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The effect of ZnO (zinc oxide) and glycerol concentrations on the mechanical properties of bioplastics made from Canna tuber (*Canna edulis*) starch

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KEYWORDS

Bioplastic
Canna starch
Glycerol
Mechanical properties
ZnO

ABSTRACT

The problem of plastic waste in Indonesia is increasingly worrying due to its long degradation duration. Bioplastics made from starch are easily degradable in nature and have a lower contribution to environmental pollution. This study aimed to determine the effect of ZnO and glycerol additions on the thickness, tensile strength, elongation, Young's Modulus, water absorption, and biodegradation of bioplastics. The results indicate that adding ZnO and glycerol has significant effects on thickness, tensile strength, elongation, Young's Modulus, water absorption, and biodegradation. A high concentration of ZnO and glycerol was parallel to an increase in the thickness of bioplastic. A high ZnO concentration and low glycerol concentration increases the tensile strength and Young's Modulus, but decreases the water absorption. Glycerol at high concentration and ZnO at low concentration increases the elongation. The addition of ZnO in a small amount positively affects the biodegradation of bioplastics.

Introduction

Environmental pollution due to plastic waste is a problem faced in Indonesia and the world. Data from The Ministry of Environment and Forestry (2019) shows that the national waste stockpile reaches 175,000 tons/day, which is 15% of the total waste. Plastic waste originates mainly from food and beverage packaging, consumer goods, shopping bags, and other packaging materials. According to the Indonesian Institute of Science (2016), the level of plastic consumption in Indonesia per capita reaches 17 kg per year, with consumption growth of 6-7% per year. Plastic waste originating from petroleum is resistant to decomposition and takes 500-1000 years (Ncube et al., 2020)

The solution to plastic waste is replacing it with biodegradable plastic (bioplastic), which can be decomposed readily by bacteria. Bioplastic components come from renewable raw materials, such as starch and cellulose. One tuber starch producer locally found in Indonesia is canna tuber, which is still underutilized. Canna tuber (*Canna edulis*) has the potential to be used as a raw material for making bioplastics because of its high starch content. According to Aprianita et al. (2014) the starch content in canna starch is quite large, as much as 7%. In addition, canna starch has a reasonably high amylose content compared with starch from other tubers, which is 37,1% (Hung and Morita, 2005). According to Thuwall et al. (2006), amylose provides stronger mechanical properties in bioplastics. Watcharatewinkul et al. (2009) added that canna starch would form a gel. The clear liquid has a high viscosity and retrogradation rate, and is resistant to hydrolysis by alfa-amylase enzymes.

Starch-based bioplastics have several weaknesses, such as brittleness and high-water absorption, thus some reinforcements and plasticizers can be added to bioplastic production. One of the reinforcing materials that can be added to the bioplastic matrix is ZnO (zinc oxide). Thirumavalavan et al. (2013) stated that ZnO is also a green material that is bio-safe, biocompatible, and biodegradable, thus it can be used for bioplastic production. US Food and Drug Administration (2020) has also categorized ZnO as a generally safe substance. In addition, ZnO will produce a non-transparent film in accordance with the aim of this research. Meanwhile, one of the plasticizers that can be added is glycerol. Oses

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et al. (2009) stated that the use of glycerol is better than sorbitol because the resulting film is more flexible and not brittle, the fiber's mechanical properties and its appearance do not change during storage. This study focuses on the effect of ZnO and glycerol concentration on bioplastic production to produce plastics that are elastic, have water resistance, and easily decomposed by microorganisms.

Table 1. Variation ZnO and Glycerol concentrations

Glycerol Concentration (G)(%)	ZnO Concentration (Z) (%)		
	1	3	6
15	Z1G15	Z3G15	Z3G15
20	Z1G20	Z3G20	Z3G20
25	Z1G25	Z3G25	Z3G25

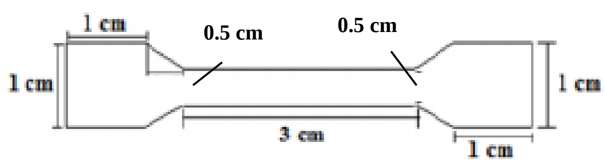

Figure 1. Sample shape and size for tensile strength and elongation tests

Research Methods

Materials and equipment

The materials used in this study are canna tuber starch as the main material in bioplastics ZnO as additional material, glycerol as a plasticizer, distilled water as a solvent, EM4 culture as a biodegradable agent, plantation land as biodegradation media. The experimental works used a hot plate and magnetic stirrer (GSA MS-H-Pro), cabinet dryer, analytical balance, glass plate measured 11x11cm, and ruler. Bioplastics analysis were conducted using *Tensile Strength (IMADA ZP-200*N), plastic cups, and analytical balance.

Bioplastic production procedures

Bioplastics were made by mixing 5 grams of canna starch, 50 ml of distilled water, ZnO (1%, 3%, 6%), and glycerol (10%, 15%, 20%) according to variations as shown in Table 1. Then, all the ingredients were poured into a beaker with the stirring. The mixture solution was dissolved on a hot plate magnetic stirrer at 135^0C for 15±1 minutes. The gelatinized mixture was printed on a glass plate with a dimension of 11x11cm. Then, the bioplastics were dried in a cabinet dryer at 60^0C for 3 hours 15 minutes. The bioplastics film then rested for 24 hours at room temperature for further analysis, including thickness, tensile strength, elongation, Young's Modulus, water absorption, and biodegradation.

Methods

The thickness measurement of bioplastic was performed at 5 different points using a screw micrometer-scale 0-25 mm with an accuracy of 0.01 mm. Thickness results are presented by giving average values of measurements.

The samples were conditioned at a standard relative humidity temperature for 24 hours before tensile measurement. The sample was cut following the size as shown in Figure 1. Then both ends of the samples were clamped on a tensile tester, and the start knob was turned on. The values of the tensile strength (f) and the elongation at break (elongation) were recorded. The calculations were made according to Equation 1 and Equation 2, respectively.

$$\text{Tensile strength}\left(\frac{\text{N}}{\text{m}^2}\right) = \frac{\text{maximum pulling force (N)}}{\text{cross sectional area (m}^2\text{)}} \quad (1)$$

$$\%\text{elongation} = \frac{(\text{final length} - \text{initial length})}{\text{initial length}} \quad (2)$$

Young's Modulus values were calculated using Equation 3

$$\text{Young's Modulus (MPa)} = \frac{\text{Tensile strength (MPa)}}{\text{Elongation at break (\%)}} \quad (3)$$

A water absorption test was carried out by cutting the sample into a size of 2.5x4cm. Then, the sample was soaked in a container having aquadest for 10 seconds, removed, and weighed again. These steps were repeated until a final constant weight was obtained. Water absorption was calculated by Equation 4:

$$\text{Water absorption (\%)} = \frac{(\text{final weight} - \text{initial weight})}{\text{initial weight}} \times 100\% \text{..................} (4)$$

The biodegradation test was carried out by cutting samples with a size of 2.5 cm x 4 cm. After the initial mass measurements (at day 0), the soil was prepared with 10% EM4. The soil was placed into a plastic cup and the sample was buried. Changes in the mass of samples were observed every 2 days. The rate of biodegradation was calculated by Equation 5

$$\text{\% weigth loss} = \frac{(\text{initial weight} - \text{final weight})}{\text{initial weight}} \times 100\% \text{.................} (5)$$

Results and Discussion

Characteristics of Bioplastics with Variation of ZnO and Glycerol Concentration

a. Thickness

Variations in ZnO addition generated different physical appearances of bioplastics, as shown in Figure 2.

Figure 2 shows that bioplastic without ZnO addition has clear and transparent optical properties. Bioplastic with the addition of ZnO white and not transparent optical property. Discoloration on the samples showed that ZnO particles were well dispersed into the starch matrix.

Changes in thickness at different glycerol and ZnO addition are shown in Figure 3. Based on Figure 3, the thickness average of bioplastics ranged from 0.160mm to 0.256mm. The smallest thickness in bioplastic was obtained with the addition of 1% ZnO and 15% glycerol. On the other hand, the greatest thickness was observed after the addition of 6% ZnO and 25% glycerol. The results indicate that adding a high concentration of ZnO and glycerol increases the thickness of bioplastic. Park et al. (1996) stated that the thickness of bioplastic is influenced by the number of dissolved solids and the surface area of the glass plate. AhHigh concentration of plasticizers may increase the function of film as a humectant that can be water-binding, thus the water is hardly evaporated during the drying process (Shah et al., 2016)

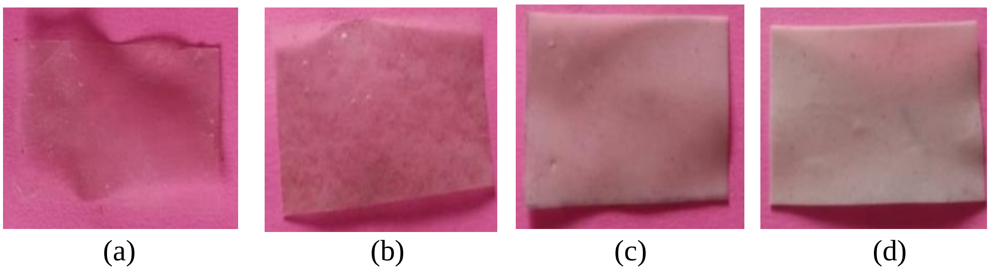

Figure 2. Bioplastic with Variation of ZnO (a) 0% (b) 1% (c) 3% (d) 6%.

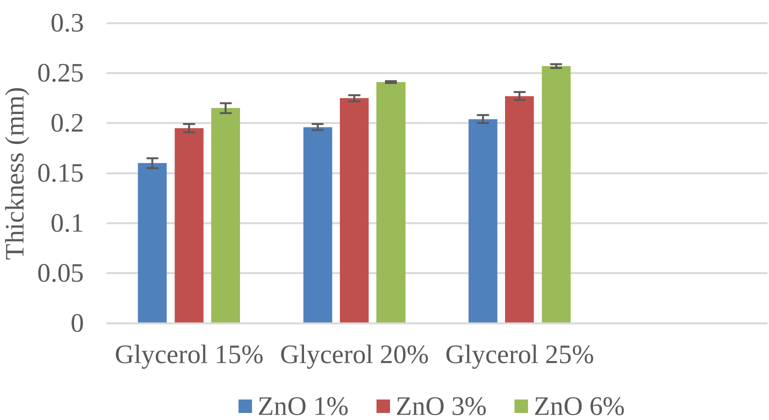

Figure 3. The Effect of ZnO and Glycerol Addition on Bioplastic Thickness. Error bars represent standard deviation from three measurements.

b. Tensile Strength

Tensile strength is the maximum force that can be held by bioplastics, which affected by the addition of plastic material (Sagnelli et al., 2017). Tensile strength test was performed using *Universal Tensile Machine*. The effect of ZnO and glycerol addition on tensile strength are presented in Figure 4.

The tensile strength values ranged from 9 N/m^2 to 18 N/m^2 at various ZnO and glycerol concentration added. At a concentration of 1% ZnO and 25% glycerol, the tensile strength was 9 N/m^2 and it increased to 18 N/m^2 at a concentration of 6% ZnO and 15% glycerol. From these results, it could be concluded that the higher addition of ZnO and the lower addition of glycerol enhance the tensile strength of bioplastic. In bioplastic, ZnO functions as an amplifier which can improve the bond in the starch polymer matrix since Zn^{2+} metal acts as a filler in the matrix and reconnects the secondary bonds in the starch polymer (Agustin and Padmawijaya, 2017). Abdullah et al. (2020) added that the moisture content strongly affects the mechanical properties of bioplastics. However, bioplastics' tensile strength decreases with the addition of glycerol as its function as a plasticizer. In this case, glycerol plays a role in reducing the intermolecular strength of bioplastics and increasing the elasticity of bioplastics (Lestari et al., 2020)

c. Elongation

Elongation is a change in the length of samples after testing the tensile strength. Elongation was measured using the *Universal Tensile Machine*. Figure 5 shows that the elongation value of bioplastics was 4.23% to 7%. At concentration of 15% glycerol and 6% ZnO elongation value 4.23% and increased to 7% at concentration of 25% glycerol and 1% ZnO. The greater addition of glycerol concentration and the smaller addition of ZnO has positively affect the elongation of bioplastic. Lee et al. (2013) stated that adding glycerol could also increase flexibility by decreasing intermolecular forces in the bioplastic polymer chain. Meanwhile, ZnO reduces elongation because ZnO as ceramic has brittle properties and has low elongation (Desai et al., 2007).

d. Young's Modulus

Young's modulus is the ratio between tensile strength and percent elongation at break. Young's modulus describes the stiffness of a material. Based on Figure 6, the value of Young's Modulus bioplastics ranged between 1.29 to 4.26MPa. Bioplastic with a concentration of 1% ZnO and 25% glycerol has Young's modulus of 1.15 MPa. Bioplastic with a concentration of 6% ZnO and 15% glycerol has Young's modulus of 4.26 MPa. From these results, it can be concluded that a high ZnO concentration and a low glycerol concentration increase Young's modulus value. This trend was opposite to the elongation value, but comparable to the tensile strength value. In this case, glycerol plays a role in reducing the intermolecular strength of bioplastics and increasing the elasticity of bioplastics (Lestari et al., 2020).

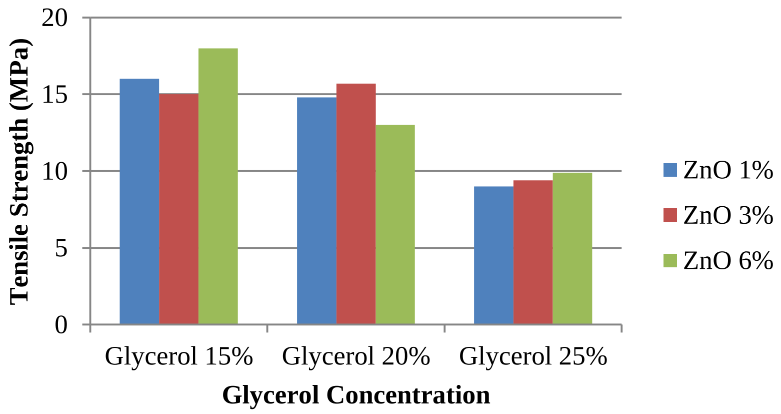

Figure 4. The Effect of ZnO and Glycerol Addition on Bioplastic Tensile Strength

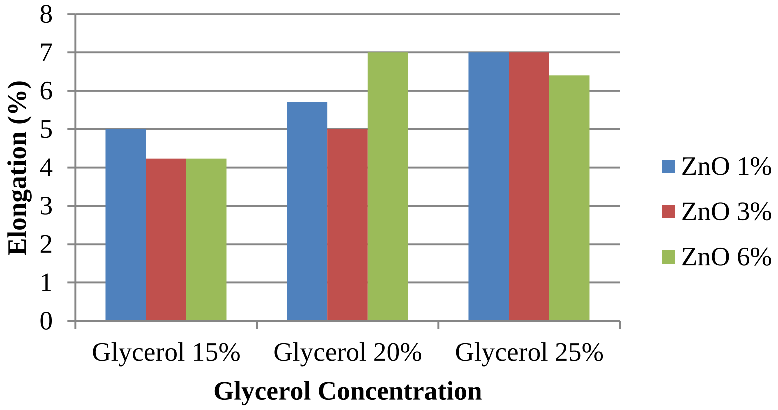

Figure 5. The Effect of ZnO and Glycerol Addition on Bioplastic Elongation

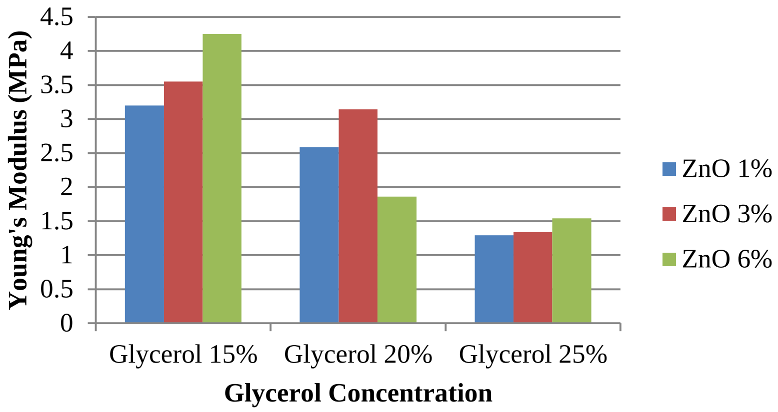

Figure 6. The Effect of ZnO and Glycerol Addition on Bioplastic Young's Modulus

e. Water Absorption

Water absorption testing was done by dipping the sample into distilled water to obtain a constant weight. The water absorption value of canna starch bioplastic with various ZnO concentrations and glycerol concentrations ranged from 26.53 to 47.8%. The highest absorption occurred in bioplastics with a concentration of 1% ZnO and 25% glycerol at 47.8%. The lowest water absorption occurred in bioplastics with the addition of 6% ZnO and 15% glycerol at 26.53%.

As shown in Figure 7, high ZnO and low glycerol concentrations decrease water absorption capacity. ZnO has hydrophobic properties and water cannot easily bind, and ZnO can cover the cavities or pores on the film's surface (Maslahah et al., 2021). Abdullah et al. (2020) added that water contact angle exhibited a larger value with the addition of ZnO, indicating the increase of bioplastics hydrophobicity. Meanwhile, water absorption increases with increasing glycerol concentration due to the easy absorption of water by hygroscopic glycerol. An increase in glycerol will create free volume in bioplastics, thus increasing the gap in bioplastics to be occupied by water molecules (Lestari et al., 2020).

f. Biodegradation Rate

The effect of additions of ZnO and glycerol on bioplastics's biodegradability is shown in Figure 8. Bioplastic with the greatest biodegradation rate was with the concentration of 1% ZnO and 25% glycerol. However, the lowest biodegradation rate was obtained at a concentration of 6% ZnO and 25% glycerol.

Based on Figure 8, a low ZnO and a high glycerol concentration increase biodegradation rate. Maslahah et al. (2021) stated that the more ZnO added, the slower biodegradation rate. This condition is because ZnO can act as a microorganism attack agent (Abdullah et al., 2020).

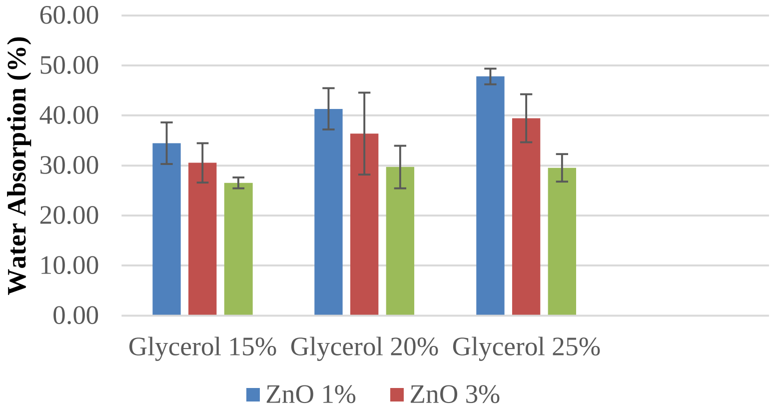

Figure 7. The Effect of ZnO and Glycerol Addition on Bioplastic Water Absorption. Error bars represent standard deviation from three measurements.

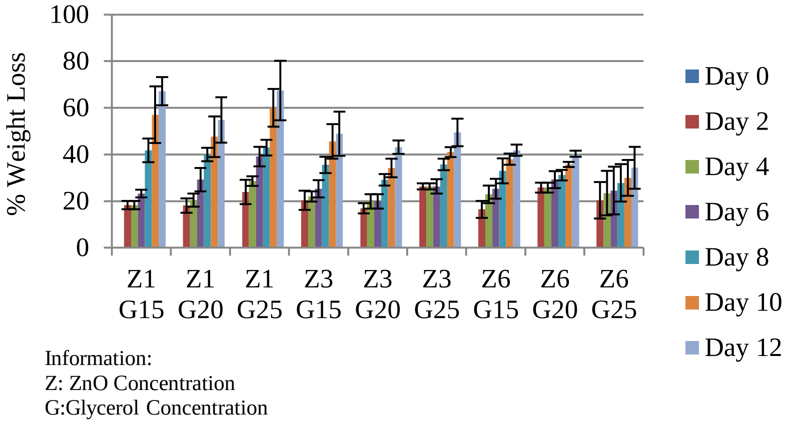

Figure 8. The Effect of ZnO and Glycerol Addition on Bioplastic Biodegradation. Error bars represent standard deviation from three measurements.

Bioplastics with higher ZnO additions have lower biodegradation rates because Zn^{2+} ions will become a bridge and substitute for the loss of the intra- and intermolecular hydrogen bonds (Agustin and Padmawijaya, 2017). The ability of bioplastic biodegradation is related to the ability of water absorption. Water absorption is influenced by the concentration of glycerol. The greater glycerol concentration increases the degradation process. The organic material in bioplastics is broken down into water (oxygen under aerobic conditions, methane under anaerobic conditions), CO, and biomass (Averous, 2004).

Conclusion

This study shows that adding ZnO and glycerol significant affects thickness, tensile strength, elongation, Young's Modulus, water absorption, and biodegradation of bioplastics. A high ZnO and glycerol concentration increased the thickness of bioplastic from 0.160mm to 0.256mm. A high ZnO and a low glycerol concentration improved the tensile strength from 9.4 N/m^2 to 18 N/m^2 and Young's Modulus 1.29 from MPa to 4.26 MPa. Adding glycerol at a high concentration and ZnO at a low concentration increased the elongation from 4.23% to 7%. A high ZnO and a low glycerol concentration decreased water absorption from 60.19% to 16.28%. Finally, adding ZnO can reduce the biodegradation rate of bioplastics from 67.4% to 34.3%.

Declarations

Conflict of interests The authors declare no competing interests.

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