Surface morphology and water vapour transmission rate analysis of protein-based bioplastic

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Abstract. Protein-based bioplastic from sweet sorghum has successfully synthesized. This study was aimed to identify and analyze the surface morphology structure of bioplastic by using SEM and water vapour transmission rate analysis. Plastics produced from protein extracted at 60 °C showed smoother surface compared to plastics produced from protein extracted at 25 °C. All bioplastics had a various particle size in the range of nanometer, protein-based bioplastic ranges from 3.51 to 3.85 g/m².24 hours.

Keywords: Bioplastics, Protein, Sweet sorghum

1. Introduction

Plastic films, commonly known as plastics, have wide range of applications, ranging from food packaging and merchandise materials to agricultural and medical applications[1]. Most of plastics used nowadays are of synthetic ones. The excessive usage of synthetic plastics results in environmental issues. Synthetic plastic waste is non-renewable waste and difficult to decompose in the soil. Taking long enough to decompose, the accumulation of plastic waste became one of the greatest concerns to the environment[2]. Indeed, synthetic plastic waste can also produce toxins during the decomposition process so that can pose a risk to health and ecosystem. Therefore, it is necessary to reduce the use of synthetic plastics, by applying the use of biopolymer-based plastics or called bioplastics. Bioplastics is one of the material engineering innovations which is made from renewable, biodegradable, and safety material, such as proteins, polysaccharides, lipids, and resins[3].

An approach to solve the environmental issue of the synthetic plastic usage includes the use of bioplastics which made of protein. Currently, protein is one of the potential materials for bioplastics. Its properties are unique, stable, and reinforced by hydrogen bonding, as well as having hydrophobic interactions and disulphide bonds[4][5]. There are various sources of protein which is derived from rice, soybean, and wheat[6][7][8].

In this study, sweet sorghum was used as protein resources in synthesizing plastics. Sweet sorghum is one of the cereal plants that can live on dry land. In Indonesia, this plant is commonly found in Java[9]. Sweet sorghum seeds are widely used as food needs, animal feeds, and industrial substances. While the sweet sorghum stalk and fiber are used as a raw material for making sugar and ethanol and used as a manufacture for composite boards[9]. Sorghum starch has been used as a raw material for
plastics; however, the physical properties of bioplastics still have not significantly enhanced which is indicated by the uniformity of the bioplastic surfaces\cite{10}.

Therefore, this study investigated the use of sweet sorghum protein as raw materials for plastics. The addition of carrageenan is also required to improved the mechanical properties of the film that will be produced\cite{11}. Furthermore, the surface morphology and water vapor transmission rate analysis was investigated at bioplastics synthesized with and without ultrasonication.

2. Methods

2.1 Materials
Sweet sorghum (containing 11% of proteins) was provided by PT Agro Indah Permata 21 (Bogor, Indonesia). The other materials such as carrageenan was provided by CV Ocean Fresh (Bandung, Indonesia), sorbitol as a plasticizer is used to increase the flexibility of bioplastic film, and sodium hydroxide (NaOH) (MW 40.00 g/mol).

2.2 Preparation of bioplastics
The protein-based bioplastics were synthesized using casting method. Firstly, the blends 40.0 g of sweet sorghum powder and 55 mM NaOH were magnetically stirred by using hot plate stirer at 25 °C and 60 °C and 120 rpm for 24 hours, following previous study\cite{12}. The sample was then centrifuged for 15 minutes by using centrifuge (HIMAC R12 A) at 10,000 rpm to separate the precipitant and supernatant phases. The blends between protein extract in supernatant phase and carrageenan (P/C) were mixed in 3/7 in 100 ml total solution for 2 hours using hot plate stirer. An additional of 16% sorbitol were then mixed into those solutions in the 20th minute at stirring time\cite{13}. The solutions were sonicated for 60 minutes at the 20 kHz and amplitude 40% before casting process. Finally, the bioplastics were prepared by casting method by using glas mold in a 20 x 20 cm$^2$ at 70 °C.

2.3 Morphological analysis
The cross-section image of bioplastic samples at magnification of 20,000 times was observed by using scanning electron microscope, CARL ZEISS EVO MA10, UK. The bioplastics were coated with gold before the process. All bioplastic samples were prepared in a 1 cm x 1 cm for the test.

2.4 Water vapor transmission rate test
The rate of water vapor transmission is one of the properties of bioplastic film test to determine the permeability of material to water vapor. To perform in this test, bioplastics samples were prepared in the size of 1.5 x 1.5 cm$^2$ and stored in a sealed-silica containing-container. The whole sample was then prepared into the desiccator that has been filled with the aquadest. The water vapor transmission test of bioplastics was carried out for 24 hours. In this test, the RH is about 80%. The wvtr analysis was calculated by dividing between the bioplastic mass probe ($\Delta m$) and multiplying the area of the bioplastic (A) by 24 hours of time (t) as shown in Eq. (1).

$$ wvtr = \frac{\Delta m}{At} \tag{1} $$

3. Results and Discussion
Fig.1 below showed the protein-based bioplastics synthesized using casting method. Casting solution method is the wet process to fabricate the film-formation which is started by hydrocolloid dispersed process in aqueous suspension\cite{14}. The bioplastics thickness range from 0.1 mm to 0.2 mm. The inhomogeneous of their thickness depends on the application technique to perform its casting process\cite{15}.
3.1 Morphological analysis

The morphology of bioplastic was investigated by using SEM. Fig.2 showed that the surface morphology of bioplastics at magnification of 20,000 times. Fig.2 (a) and (c) are SEM images of bioplastic samples with protein extracted at 25 and 60 °C for 24 hours, respectively. Both of them did not follow sonication treatment. In contrast, the other samples in Fig.2 (b) and (d) are morphology of bioplastics that were following sonication treatment. Plastics produced from protein extracted at 60 °C showed smoother surface compare to plastics produce from protein extracted at 25 °C. Moreover, additional sonication treatment only affected the plastic surface which were synthesized at 25 °C (sample B). Contrasting Fig.2 (c) and (b), it can be inferred that sonication at 60 °C did not give significant changes in the morphology. Different with starch-based bioplastic from sweet sorghum, surface morphology structure from this product has not homogenoues yet due to its property insoluble in organic solvents\[6\].
Both of protein from sweet sorghum and carrageenan, they are hydrophobic and hydrophilic bonding which are relatively difficult to binding each other. But, an additional of sorbitol as a plasticizer to the protein-carrageenan-solution could be improve the binding the polymerics chains between protein and carrageenan. In addition to the morphology, SEM microscopy also provided data on the particle size. Table 1 indicated the particle size of each bioplastic determined from SEM microscopy.
Table 1. particle size bioplastics

| SAMPLE                    | Particle Size (nm) |
|---------------------------|--------------------|
| 25 °C without sonication  | 135.8-312.6        |
| 25 °C with sonication     | 61.6-111.8         |
| 60 °C without sonication  | 111.7-190.0        |
| 60 °C with sonication     | 122.8-223.6        |

3.2 WVTR analysis

The wvtr test aims to determine the bioplastic permeability by calculating how much water vapor transmits into the film. In this analyzing, all bioplastic samples were separated in 1.5 x 1.5 cm$^2$ and stored on the container which was filled by 10.0 g silica gels. Whole containers were stored in the desicator. To prevent the air from the environment, the desicator was covered by using parafilm.

![Figure 3. Water vapour transmission rate of protein-based bioplastics at various conditions](image)

Fig. 3 informed that the wvtr of the protein-based bioplastic ranges from 3.51 to 3.85 g/m$^2$.24 hours. The data indicated that bioplastics synthesized from protein extracted at 25 °C without sonication had the highest wvtr. Furthermore, sonication conducted during bioplastics preparation with protein extracted at 25 °C resulted in decreased of wvtr. However, a contrary phenomenon was occurred at bioplastics synthesized from protein extracted at 60 °C. The sonication resulted in an increase of wvtr.
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