 17,090    |
| Df                   | 5        | 5        | 5        | 5        | 5         | 5         | 5         |
| Asymp. Sig.          | 1.000    | 0.008    | 0.008    | 0.008    | 0.004     | 0.007     | 0.004     |

The analysis showed that the effect of the addition of ZnO on the biodegradation rate was significant on each test day. This indicates that variations in the addition of ZnO produce a significant impact on the decrease in bioplastic weight loss.

3.3.3. Comparison of biodegradation rates. Based on Figure 8., the bioplastic biodegradation rate that has been made on soil pH 5 is faster than soil pH 6. This can be proven by the slope of the biodegradation linear equation on soil pH 5 is 0.2426, while on soil pH 6 is -0.0171.
In the biodegradation testing process in bioplastics, small patches are found on the surface of the bioplastic film, which is a sign of microorganism activity [22]. One factor that can affect degradation is pH, where plastic degrading microorganisms can degrade only at optimum pH. If the pH conditions are not optimum, it can cause microorganisms that are in will die [22].

4. Conclusion
The addition of ZnO filler affects the physical and mechanical properties of bioplastic based on arrowroot tuber starch with varying strength relationships. The physical appearance of bioplastic films without the addition of ZnO is colorless/transparent, while increasing variations of ZnO fillers, show the colors to be white and not too transparent. The thickest bioplastic is produced at a variety of ZnO 1% by 0.0945 mm, while the thinnest is at ZnO 3% by 0.055 mm. The value of tensile strength decreases with increasing ZnO. The highest tensile strength value at 0% ZnO variation was 11.1779 MPa, while the lowest tensile strength value at 5% ZnO variation was 2.5425 MPa. Modulus young value decreases with increasing ZnO. The highest modulus young at 0% ZnO variation was 291,3837 MPa, while the lowest modulus young at 1% ZnO variation was 32,68601 MPa.

Bioplastic biodegradation test based on arrowroot tuber starch on soil media pH 5 and 6 from day 1 to day 15 has decreased mass. The more the number of ZnO increases, the slower the rate of biodegradation. Fastest bioplastic mass reduction in bioplastics without the addition of ZnO. Meanwhile, the ratio of biodegradation rate in pH 5 soil media is faster than in soil pH 6.

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