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Analysis of Biodegradation of Bioplastics Made of Cassava Starch

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ABSTRACT

Environmental pollution due to plastic waste taking too long to decompose has become a global problem. There have been numerous solutions proposed, one of which is the use of bioplastics. The use of cassava starch as the main ingredient in the manufacture of bioplastics shows great potential, since Indonesia has a diverse range of starch-producing plants. The aim of the present study is to analyse the effect of glycerol on microbial degradation. This experimental research investigated the use of cassava flour mixed with glycerol plasticizer at various concentrations (0, 2, 2.5, 3%) in the synthesis of bioplastics. The aspects studied were biodegradability, moisture absorption (using ASTM D 570), shelf life, and morphological properties (using a camera equipped with a macro lens) and SEM. This study revealed that complete degradation could be achieved on the 9th day. The addition of a large concentration of glycerol would accelerate the microbial degradation process, increase moisture, and extend the shelf life of bioplastics in a dry place.

Keywords: Bioplastics, Cassava starch, Glycerol, Degradation, Microorganism

I. Introduction.

Plastic waste has become a worldwide problem. Indonesia is the world's second-largest contributor of plastic waste after China [1], since it produces approximately 100 million tons of plastic for various industrial sectors [2]. According to the most recent data provided by INAPLAST (Indonesian Oleafin Aromatic Plastic Industry Asociation), the annual consumption of plastics in Indonesia was 4.7 million tons in 2015, rose to 5 million tons in 2016 [3], and is predicted to hit 9.52 million tons in 2019 [4]. One remedy to overcome the problem of plastic waste is by creating an environmentally friendly alternative to conventional plastics, i.e. bioplastics (biodegradable plastics). The use of non-biodegradable plastics and biodegradable plastics has been calculated to be 69.1% and 39.1% respectively [5]. Bioplastics are biodegradable plastics which can be degraded by microorganisms from plant-derived compounds, such as starch, cellulose, and lignin [6]. Biodegradable plastics have the same functional quality like conventional plastics, but they can be decomposed by the action of microorganisms, which produces water (H2O), carbon dioxide (CO2), and methane (CH4) [7]. In other words, they can return back to nature after its use because it can be broken down in the environment, hence eco-friendly plastics [8]. Conventional plastics take 50 years to decompose in nature, while bioplastics can be degraded 10 to 20 times faster [9]. Starch is a natural polymer extracted from plants and can be used to produce biodegradable plastics due to its eco-friendliness, abundance, and low cost [10]–[12]. Cassava contains a large amount of starch, which can be suitably used for the production of bioplastics. This potential is a great opportunity to add value to cassava as the raw material in the manufacture of eco-friendly plastics [13]. In fact, cassava holds huge potential for the production of bioplastics since Indonesia is the third-largest producer of cassava in the world [14]. Nonetheless, there has been a lack of attention and appropriate treatment towards it, and indeed further exploration should take place. Thus, this paper takes a closer look at the degradation of bioplastics composed from cassava starch added with glycerol as a plasticiser.

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II. Method

A. Synthesis of Bioplastics

A 5% cassava starch (b/v) was added to each of four different amounts of distilled water/aquades (98.5, 98, 97.5, and 97 ml), then the solutions were stirred using a magnetic stirrer for 5 minutes at 900 rpm. Next, glycerol at various concentrations, i.e. 1.5%, 2%, 2.5%, 3% (v/v), was added to each solution, and then the solutions were stirred again for 5 minutes at 900 rpm. The solutions were heated in a magnetic stirer at a temperature of ± 80 ° C, while being stirred with a magnetic stirrer for ± 45 minutes at 900 rpm. Each stirred solution was poured into a mould with a diameter of 88 mm, then dried in an oven with a temperature of 50°C for 24 hours, and finally placed at room temperature (27°C-30°C) until dried.

B. Observation of Morphological Properties of Bioplastics

The surface morphology of bioplastics was observed using an electron microscope, FEI Inspect S50. Scanning Electron Microscope (SEM) was used to observe the surface of specimens (bioplastics). Before being observed, the specimens were coated with a 10-nm-thick gold.

C. Moisture Absorption

The moisture absorption test identified the ability of bioplastics to absorb water (H2O) as determined by standard ASTM D 570. Bioplastics, which had been previously dried for 24 hours in an oven at 50°C, cooled in a desiccator, and weighed, were cut into 10mm x 10mm. The moisture absorption data of bioplastics was obtained by soaking them in water for 24 hours. After that, the bioplastics were dried with a cloth and immediately weighed. The water absorption capacity of bioplastics can be calculated as follows [17].

$$\text{Moisture Content (\%)} = \frac{(Post\!-\!Bake\ Weight)-(Initial\ Weight)}{Initial\ Weight} \times 100 \qquad (1)$$

D. Biodegradability

Biodegradable behaviour of bioplastics was determined using soil burial degradation test, i.e. bioplastics were buried in the soil, so that it would be degraded completely [18]–[20]. Degradation testing serves to determine the extent of damage of bioplastics. The damage can be seen from the mass reduction of respective specimens buried in the ground.

Bioplastics were cut into 10 mm x 10 mm. Then, they were buried into the ground at 8-cm depth; the burial duration varied (3, 6, 9, and 12 days). Prior to burial, the initial mass (mass before degradation) was determined. The final mass (mass after degradation) of the bioplastics was measured afterwards. Any changes in mechanical properties due to degradation process were observed and when the bioplastics were completely degraded, the biodegradability was measured [21].

$$\text{Microbial Resistance (\%)} = \frac{Final\ mass\ - Initial\ mass}{Initial\ mass} \times 100 \qquad (2)$$

E. Shelf Life Testing

Shelf life testing aims to determine the durability level of bioplastics as plastic packaging. The use of organic materials in manufacturing bioplastics causes low tensile strength, short shelf life (not durable), and mould damage [22]. In this study, the shelf life test was performed through observation using a camera equipped with macro lens. Bioplastics were placed in a plastic box with limited oxygen or humidity of 45-60% RH to determine the damage caused by microorganisms. By doing so, the shelf life of bioplastics under certain environmental conditions could be identified. The testing process lasted for 90 days. The results were analysed through visual observation.

F. Chemical Reaction of Bioplastics

A chemical reaction aims to determine the transformation/change in the structure of molecules involved in the reaction. The chemical reaction combines elements into compounds, decomposes compounds back into elements, and transforms existing compounds into new compounds. The reaction produces chemical combinations to form larger molecules. The splitting of a molecule into two or more smaller molecules and rearrangement of atoms in molecules.

III. Findings and discussion.

A. *Synthesis of Bioplastics*

The bioplastics produced were hard, smooth and transparent. The surface morphology of bioplastics observed with SEM is shown in Figure 1. Cassava starch consists of semi-crystalline structures because its granules are disrupted as a result adding specific heat and solvents. Then, the semi-crystalline structures will turn into amorphous forms determined to be a fragile.

B. *Moisture Absorption*

Figure 2 shows that changes in water absorption of bioplastics varied depending on the variations in the concentration of glycerol. The more the glycerol is, the higher the water-swelling ratio will be [23]. It is associated with hydrophilic properties of glycerol and starch [24] [25]. These properties increase the affinity between glycerol and water, hence the increase of water absorption [26]. Higher water affinity demonstrate by adsorption and desorption isotherms [25]. The fact that cassava starch contains hydroxyl (OH), carbonyl (CO), and ester (COOH) indicates that the concentration of hydrophilic properties in the bioplastics is high; high concentrations of hydrophilic starch and glycerol cause faster degradation in the soil [20].

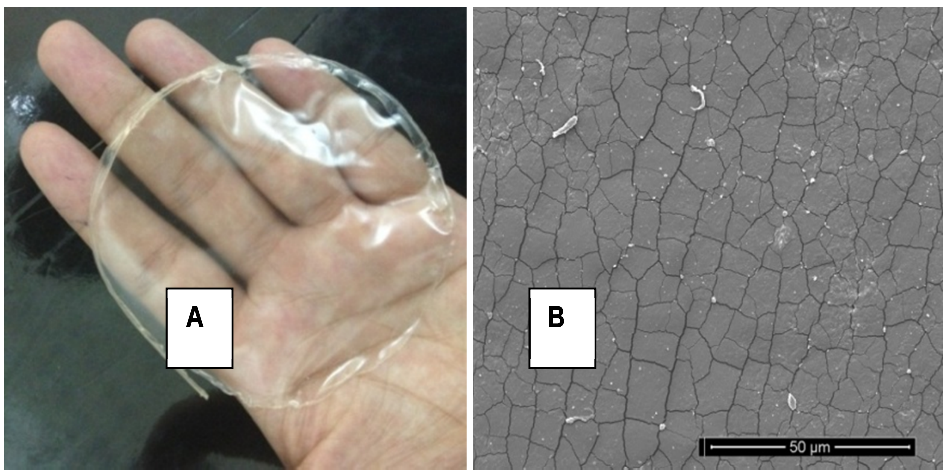

Fig. 1.Surface Morphology of Bioplastics (A), Result of Bioplastic Production (B) Result of Observation using SEM

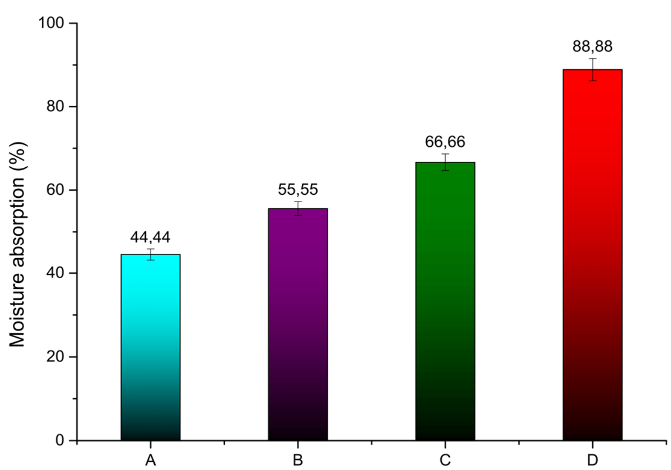

Fig. 2.Result of Moisture Absorption Testing at Various Concentrations of Glycerol (A), 1,5% (v/v); (B), 2% (v/v); (C), 2,5% (v/v); and (D) 3% (v/v)

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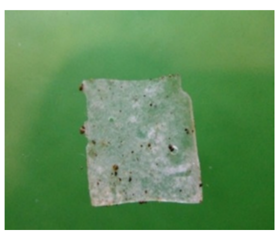
Table 1. Results of the Degradation of Bioplastics with various concentrations of Glycerol

Glycerol Amount (v/v)	**Degradation of Bioplastics**			
	3 Days	**6 Days**	**9 Days**	**12 Days**
1,5%				Completely Degraded
2%			Completely Degraded	Completely Degraded
2,5%			Completely Degraded	Completely Degraded
3%			Completely Degraded	Completely Degraded

C. Biodegradability

Biodegradability testing was carried out to determine the degradation level of bioplastics in the environment [27] as a parameter of an environmentally friendly material [28]. Table 1 shows the mass reduction in bioplastics for 3, 6, 9, and 12 days.

The mass of bioplastics buried for 6 days was reduced by more than 50% (as shown in Figure 3). This mass loss happened because the bioplastics were composed from natural materials which were easily digested by microbes [29]. Bioplastics broke down into small pieces in 7 days, but the complete degradation occurred on the ninth day. After absorbing water from the soil, hydroxyl group in the cassava starch initiated the hydrolysis reaction; due to this reaction, cassava starch was decomposed into small pieces and quickly disappeared [30].

A high concentration of glycerol contained in bioplastics led to rapid mass reduction. The hydrophilic nature caused bioplastics to be degraded more easily [26], making bioplastics an eco-friendly packaging material. The degradation process of bioplastics was done with the help of

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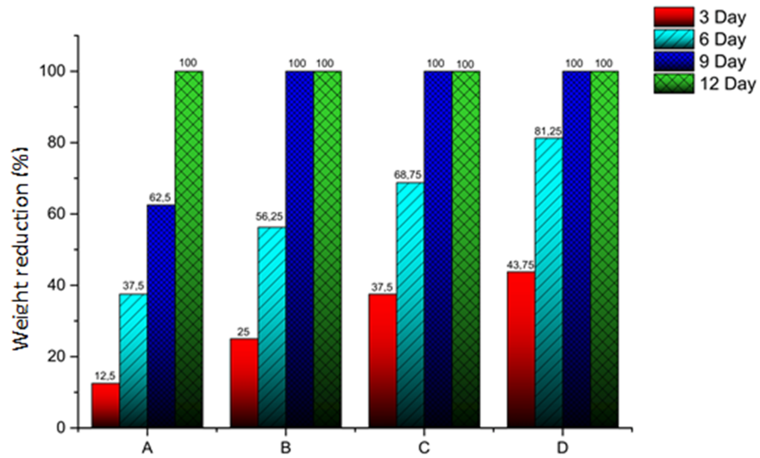

Fig. 3.Results of Bioplastics Degradation Testing with Various Amounts of Glycerol (A), 1,5% (v/v); (B), 2% (v/v); (C), 2,5% (v/v); and (D) 3% (v/v)

microorganisms such as bacteria and fungi [31], mechanical degradation (wind and abrasion), and light (photo-degradation) [20].

The degradation level of a compound depends not only on the durability of the molecules, but also the pH, temperature, humidity, and oxygen content in the environment [32] and [33]. The surrounding environment can affect pH, redox potential, presence of suitable microorganisms, availability of adequate nutrition, and concentration of the compound [20].

Biodegradation of bioplastics can be done by several bacteria found in the soil such as Pseudomonas sp., Streptococcus sp., Staphylococcus sp., Bacillus sp., and Moraxella sp [34]. Moreover, it can be done due to the breaking of polymer chain of cassava starch containing hydroxyl (OH) carbonyl (CO), and also ester (COOH) into monomer [35]. The addition of more glycerol can increase the degradation of bioplastics, since glycerol has the ability to absorb hydroxyl water [25] or absorb water easily. Water is the medium of most bacteria and microbes, particularly those in the soil. As a result, water content results in plastics becoming degraded more easily [26]. The more the amount of glycerol, the more the amount of water that can penetrate through the structure of bioplastics and assist in the biological/microbial processes [36]. The more the glycerol and the starch, the easier the degradation [26]. The degradation process then continues by expanding the surface through erosion and perforation; these methods can increase the speed of degradation because the holes formed accelerate the diffusion of oxygen and enzymes into the bioplastics [20].

D. Shelf Life Testing

Bioplastics made of organic cassava starch had a low level of tensile strength, making them ineffective packaging materials. The shelf life of bioplastics was quite low; it will damage food stuff being packed due to the migration of spoilage bacteria to the food. The growth of fungi in bioplastics without the addition of natural preservatives can accelerate the deterioration of food [22].

As shown in Figure 4, bioplastics have been covered with white fungi, so that the polymer chains split as a result of reducing weight, so enzymes which depolymerise the polymers it can be excreted outside the cell [37], [7]. Depolymerisation occurs because of the working process of extracellular enzymes (consisting of endo and exo enzyme). Endo enzymes break the internal bonds in the main polymer chain randomly, while exo enzymes break the monomer unit in the main chain sequentially [38].

The fungal growth in bioplastics caused by fungi from glycerol as a plasticiser, i.e. Aspergillus niger, A. versicolor, Cladosporium sp., Fusarium sp., Penicillium sp., Trichoderma sp., and Verticillium sp [39] and [40] is influenced by environment, catabolism of bioplastics, and temperature [33] and [22]. The storage temperature can affect the activity of microbes and fungi. Generally, storage temperature can accelerate the migration of additives in bioplastics [41].

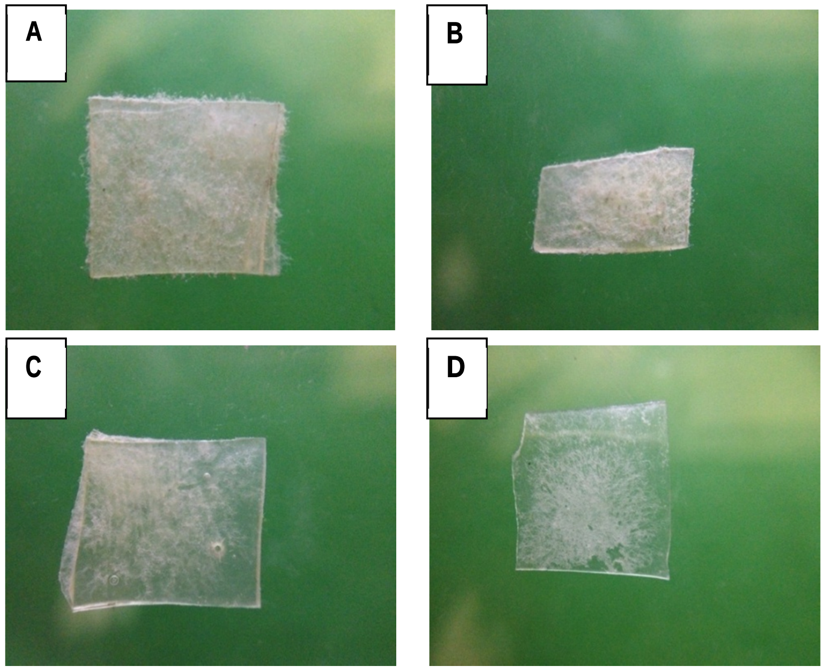

Fig. 4. Shelf Life Testing for 90 Days with Various Concentrations of Glycerol (A), 1,5% (v/v); (B), 2% (v/v); (C), 2,5% (v/v); and (D) 3% (v/v)

A high concentration of glycerol serves as an anti-fungal for bioplastics, hence an increased shelf life. Anti-fungal ingredients in bioplastic can control the growth of fungi and extend the shelf life [41]. The use of natural anti-fungal substances is likely to increase, as consumers are getting more aware of their health and potential dangers of synthetic preservatives [42] and [43]. The advantage of adding additives or anti-fungal agents into bioplastics is to increase the shelf life. In addition, glycerol layers reinforced with anti-fungal components can inhibit bacterial spoilage and reduce health risks [43].

IV. Conclusions

The degradation of bioplastics is affected by water content, moisture, and oxygen level. Resistance to degradation of bioplastics made of cassava starch was strongly influenced by the amount of glycerol used as the plasticiser. The greater the amount of glycerol was used, the faster the degradation process (the complete degradation occurred on the 9th day), the higher the moisture absorption, and the longer the shelf life (in a dry place) would be.

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