

The Effect of Glycerol on the Production of Environmentally Friendly Bioplastics From Cassava Peel (*Manihot Esculenta*) and Corn Cobs (*Zea Mays*)

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Abstract

Conventional plastics made from synthetic polymers have a low biodegradation rate, which contributes greatly to environmental pollution. The use of agricultural waste such as cassava husks (*Manihot esculenta*) and corn cobs (*Zea mays*) as bioplastic raw materials is one of the alternatives for the development of environmentally friendly materials. This study aims to determine the effect of variations in the amount of glycerol and the length of decomposition time on the biodegradability of bioplastics made from cassava husks and corn cobs. The study used an experimental method with a Two-Way Factorial Design, covering three concentrations of glycerol (0 mL, 15 mL, and 30 mL) and three decomposition times (3, 6, and 9 days). The results showed that the treatment without glycerol (0 mL) did not form bioplastics so it could not be analyzed. The data was tested using Two Way ANOVA. The results of the biodegradability test showed that the glycerol concentration had a significant effect, and the 30 mL formulation resulted in the highest degradation rate of 91.026% on day 9.

Keywords: Bioplastics; Glycerol; *Manihot esculenta*; *Zea mays*; Biodegradability

INTRODUCTION

Practicality in various aspects of life tends to be a top priority in the lifestyle of modern society. Plastic is very closely related to human life in this modern era which demands fast-paced and practical (Wiranata, 2020). All community activities, for example, to consume snacks and buy various items require packaging or wrapping tools such as cracker bags made of plastic. Plastic is a packaging material that is widely used and widely developed. Plastic is used as a packaging because it is lightweight, strong, malleable, and affordable (Arwini, 2022). Plastic has become an indispensable part of human life today. Therefore, plastic has become a daily necessity (Rahardiyan et al., 2023).

Plastics that are commonly used today are derived from synthetic polymers obtained from petroleum (Aripin et al., 2017). Plastics made from petroleum-based synthetic polymers include *polyethylene terephthalate* (PET), *polyvinylchloride* (PVC), *polyethylene* (PE), *polypropylene* (PP), *polystyrene* (PS), and *polyamide* (PA). The disadvantage of plastic with synthetic polymer materials is that they are limited in number and difficult to recycle. Plastics derived from petroleum are increasingly limited in number and cannot be easily degraded even though they have been stored for decades (Wiranta, 2020).

Plastic waste takes about 200 to 1,000 years to decompose (Trisunaryanti, 2018). As a result, the accumulation of plastic waste will be the cause of environmental pollution. Plastic waste has a negative impact and causes quite serious problems for the environment, for example, it can produce greenhouse gas emissions that are large enough to trigger global warming, inhibit water absorption, cause flooding, and damage soil fertility. The recycling process cannot overcome the problem of plastic waste that has accumulated (Yuniarti et al., 2014). Burning plastic is also not a good option because plastic that does not burn completely below 800°C will form dioxin which is a harmful compound for the body (Saputro & Ovita, 2017).

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According to the 2022 National Waste Management Information System (SIPSN) data of the Ministry of Environment and Forestry (KLHK), input results from 202 districts/cities throughout Indonesia said that the number of national waste piles reached 21.1 million tons. Of the total national waste production, 65.71% (13.9 million tons) of waste can be managed, while the remaining 34.29% (7.2 million tons) of waste has not been managed properly. In addition, according to data from the Indonesian Olefin Aromatic Plastic Industry Association (INAPLAS), plastic consumption in 2020 reached 6.2 million tons, an increase of 5% when compared to plastic consumption in 2019 of 5.9 million tons. Excessive consumption of plastic, resulting in an increase in the amount of plastic waste.

One way to overcome this problem is to use natural materials in the manufacture of plastics that can decompose naturally in a faster time than plastic with petroleum raw materials. Plastics made with natural raw materials are called bioplastics. Bioplastics are one of the efforts made to become a solution to the problem of using conventional plastic packaging. *Biodegradable plastic* or bioplastic is a plastic composed of natural polymers that are capable of being degraded by both microorganisms and weather (Aripin et al., 2017).

Bioplastics are made from natural materials that can be broken down by microorganisms, making them more environmentally friendly when compared to commercial plastics (Agustin & Padmawijaya, 2016). Bioplastics are plastics whose all or almost all components come from renewable raw materials. Bioplastics have environmentally friendly properties because of their properties that can return to nature. Bioplastics are designed to facilitate the degradation process against the enzymatic reactions of decomposing microorganisms such as bacteria and fungi (Wiranta, 2020).

The raw materials that can be used for the manufacture of bioplastics are cassava husks and corn cobs. Cassava husks and corn cobs are abundant agricultural waste. In food processing, cassava husks and corn cobs are often ignored or simply thrown away. Cassava plantations in Indonesia are quite extensive. According to the Central Statistics Agency in 2018, the area of cassava plantations in Indonesia reached 792,952 hectares. Looking at the size of cassava plantations, there are also many cassava harvested so that a lot of cassava peel waste will be discarded. Cassava peel waste that is simply dumped around the production site can harm the environment and produce a bad smell. If the waste is left unchecked, it will have a negative impact on health (Mugandi, 2023).

The manufacture of bioplastics requires the addition of other supporting materials such as *plasticizers* for the improvement of physical properties, mechanical properties and resistance to water of bioplastics. *Plasticizer* is a compound that allows the plastic produced not to be easily brittle and stiff (Kurniawati et al., 2022). *The plasticizer* used is glycerol, because glycerol is a cheap material, the source is easy to obtain, renewable and also easily degraded by nature. Glycerol can weaken the stiffness of polymers while increasing the flexibility and extensibility of polymers (Wiranata, 2020). Based on this background, this study will utilize cassava husk (*Manihot esculenta*) and corn cob waste (*Zea mays*) as the basic material for making bioplastics with the addition of variations in *plasticizer concentrations* in the form of glycerol.

RESEARCH METHODOLOGY

Research Tools and Materials

The tools used in this study were a 1000 ml *glass beaker*, oven, knife, analytical scale, *blender*, filter cloth, 60 mesh sieve, *5x5 cm glass plate*, tongs, *thinwall*, measuring cup, stainless spatula, *15x20 polybag*, *thread*, *sterile gloves*, and *masks*. The ingredients used in this study were cassava husk (*Manihot esculenta*), corn cob (*Zea mays*), glycerol, aquades, soil, NaOH 10%, NaOCl 5%, and water.

Research Procedure

Preparation of Making Starch from Cassava Peel (Kelibay, 2020)

The cassava peel is first separated from the brown outer shell, then the white cassava peel is washed with water until clean. After that, the clean cassava peel is dried in the sun for 12 hours until the moisture content decreases. The dried cassava peel is then mashed using a blender, then sifted to obtain a more homogeneous powder. The sifted cassava peel powder is weighed 40 grams and put into a 1000 mL beaker glass.

Next, a solution of 400 mL of NaOH is added, then cassava peel powder is soaked in a NaOH solution for 24 hours for a chemical treatment process, after which it is washed with running water until clean. The cassava peel powder is then re-soaked using a 5% NaOCl solution for 3 hours, then filtered using a filter cloth to separate the deposits. The resulting cassava peel deposits are dried using an oven at 50°C for 8 hours. The cassava peel starch that has been produced is then ready to be used in the polymerization process of the mixture.

Preparation for Making Starch from Corn Cobs (Kurniawati et al, 2022)

The corn cobs are first washed using running water to remove any dirt that still sticks, then dried in the sun for two days until they are completely dry. The dried corn cobs are then cut into smaller pieces using a sharp knife, then crushed using a blender. The results of the destruction were sifted using a 60-mesh sieve to obtain uniform particle sizes. The obtained corn cob powder is then soaked in a 10% NaOH solution for 24 hours, after which it is filtered using a filter cloth.

The corn cob powder is then re-soaked in a 5% NaOCl solution for 3 hours. The resulting mixture is then filtered and washed using aquadest that has been boiled until the hypochlorite smell disappears. The residue obtained is dried in the oven at a temperature of 60°C. After drying, the residue is again mashed using a blender and sifted using a 60 mesh sieve so that corn cob powder is obtained that is ready to use.

Mixed Polymerization Process (Kelibay, 2020)

The starch derived from cassava husks and corn cobs is first mixed with aquadest as much as 250 mL until it forms a homogeneous mixture. Then glycerol is added with different volume variations, namely 15 mL and 30 mL, then the mixture is heated to a temperature of 80-90°C while stirring until the gelatinization process takes place well. After heating, the sample is left to sit for 24 hours to remove any air bubbles that form on the surface layer.

The sample was then printed on a 5×5 cm glass plate, then dried in the sun for 5 days until a dry bioplastic film was formed. The resulting bioplastic film is further tested according to the testing procedure.

Observation Stage

Biodegradability Test

The bioplastic sample degradation test was carried out to determine the level of plastic decomposition (Muhammad et al., 2020). Samples measuring 5x5 cm were weighed at first weight (w_0) before being degraded, then buried for 3 days, 6 days, and 9 days in a 10x15 cm polybag that had been filled with soil (Kelibay, 2020). Next, the final weight of the sample (w_1) was weighed. Biodegradability is calculated using the following formula (Dewajani et al., 2024):

$$\text{Biodegradability (\%)} = \frac{w_0 - w_1}{w_0} \times 100\%$$

Description:

w_0 = sample starting weight (g)

w_1 = sample weight after stockpiling (g)

Additional Tests

In addition to the main test in the form of biodegradability, this study is also equipped with a series of additional tests that serve to provide a more comprehensive picture of the

physical characteristics of bioplastics. The additional tests include water absorption measurements and elongation tests. Both tests are not the main focus of the research, but they play an important role in providing additional context to the performance of the resulting material.

Elongation Test

The tip of the sample measuring 5x5 cm is clamped using a clamping device at both ends and provides a gradual load until the sample breaks (Maneking et al., 2020). The maximum load ($F_{\max}$) that causes the sample to break is used to calculate the tensile strength using the formula (Wening & Amalia, 2023):

$$\sigma = \frac{F_{\max}}{A}$$

Description:

σ = tensile strength (MPa)

$F_{\max}$ = maximum force exerted on the sample (N)

A = sample area (mm²)

Water Absorption Test

The water absorption test was carried out using a simple immersion method which refers to the procedure for measuring water absorption in bioplastics. Bioplastics with high water absorption have low water resistance. The sample was cut to a size of 5x5 cm, weighed as initial weight (w_0), then immersed in water for 2 hours. After that, the sample was lifted, dried using a rag, and weighed again as the final weight (w_1) (Muharam et al., 2022). The percentage of water absorption is calculated using the formula (Dewajani et al., 2022):

$$\text{Water Absorption (\%)} = \frac{w_1 - w_0}{w_0} \times 100\%$$

Description:

w_0 = sample starting weight (g)

w_1 = sample weight after immersion (g)

RESULTS AND DISCUSSION

Results

The data of the research results are presented in the form of a table, namely the percentage of biodegradability test results (Table 4.1), as well as a table of additional test results in the form of elongation test results (Table 4.2), and the percentage of water absorption test results (Table 4.3).

The results of the *Two Way* ANOVA analysis on biodegradability testing showed that the variation in the amount of glycerol had a significant effect on the degradation rate of bioplastics with a value of $p < 0.001$ ($p < 0.05$), and the length of decomposition time also had a significant effect with a value of $p = 0.003$ ($p < 0.05$). The interaction between the two factors showed no effect along with the value of $p = 0.236$ ($p > 0.05$).

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Table 1. Percentage of Biodegradability Test Results

Biodegradability Test Results			
Treatment Groups	Before Testing	After Testing	Yield (%)
M17A			18,269 %
M27A			49,874 %
M18A			36,218 %
M28A			81,731 %
M19A			57,286 %
M29A			91,026 %
M17B			18,269 %
M27B			71,357 %

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M18B			36,218 %
M28B			75,221 %
M19B			63,782 %
M29B			78,589 %

Description: A is the first repeat symbol, and B is the second repeat symbol. M17A, M27A, M17B, and M27B are 3rd day treatments; M18A, M28A, M18B, and M28B are 6th day treatments; and M19A, M29A, M19B, and M29B are the 9th day treatments.

The results of the analysis of additional tests, namely elongation (tensile strength) testing, showed that bioplastics with the addition of 15 mL glycerol had an elongation value in the range of 0.014-0.028 MPa, with an average of around 0.021 MPa. Meanwhile, bioplastics with the addition of 30 mL of glycerol showed an elongation value in the range of 0.012-0.027 MPa, with an average of about 0.020 MPa. The difference in elongation values between treatments illustrates the variation in the stretch ability of bioplastics due to differences in glycerol formulation and the length of time the sample is stored.

Table 2. Elongation Test Results (Tensile Test)

Elongation Test Results (Tensile Test)			
Treatment Groups	Before Testing	After Testing	Yield (MPa)
M14A			0,028 MPa

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M24A			0,027 MPa
M15A			0,020 MPa
M25A			0,016 MPa
M16A			0,019 MPa
M26A			0,012 MPa
M14B			0,027 MPa
M24B			0,026 MPa
M15B			0,020 MPa

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M25B			0,025 MPa
M16B			0,014 MPa
M26B			0,012 MPa

Description: A is the first repeat symbol, and B is the second repeat symbol. M14A, M24A, M14B, and M24B are the 3rd day treatment; M15A, M25A, M15B, and M25B are 6th day treatments; and M16A, M26A, M16B, and M26B are the 9th day treatments.

The results of the additional test, namely the water absorption test, showed that bioplastics with the addition of 15 mL glycerol had water absorption in the range of 49.874-90.705%, with an average value of around 79.86%. Bioplastics with the addition of 30 mL of glycerol show water absorption in the range of 49.874-127.244%, with an average value of around 90.88%. The addition of glycerol as a plasticizer also affects the ability of bioplastics to bind water, because glycerol has hygroscopic properties that can increase the penetration of water into the polymer matrix.

Table 3. Percentage of Water Absorption Test Results

Water Absorption Test Results			
Treatment Groups	Before Testing	After Testing	Yield (%)
M11A			78,589%
M21A			49,874%
M12A			90,705%

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M22A			127,244%
M13A			78,589%
M23A			94,510%
M11B			90,705%
M21B			127,244%
M12B			49,874%
M22B			90,705%
M13B			90,705%
M23B			55,686%

Description: A is the first repeat symbol, and B is the second repeat symbol. M11A, M21A, M11B, and M21B are 3rd day treatments; M12A, M22A, M12B, and M22B are 6th day treatments; and M13A, M23A, M13B, and M23B are the 9th day treatment.

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Bioplastics at a glycerol concentration of 0 mL are not formed so that all parameters in the group cannot be tested. This condition occurs because the absence of a *plasticizer* causes the polymer structure of starch and cellulose to be unable to form a flexible matrix, so that the bioplastic film cannot be printed and produce N/A measurement results.

The results showed that the variation in the amount of glycerol and the length of decomposition time had a different influence on the characteristics of bioplastics made from cassava husks and corn cobs. Based on the three parameters tested, biodegradability is the main focus of this study, as it is directly related to the goal of making environmentally friendly materials that can be decomposed naturally. Meanwhile, the elongation and water absorption tests function as supporting tests to provide an overview of the physical properties of bioplastics.

Biodegradability is the most important parameter because it shows the ability of bioplastics to decompose by soil microorganisms. The level of biodegradability increases consistently from day 3, day 6, to day 9 of each treatment. The largest improvement was obtained in the M2 formulation (30 mL glycerol) with a degradation rate of 91.026% on day 9, which was the highest value of all treatments. This result is in line with the research of Kelibay (2020) which reported an optimal degradation rate of 85.71% at 30 mL glycerol in 9 days, and is consistent with the findings of Kanani et al. (2023) which stated that bioplastics made from corn cob cellulose and cassava peel starch were able to decompose up to 60.19% in 7 days.

This high degradation rate is caused by the role of glycerol in increasing porosity and water absorption ability, making it easier for soil microorganisms to depolymerize (Masahid et al., 2023). The addition of glycerol will accelerate the degradation process in plastics but reduce the percentage value (%) of water resistance and tensile strength value. Glycerol is a hydrophilic *plasticizer* that is added to bioplastics to help make the resulting film flexible and non-brittle by helping to absorb water and retain moisture content during the retrogradation process and *glass transition* of bioplastic starch (Timbuleng et al, 2023).

The mixture of cassava peel starch and corn cob cellulose itself is a very easily degradable material because both consist of polysaccharides with glycosidic bonds that are easily broken down by soil microbial enzymes (Natalia et al., 2019). Therefore, the formulation of 30 mL of glycerol proved to be the most effective in achieving the main goal of the study, which is to produce environmentally friendly bioplastics with high degradability.

Additional testing in the form of elongation tests showed that storage time had a significant effect on the tensile strength of bioplastics, while glycerol variations did not make a significant difference. The tensile strength values in this study ranged from 0.012-0.028 MPa, and the trend decreased as the storage time increased (from day 3 to day 9). This is consistent with the research of Akbar et al. (2013) which reported that cassava peel starch film experienced a decrease in tensile strength during the aging period due to *plasticizer* migration and moisture absorption from the environment. This phenomenon is a natural characteristic of starch-based bioplastics that are hydrophilic and easily absorb moisture.

The results of the water absorption test showed that the percentage of water absorption obtained ranged from 49.874-127.244%, which is still in accordance with the characteristics of starch and cellulose-based bioplastics that are hydrophilic (Muharam et al., 2022). The addition of glycerol increases the absorption of water because glycerol itself is very hygroscopic and can bind large amounts of water. When glycerol is added to the bioplastic film, the distance between the polymer chains increases so that porous microspaces are formed that facilitate water penetration (Anita et al., 2013).

The surface morphology of bioplastics shows a texture that is not homogeneous, rough looking, and has pores. These characteristics are commonly found in starch and cellulose-based bioplastics from agricultural waste such as cassava husks, taro husks, and corn cobs. These materials have a high fiber and cellulose content, so the gelatinization process often does not

take place evenly and produces a film with a rougher and more porous surface structure (Wening & Amalia, 2023). This unevenness of gelatinization causes some starches to disperse well, while others are aggregated to form *micro-voids* or small cavities.

Some studies have shown that porous morphology can be improved through the addition of additives in addition to glycerol. Wening and Amalia (2023) report that the combination of cassava peel starch, corn cob cellulose, PVA, and TiO₂ results in a film with a tighter surface, fewer pores, and higher mechanical strength. PVA acts as a compatibilizer that smooths the matrix structure, while TiO₂ acts as an inorganic *filler* that increases the density and strength of the film. Other studies have shown that microcrystalline cellulose, *nanocellulose*, chitosan, and ZnO can be used as structural reinforcers to reduce porosity and increase tensile modulus (Hendri et al., 2017; Kurniawati et al., 2022). The use of organic *cross-linkers* such as citric acid is also reported to be effective in strengthening the bonds between polymer chains so that the surface structure becomes more homogeneous.

CONCLUSION

Variations in the amount of glycerol and the length of decomposition time affect the biodegradability level of bioplastics, where the formulation of 30 mL of glycerol results in the highest level of biodegradability, which is 91.026% on day 9.

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