Properties of cassava starch-based bioplastics and CMC with sorbitol as a plasticizer

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Abstract. This research aims to synthesize and characterize the properties of starch and starch/CMC-based bioplastics and to know the effect of sorbitol concentration on bioplastics produced. Characterization the bioplastics used SEM, FTIR and XRD as well as thickness, tensile strength, elongation at break, and resistant to water and acid. The result showed that synthesis of starch and starch-bioplastic success and the surface of bioplastics is uniform, except bioplastic from pure starch. Starch/CMC-based bioplastics is thinner (106.67 ± 5.13 μm), lower tensile strength (8.95 N), more easily degraded by water (33 hours) and acid (15 hours) but highest elongation at breaks (48.15%) than starch-based bioplastics. Sorbitol concentration is proportional to the level of elongation at break and the optimum concentration which added to starch-based bioplastic is 15 mL/20g starch.

1. Introduction

Plastic is a powerful material because it’s lightweight, highly malleable, water resistant, can be molded easily, and resistant to the kind of chemical reaction. Production of plastics was reached 8300 million ton in 2015 however 55% of its was thrown [1]. Besides it is non biodegradable material which is caused negative impact to environment [2, 3]. Therefore research of bioplastics to replace conventional material increase.

Cassava starch is one of the potential biopolymers that can be material raw to produce bioplastics. This is non-toxic, eco-friendly, abundant renewable sources, and low cost. Starch-based bioplastics is transparent, colorless, tasteless, and odorless [4-6]. But the similar study also reported that bioplastics from starch are brittle, rigid, and fragile [7]. So, it was solved by addition plasticizer and carboxymethyl cellulose.

Plasticizers commonly used are glycerol and sorbitol [8-10]. However Li & Huneault [11] suggested that the addition of sorbitol made PLA matrices were greater at tensile strength and modulus Young than glycerol. Besides sorbitol are non toxic, non volatile, degraded easily, easy to found, and food grade. Then the addition of CMC is helpful to improve the film flexibility and gas barrier properties [12]. Owing to it is good film-forming ability, biodegradability, and non-toxicity. The concentration of plasticizers and CMC is affecting to the bioplastics properties [13].

This research aims to synthesize and characterize the properties of starch and starch/CMC-based bioplastics and to know the effect of sorbitol concentration on the properties of bioplastics. The starch prepared from Cassava variety ADIRA-1. Bioplastics were characterized by using SEM, FTIR, and XRD also analyzed the bioplastic resistant to water and acid, thickness, tensile strength, and elongation at break.
2. Methods

2.1. Materials
Cassava was used ADIRA-1 species from Probolinggo, Indonesia. Carboxymethyl cellulose (CMC) food grade as an additive, sulfuric acid 98%, and deionized water was purchased from Duta Jaya (Malang, Indonesia). Sorbitol as a plasticizer and NaOH by Sigma was kindly provided by SIP (Malang Indonesia).

2.2. Extraction starch from ADIRA-1 cassava
The detail procedure of extraction starch from ADIRA-1 cassava using traditional method. 3000 g cassava was washed with water. After that, cassava was grated then added 2000 mL water. The mixture filtered and the remaining solid mass was put into basin. The step repeated seven times to get more starch. The mixture contains starch and water was allowed to settle for 10 min then filtered it. Afterwards the starch added with 1000 L water and this step repeated many times until the colour of the blends change from yellow to white. The starch was separated from the water and continue to dried in the sun until the weight constant.

2.3. Production of bioplastics
Production of bioplastics was modified from Bergo et al [14]. Starch-based bioplastics were prepared with 20g/200mL of deionized water and sorbitol with variation volume 0, 5, 10, 15, and 20 mL. To obtain starch/CMC bioplastic, CMC with variation mass 4, 12, and 20g diluted with 800mL of deionized water at 50°C. Then, CMC was mixed with 20g starch and 5mL sorbitol. The all mixtures were stirred using hotplate stirrer at 70°C until gelatinization. The gel was poured in an acrylic plate 21 x 25 x 0.2 cm\(^3\) and were dehydrated in an oven at 70°C/18-24 h.

2.4. Characterization

2.4.1. Bioplastics morphology. Morphology of bioplastics were determined using a SHIMADZU scanning electron microscope (SEM) with acceleration voltage 20.00 kV, magnification 10000x, and WD 9.9 mm.

2.4.2. FTIR. Absorbance spectrum of the starch-based bioplastics and CMC with sorbitol were recorded on Shimadzu Fourier Transform Infrared (FTIR). The spectra were obtained at band 500 – 4000 cm\(^{-1}\).

2.4.3. XRD. Bioplastics were submitted to x-ray diffraction using Cu Kα radiation wavelength (λ\(_1\)=1.54060 Å, λ\(_2\)=1.54443Å) and diffractometer system XPERT-PRO. Scattered radiation was detected in the angular range 10-90° (2θ) and scan step time 0.7 s.

2.4.4. Mechanical properties. The uniaxial thickness, tensil strength, and elongation at breaks were determined using IMADA tension testing with maximum force 5 Newton and minimum force 50 Newton. Samples were cut into a dumbbell shape with width 1 cm and distance grip separation of 6 cm. The sample were calculated at temperature room.

2.4.5. Bioplastics resistant to water, acid, and base. Procedure was modified from Mostafa et al [15]. Test of bioplastics resistant to water, acid, and base were prepared with 1 g bioplastics was poured onto beaker glass 500 mL consists 400 mL water, beaker glass 250 mL consists 70 mL sulfuric acid 20% (v/v), and beaker glass 250mL consists 70 mL sodium hydroxide 20%. Then it was covered with wrap plastic and write the times when bioplastics fully degraded. The steps repeatedly three times.
3. Results and discussions

3.1. General appearance of starch-based bioplastics and CMC with sorbitol

Figure 1 shows the photograph of bioplastics produced. The surface of bioplastics almost uniform, but bioplastic from pure starch (CS20) has cracks and granules as well as starch-based bioplastics with addition 10 mL sorbitol (CS20/SOR10) has bubbles. Granules and bubbles could be formed as consequent from the starch not gelatinization completely. So the optimum times and temperature to mixed the compound is really important to obtain bioplastics with the smooth and uniform surface. The visualization of bioplastics photograph is depicted in Table 1.

![Figure 1. Photograph of bioplastics with variation a)CS20, b)CS20/SOR5, c)CS20/SOR10, d)CS20/SOR15, d) CS20/SOR20, e)CS20/CMC4/SOR5, f)CS20/CMC12/SOR5, g)CS20/CMC20/SOR5](image)

(CS20) is brittle, fragile, rigid, surface cracks, and difficult to peel could be attributed to the strong inter/intra molecular hydrogen bond of starch so the mobility of molecular chains is less. Based on the Tabel 1, bioplastics prepared with 5 mL sorbitol (CS20/SOR5) is more flexible than CS20, peelable, an no granules. The addition of sorbitol improve the properties of bioplastics. Sorbitol formed hydrogen bond with starch thereby reduced the interaction stress to intensify the mobility of molecular chains. It can be assumed that sorbitol is relatively easier to interpose itself within the intra/intermolecular spaces of the starch because of its smaller molecular weight. Also the strong bond between starch and sorbitol reduced the cohesive tension of the starch molecule, thus the bioplastics easy to peel. However transparency bioplastics were decreased whereas the concentration of sorbitol were increased. The optimum sorbitol concentration for 20g starch is 15 mL, because appearance of CS20/SOR20 is oily. It was attributed that CS20SOR20 produced sorbitol excess.

CMC has similar structure with starch, thus CMC and starch formed strong hydrogen bond and other intramolecular. Beside that CMC can change starch’s three dimensional molecule structure. So it reduced rigidity of starch-based-bioplastics.
Table 1. Appearance of starch-based bioplastics and CMC with sorbitol

| Sample          | Sorbitol volume (mL) | CMC mass (g) | Appearance of bioplastics                           |
|-----------------|----------------------|--------------|-----------------------------------------------------|
| a               | CS20                 | 0            | More transparent than b-d, brittle and fragile,      |
|                 |                      |              | granulate, surface cracks, rigid, and difficult to   |
|                 |                      |              | peel                                                |
| b               | CS20/SOR5            | 5            | More transparent than c-d, flexible, surface        |
|                 |                      |              | uniform, and peelable                               |
| c               | CS20/SOR10           | 10           | More transparent than d, flexible, bubbles exist,    |
|                 |                      |              | and peelable                                        |
| d               | CS20/SOR15           | 15           | Less transparent than a-c, flexible, sticky, peelable|
|                 |                      |              |                                                     |
| e               | CS20/SOR20           | 20           | Less transparent than a-c, flexible, stickier, oily,|
|                 |                      |              | peelable                                            |
| f               | CS20/CMC4/SOR5       | 5            | Transparent, thin, sticky and flexible than a-d,     |
|                 |                      | 5            | and peelable                                        |
| g               | CS20/CMC12/SOR5      | 5            | Transparent, sticky, thinner and more flexible than  |
|                 |                      | 10           | e, and peelable                                     |
| h               | CS20/CMC20/SOR5      | 5            | Transparent, sticky, thinner and more flexible than  |
|                 |                      | 15           | f, and difficult to peel                             |

3.2. Morphology of bioplastics

Morphology of all bioplastic shows in Figure 2 at magnification of 10000x. Surface feature of pure starch bioplastic (Figure 2a) consist of granules, which means that the starch not fully gelatinized during the formation process. Their general appearance is similar to that previously mentioned by López et al[16]. Jaimes et al. also reported in their study that SEM image depicted insoluble remnants because of starch granule swelling [17]. Besides, there are fracture surface areas that will be influence the mechanical properties of it. Few cracks propagation indicates poor bonding between the components. The addition of sorbitol only as a plasticizer helping in solubizing granule starch completely and then presenting a homogeneous surface without cracks (Figure 2b). Bioplastic with addition CMC have a uniform surface. This occured because CMC undergo crosslinking and formed network structure with starch[18]. It’s concluded that starch compatible with CMC and sorbitol.

![Figure 2](image-url) SEM photograph of starch bioplastics (a) pure starch, (b) with sorbitol, (c) with sorbitol and CMC

3.3. FTIR

Spectrum of bioplastics used to investigate the interaction between starch, sorbitol, and CMC. Bioplastics from pure starch have broad band at 3649 and 3500 cm\(^{-1}\) which described hydrogen bond from the interaction O-H groups starch-water and between starch molecules (Figure 3). Similar peaks were reported by Vercino and Gracia [19]. Addition of sorbitol and CMC decrease the band of O-H stretching vibration. It is indicating that hydrogen bond were formed between starch and sorbitol or starch, sorbitol, and CMC as a consequence the distance O-H bond between starch molecules even
further. Besides that, the peak frequency of C-H bond stretching is also decrease because of Van der Waals bond between the components. The result presents that starch, sorbitol, and CMC is compatible as a matriks. Then, the lower of the peak frequency signify the stronger interaction intramolecule [20, 21].

![Figure 3. Spectrum of bioplastics](image)

3.4. X-ray diffraction

Figure 4 inform that the XRD pattern of all bioplastics is similar. As observed, the peaks of bioplastic from pure starch show a large amorphous area and crystalline peaks. Amorphous area is location at 2θ 15 - 20° and the crystalline peaks at 26.3667°. The peaks of starch-based bioplastic with addition sorbitol and also sorbitol and CMC only have amorphous area. The intensity of amorphous area at XRD pattern of starch-based bioplastics with sorbitol higher than bioplastic from pure starch. Simmiliar observation was made by Garcia et al [22], who suggested that intensity of diffraction peaks increased as glycerol concentration from 0 to 45%. Sorbitol and CMC change three-dimensional organization molecular and reducing the energy needed for molecular motion and hydrogen bonds between chains of starch as a result of increased molecular mobility and decreased degree of crystallinity [23].

![Figure 4. XRD patterns of cassava starch-based bioplastic](image)

3.5. Mechanical properties

Tabel 2 ilustrated the influence of sorbitol and CMC concentration on thickness, elongation at breaks, and tensile strength of bioplastics. The elongation at breaks was increased when sorbitol and CMC concentration increased. Elongation at breaks inverse with tensile strength. This probably occured because sorbitol and CMC reduced inter/intra molecular hydrogen bond in starch chains, as a results the molecular mobility was increased and the matrices more flexible [24].
### Table 2. Mechanical properties of starch-based bioplastics

| Bioplastics       | Thickness (μm) | Elongation at breaks (%) | Tensile Strength (N) |
|-------------------|----------------|--------------------------|----------------------|
| CS20/SOR5         | 319.33 ± 32.62 | 21.05                    | 18.37                |
| CS20/SOR10        | 394.33 ± 3.060 | 4.170                    | 47.87                |
| CS20/SOR15        | 393.33 ± 23.54 | 43.75                    | 13.95                |
| CS20/SOR20        | 373.00 ± 41.62 | 26.09                    | 7.29                 |
| CS20/CMC4/SOR5    | 276.00 ± 31.32 | 16.67                    | 58.14                |
| CS20/CMC12/SOR5   | 180.67 ± 10.07 | 16.50                    | 58.80                |
| CS20/CMC20/SOR5   | 106.67 ± 5.13  | 48.15                    | 8.95                 |

3.6. Resistant of bioplastics.

Bioplastics resistant in water and acid liquid are essential properties that must be analyzed. Figure 5 attribute that sorbitol and CMC rapidly the time degradation of bioplastics. Choi et al. also reported that the addition of CMC in apple skin particle maticks was increased water solubility [25]. Due to the hydrophilic of sorbitol and CMC, they weakening the hydrogen bond between the components and increasing the free spaces in molecule chains as a consequences increasing the solubility of bioplastics.

![Figure 5. Water resistant of bioplastic with variation concentration of a)sorbitol, b)CMC](image)

The bioplastics degraded rapidly by sulfuric acid than water. Starch is polymeric carbohydrate consisting of numerous glucose units joined by glicosidic bonds. Sulfuric acid caused acid hydrolysis of starch. The acid works on the starch granule surface prior to entering the inner region starch. Proton from acid attacks oxygen from glycosidic bond which connected the two glucose units. C-O bonds and conjugate acid from cyclic carbonium ion broken down into free sugars and unstable carbonyl groups. Carbonium from carbonyl groups was interacted with water molecule produced glucose and proton. Based on Figure 6 the time of bioplastics to degraded was increased when the sorbitol and CMC concentration was increased too because sorbitol and CMC prevent interaction between proton from acid with starch molecules.

![Figure 6. Acid resistant of bioplastic with variation concentration of a)sorbitol, b)CMC](image)
4. Conclusion
Starch/CMC-based bioplastic have better mechanical properties and biodegradibility than starch-based bioplastics. The sorbitol addition improves the properties of starch-based bioplastics.

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