Characterization of bioplastic based from cassava crisp home industrial waste incorporated with chitosan and liquid smoke

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Abstract. Cassava peel (Manihot utilissima) is waste of agricultural result that is much potential as raw material of bioplastic making. This research focuses on bioplastic making from cassava peel. It aims to characterize the resulted bioplastic (mechanical and physical properties, SEM analysis, FTIR analysis and time test of bioplastic degradation). The bioplastic preparation takes place by mixing starch of cassava peel and chitosan (20, 30, 40 and 50% w/w), glycerol 30% w/w as plasticizer, and liquid smoke (0, 1 and 2 mL) as antimicrobial agent. The research result shows the highest value of tensile strength is 96.04 MPa, the highest elongation at break is 52.27%, and the value of water-resistant test is 22.68%. Morphology analysis by using SEM shows uneven surface and there is fracture in its cross-section. The analysis of functional group by FTIR shows the presence of functional groups of O–H (hydroxyl), N–H (amine), dan CH3–O (ether). The fastest complete degradation of bioplastic occurs in 45 days, and the longest occurs in 57 days.

1. Introduction
The usage of plastic as packaging keeps increasing, so that it could cause plastic waste accumulation. The waste has impact on environmental pollution because it is hard to degraded by microorganism [1]. Various industrial sectors produces synthetic packaging plastic about 100 million tons/year. They produce plastic waste about as much as that amount every year. Meanwhile the need of packaging plastic achieves 2.3 million tons/year [2]. Therefore, development of biodegradable plastic technology is necessary, because biodegradable plastic can decompose faster than commercial plastic in the soil that can reduce a plastic waste.

Biodegradable plastic is plastic that could be degraded by degrading-microorganism activity. Biodegradable plastic has benefit that is the same as synthetic plastic or conventional plastic. It is bioplastic, namely plastic that all or almost all of its components are from renewable raw materials. They are environmentally friendly because of their properties that could be back to nature. Biodegradable packaging is packaging film that could be recycled and destroyed naturally [3]. Raw material often used in biodegradable plastic is tuber that has starch such as sweet potato and cassava [1].

Chitosan is another polymer that is the second most natural polymer occurring after fiber. It has interesting biological activities and biodegradable, non-toxic, excellent strength and elongation properties. Chitosan combined with cellulose increases the mechanical strength of paper board [4].

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advantageous properties cover hydrophilicity, bio-compatibility, degradability, and anti-bacteria. It is hydrophobic, water-resistant in its structure, forms gel spontaneously and membrane or film easily [5]. Liquid smoke is liquid that has anti-microbe property. Liquid smoke so far is useful as preservative because acid content contained inside is anti-microbe. Compounds of phenol and acetic acid could inhibit bacterial growth. Liquid smoke with such property could be additive in making biodegradable plastic [6].

Waste in the form of cassava peel from cassava-chip industry could be raw material of bioplastic. According to Badan Pusat Statistik (2016), cassava production in Indonesia in 2015 is 21.8 million tons/year [7]. Cassava peel has starch content of 4 – 59% [8]. Up to present, not many industries benefits cassava peel maximally. It is just thrown away so that it becomes waste that pollutes environment. Therefore, improvement of bioplastic from solid waste of cassava-chip industry needs to be further investigated.

2. Materials and Preparation

2.1. Materials

Materials used were cassava peel, distilled water, chitosan (20, 30, 40, and 50% w/w), glycerol PA (30% w/w) as plasticizer, acetic acid as chitosan solvent, sodium metabisulphyte, and liquid smoke (0, 1, and 2 mL) as anti-microbial agent. Equipments used were blender, oven, hot plate, magnetic stirrer, thermometer, desiccator, digital balance, and mirror plate.

2.2. Procedure

2.2.1. Extraction of Cassava Peel, Cassava peel of 100 grams was washed and soaked in sodium metabisulphyte 1% for 1 hour. The next process was separation process between cassava peel and sodium metabisulphyte. It was continued by crushing of cassava peel by blender, added 100 ml water to ease crushing. Slurry resulted was mixed by water with ratio of 1 : 1 to extract starch in cassava peel. After that it was filtered by using gauze and the result was called filtrate I. The extract was added with water at the same ratio and filtered so that filtrate II was obtained. The rest of the waste was thrown away. Filter results (filtrate of I and II) were precipitated for 3 hours. The starch precipitation was taken and the filtrate was thrown away. The starch precipitation was dried in oven at temperature of 70°C for 30 minutes [9]. Dried precipitate was refined by grinding and screened by gauze. The screening results in cassava starch that was ready used.

2.2.2. Bioplastic Making, Cassava-peel starch of 5 grams was put into Erlenmeyer I, and added by aquadest until 50 grams. It was stirred by magnetic stirrer for 25 minutes. Chitosan was put into Erlenmeyer II and dissolved with glacial acetic acid 1% (%v). Chitosans of 20, 30, 40, and 50% of starch solution mass was put into Erlenmeyer I. They were put in hot plate and heated at temperature of 70°C while stirred for 15 minutes. Glycerol was added 30% mass of starch solution, and various volumes of liquid smoke of 0, 1, and 2 mL. Furthermore, it was stirred back until homogeneous. Casting was carried out on glass plate of 0.02 mm thickness [10] to form thin sheet of bioplastic. Thin sheet (bioplastic) was removed from glass plate, kept in desiccator and ready for analysis.

2.3. Sample Characterization

2.3.1. Mechanical Properties, Tensile strength and elongation at break were determined with ASTM D 882-10 (Standard Test Method for Tensile Properties of Thin Plastic Sheeting). Tensile strength test measured the highest tensile stress attained by a sample during test. It also determined elongation of the sample at rupture, and expressed as percent of the gage length. Tensile strength and elongation at break used Equations of (1) and (2) [4].
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\[ Tensile\ strength\ (\sigma) = \frac{F}{A} \]  

(1)

\[ Elongation\ (\varepsilon) = \frac{L - L_0}{L_0} \]  

(2)

\( F \) is the highest tensile; \( A \) is the cross-section of the gage section; \( L_0 \) is the initial gage length; \( L \) is the final length.

2.3.2. Physical Properties (Water Resistance). Test of water resistance was carried out by cutting plastic film of 1 cm × 1 cm. Initial mass was weighed and put into measuring cup that contained distilled water in 10 seconds. Sample was lifted from measuring cup, removed from distilled water by tissue, after that just weighed. Sample was put back into measuring cup that contained distilled water for 10 seconds. Then sample was lifted from measuring cup and weighed back. Procedure of soaking and weighing was carried out back until final sample mass was constant. Test of water-resistant was calculated as the following Eq. (3) [11].

\[ Water\ Resistance\ (W') = \frac{W - W_0}{W_0} \times 100\% \]  

(3)

\( W_0 \) is the initial sample mass; \( W \) is the final sample mass.

2.3.3. Morphology Analysis by Using SEM (Scanning Electron Microscope). Analysis of sample morphology was in Geology Laboratory of Institut Teknologi Bandung. Sample was cut in size of 2 × 3 cm then it was adhered in holder. Sample was put into chamber of SEM equipment for setting place and recording picture. Photos of SEM taken were top and cross sections of film with magnitude of 5000 × [11].

2.3.4. Analysis of Functional Group by Using FTIR (Fourier Transform Infrared Spectroscopy). Functional group was analyzed in Chemistry Laboratory of Universitas Negeri Padang. It was done by Fourier Transform Infrared Spectroscopy PerkinElmer® (FTIR). Sample of film was placed into set holder, and then appropriate spectrum was searched. The result was in the form of diffractogram of relation between wave number and intensity. Spectrum of FTIR was recorded by using spectrometer at room temperature [12].

2.3.5. Test of Biodegradability on Environment. Biodegradability was tested by method of soil burial test by cutting plastic film in size of 3 × 3 cm. After that plastic was put in desiccator for 24 hours then it was weighed. Plastic burial used soil with soil depth of 5-cm. Sample checking took place once in every three days, followed by weighing and putting back in soil. Observation was carried out until sample was degraded completely in soil [13].

3. Result and Discussion

3.1. Mechanical Properties of Biodegradable Film

Tensile strength is the highest stress needed by a specimen to suppress force which given [5]. The highest tensile strength obtained is at chitosan of 30% without liquid smoke namely 96.04 MPa. The lowest strength is at chitosan of 40% without liquid smoke namely 35.28 MPa as in Figure 1. The high value of tensile strength indicates that film has strong structure and not easy to break. It is because
chitosan could form inter-molecular hydrogen bond that makes bioplastic denser, strong, and hard to break [11].

Figure 1. The effect of chitosan on tensile strength of bioplastic at various liquid smoke.

Figure 2. The effect of chitosan on elongation of bioplastic at various liquid smoke.

Elongation means the residual relative change in length compared with the starting length after the break of the test piece in a tensile test [14]. The highest elongation obtained is at chitosan of 30% with liquid smoke volume of 2 mL namely 52.27%. The lowest is 14.87% at chitosan of 40% without liquid smoke as indicated in Figure 2. The lowest elongation value indicates that film’s structure is not plastic (stiff) and hard to stretch. Strong interaction between starch and chitosan makes molecule bond denser and strong. Therefore, film is hard to stretch or elongate [11].

3.2. Physical Properties (Water Resistance of Biodegradable Film)
Water resistance of the cassava starch-based film increases as chitosan concentration increases (Fig. 3). Hydrophobic chitosan property and the film that could not be in water cause it [3].

Figure 3. The effect of chitosan on swelling at various liquid smoke volumes.

The highest water resistance obtained is at chitosan of 20% without liquid smoke namely 78.40%. The lowest water resistance is 22.68% at chitosan of 50% and liquid smoke of 2 mL.
3.3. Analysis by SEM

Analysis of bioplastic morphology carried out is to explain morphology of bioplastic formed. The part of sample analyzed is top and cross sections as shown in Figures of 4 and 5. Micro-structure of bioplastic with chitosan of 30% and liquid smoke of 1 mL is in Figure 4. It is not distributed completely (uneven) as shown by agglomerating part (laminar).

Disorder while casting causes uneven sample so that its morphology structure is not homogeneous. It is also caused by the presence of insoluble chitosan in organic solvent [15]. Film layer is formed based on chemical bond of polymer and another compound added. Chemical bond that occurs is interaction of H–H or hydrogen bond [16]. In Figure 5, it could be observed that bioplastic resulted is non-porous. It seems fracture (wrinkle) caused by the presence of irregularity at the time of casting.

3.4. Analysis by FTIR

Bioplastic functional group is analyzed to identify its structure (organic and inorganic compounds). Figure 6 shows the result of functional group analysis. It also shiws that product resulted is bioplastic (based on standard IR spectrum). It indicates strong absorption at wave numbers of 3294.31 and 3291.54 cm\(^{-1}\) from O–H vibration. At the same wave number, it seems N–H group that shows the N-acetyl presence. Sharp absorption at wave number of 1645.45 and 1645.86 cm\(^{-1}\) indicates vibration of C=O. Sharp absorption at wave number of 1018.84 and 1020.66 cm\(^{-1}\) is from vibration of C–O.

Based on result of FTIR, it seems specific functional group contained in its constituent part. Groups of O–H show the material presence of bioplastic composing i.e. glycerol [5]. Meanwhile, the N–H group identification shows the presence of chitosan. The new functional group is not found (no chemical reaction occurs). For sample without liquid smoke addition, CH\(_3\)–O group does not appear. It is because at the chitosan concentration, the sample uses liquid smoke whose part is ether.

3.5. Degradation Time of Bioplastic

Degradation time of the cassava-starch- based film increases as liquid smoke volume increases (Fig. 7). A decrease of film mass marks it until the film completely degraded. It occurs because in liquid smoke there is active substance namely phenol. In liquid smoke, it could inhibit bacterial growth, so that the more liquid smoke, the longer degradation time needed.
Figure 6. FTIR spectrum of bioplastic with chitosan concentration of 30% and liquid smoke of 1 mL.

Figure 7. The correlation of bioplastic mass reduction and time at chitosan of 30% and various volume of liquid smoke.

In Figure 7 the fastest degradation is in 45th day for film with chitosan of 30% and without liquid smoke. The longest degradation is at film with chitosan of 30% and liquid smoke of 2 mL in 57 days.
4. Conclusion
This research focuses on characteristic of cassava-peel-starch bioplastic with chitosan and various volumes of liquid smoke. Bioplastic with chitosan of 30% without liquid smoke has the highest tensile strength of 96.04 MPa. Bioplastic with chitosan of 30% and liquid smoke of 2 mL has the highest elongation of 52.27%. Bioplastic with chitosan of 50% and liquid smoke of 2 mL has the lowest water absorption of 22.68%. SEM analysis of bioplastic with chitosan of 30% and liquid smoke of 1 mL indicates uneven surface. There is fracture in its cross-section. FTIR analysis of bioplastic with chitosan of 30% and liquid smoke 1 mL indicates O–H, N–H, and CH3–O groups. Such groups show glycerol, chitosan, and liquid smoke presence in film. Degradation test shows that liquid smoke could prolong degradation time. For bioplastic with chitosan of 30% without liquid smoke, the fastest degradation time is 45 days. For bioplastic with chitosan of 30% and liquid smoke of 2 mL, degradation is longer namely in 57 days.

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