Article

Fabrication of Bioplastic from Rice Straw

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Abstract. This work was aimed to fabricate bioplastics from rice straw, with addition of carboxymethyl cellulose (CMC) and glycerol. Prior to the bioplastic fabrication, cellulose was extracted from rice straw through digestion process using ethanol solution 50% (w/w) and sodium hydroxide solution 8% (w/w) as catalyst. Digestion process was held for 60 minutes at temperature of 120^{o}C. Bioplastics were produced by blending dried pulp, CMC, and glycerol. Each bioplastic sample with size of 2.5 cm x 5 cm were mainly made from 5 grams of dried cellulose that was dissolved in 100 ml of water. The amount of CMC and glycerol added to the pulp solution were varied from 1 ml to 2 ml and 0.5 to 1.5 grams, respectively. Swelling test (both in water and oil) and biodegradability test were conducted to study the performance of the bioplastics. Results showed that bioplastics were dissolved easily in water. During oil swelling test, it showed that higher glycerol content increases the oil resistant characteristic of the bioplastic. Meanwhile, the CMC content has no impact during the oil swelling test. The best composition of the bioplastic was achieved with the CMC and glycerol contents of 1.382% (w/w) and 2.323% (w/w), respectively, with the lowest oil swelling test result of 68%. Biodegradability of the bioplastics were lower at higher CMC and glycerol contents. The best composition with maximum weight reduction of the bioplastics was achieved by the bioplastic with 0.469% (w/w) of CMC content and 0.939% (w/w) of glycerol.

Keywords: Bioplastic, Rice Straw, CMC, Glycerol, Swelling, Biodegradability

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1. Introduction

Plastics are materials that are formed from synthetic or semi-synthetic polymerization products that have unique and extraordinary properties. The polymerization process that produces straight chain polymers has a low polymerization rate and the basic framework that binds between carbon atoms and bonds between chains is greater than the hydrogen chain. Materials produced with low polymerization rates are rigid and hard.[1].

Bioplastic technology is one of the efforts made to contribute in overcoming of problems caused by conventional plastic for packaging. Furthermore, bioplastics also can be used in the medical and pharmaceutical fields, among others, for surgical equipment, surgical sutures, swabs, wound dressing, bone and plate replacement, and so forth. Bioplastics can be produced through fermentation process by bacteria or by a simpler method of mixing natural polymers such as cellulose with additives such as plasticizers [2]. Bioplastics are plastics that can be used like conventional plastics, but will be broken down by the activity of microorganisms into the end result in the form of water and carbon dioxide after being used up and discharged into the environment without leaving toxic residues. Because of its nature that can return to nature, biodegradable plastic is an environmentally friendly plastic material [3].

In recent years, the development of bioplastics has been carried out by utilizing cassava as the main raw material. However, the use of cassava for bioplastics is in conflict with government policies regarding food security. In addition, the physical and mechanical properties of bioplastics from cassava have not been able to compete with synthetic plastics. Therefore, cellulose based raw material is required as it can be used to produce stronger bioplastics and it can be derived from natural fibers [4].

Rice straw is one of the most available agro-industrial wastes in Indonesia. Based on data from Badan Pusat Statistika [5], the rice production in Indonesia in 2018 was almost 56,54 million tons of dry unhusked rice (MPD). From dry unhusked rice, the rice straw produced could reach 50% or about 28.27 million tons. However, utilization of rice straw by farmers, in general, is still low. Rice straw is usually used as animal feed or as compost. In addition, the majority of farmers burn paddy straw in their paddy fields after harvesting. Burning of crop residue may harmful for environment as it emits greenhouse gases, increases levels of particulate matter and smog. In other words, burning of crop residue causes health hazards, deterioration of soil fertility, and loss of biodiversity of agricultural lands [6]. Therefore, it is necessary to intensively utilize paddy straw as component for bioplastic production.

Bioplastics are grouped into two groups and four different families [7], i.e. group of agro-polymers consisting of polysaccharides, proteins, etc., and group of biopolyester (biodegradable polyester), such as poly lactic acid (PLA), polyhydroxy alkanoate (PHA), aromatic and aliphatic co-polyester. Agro-polymers are biomass products obtained from agricultural materials. Biopolymer can be grouped according to source. PHA group is obtained from microorganism activity by means of extraction. Another group is biopolyester obtained from the application of biotechnology, namely by conventional synthesis of biologically obtained monomers, called polylactides. Examples of polylactides are poly lactic acid. The final group is derived from petrochemical products synthesized conventionally from synthetic monomers (polycaprolactones, polyester amides etc.).

Biodegradable polymers are polymers that are able to decompose into CO_2, CH_4, H_2O, inorganic compounds or biomass through enzymatic reactions by microorganisms. Some polymers can be decomposed at certain places with different decomposing speeds [8]. Protein, lipids, plant extracts, and polysaccharides have been used extensively in the production of biodegradable plastics [9].

Ethyl cellulose can be used for laminating or printing after adding plasticizers or other polymers [10]. Cellulose as one of the plastic constituent polymers contains high levels of fiber. The mechanical strength of cellulose fibers is influenced by the size of the fiber diameter. The greater the diameter of the fiber, the lower the value of the tensile strength and modulus of elasticity and vice versa.[11].

Carboxymethyl cellulose (CMC) is a derivative of cellulose and is often used in the food industry, or used in food to prevent retrogradation [12]. There are four important functions of CMC, i.e., as thickener, stabilizer, gelling agent and emulsifier. In the hydrocolloid emulsion system, CMC does not function as an emulsifier but rather as a compound that provides stability [13].

Glycerol is a chemical that is widely used in the pharmaceutical, cosmetic and food industries. It is non-toxic, edible, and biodegradable so it has important benefits to the environment [14]. The functions of glycerol are to absorb water, as a crystallizing agent and a plasticizer. Plasticizer is a compound that has ability to increase flexibility, strength, and distortion of a biopolymer matrix by reducing the electrostatic charge and at the same time increasing flexibility, crack resistance, and dielectric constant [15].

This research was aimed to fabricate bioplastic from rice straw and to study the effect of glycerol and CMC on its oil resistance, water resistance, and biodegradability.

2. Methodology

2.1. Extraction of Cellulose from Rice Straw

Prior to bioplastic fabrication, cellulose was extracted from rice straw that was obtained by removing leaves from paddy rice. Straw was then cut into 2-3 cm length and being dried under the sun.

Dried rice straw was cooked in a digester with a cooking solution of 50% (w/w) ethanol solution and 8% (w/w) NaOH solution as catalyst, with ratio between dried rice straw and ethanol solution was 10: 1 (ml:gram). Digester was operated for 60 minutes at 120 ºC. The residue and filtrate from the digester were then separated a sieve. The residue was then washed with 50% (w/w) ethanol solution and then using hot water until the filtrate was clear and neutral. The 'clean' residue was then dried in an oven at 70 ºC for 24 hours. The dried residue, i.e. pulp, was then pulverized using a blender to reduce the size and break down the cellulosic fibers.

2.2. Cellulose analysis

The pulp was dried in an oven at 105 ºC for 1 hour. Three grams of dried pulp was macerated using 15 ml of 17.5% (w/w) NaOH solution in an erlenmeyer for 1 minute. Ten ml of 17.5% (w/w) NaOH solution was poured into the erlenmeyer and then the mixture was stirred 15 minutes and being rested for 3 minutes. Solution of 17.5% (w/w) NaOH was then added sequently into the mixture at 2.5, 5, and 7.5 minutes. Volume of NaOH solution added for each time was 10 ml. The mixture was the put in a rest for 30 minutes. Next step was adding a 100 mL of water and let them in rest for 30 minutes, and then the mixture was filtered using filter paper. The formed precipitated solid was washed with 50 mL of water. This washing step was repeated for 5 times. The precipitated solid left on the filter paper was transferred to another flask and then was washed using 400 mL of water. Acetic acid solution with concentration of 2 N was poured to the precipitated solid and the mixture was stirred for 5 minutes. Washing step was repeated until the solid was not in acidic condition. The remaining precipitate was then dried in an oven at 105 ºC until the weight of the solid remained constant. The cellulose content can be calculated using equation (1)

$$Percentage\ of\ Cellulose = \frac{weight\ of\ precipitated\ solid\ (g)}{weight\ of\ raw\ pulp\ (g)} x\ 100\% \quad (1)$$

2.3. Bioplastic Synthesis

Bioplastics were prepared with same amount (5 grams) of rice straw cellulose which was dissolved in 100 ml of water with variation of the glycerol and CMC content. The amount of glycerol added to the mixture were 1 ml, 1.5 ml, and 2 ml, while the CMC amount were 0,5%, 1%, and 1,5%. So, in this experiment we prepared 9 samples (solution of rice straw cellulose, glycerol, and CMC in water). Prior the molding, the solutions were filtered to remove coarse solids. Bioplastics were molded on plastic-wrapped ceramic and dried in room temperature for 2x12 hours. Size of each bioplastic sample was 2.5 cm x 5 cm. Name and additive content of bioplastic solutions is presented in Table 1.

Table 1. Additive Content of Bioplastic Solution

Sample Name	CMC [gram]	Glycerol [% mass]
C1G1	0.5	1.183
C1G2	0.5	1.766
C1G3	0.5	2.344
C2G1	1	1.178
C2G2	1	1.758
C2G3	1	2.333

Sample Name	CMC [gram]	Glycerol [% mass]
C3G1	1.5	1.172
C3G2	1.5	1.750
C3G3	1.5	2.323

2.4. Analysis

Water, oil swelling test and biodegradability tests were conducted for all samples. In water and oil swelling test, samples were submerged into the water and oil. In biodegradability test, samples were buried under dry soil. Duration for oil swelling test and biodegradability test were 6 and 15 days, respectively. In oil swelling test, samples were weight in daily basis. For biodegradability test, the weights of samples were measured in every 5 days. Level of biodegradability by was calculated using Eq (2)

$$\%weight\ degraded = \frac{Wi-Wf}{Wi} x100\% \quad (2)$$

With w_i and w_f are initial weight of sample before degraded (Day-1) and weight of samples after degraded, respectively.

3. Results and Discussion

During water swelling test, all bioplastic samples decompose immediately when they were submerged in water. This happened because the bioplastic binding agent, i.e. CMC, is hydrophilic and its molecules were also easily dispersed in water.

Figure 2 shows the results of oil swelling test. The values recorded was based on the last day of experiment (day-6). It is shown, in general, the higher glycerol content of bioplastic the resistance toward oil was higher. It was recorded that the amount of oil absorbed by the bioplastics reduced significantly in higher glycerol content.

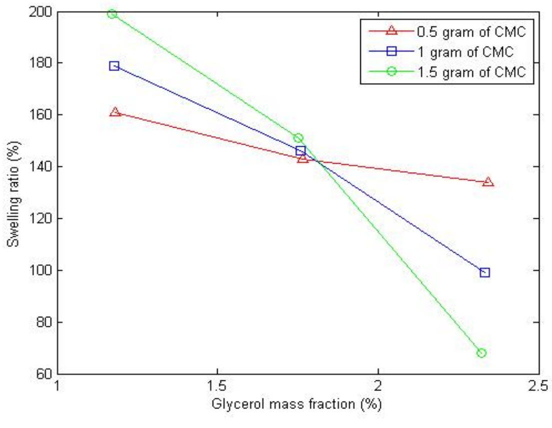

Fig. 2. Oil swelling test result for each sample

Those phenomena happened as glycerol is a plasticizer that has character as oil resistantThe effect of CMC content was observed during the fabrication of bioplastic. The higher CMC content, the bioplastics became thicker, and vice versa. The best bioplastic sample was the bioplastic with the lowest glycerol content (2.323%) at 1.5 gram (1.382%) of CMC in the bioplastic composition.

Degradation test was observed for 15 days on burial of the bioplastic samples in dry soil. Figure 3 shows the results of the biodegradability test of the samples, measured at 0-day, 5th day, and 10th day. On weighing the sample on the 15th day, it was found that all samples no longer experienced weight reduction. This means that there were undecomposed samples after 15 days burial.

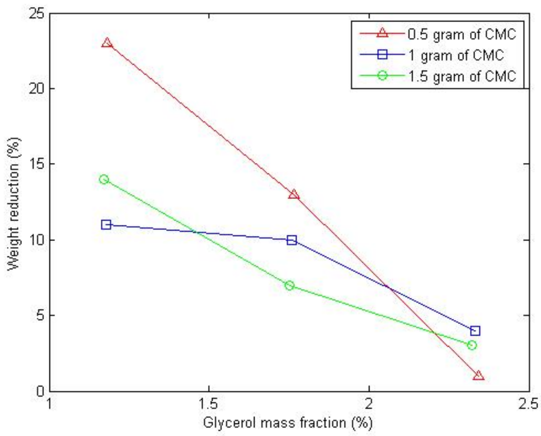

Figure 3. Biodegradability test under dry soil

The test results showed that in all bioplastic samples undergoing changes in mass reduction with different percentages. The smaller the CMC content, the greater the average percent depreciation per day. This happened as amount of CMC, which is a bioplastic binding agent, caused the different sample's densities. The higher the density of the sample, the more difficult to be decomposed.

4. Conclusion

Based on the results of research that has been done can be concluded as follows:

1. Bioplastics can be fabricated from rice straw cellulose with addition of CMC and glycerol.
2. Bioplastics with additives such as CMC and glycerol are not waterproof.
3. At the same CMC content, the oil resistance of the bioplastic was higher in bioplastic with higher glycerol content. CMC and glycerol content that produced bioplastic with highest oil resistance (68%) were 1.382% (w/w) and 2.323% (w/w), respectively.
4. Lower of CMC and glycerol content the bioplastics were easier to be degraded. Best bioplastic with maximum weight reduction was achieved at CMC and glycerol content of 0.469% (w/w) and 0.939% (w/w), respectively.

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