Study of SEM, XRD, TGA, and DSC of Cassava Bioplastics Catalyzed by Ethanol

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Abstract. This study aims at preparing and characterizing of bioplastics that utilized cassava biomass which was available abundantly in Indonesia. The bioplastic synthesis was conducted with two variations of the reactant, namely cassava + starch + glycerol + water + acetic acid (vinegar) and cassava + starch + glycerol + water + acetic acid + ethanol. Bioplastic obtained was characterized by employing scanning electron microscopic (SEM), X-Ray diffraction (XRD), Fourier transform infra-red (FTIR), thermogravimetric analysis (TGA), and differential scanning calorimetric (DSC). The results show that bioplastics with the second combination have a high degree of degradation, whereby they were consistent with XRD analysis, appearing a low crystallinity value. The functional groups have shown IR spectra presented the existence of C-H alkanes, C = O esters, and C-H alkene groups. While the surface morphology displayed a flat surface, which was relatively comparable to both samples and the reduction of sample mass during heating was at 2.32 mg.

1. Introduction

Plastic is one type of material formed by the polymerization process, which is the process of combining several simple molecules (monomers) through a chemical process into more complex molecules [1]. This material is widely used in modern society for has several advantages such as durable, lightweight, waterproof, and the price is relatively low. Every year around 265,000,000 tons of plastic are produced and used worldwide for industrial and household [2]. However, plastic currently that massively is utilized a synthetic polymer which cannot be decomposed in a short time, causing environmental problems. Plastic waste tends to create a buildup of soil pollution, causing land degradation, environmental damage, and floods [3].

Recently, scientists have been giving more attention to the development of renewable resources, such as starch, lignocellulose, and ethanol [4-7]. Those materials could be improved, becoming the
bioplastics that can be decomposed by microorganisms [8]. The development of bioplastics has focused on starch, which is available abundantly in nature [9]. The potential for bioplastic development is immense because the raw material is available in the environment. The bioplastics have been reported by authors in which they were processed from great range sources, such as cassava [10].

The present study utilized the cassava (*Manihot esculenta*) as the raw material with some considerations. Indonesia is the third-largest cassava producing country in the world with production capacity in 2014, reaching 26 million tons, meanwhile based on the FAO report in 2017, the world capacity attained at 278.0 Million Tons. The huge cassava is an excellent opportunity to increase its value, becoming bioplastic.

As described previously, that bioplastics had been prepared from many biomass. It was known generally that bioplastic was obtained by reacting reactants, cassava, glycerin, which is enhanced by a catalyst. Meanwhile, the properties and improvement of bioplastic also were reported by many authors. The deficiencies of this material from starch were low mechanical properties (tensile strength, strain, and young modulus) and hydrophilic nature. The increase of bioplastic quality was the addition of biopolymers such as glycerol and sorbitol. The addition of glycerol provides a higher solubility in plastic films than sorbitol. Bioplastics made from cassava starch and glycerol plasticizers are transparent, bright, homogeneous, flexible, and easy to handle [11].

Based on the reference survey as described above, the preparation and characterization of plastic films synthesized with a combination of cassava starch + glycerol + water + acetic acid and cassava starch + glycerol + water + acetic acid + alcohol are needed to be studied and analyzed. Bioplastics were characterized by using instruments. SEM was to observe the surface morphology; XRD was to determine the crystallinity; FTIR was to examine the functional groups formed; TGA and DSC were to identify the thermal properties of plastic films.

2. Materials and Methods

2.1 Chemicals

The ethanol employed in this work was fermented from *Arenga pinnata* sap and distilled using reflux distillation. Glycerol was purchased from a drug store and produced by One Med Health Care, Jayamas Medica Industry, Indonesia. Acetic acid used an industrial-grade with purity was 99.8%, and the solvent water was obtained through simple distillation. The cassava was obtained from a farmer in Minahasa Regency and then was milled until particle sizes were ranged 100 – 120 mesh. Before using, the cassava was dried under sunlight until the weight was constant in which the water content was reduced significantly.

2.2 Instruments

The tools used were an electrical stove equipped by magnetic stirring, aluminum pan 100mL. Apparatuses XRD and FTIR used were the Analytical X’pert Pro (Almelo, Netherlands) and Shimadzu PRESTIGE 21 (Tokyo, Japan), respectively.

SEM measured the characterization of surface morphology with specification FEI Inspect S50 SEM (Tokyo, Japan), which is available at Central Laboratory, Universitas Negeri Malang (UM), East Java, Indonesia.

The XRD procedures followed the steps as described below. The degree measurements were set from 20 = 10.01 until 89.9° with beam wavelengths were Kα (λ = 1.54 Å) and Kβ (λ = 1.39 Å) at 25 °C. The operating current and potential differences were set at 35 mA and 40 kV, respectively. The functional vibrations of the substrates were detected by instrument FTIR, whose frequencies were in the range of 400 to 4000 cm\(^{-1}\).
The SEM pictures were taken employing an electrical potential for accelerating operating at 15 kV, and picture magnifications were set at 5000x. The working distance (WD) and the spot calibration were 10.8 mm, and 5.5, respectively.

2.3 Procedures

The work was conducted in two phases, such as the manufacturing of bioplastic films and characterizing the sample. The preparation employed two combinations: The 50 grams of cassava starch, 25 ml of glycerol, 25 ml of acetic acid (vinegar), and 50 ml of water; the 50 grams of cassava starch, 25 ml of glycerol, 25 ml of acetic acid (vinegar), 50 ml of water and the addition of 25 ml of alcohol.

The ingredients were mixed inside a flask equipped by a reflux column and heated at 80 °C under gentle stirring. After that, the mixture was cooled down for minutes and printed on a wooden board laid on the aluminum foil. The biodegradable plastic mold was dried under sunlight for hours. After drying, the plastic was removed from the frame; then, the process was repeated for variation 2.

For characterization purposes, the film was cut into small pieces with a size of 2 × 2 cm². The characteristics of films were analyzed using instruments XRD, SEM, FTIR, TGA, and DSC. The measurement employing TGA and DSC used the device manufactured by Toledo Mettler at Energy Laboratory, ITS, in Surabaya.

The crystallinity value (Cr) was calculated using the Herman method, which was followed from the previous report [12] as presented in Eq.(1) and employing the Origin Lab and Microsoft Excel software.

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Cr = 100 \left( \frac{l_{\text{crystal}}}{l_{\text{amorphous}} + l_{\text{crystal}}} \right) \%
\]

3. Results and Discussion

3.1 Surface Morphology

The bioplastics grown was a printed sheet whose properties were a light brown, transparent, and elastic, as shown in Figure 1. The investigation of surface morphology was carried out at determining the surface structure, cracks, and surface smoothness. The study was intended to study a comparison of two combinations, namely cassava starch +glycerol+water+acetic acid and cassava starch+glycerol+water+acetic acid+ alcohol. Figure 2 show the surface morphology of the samples grown employing two combinations cassava starch+glycerol+water+acetic acid (A), cassava starch+glycerol+water+acetic acid+ethanol (B) and images are magnified 50,000x.

Figure 1. The bioplastic obtained by employing ingredients 50 grams of cassava starch, 25 ml of glycerol, 25 ml of acetic acid (vinegar), 50 ml of water, and 25 ml of ethanol
The image showed that the surface structures were fractured and cracked both samples, but the ethanol addition appeared smoother compared to the first variation. The cracks might be caused by the starch bonds α-1,4-glucosidic connection, which was more amorphous. Another reason could be explained that the size of amylopectin was large in which the particles were not dense in the starch matrix. The addition of ethanol influenced surface morphology, which was more compact and homogeny.

![Figure 2](image1.png)

**Figure 2.** The surface morphology of bioplastic prepared by using first combination cassava starch+glycerol+water+acetic acid (A); cassava starch+glycerol+water+acetic acid+ethanol (B) and the images were magnified at 50000x

![Figure 3](image2.png)

**Figure 3.** The fingerprint of the bioplastics reacted from cassava starch+glycerol+water+acetic acid (red) and cassava starch+glycerol+water+acetic acid+ethanol (blue)

### 3.2 Functional Groups Analysis

The FTIR (fingerprint) is a characterization based on the vibrations of atoms or molecules by passing infrared radiation through a material or sample in which the energy corresponds to the wave frequency. The absorbance bands of the functional groups in the material are used to identify the substance properties. Figure 3 is the FTIR spectra of the bioplastics prepared by reacting ingredients cassava starch+glycerol+water+acetic acid (red) and cassava starch+glycerol+water+acetic acid+ethanol (blue).
Both fingerprints showed similar peaks and valley, but the transmittances or absorbances were significantly different. Generally, the transmittance of bioplastic derived from the second variation was higher compared to that of the first sample. It was indicative that the first substrate which was prepared from in which ethanol did not exist was a different structure with the second sample. It was also supported by SEM images and XRD spectra, as described in the next section.

The spectra showed that the wave absorbed profoundly in the range of 675-995 cm\(^{-1}\) and 2966.52 cm\(^{-1}\) positioned in the variety of 2850 - 2970 cm\(^{-1}\) belonged to the C-H alkene groups. According to work conducted by [13] showed the C-C, C-O, C-O (ester), and C-O-H (carbonic acid) bonds appeared at energy bands between 800 and 1300 cm\(^{-1}\) which was relatively comparable with present spectra in the range of 1050 - 1300 cm\(^{-1}\). The absorbance whose wavelengths were of 1000 - 300 cm\(^{-1}\) were typical of the C-O (ester group), which was an indication of the ability to decompose. The bonds also are hydrophilic groups whereby water can cause microorganisms entering the bioplastic matrix for decomposing [14].

3.3 Crystallinity

The XRD was employed to investigate the crystalline structures and particle size of samples. Fig. 4 is the XRD spectra of bioplastics grown from combining of cassava starch+glycerol+water+acetic acid (red) and cassava starch+glycerol+water+acetic acid+ethanol (blue). The XRD patterns of each sample, as shown, are the characteristics of bioplastic and have peaks, which are known as a crystalline region [15].

The vivid peak of the first combination was at 22.30° and shifted slightly to 22.27° of the second variation in which ethanol was added. Meanwhile, the valley of both samples was located at 12.5°. The present result has a similarity to the previous study about lignocellulose crystallinity, as published by researchers [16].

Table 1 presents the crystallinity values of substrates grown from cassava starch + glycerol + water + acetic acid (Bioplastic 1) and cassava starch + glycerol + water + acetic acid + ethanol (Bioplastic 2). Based on the results obtained, that crystallinity of the bioplastic employing Eq. (1) was of 0.67, which was higher than that of the second bioplastic observed at 0.63. Even though the surface morphology of the second bioplastic characterized by SEM was smoother than the first substrate, its crystallinity was less compared to that of the first bioplastic as resulted. For the second bioplastic was more amorphous than the first one, so it is better to be decomposed.

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Figure 4. The XRD spectra of bioplastics obtained from reacting of cassava starch+glycerol+water+acetic acid (red) and cassava starch+glycerol+water+acetic acid+ethanol (blue)
Figure 5. The TGA diagram of the bioplastic derived from cassava starch+glycerol+water+acetic acid (A) and cassava starch+glycerol+water+acetic acid+ethanol (B)
Table 1. The crystallinity values of bioplastics prepared from cassava starch + glycerol + water + acetic acid (Bioplastic 1) and cassava starch + glycerol + water + acetic acid + ethanol (Bioplastic 2)

| Substrate       | Crystal intensity (Cs) | Amorphous intensity (Cs) | Crystallinity |
|-----------------|------------------------|--------------------------|---------------|
| Bioplastic 1    | 134                    | 67                       | 0.67          |
| Bioplastic 2    | 182                    | 108                      | 0.63          |

3.4 Thermo Gravimeter Analysis (TGA)

To investigate the thermal property of bioplastic concerning temperature was measured by employing the methods *Thermo Gravimeter Analysis* (TGA) and *Differential Scanning Calorimetric* (DSC).

This work analyzed the change of weight of both substrates due to the influence of temperature on the material [17]. The 10 mg each sample was heated in a temperature range from 27 °C to 190 °C at a rate of 10 °C / min, as presented in Figures 5a and 5b.

When the heat was supplied into the bioplastic, the temperature increased as time inclined. It was discovered that the weight of bioplastic decreased as the temperature went up, which was comparable to the investigation of the authors.

The first substrate occurred the thermal decomposition at 27.49 - 122.44 °C, and the mass decreased by around 19.71%, which was similar to 2.11 mg. Meanwhile, the mass decline of the second sample with the range of temperature 27.67 - 173.98 °C was 21.51%, which was of 2.32 mg. These results were comparable to those that were obtained from XRD in which the second bioplastic was more amorphous than the first one.

3.5 Differential Scanning Calorimetric (DSC)

The DSC method is at analyzing the caloric value required entering the material as temperature inclines. Figure 5 shows the DSC diagram of the bioplastic derived from cassava starch + glycerol + water + acetic acid (A) and cassava starch + glycerol + water + acetic acid + ethanol (B). The diagrams give information about critical temperatures. Both diagrams presented that the bioplastics prepared were semicrystalline forms since many peaks were appearing do the glass transition was difficult to be determined. The glass transitions (Tg) the first- and the second substrate could be relatively similar at 62 °C. The second diagram representing the second sample displays more amorphous compared to the first one, whereby it is comparable with the XRD spectra. The temperatures which are points to valleys and peaks correlate to the crystallization and melting points of the material. The diagrams showed that the first bioplastic was decomposed with temperatures which are higher than 185 °C, while the second was destroyed above 195 °C. The first material showed the melting point was at 175 °C; meanwhile, the second sample was at 180 °C, respectively.

The samples, as shown in the diagram, were occurred multiple phase transformations in which it could be seen from peaks and valleys formed. The least valley gave information about crystallization, while the peaks showed that the material transformed from solid to liquid and finally was destroyed at high temperatures. The findings verified the investigations on the bioplastics, as reported previously [18-22]. The present work is an alternative technique to improve the quality of bioplastics. It is crucial to change the synthetic plastics which have been utilized by people for a hundred years. It is possible since the raw material; cassava can be planted in most tropical countries. The urgent action now is to overcome the damage of the environment because of plastics, especially oceans. Much big fish had been found dead whose bellies contain plastics. The most problematic to develop bioplastic is the price of cassava, which is higher than fossil oils, and the properties of bioplastics are not fulfilling the requirements of a daily application for people.
Figure 6. The DSC diagram of the bioplastic derived from cassava starch+glycerol+water+acetic acid (A) and cassava starch+glycerol+water+acetic acid+ethanol (B)
4. Conclusion

The bioplastics which were prepared from a combination of cassava starch+glycerol+water+acetic acid and cassava starch+glycerol+water+acetic acid+ethanol were synthesized successfully. The SEM images showed that the surface morphology of the second bioplastic was smoother than that of the first one. The XRD presented that the bioplastic employing the second combination was more amorphous in which TGA and DSC measurements supported the claim. The Cr value of the first sample was 0.66, while the second was recorded at 0.63. The biodegradable material was established since the existence of the functional ester, which was easily trimmed by micro-organisms. The bioplastic obtained was semi-crystalline structure and was occurred multiple phase changes.

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