

MECHANICAL PROPERTIES OF BIOPLASTICS JANENG STARCH (*Dioscorea hispida*) FILM WITH GLYCEROL AND ZINC OXIDE AS REINFORCEMENT

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ABSTRACT

The biodegradable plastics have been synthesized from janeng starch with the addition of ZnO and Glycerol as plasticizers. The process has used ZnO with variation of concentration by 1%, 3% 6%, then Glycerol with volume 1 ml, 3 ml, and 6 ml. The utilization of 6% ZnO and 3 ml of glycerol showed the highest tensile strength of 2.8 kgf/cm²; conversely, the highest percent elongation was obtained at 1% ZnO with addition 6 ml glycerol to be 4.5%. The lowest water absorption was captured in the composition of 6% ZnO with the addition of 1 ml of glycerol, which was equal to 2.9%, and the decomposition process occurred for 27 to 36 days.

Keywords: Bioplastics, Janeng (*Dioscorea hispida*), Plasticizers, Tensile Strength

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INTRODUCTION

Polymers are the most widely used plastic raw material for people in food packaging. This is due to the superiority of plastic polymers compared to other materials.^{1,3} Some of the advantages of plastic include having excellent mechanical properties (strong), is a barrier that is good for water and air, cheap, lightweight compared to other materials, in the form of sheets so that it can be made pockets, and ease in the process and application. In contrast, plastic still has disadvantages that are less favorable because plastic is not easily broken down by the environment, both by the weather of the rain and heat of the sun and microbes that live in the soil. Plastic material cannot be recycled naturally quickly.²

This causes a lot of garbage accumulation. It takes 300-500 years to decompose or decompose completely. Burning plastic is not the right choice either, because imperfectly burned plastic, under 800 degrees Celsius, will form dangerous dioxin. Plastics that are widely used are petroleum-based plastics whose existence is becoming thinner.⁵ On the other hand, the use of petroleum also causes environmental impacts in the form of global warming. Plastics made from petroleum can not decompose naturally, causing environmental pollution. Therefore, it is necessary to develop plastic that is biodegradable.^{4,6,7}

Starch has several disadvantages, namely strong hydrophilic behavior and inferior mechanical properties when compared to synthetic polymers. Starch is also mostly soluble in water and will be decomposed before undergoing the gelatinization process. To provide resistance and mechanical strength to starch, several fillers (reinforcement) in the form of metal and natural materials are usually added to the polymer matrix. The supporting material in other biodegradable plastic makers is ZnO. ZnO is a metal amplifier that is often used because ZnO is a piezoelectric ceramic and is antimicrobial.³ In this research, bioplastics will be made by materials from Janeng starch. Some of the most recent experimental experiments have been carried out by adding Janeng starch, but starch has deficiencies including lack of water resistance and mechanical properties. Addition of glycerol is one way to reduce hydrophilic properties so that plastic can maintain its strength.^{2,7,8}

This study using glycerol as plasticizing. Therefore this research uses Jeneng starch as the main ingredient in making environmentally friendly biodegradable plasticizers added with ZnO.

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EXPERIMENTAL

Material

Janeng, Acetic Acid (CH_3COOH), ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$), sodium hydroxide (NaOH), Aquades, Zinc Oxide (ZnO) were supplied by Sigma Aldrich and Glycerol.

Synthesis of Biodegradable Plastics from Pati Janeng

The among of 5 grams Starch janeng was dissolved in 100 ml aquadest and stirred for 25 minutes. The ZnO with concentration at 1%, 3%, and 9% was mixed into glacial acetic acid. Starch was heated at 80°C during 15-20 minutes. Then, the plasticizers (glycerol) was added into this mixing. The starch solution must be stirred to an average temperature of around $25\text{--}30^\circ\text{C}$ for 30 minutes so that the viscosity was maintained. The thin layer that formed on the glass was put into the oven with a temperature of 70°C until 4 hours. The plastic was putted to the desiccator and stored that was not in direct sunlight, until 24 hours.

Tensile Strength (TS) and Elongation at Break (%E) Analysis

All plastic films are conditioned before they are subjected to permeability and mechanical tests according to the Standard method, ASTM D 618-61. Plastic film is tested by Water Vapor Permeability (WVP), Tensile Strength (TS) and Elongation at Break (%E) which are conditioned on 75% and 25°C relative humidity, this is done by placing it in a desiccator oversaturated solution $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 24 hours or more. Tensile Strength (TS) and Elongation at Break films were measured using a computer type universal testing machine (HUNG TA, TH-8503). The tensile sample is placed in a folded aluminum mold based on the ASTM D638 standard for tensile testing.

RESULTS AND DISCUSSION

The essential mechanical character of a plastic as a measure of the quality of the plastic is tensile strength and percent elongation. Tensile strength testing is carried out using Electronic System Universal Testing Machines based on the ASTM D638 standard. Data on the results of tensile strength testing can be seen in graph 1.1 below.

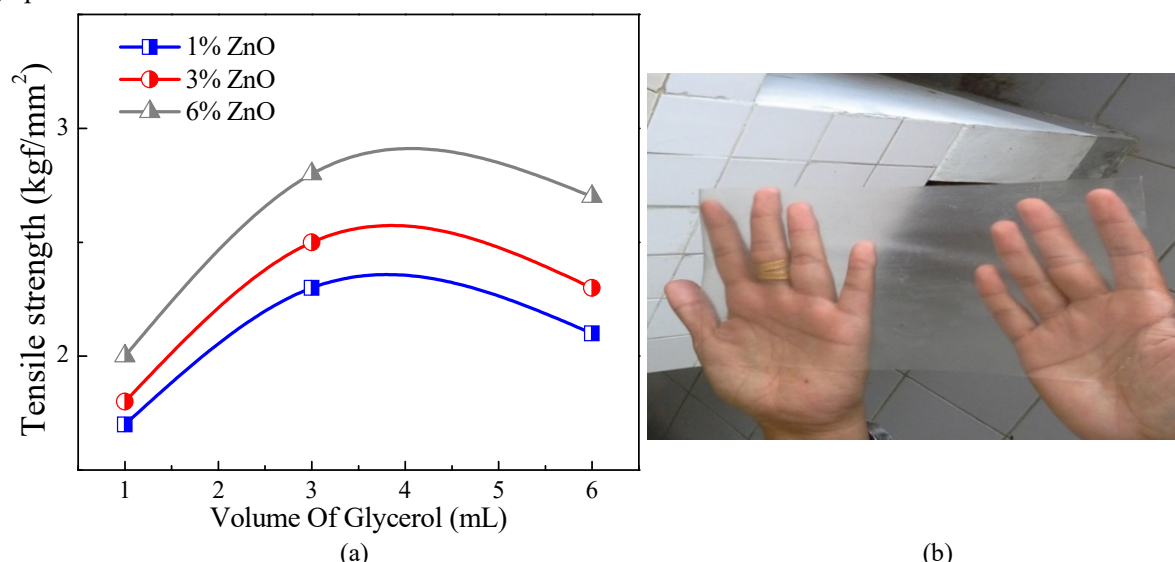


Fig.-1: (a) Tensile Strength of Plastic Film with a Various Additive Concentration (b) Plastic film synthesized

The highest tensile strength value was obtained by adding 3% ZnO with the addition of 3 ml Glycerol, which was 2.8 kgf/mm^2 (Figure 1). The added plasticizer content strongly influences the tensile strength of plastic films. The tensile strength of plastic films will be lower when the concentration is higher. This is due to the decrease in hydrogen bonds that occurs in the film, thereby increasing flexibility. Therefore, the tensile strength of the film gets smaller. Besides that, the resulting film is softer and more flexible.^{9,12}

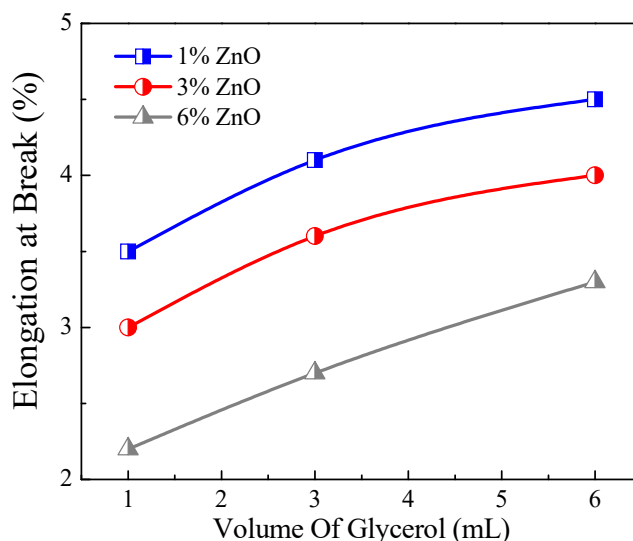


Fig.-2: Elongation at Break of the Bioplastic Film with Variation ZnO Concentration.

The elongation of break test is carried out to determine the magnitude of the increase in the length of a polymer before finally breaking up. Measurement of elongation of the break was carried out together with the analysis of tensile strength. Figure-2 above shows that the percentage of elongation is directly proportional to the concentration of addition of glycerol. Where the more significant the intensity of glycerol, the higher the percentage of elongation. From the results of the observations obtained the highest percentage of elongation at the mixture ratio between 1% ZnO and 6 ml Glycerol with a yield of 4.5%. This is caused by the decreasing distance of intermolecular bonds due to the high addition of glycerol as a platilizer.¹¹

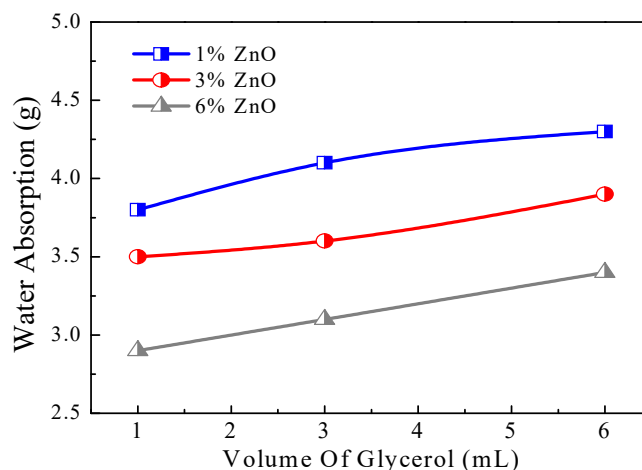


Fig.-3: The Water Absorption of Plastic Film

Liquid impermeability is one of the conventional properties of plastic. Water absorption can be defined as the amount of water absorbed by plastic film in percent units, after being immersed in water at room temperature for up to 24 hours. Water will fill the empty space contained in the plastic film. The lower the percentage of water absorption obtained, the better the quality of the plastic. Water absorption values obtained from this study ranged from 2.9% to 4.3%.

From Fig.-3, the value of the lowest water absorption is at a concentration of 6% ZnO with the addition of 1 ml of glycerol with a yield of 2.9% and the highest absorption of water is at a concentration of 1% ZnO with the addition of glycerol 6 ml. From the research that has been done, it can produce 4.3%, the more

plasticizer is used, the intermolecular adhesive properties increase, this causes the amount of water bound to the polysaccharide compound will increase, the water content will also be higher..^{9,10}

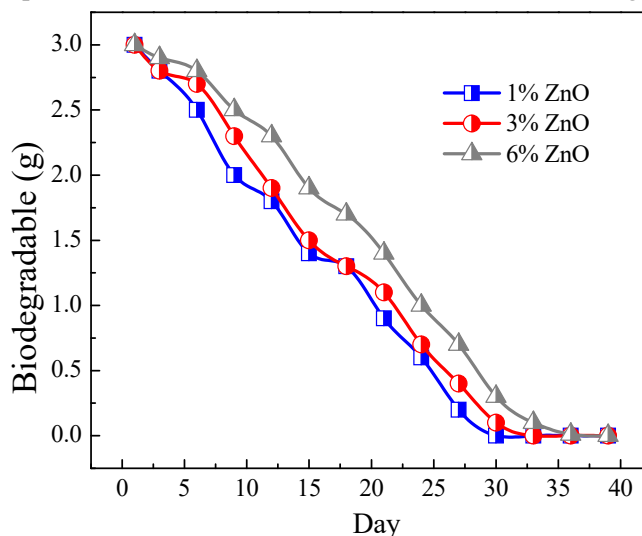


Fig.-4: Study of Biodegradable Activity

In this study, biodegradation tests of bioplastics were carried out by burial (composting) in soil media. The land used is land sourced from landfills. Experiments are carried out on all samples, and weighing is carried out every 3 days. This test is carried out for a maximum of 36 days until the sample is degraded. Reducing the sample weight in each bioplastic can be seen in Fig 4. From the graph above shows that the more ZnO added can affect the biodegradation time of the sample. Bioplastics with a ratio of 1% ZnO have been entirely degraded on the 30th day. While bioplastics with a rate of 6%, ZnO experienced a more extended degradation, on day 36. This is due to the large amount of ZnO contained in bioplastics which makes the plastic more durable because ZnO has metal reinforcing properties that are often used because ZnO is a piezoelectric ceramic and is antimicrobial.^{3,8}

Thermal Testing

At some point molecules can gain enough freedom of motion to spontaneously arrange themselves into crystal form. This is known as the crystallization temperature (Ct). This transition from amorphous solid to crystalline solid is an exothermic process. The physical properties of polymers are determined by their chemical structure. The movement of the polymer chain depends on the ability to rotate around the main chain, which is determined by the flexibility and interaction of the chain. The main chain consisting of a single bond (saturated) is very easy to move so that it has a low Tg. Crystallinity also greatly influences the physical and mechanical properties of polymers. With crystallinity shows the amount of crystalline area in a polymer (Fig.-5). The greater the degree of crystallization of the polymer, the mechanical properties of the polymer will increase.

The results of the DSC thermogram shown in Fig.-5. Can be seen that the thermal degradation temperature of plastic with 6% ZnO has the highest value of 390.56 °C far above the addition of 1% and 3% ZnO with values, 361.53 °C and 362.15 °C. This shows that plastics with higher ZnO concentrations have better thermal resistance. DSC analysis results from a polymer material will provide information on the glass transition point (Tg), the temperature at which the polymer changes from glassy to rubbery, crystallization point (Tc), ie when the polymer is crystalline, melting point TM, that is, when the polymer is liquid and the decomposition point (Td), which is when the polymer begins to break down.^{4,7,9}

Adding ZnO to the material can increase the Tg of the plastic. This can be caused by the unique nature of ZnO which is hydrophobic at temperatures above 32 °C, so that the structure becomes denser. The higher Tg value indicates that the plastic is more resistant to heat and does not melt easily. The increasing the concentration of glycerol can reduce Tg because the polymer matrix becomes tenuous and the movement of the polymer chain is easier with the addition of plasticizers.⁸

The important parameter related to the state of the polymer is the glass transition temperature (T_g), which is defined as the temperature at which the transition from a glassy state to a rubbery state. The price of T_g depends on the flexibility of the chain and the interaction of the chain. The more flexible a polymer is, the segmental movement within it will be more flexible and easier to occur, resulting in a relatively low T_g polymer price, in other words at room temperature the polymer tends to be in a rubbery state.¹⁵

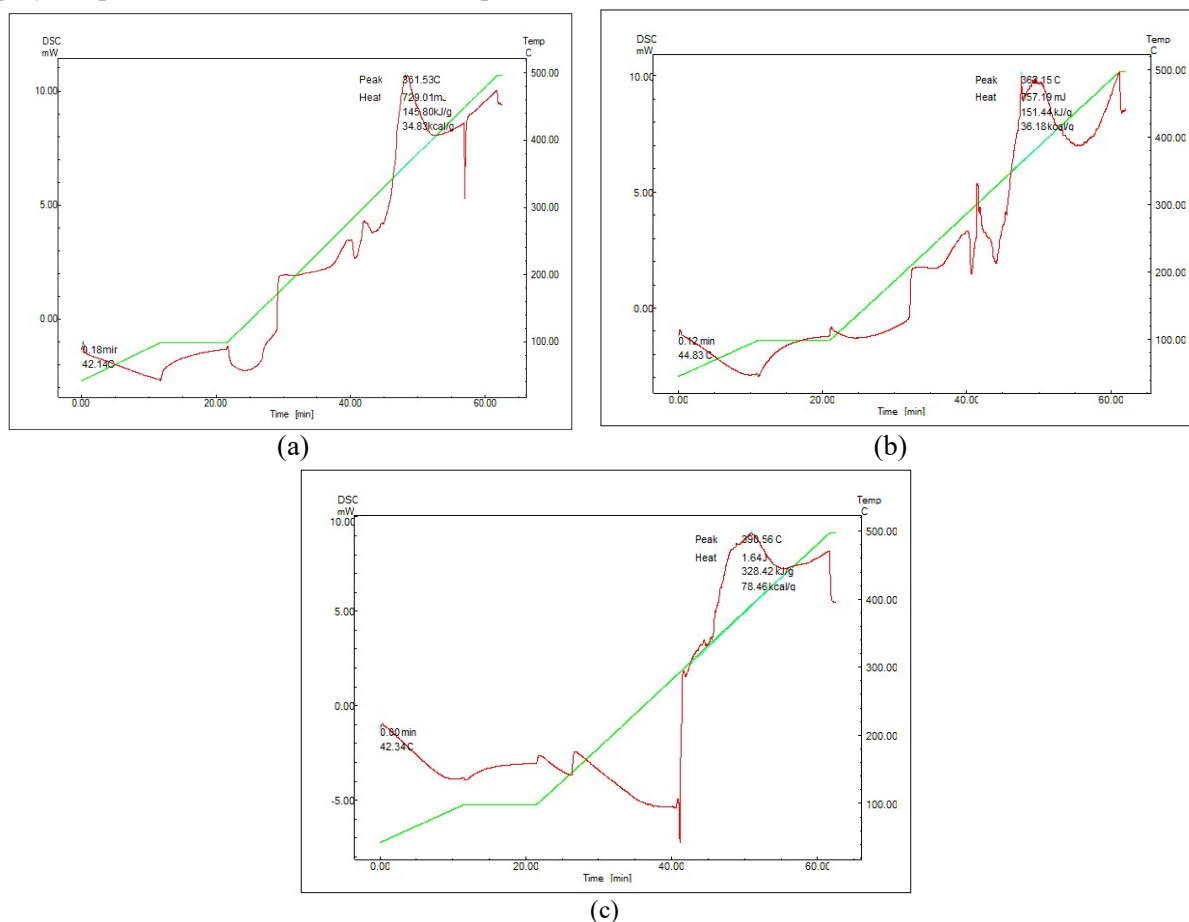


Fig.-5: Biodegradable Plastic DSC Thermogram with Variations in ZnO (a) 1% (b) 3% and (c) 6%

The glass transition temperature is a narrow temperature range, below that temperature the polymer is glassy and above it is rubbery. Polymers can be glassy or rubbery depending on the situation above or below the glass transition temperature.^{13,15} In general the glass transition temperature of polymers depends on the polymer-free volume, intermolecular attractions, the internal tendency of the chain, and polymer chain stiffness. Generally plastic has T_g above room temperature if not many have cross-linked ties. The biodegradable plastic melting point obtained from this study has a high value $^{\circ}\text{C}$. Previous research found that the melting point of chitosan ranges from 264-266 $^{\circ}\text{C}$.¹³

Morphology of Biodegradable Plastics

In Figure-3 it can be seen the morphology of biodegradable plastics, from the addition of ZnO by 1% 3% and 6%, however, biodegradable plastics with the addition of 1% ZnO all mixed in starch so that it cannot be separated, whereas at 6% ZnO is not too soluble in starch it is suspected granules are less homogeneous with a mixture of other ingredients. There are several possible reasons for the lack of homogeneity in the ingredients.^{14,16} One of them is due to the addition of ingredients in the Glycerol process that interacts with starch to form granules that are difficult to dissolve (Fig.-6).

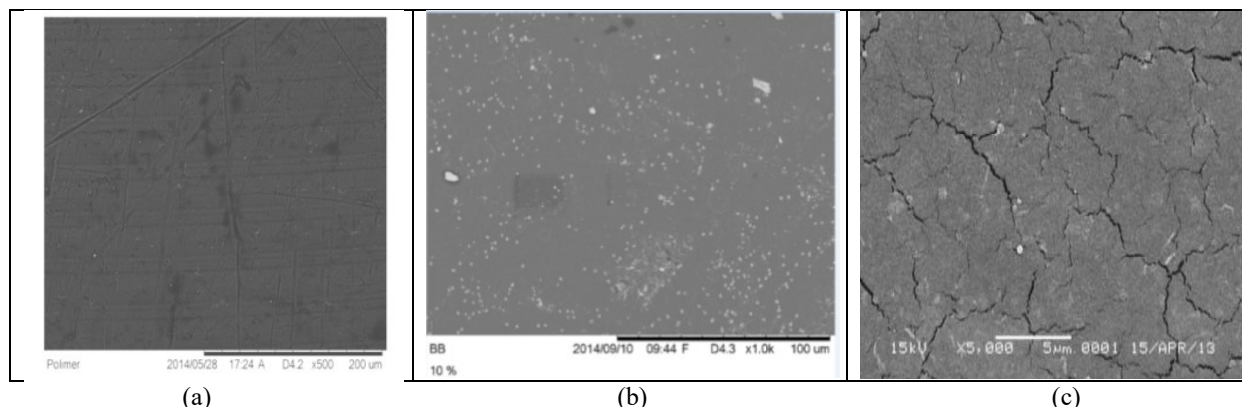


Fig.-6: Display of Biodegradable Plastic SEM with the Addition of ZnO (a) 1% (b) 3% and (c) 6%.

CONCLUSION

The highest tensile strength value was obtained at the concentration of 3% ZnO starch with the addition of 3 ml glycerol, which was 2.8 kgf/cm². Percent elongation increases with increasing concentration of plasticizer, at a concentration of 1% ZnO with the addition of 6 ml glycerol, which is equal to 4.5%. The lowest water absorption is obtained at 1% ZnO concentration with the addition of 1 ml glycerol of 2.9. The process of plastic film degradation occurs for 30 to 39 days. The results of the DSC thermogram shown the thermal degradation temperature of plastic with 6% ZnO has the highest value of 390.56 °C far above the addition of 1% and 3% ZnO with values, 361.53 °C and 362.15 °C. This shows that plastics with higher ZnO concentrations have better thermal resistance.

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