Characteristics of bioplastic made from modified cassava starch with addition of polyvinyl alcohol

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Abstract. Food packaging plastic from petroleum-based sources can be a problem to the environment due to its non-biodegradability. The development of bioplastic from modified cassava-starch will be an alternative to overcome that problem. Since starch-based bioplastic usually has low mechanical strength and damage if exposed to water, it’s modification with polyvinyl alcohol (PVA) and citric acid is necessary. Bioplastics are made by heating a solution of modified cassava starch at 75 °C for 1 hour. After starch solution was gelatinized, glycerol (5% based on starch weight) was added, and then PVA solution (25, 50, 100% based on starch weight) was inserted gradually. While stirring was continued, citric acid (5% based on starch weight) was added into the solution. The bioplastic solution was then poured into a 20 x 20 cm acrylic sheet and cooled at room temperature for 3 days, so that the bioplastic sheet was ready for mechanical strength test (ASTM D 882-75b Tensile Properties of Thin Plastic Sheeting) and for thermal properties test with Thermo Gravimetric Analyzer. The results suggested that the addition of 25% polyvinyl alcohol (PVA) into bioplastic made from modified cassava starch produced bioplastic with higher tensile strength compare to that without PVA addition. On the other hand, the addition of 100% PVA could slightly increase bioplastic elongation. The decomposition temperature of bioplastic made from modified cassava starch with 50% PVA was higher than that of the bioplastic without PVA addition, indicated that bioplastic with 50% PVA was more thermally stable.

1. Introduction

Petroleum-based plastic is difficult to degrade naturally, thus it will produce carbon emissions when burned after usage and to cause environmental pollution. The development of bioplastics made from renewable bio-based materials such as starch, cellulose, collagen, or casein have been carried out to produce bioplastics that are easily decomposed naturally after their use. At first, starch-based bioplastics were originally developed by adding starch in polyethylene to improve its biodegradability. However, this type of starch-based bioplastic still has weakness, i.e., the reducing of mechanical properties along with the increasing starch content.

The main components of starch granules are amylose (20% to 25%), amylopectin (70% to 85%), and other materials such as protein and fat (5% to 10%). Amylose is a straight-chain glucose polymer that binds to α-1,4, while amylopectin is a branched glucose chain consisting of short-chain α-1,4 which binds to β-1,6. Amylose is easier to form entanglement when starch is heated, compared to amylopectin. The linear amylose molecules are said to form more effective entanglements than the highly branched amylopectin molecules that resulting in a better performance, such as an increase in
tensile strength [1]. The tensile properties of the bioplastics would rise when the amylose content was increased [2]. Therefore, the production of bioplastic using high amylose content will be beneficial. Starch modification to convert amylopectin to amylose was conducted as one way to make optimal use of starch.

So far, starch-based bioplastics utilize cassava starch as raw material. Moreover, bioplastics from cassava starch have been produced commercially. The disadvantages of starch-based bioplastics are low water stability, high moisture sensitivity, brittle behavior at room temperature [3]. Efforts to improve the properties of starch-based bioplastics include the addition of additives and/or fillers.

Polyvinyl alcohol (PVA) is a biodegradable synthetic material which has hydroxyl groups (-OH) in its structure, so that it can form the intermolecular and intramolecular hydrogen bonds with thermoplastic starch, thereby increasing the integrity of the mixture [4]. PVA has the advantages of good film forming, strong conglutination, and high thermal stability, therefore it has been widely used in the materials industry [5-7]. PVA is also widely used in packaging industry because it is tasteless, odorless, nontoxic, dissolvable in water, and resistant to oil and fat.

As a multi-functional food additive, CA is utilized in the processes of producing different foods due to its antibacterial and acidulant effect, and also can strengthen the antioxidant action of other substances, and improves the flavors of juices, soft drinks, and syrups. Yu et al. [8] reported that the water-resistant and thermal stability properties of citric acid (CA) modified thermoplastic starch (TPS) resins were significantly better than those of TPS resins. In which, CA modified TPS resins were prepared by blending proper amounts of CA with cornstarch, glycerol and water using a single-screw extruder.

The purpose of this current research is to improve mechanical properties of modified cassava starch bioplastic by addition of polyvinyl alcohol and citric acid. The manufacturing method was carried out in the order of cassava starch modification, the preparation of starch-based polymer solution with the addition of plasticizer glycerol, polyvinyl alcohol and citric acid, film casting to produce sheet of bioplastics. Tensile strength and thermal properties of bioplastics were analyzed to explain the effect of addition polyvinyl alcohol into starch-based polymer.

2. Materials and methods

2.1. Materials

The materials used in this study were cassava starch, sodium acetate technical grade obtained from PT Trijaya (Bandung, Indonesia), acetic acid glacial obtained from Merck (Merck KGaA, Germany) and distilled water. Glycerol and polyvinyl alcohol were used at technical grade without further purification. Anhydrous citric acid for synthesis was obtained from Merck (Merck KGaA, Germany).

2.2. Modification of cassava starch

Modification of cassava starch was carried out using acetate solution (CH₃COOH + CH₃COONa) at pH 7. Preparation of acetate solution was carried out by dissolving as much as 44.52 g sodium acetate in 50 ml of distilled water. After sodium acetate dissolved, acetic acid was added into the solution, gradually until it reaches pH 7. Distilled water was added into the solution until the volume reached 1 l. The modification of cassava starch was carried out by dissolving 100 g cassava starch into 200 ml acetate buffer solution in a beaker glass, then the mixture was stirred and heated on a hot plate stirrer at a temperature of 40 °C to thicken, after which it is dried at room temperature. After drying, the modified starch was mashed and sieved at 80 mesh.

2.3. Production of bioplastic from modified cassava starch combined with polyvinyl alcohol and citric acid

The modified cassava starch was dissolved in distilled water with a ratio of 1: 20. As much as 2.5 g of starch was dissolved with 50 ml of distilled water into a beaker glass. The solution was heated on a water bath at 75°C for 1 hour. The solution was stirred at a constant speed of a mechanical stirrer 200 rpm, until it’s shaped was like a clear gel. At the same time, in a separate beaker glass, polyvinyl alcohol was dissolved in 50 ml distilled water using a hot-plate magnetic stirrer. The amount of PVA
was 0.625 g, 1.25 g and 2.5 g (25%, 50% and 100% of starch dry weight). After the starch solution was gelatinized, glycerol plasticizer (0.3% of the dry weight of starch) was added, followed by dissolved polyvinyl alcohol and continued stirring for 10 min. Finally, citric acid (5% of the dry weight of starch) which dissolved in 5 ml distilled water was added into the solution. The mixture was stirred again until homogeneous for ± 15 minutes at the same speed and temperature.

The mixture solution was then poured into a mold (flexi glass) with a dimension of 20 x 20 cm and a thickness of ± 5mm. Spread the mixture solution evenly on the surface of flexy glass. The solution was then air-dried at room temperature for ± 3 days, until it formed film sheets (bioplastic). The bioplastic was removed from the mold using tweezers and the film was ready to be characterized.

2.4. Analysis of bioplastic characteristic

2.4.1. Evaluation of bioplastic mechanical properties. Tensile strength test was carried-out in accordance with ASTM-882-75b “Tensile Properties of Thin Plastics Sheeting”. The Samples were cut in sizes of 2 x 10 cm. Tensile strength was measured with Universal Testing Machine (UTM) Shimadzu Autograph 50kN (Shimadzu Corp., Japan), the speed testing was 1 mm/min. The test results will be read after sampling. This test was carried out 4 times.

2.4.2. Evaluations of bioplastic thermal properties. The thermal properties test was performed using the Thermogravimetric Analyzer (TGA) 4000 Perkin Elmer (PerkinElmer Inc., USA). A 8 mg bioplastic was placed on a ceramic crucible. The test was carried out by heating the sample at a temperature of 25-500°C with a heating speed of 10°C / min.

3. Results and discussion

3.1. Bioplastic mechanical properties

Modified cassava starch powder (Figure 1a) with water content of 11.16% and solubility in water of 21.38% was used to produced bioplastic (Figure 1b). The effect of the addition of polyvinyl alcohol (PVA) in modified cassava (mocaf) starch on bioplastic tensile strength is presented on Figure 2 as follows.

![Figure 1. The modified cassava starch (a), the bioplastic of the modified cassava starch (b).](image)

Bioplastic film with the addition of 25% PVA presented the highest tensile strength value than other modified cassava flour (mocaf) bioplastic film. Bioplastic with addition of 50% and 100% PVA show lower tensile strength when compared to bioplastic without addition of PVA. Bioplastic tensile strength analysis showed that the bioplastic with the addition of 25% PVA was the best tensile strength value (13.03 N/mm²). The tensile strength was improved almost 10 times compare to that without the addition of PVA.

On the other hand, bioplastic elongation showed that the addition of 100% PVA produced mocaf bioplastic with the highest value, which was 6.07 % compare to those with no addition of PVA or with the addition of 25% and 50% PVA, which were 0.77%, 2.26%, 3.43%, respectively.
Mocaf bioplastic (M0) was brittle (low tensile strength and low elongation) as presented on Figure 2. The addition of PVA could improve the mechanical properties of mocaf bioplastic. Ismail and Zaaba [9] reported that the remarkable increase in the tensile strength of the blend films indicated the presence of intermolecular interactions of the components by way of hydrogen bond formation, which strengthened the bonding of the PVA with sago starch. In our current study, the addition of PVA with ratio of starch: PVA = 1:0.25 was produce the highest bioplastic with the highest tensile strength. However, when PVA was added with the ratio of 50% or 100% from starch weight, the bioplastic tensile strength was decreased. The reduction in the tensile strength was because mocaf tended to agglomerate when addition of PVA was 50% or exceed, which caused poor dispersion of PVA in the mocaf matrix.

![Figure 2. The tensile strength and elongation of mocaf bioplastic with varied addition of polyvinyl alcohol: 25% (M1), 50% (M2) and 100% (M3) of the dry weight of mocaf.](image)

The interesting result of our present study was the bioplastic elongation tended to increase along with the increasing of PVA addition. Modified cassava starch produced very brittle bioplastic (tensile strength of 1.35 N/mm² and elongation of 0.77%). Although the addition of 100% PVA could improve bioplastic elongation to be 6.07%, the elongation value was far below that of blend sago starch and PVA bioplastic [9]; or modified cassava starch and PVA bioplastic [10], in the same portion which were 151%, 37%, respectively. Guimaraes et al. [10] also reported that modified cassava starch biofilm was 2.7%. The low value of bioplastic elongation at break, was because mocaf and PVA showed partial compatibility. According to Lawton [11], the amount of amylose present on starch interferes on the compatibility of this polysaccharide with PVA during the formation of blends. Meanwhile, the high concentration of PVA in relation to starch makes the system more stable and compatible, thus it improves the bioplastic elongation at break.

3.2. Bioplastic thermal properties

Thermal degradation testing was carried out by Thermo Gravimetric Analyzer (TGA) which aimed to determine the change in mass of the bioplastic on temperature rise. This test could also provide information on the results of thermal decomposition of the bioplastics produced in this study. The TGA curve showed the changes in the mass of mocaf bioplastic with the addition of PVA (Figure 3 and Figure 4) to the temperature increment.

Based on the TGA curve on Figure 3, the mass loss after heating of mocaf bioplastic (MSO) and mocaf bioplastics with the addition of 5% citric acid (MS) showed no significant difference. By the addition of 50% PVA (M2), the mass loss of bioplastic after heating over 450° was lower compare to that with the addition of 5% citric acid only (MS).
Figure 3. The TGA thermogram of the bioplastic made from modified cassava starch only (MSO), with the addition of 5% citric acid (MS), 5% citric acid and 50% polyvinyl alcohol (M2).

The same trend was shown by mocaf bioplastic on Figure 4. Mocaf bioplastics with the addition of 50% PVA (M2) presented lower decrease in mass due to heating compared to that without the addition of PVA (M0). This result showed that the bioplastics with the addition of PVA had better resistance to the heat compared to those without the addition of PVA.

Figure 4. The DTG thermogram of the bioplastic made from modified cassava starch only (MSO), with the addition of 5% citric acid (MS), 5% citric acid and 50% polyvinyl alcohol (M2).

Liu et al [12] analyzed the waxy starch thermal decomposition with TGA. They found that there are two major weight loss steps. The first one is the evaporation or hydration that starts when the temperature increases and ends at around 110°C. The second weight loss step relates to thermal decomposition of starch at around 320°C. Generally, starch thermal decomposition mechanism can be separated into three stages. The first stage is physical dehydration, which depend on absorbed and abounded water in starch. The second stage is chemical dehydration and thermal decomposition, which start at around 300°C with the condensation of starch hydroxyl groups to form ether segments and release water molecules and other small molecular species. The last stage of carbonization reactions is occurred at temperature above 500°C [13, 14].
Based on the TGA data presented in Table 1, the initial thermal decomposition of mocaf bioplastic was occurred at 89.38°C, and at 93.48°C for that with the addition of 50% PVA. The temperature decomposition of mocaf bioplastic with the addition of 50% PVA (M2) when 50% degraded was higher (333.71°C), compare to that of mocaf bioplastic without PVA addition (M0), which was 323.31 °C. Thus, mocaf bioplastics with the addition of 50% PVA (M2) showed better thermal resistance compared to those without PVA addition (M0).

Table 1. Thermal properties of mocaf bioplastic.

| Bioplastic | T_onset (°C) | T_max (°C) | T_end (°C) | T5 (°C) | T50(°C) | Char residue at 450 °C (% weight loss) |
|------------|-------------|------------|------------|---------|---------|--------------------------------------|
| M0         | 276.72      | 316.17     | 351.11     | 89.38   | 323.31  | 24.12                                 |
| M2         | 277.43      | 312.50     | 363.94     | 93.48   | 333.71  | 23.01                                 |

Mocaf bioplastic without and with the addition of PVA, the curing temperatures were 78.75 °C and 80.78 °C, respectively. An increase in curing temperature indicated that the gelatinization temperature can be reached at a higher point. Thus, the energy needed for gel formation from mocaf starch with the addition of PVA in the process of making bioplastics was higher, compared to that without PVA addition.

4. Conclusion
The addition of 25% polyvinyl alcohol (PVA) into bioplastic made from modified cassava starch produced bioplastic with higher tensile strength compare to that without PVA addition. On the other hand, addition of 100% PVA, could slightly increase bioplastic elongation. The decomposition temperature of bioplastic made from modified cassava starch with the addition of 50% PVA was higher than of that without PVA addition, indicated that it was more thermally stable.

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