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Bioplastic from Cassava peel and eggshell waste

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Abstract

The accumulation of plastic waste and excessive use of plastic is a common environmental issue in Indonesia. Plastics are synthetic polymers that are stable, water-resistant, light, flexible, and firm but very difficult to break down by microorganisms. Decomposition of plastic waste by burning can cause other environmental issues and, during the combustion process can produce dioxin compounds that are harmful to health. An available and affordable alternative to reduce the use of plastic is by using bioplastics. Bioplastics are plastics made from natural materials that microorganisms can break down, so they are more environmentally friendly than commercial plastics. Generally, the main ingredients for making bioplastics are starch or chitosan. The source of starch used in this project comes from cassava peel waste. In this project, researchers also utilize waste from chicken eggshells. The function of adding eggshell waste is to give biodegradable plastic complex characteristics. The ratio between cassava peel and eggshell used was 1:0, 1:1, 1:3, and 1:5. With a 1:1 ratio is the most optimal. The addition of eggshells with the correct ratio (1:1) increased the ability of biodegradation of bioplastics. The results of the Tensile Strength Test of Bioplastic Samples with a ratio of 1:0, 1:1, 1:3, and 1:5 are 9.2 x10^{-3} kgf/cm^2, 4.4 x10^{-3} kgf/cm2, 2 x10^{-3} kgf/cm^{2,} and 2 x10^{-3} kgf/cm^2.

Keywords: *biodegradable plastic; cassava peel; eggshell*

1. Introduction

The accumulation of plastic waste and the excessive use of plastic are common environmental issues in Indonesia. According to the Indonesian Plastic Industry Association (INAPLAS) and the Central Bureau of Statistics (BPS), plastic waste in Indonesia reaches 64 million tons per year. As much as 3.2 million tonnes of plastic waste is dumped into the sea [1][2]. Plastics are synthetic polymers that are stable, water-resistant, lightweight, flexible, and strong but difficult to decompose by microorganisms. The decomposition of plastic waste by burning can cause other environmental issues and during the combustion process, it can produce dioxin compounds which are harmful to health [3][4]. An available and affordable alternative to reduce plastic use is by using bioplastics. Bioplastics are plastics made from natural ingredients that microorganisms can break down, so they are more environmentally friendly than commercial plastics [5][6].

In general, the main ingredients for making bioplastics are starch or chitosan. Starch is a carbohydrate that is a glucose polymer consisting of amylose and amylopectin in a ratio of 1:3. The ratio of amylose and amylopectin varies depending on the type of starch [4][7]. Starch is brittle and difficult to process because of its physical properties, namely its glass transition value and relatively high melting temperature. The Tg (Transition glass) of pure dry starch is estimated to be around 240 °C, above the initial point of their thermal degradation (about 220 °C). Starch's high Tg and friability are mainly due to intra-molecular hydrogen bonds between starch macromolecules. These drawbacks limit the formation of films with good mechanical properties. Therefore, starch must be modified to break down crystal grains and lower Tg and melting temperature (Tm) by adding plasticizers, mixing with other polymers, modifications, or chemical combinations before it can be processed into plastics/films [8]. To increase starch's mechanical strength, add filler (substance fillers) into bioplastics. Several studies have been conducted to look for additional filler which produces the characteristics best. One of them was done by Udjiana et al. [9], which used chitosan and CaSi. Results experiments showed that the highest degradation ability was 42.86% for bioplastics with 6% calcium silicate filler. Moderate water resistance test results show a value of 88.24% with chitosan filler 8%. Tensile strength test obtained the most significant value of 9.56 Mpa on 6% calcium silicate filler.

The source of starch used in this project comes from cassava peel waste. Cassava peel obtained from cassava (*Manihot utilissima*) is a significant food waste in developing countries, the starch content in cassava peel is relatively high, allowing it to be used as a biodegradable plastic film. The amylose and amylopectin content of cassava peel starch is 15/73 [10][11]. From the background above, bioplastics must be modified to control mechanics properties and skills of biodegradability. It is crucial to research on the influence addition of organic filler and inorganic as an innovation such as $CaCO_3$ [12-14]. Therefore, in this research will $CaCO_3$ filler is used.

Today, egg shells are used in bioplastic mixtures to increase the flexibility of bioplastics. Adding chicken eggshell waste can also form delicate pores as air cavities so bioplastics are more easily decomposed. This can happen because egg shells contain $CaCO_3$, which affects the structure of bioplastics by chelating proses. Chicken egg shells were chosen because of their abundant availability and very cheap price [15][16]. In this study, researchers used waste from chicken egg shells.

2. Experiments Procedure

Materials

Beaker 250 mL, Beaker 100 mL, Volumetric flask 100 mL, Volume pipette, Test tube racks, Stirring rods, Spatulas, Storage containers (moulds), and Digital balances. While the ***ingredients***: Glycerin 1000 mL (E. Merck), Cassava peel, Eggshell, Food colouring, Essential oil, Acetic acid, Acetone, and Aluminum foil.

Experiment

The cassava peel is cleaned until the white part without the epidermis remains, then the clean skin is dried and it is easy to make powder. The eggshells that have been collected are washed and then peeled off the inner epidermis. After cleaning, the shells are dried in the oven and then crushed to a powder. Cassava skin extract and egg shells are mixed until evenly distributed. The main ingredient mixture is added glycerin and 25% acetic acid, then stirred until mixed. Add food colouring and essential oil to the dough, then add acetone. The bioplastic dough is put into the mold and then dried using an oven.

Methods

Water Resistance Test

The analysis carried out to determine occurrence of the bonds and degree or regularity in the polymer. It is determined by the percentage addition of polymer weight after water absorption occurred [17].

Tensile Strength Test

The tensile test is carried out to know a material's strength level and identify the material's characteristics. This tensile test is carried out by providing a maximum tensile force with a specific weight (calculated, measurable) on one axis until the material being tested breaks or reaches the material's tensile limit. Often this test is performed on rubber or metal objects [18]. The material test result will be compared with standard plastics or bioplastics on the market.

Biodegradable Test

The basic principle of the biodegradable test is the ability of bioplastics to be degraded in soil. This test was carried out to prove that the material being tested can degrade completely when buried or implanted in the soil and determines the time it takes for plastic to decompose[19]. The basic concept of material degradation is based on soil moisture, and heat in the soil due to sunlight, this occurs over time and can accelerate the weathering of bioplastics. Usually, bioplastics decompose into carbon dioxide, water, and organic matter that are harmless to the environment.

3. Result and Discussion

Based on data [20], it is known that cassava peel has a high cellulose content, which is 57% and 22% lignin, and the remaining 20% is starch and other ingredients. This is because cassava skin is a tuber protector so it has a high cellulose cell wall. The main ingredient for making bioplastics is cassava peel. The cellulose contained therein needs to be converted into amylose and amylopectin. This is done by changing the type of glucose from beta-glucose to alpha-glucose through a mutarotation process. First, the 60°C heating process which was carried out for 30 minutes allowed the reaction of cellulose to become cellulose acetate by changing the functional groups due to the addition of acetic acid. Then the cellulose acetate that has been formed will dissolve in the acetone added during the heating process. When it dissolves, the cellulose bonds will be broken and the acetate functional group will return to hydroxide, after which beta-glucose monomers will be formed. The dissolved beta-glucose will then undergo mutarotation through the equilibrium reaction in Figure 1.

When alpha glucose species are formed, they will immediately polymerize into amylopectin or amylose. This will cause the reaction to shift towards alpha glucose, converting almost all of the beta glucose to alpha glucose and bioplastic synthesis has been successfully carried out. Adding glycerol to the mixture of bioplastics serves as a plasticizer that can reduce internal hydrogen bonds in intermolecular bonds. Meanwhile, adding acetone in the heating process functions as a cellulose solvent. This is due to the volatile nature of acetone (maximizing the process of dissolving and evaporating the solvent elements) [8].

Water Resistance Test

The water resistance test show in Figure 2. It is carried out by immersing it in hot water at 60 °C and ordinary water at 25 °C. The bioplastic sample was cut to a size of 2.5 cm x 5 cm which was soaked for 5 minutes. After immersion for 5 minutes, the bioplastic samples were then agitated and the changes observed were observed. The observations obtained from the water resistance test are summarized in Table 1.

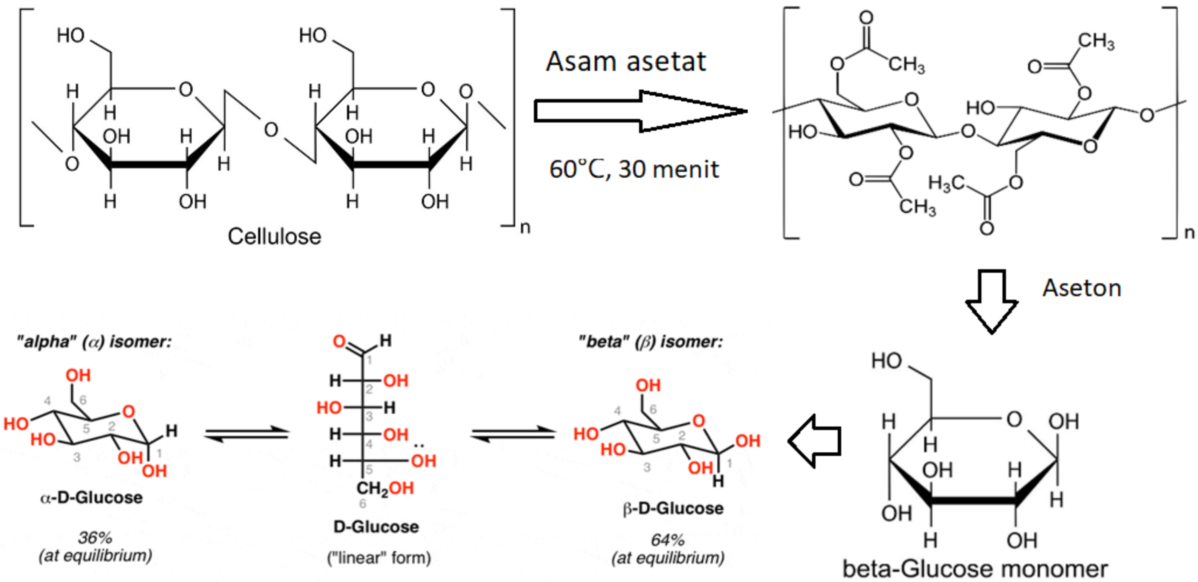

Figure 1 The Process of Forming Alpha-Glucose from Cellulose

(a) (b)

Figure 2 Water resistance test of bioplastic samples of (a) before soaked for 5 minutes; (b) after soaked for 5 minutes

Table 1 Bioplastic Sample Solubility Test Results

No	Variation (Cassava Peel: Eggshell)	Results
1	1:0	Shows relatively good flexibility and water resistance
2	1:1	Harder bioplastics and low water resistance (tears easily)
3	1:3	Bioplastics that are too hard so they lack adhesion between the elements in them have low flexibility, and meager water resistance (reforming mush)
4	1:5	Bioplastics that are too hard, so they lack adhesion between the elements in them have low flexibility, and meager water resistance (reforming mush)

The resistance properties of plastic films to water are determined by the swelling test, namely the percentage of swelling of the film by the presence of water, the lower the water absorption value, the better the plastic properties, while the higher the water absorption, the plastic properties will be easily damaged [21]. The experimental results found that the 1:0 bioplastic composition variation had the best water resistance among the other variations. In contrast, the lowest water resistance was the sample with eggshell content of 1:3 and 1:5. The addition of eggshells decreases the resistance of bioplastics to water. Bioplastics without eggshell content have relatively good water resistance.

Tensile Strength. The tensile strength test was carried out by cutting the bioplastic sample with a size of 2.5cm x 5cm, then punching a hole with a hole position of 1.5 cm (top), 1 cm (right), and 1 cm (left) with a hole diameter of 0.5 cm. . Then, the bioplastic sample is hung on a luggage scale which is then withdrawn. The highest measurement data is obtained before it is torn. Because aluminum foil was included in the test during this test, we measured the strength of the aluminum foil itself so that a value of 20 g was obtained, and reduced the strength of aluminum foil with the results of the previous measurements. The following is the data collected from the tensile strength test results.

Table 2 Tensile Strength Test Results for Bioplastic Samples

Variation	Maximum weight (g)	*Tensile strength* (10^{-3}kgf/cm^2)	*MPa*
1:0	115	9.2	1.216
1:1	55	4.4	0.903
1:3	25	2	0.432
1:5	25	2	0.432

Table 2 shows the best comparison between cassava skin and eggshells in the 1:0 formula. The addition of eggshells does not increase the strength of the synthesized bioplastic. Figure 3 show the graph of a decrease in tensile strength value with adding egg shells.

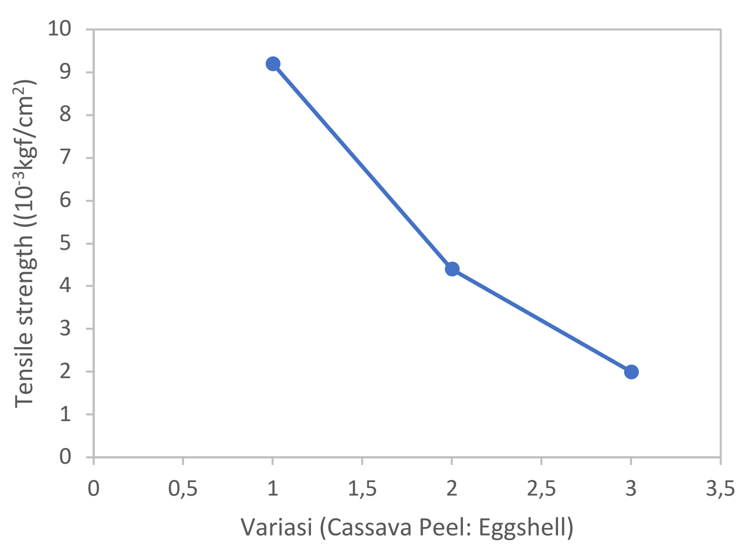

Figure 3 Graph of Variation vs Tensile Strength

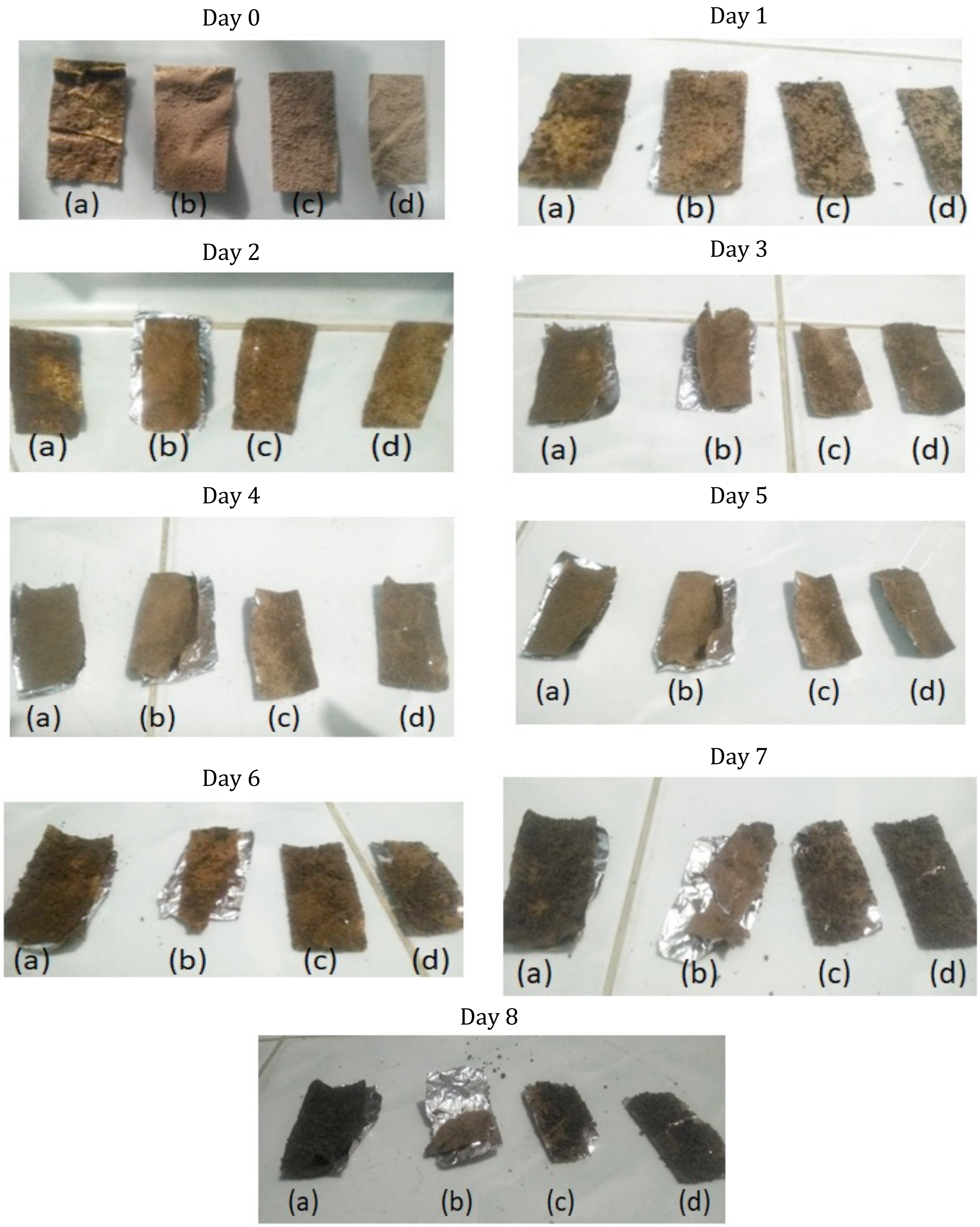

Figure 4 Biodegradable test results for bioplastic samples. Caption: From the far left, sample variations 1:0 (a), 1:1 (b), 1:3 (c), and 1:5 (d).

Adding $CaCO_3$ tends to be the opposite of the tensile strength value. The more significant the percentage of $CaCO_3$, the less the tensile strength value tends to get smaller. This means that adding $CaCO_3$ causes putative bioplastic molecular structure to be amorphous. On the molecular structure amorphous, branched chains are not tightly arranged so the distance between the molecules becomes more prominent and the strength of the molecular bonds becomes weak. Weak internal molecular bond strength bioplastics cause more low force required to decide on the bioplastic [22-23].

Several previous studies have been carried out to produce bioplastics. However, starch-based plastics have several drawbacks. This bioplastic is less resistant to water (less hydrophobic/hydrophilic) and has low mechanical properties (tensile strength and Young's modulus). One way to reduce hydrophilic properties is to mix starch with other hydrophobic biopolymers, such as cellulose, chitosan, and protein [24]. Here the cassava peel is dominated by its cellulose content so, it is expected to improve the mechanical properties of bioplastics. From the experiment, it was found that bioplastic samples without egg shells had the greatest tensile strength. The addition of eggshells increases the hardness of the characteristics of bioplastics but reduces their elasticity.

Biodegradable Test

Biodegradable test results for bioplastic samples show in Figure 4.The bioplastic sample was cut with a size of 2.5 cm x 5 cm which was then immersed in the soil to be observed every day for one week. Observations aim to observe the bioplastics' *ability* to be degraded in soil media with a depth of 3 cm for each variation of the synthesis result. The biodegradation test result found that the eggshell content can make bioplastics harder and more easily degraded. This was shown from the results of bioplastic samples containing eggshells, samples 1:1, 1:3, and 1:5, which had better biodegradability than samples without adding eggshells. Based on the results of the SEM test conducted [25], it was shown that samples with a higher ratio of starch or $CaCO_3$ had a larger pore width which resulted in high vapor transmission and was more easily degraded in nature. In this study, samples with a 1:1 variation had the most effective biodegradability compared to other samples. However, in this research, it is necessary to optimize the composition more precisely so that the bioplastics' degradation ability and flexibility can be maximized according to needs.

4. Conclusion

The experiments that have been carried out, it can be concluded that bioplastic synthesis based on cassava peels and eggshells have been carried out with the comparisons between cassava shells and eggshells used are 1:0, 1:1, 1:3, and 1:5. With ratio of 1:1 is the most optimal. With the addition of eggshells in the correct ratio (1:1), the ability to biodegrade bioplastics increases.

Acknowledgments

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