Food packaging development of bioplastic from basic waste of cassava peel (*manihot utilissima*) and shrimp shell

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Abstract. Development of biodegradable plastics or bioplastics that can be degraded by microorganisms such as bacteria and fungi is one approach to solving the problem of plastic waste. Bioplastic from waste starch and cassava peel shrimp shell waste as filler or reinforcement that has been generated in previous research. This research aims to develop bioplastic packaging into food for direct consumption and packaging. Stages of the study include the manufacture of bioplastics, food safety testing, manufacture and packaging of food products, organoleptic test, and the test period. Utilization of cassava and leather waste shrimp shells for bioplastic packaging is an added value in addressing environmental problems because it is recycled into products of high economic value and environmental.

1. Introduction

The development of biodegradable plastics or bioplastics that can be degraded by microorganisms such as bacteria and fungi is one approach to solving the problem of plastic waste (Kumar, 2011; Floros and Gnanasekharan, 1993). Plastic which has been used to be a problem for the environment because the type of plastic used is poliofelin (polyethylene, polypropylene, Polyvinylechloride) (Beeler and Finney, 1982). This type of plastic is strong, lightweight, and stable but difficult overhauled by microorganisms, so when in the environment will be a very serious problem (Charles and Harper, 1999).

Generally, starch-based bioplastic in the form of a natural polymer of the extraction plant (Yuli, 2008). Bioplastics made from plants that contain lots of starch such as sweet potato (Marbun, 2012), sago (Matondang et al., 2013; Miskiyah 2011)), cassava (Pudjiastuti et al., 2012; Kaewphan and Gheewala, 2013), and potato taro (Sinaga, 2014). However, the use of these materials will reduce the portion of food. An additional value if the development of bioplastics to address environmental problems from waste as well. In previous studies, we have succeeded in making bioplastic from waste starch and cassava peel shrimp shell waste as filler or reinforcement.

In Indonesia, biodegradable polymers developed more than ten years ago, but the research and development of biodegradable plastic packaging technology are still very limited. The development prospects of biopolymers for biodegradable plastic packaging in Indonesia is very potent. This premise is supported by the lack of natural resources, especially agricultural products that are abundant and can
be obtained throughout the year. Various agricultural products with the potential to be developed into biopolymers are maize, corn, soybeans, potatoes, tapioca, cassava (vegetable) and chitin from shrimp shells (animal) and others. Wealth will be the source of basic materials such as mentioned above, on the contrary, become a serious potential problem for countries that have developed and mastered the science and technology of packaging biodegradable, particularly in Germany. The country with the mastery of science and technology high technology field of packaging, worrying shortage of basic material resources (raw materials) and will be highly dependent on countries rich in natural resources.

We develop food packaging using bioplastic skin cassava starch and chitosan shells. The advantages of bioplastics we produce are: 1) The base material in the form of starch derived from leather waste cassava whose existence is abundant in Indonesia without competing with food crops. 2) Filler using natural materials that chitosan derived from waste shrimp shell and easy to find in Indonesia (Note: chitosan for filler facilitate biodegradation by microbes and particularly advantageous in applications in bioplastics compared with synthetic material (Dhanikula and Pachagnula, 2004). 3 ) Plasticizer use of glycerol byproduct from the manufacture of biofuel (Note: on the same occasion we also develop biofuel production). 4) degraded faster than wrapping sausages bioplastics and biodegradable plastics that have been produced by several companies. 5) Has the excellent characteristics of the results of DSC characterization, SEM, FT-IR, and WVTR and can be used as a packaging material. 6) Bioplastics can be generated with a simple method. 7) Bioplastics can be produced with cheap funds (Dasumiati and Saridewi, 2014).

Forms of food packaging developed a bioplastic from cassava starch, and chitosan shell shrimp are food packaging that can be directly consumed. For packaging for direct consumption to be developed in the form of bioplastic packaging sausages.

2. Tools and material
The tools used in this study is:

- Equipment for the preparation of materials: the crankcase for chopping knife or cassava peel and shrimp, grinding to smooth the skin and shells, trays for drying the starch from cassava and flour peel shrimp shell, sieve to sift cassava starch leather, glass beaker, and spatula.
- Equipment bioplastics manufacturing process: glass beakers, Petri dishes, spatulas, measuring cups, and a pipette. Erlenmeyer, pumpkin heads of three, funnel, thermometer, magnetic stirrer, hot plate, analytical balance, oven, pan heater.
- Equipment characterization TGA, XRF, testing tools tensile strength and elongation, measurement tools proximate analysis.

Materials needed in this research is the starch peel cassava, acetic acid, distilled water, glycerol, chitosan, distilled water, the chitosan from shrimp shells dry, sausage, 1 M NaOH, HCl 2 M NaOH 20%, glycerol, and materials characterization TGA, XRF, testing tools tensile strength and elongation, measurement tools proximate analysis.

3. Method

3.1. Manufacture Bio-Plastic

3.1.1. Starch Extraction from Cassava Peel
Small pieces of skin that is clean cassava mashed into a pulp in a grinder. The composition used was 10 g cassava peel with the addition of 50 ml of water. Cassava bark extract is washed with a ratio of 1: 3 (skin manioc porridge: water). Washing was done twice. Furthermore, the juice precipitated and dried under direct sunlight to form a flour or starch.
3.1.2. Bioplastics Manufactured

Bioplastics are made from a mixture of 3 g of starch with glycerol concentration of 25% w and added chitosan with a mass of 2 and 3% w glycerol. The mixture is heated at a temperature of 80-90 °C while stirring with a stirrer for 40 minutes. The mixture is poured into the mold and then dried in an oven at a temperature of 40-50 °C for 5-6 hours. Subsequently left at room temperature until the mixture separated from the mold.

In the manufacture of bioplastics is done several treatments chitosan, which is 3, 5, 7% w. It aims to obtain a bioplastic easily separated from the mold and is plastic making it eligible to be used as food packaging for direct consumption and plastic bags.

3.1.3. Characteristic properties of Physics, Mechanical, and Thermal Bioplastics

Characterization of physical properties, mechanical, and thermal bioplastic is required to measure broad enough that there should be no cut out in the slightest, which is 15x315 cm — bioplastics which were characterized to see the quality. Characters are observed physical properties and mechanical, and thermal stability. The physical and mechanical test is elongation, permeability, and tensile strength. Testing physics, mechanical, and thermal test with TGA.

4. Food safety test

Food safety testing is determined by the determination of levels of heavy metals (Hg, Cd, Pb, Cr, etc.) contained in bioplastics produced. XRF assay performed.

5. Result and discussion

5.1. Bioplastic

Bioplastics generated in this study are bioplastics that will be used in food packaging that can be directly consumed in the form of wrapping sausages. Development undertaken is the development of the workings and development of compositions.

Starch is a carbohydrate which is a glucose polymer composed of amylose and amylopectin in the ratio 1: 3 (the amount of amylose and amylopectin ratio varies depending on the type of starch. The content of amylose and amylopectin starch cassava bark is 15/73 (Cui, 2005). The content of starch derived from the bark of a high enough cassava may be used as a biodegradable plastic film.

The skin material cassava serves as a matrix, in which he needs an amplifier (filler) and plasticizer. The amplifier used in the form of chitosan derived from shrimp shell waste, while plasticizer form of glycerol. Chitosan as reinforcement plays an important role in determining the physical and mechanical properties of bioplastics produced. In a study conducted three variations of composition addition of chitosan, which is 3, 5, 7% w. This is done to see how the effects of chitosan as a reinforcement in the form of bioplastic material. Where is expected to be applied to the two character packs, namely as a direct food wrapper (wrappers sausage unpeeled) and packaging food carrier (with a higher power)?
Figure 1. Bioplastic with chitosan 3 % w (A), 5 % w (B), dan 7 % w (C)

Figure 1 shows that the addition of chitosan composition variation can form bioplastics well, which is physically not too reveal the difference. But if it is pulled composition of 3% w texture is very weak, soft, and easily torn. While the addition of 5% chitosan has a texture that is more compact, remains soft, and not easily torn. It is possible that the addition of 5% chitosan has been able to maintain the texture of bioplastic if used as a wrapper. However, this needs to be supported by the physical and mechanical characterization is more accurate.

5.2. Characteristic properties of Physics, Mechanical and Thermal Bioplastics

Physics and mechanical properties of bioplastics is tested elongation and tensile strength. These properties determine the quality and use of bioplastics in order. Tensile strength a bioplastic tensile strength, while the elongation is the elongation at the break if the bioplastic to be withdrawn.
Table 1. Physical and mechanical properties of bioplastics from cassava peel (the reference standard ASTM D.882)

| Sample          | Elongation (%) | Average | Tensile Strength (kgf/cm²) | Average |
|-----------------|----------------|---------|----------------------------|---------|
| Chitosan 3 % w  | 31.23          | 4.35    | 3.23                       |         |
|                 | 27.24          |         |                            |         |
|                 | 29.45          | 30.37   | 4.01                       | 4.16    |
|                 | 33.52          |         | 5.66                       |         |
|                 | 30.43          |         | 3.56                       |         |
| Chitosan 5 % w  | 51.43          | 8.35    | 8.99                       |         |
|                 | 57.14          |         |                            |         |
|                 | 64.29          | 59.14   | 14.01                      | 11.67   |
|                 | 62.86          |         | 13.65                      |         |
|                 | 60.00          |         | 13.35                      |         |
| Chitosan 7 % w  | 95.21          | 29.57   |                            |         |
|                 | 107.83         |         | 31.98                      |         |
|                 | 87.67          | 94.25   | 24.01                      | 27.41   |
|                 | 90.64          |         | 26.15                      |         |
|                 | 89.90          |         | 25.35                      |         |

Table 1 shows that the addition of the sample mass variation bioplastics with chitosan has the properties of physics and mechanics are different. Bioplastics with chitosan mass of more than 5 and 7% w increased tensile strength, as well as elongating. This suggests that the chitosan increases the strength of the resulting plastic, where the main function of chitosan is an amplifier in this material. The greater the tensile strength then elongation also getting bigger. The high tensile strength and elongation which can occur in bioplastics containing chitosan 5 and 7% indicated that bioplastics produced can support the weight.

The addition of 7% w chitosan has elongation, and tensile strength is considerably higher than other additions. Value at 94% elongation and tensile strength 27 kgf / cm². This value is close to the value that is standard commercial plastic > 100% elongation and tensile strength of 10-50 kgf / cm². So bioplastics with the addition of 7% w chitosan can be used as a wrapper for carrying food, while the addition of 5% w chitosan can be used for wrapping sausages directly feed.

The tensile strength is the maximum tensile force that can be retained by the film during the measurement takes place. The tensile strength is affected by a reinforcing material is added in the process of filmmaking. While the percent elongation at break is a change in the maximum length of the film before it is disconnected (David, 1994).

5.3. Thermal test bioplastics by TGA
Thermal test bioplastics by TGA (Thermogravimetric analysis) aims to determine the nature and thermal stability bioplastic components of skin cassava has produced. This data is a reference in determining the optimum conditions bioplastic packaging when exposed to high temperatures or resistance of the packaging in wrapping the food was hot.
Figure 2. The results of the TGA thermal test bioplastics from cassava bark

TGA measurement used to predict the thermal stability. This TGA technique will show a loss or weight gain due to decomposition, oxidation or dehydration (Jon, 2001). Figure 2 shows the temperature of 101.49 °C the weight loss amounted to 8,017%. This indicates the loss of a water molecule to bioplastic material. Bioplastic material weight decreased by 6.046%, which occurs at a temperature of 205.09 °C. After passing through a phase loss of a water molecule, then an evaporation of the liquid phase of the organic pollutant material at a temperature range of 250-300 °C. This indicates that the temperature above 300 oC bioplastics have been exhausted when heated. According to Rosjidi (2010), organic materials are decomposed into gases O2, CO2 and H2O then evaporated.

It can be seen that bioplastics can withstand foods that heat up to 100 °C, but if hotter than the temperature of bioplastics decompose (broken). This shows that if bioplastic used to pack food that is too hot, it would cause degradation of the covering. If this happens then, degraded bioplastic packaging can migrate into food wraps.

5.4. Food Safety Test

Food safety testing is determined by the determination of levels of heavy metals (Cd, Pb, Hg, Cr) contained in the bioplastic packaging. Assay performed with measurement by XRF (X-Ray Fluorescence)

Table 2. The composition of bioplastic material cassava bark

| No. | Analite | Compound | Concentration(%) |
|-----|---------|----------|-----------------|
| 1   | Mg      | MgO      | 0.016932        |
| 2   | Al      | Al2O3    | 0.071485        |
| 3   | Si      | SiO2     | 0.234294        |
| 4   | P       | P2O5     | 0.141695        |
| 5   | Si      | SO3      | 0.034357        |
| 6   | K       | K        | 0.128741        |
| 7   | Ca      | CaO      | 0.513706        |
| 8   | Fe      | Fe2O3    | 0.364276        |
| 9   | Nd      | Nd2O3    | 0.122298        |
| 10  | Sm      | Sm2O3    | 0.072216        |
Measurements on a bioplastic material composition are necessary to determine the content of heavy metals, which results in food security for the reference product. Food safety testing is done by the polymer nanocomposite BPOM Head Regulation No. HK 00.05.55.6497. From Table 2 it appears that this bioplastic material does not contain heavy metals (Pb, Cd, Hg, and Cr). It showed that this bioplastic material is safe for consumption. Meanwhile, the content of which is the largest in this material is calcium in the form of CaO, followed by iron in the form of Fe2O3. Both of these materials are a source of minerals needed by the body. This is because bioplastic made from starch derived from the skin of cassava. Where cassava is a tuber group - crops with mineral content is quite high and one of the important source of carbohydrates.

From Table 2 it can be seen that bioplastics produced do not contain metals that are harmful to health, but rather the body's mineral needs can be met by consuming foods that have been packaged or wrapped in the bioplastics. For bioplastics by adding chitosan composition 5% w, bioplastic used to wrap food sausage that does not need to be peeled again when cooked (direct consumption).

The sausages are wrapped in transparent plastic that needs to be peeled before cooking. Besides less effective, the plastic also causes problems in the environment. While the use of bioplastics can provide three benefits at once, namely: more effective (no need to peel), not a waste, mineral content is good for the body.

5.5. Analysis of protein and carbohydrate content, moisture content and ash
Analysis of protein and carbohydrate content, moisture content and ash were conducted by measuring proximate.

| Analysis          | Content (%) |
|-------------------|-------------|
| Protein           | 8.44        |
| Carbohydrate      | 4.67        |
| Moisture Content  | 13          |
| Ash               | 1.5         |

Based on data in Table 3, it is known that the bioplastic material contains high protein and carbohydrates. The high content because the basic material used in this material is derived from starch (polysaccharide). While the water content of 13%, where the value is still above water levels allowed in food. This suggests that the resulting bioplastic is indeed worthy to be a plastic wrapper on groceries direct consumption (unpeeled wrapper), such as sausages. The ash content in bioplastic material is also fairly high. This is comparable with the content of minerals that have been given to the XRF results (Table 2).

6. Conclusion
Based on the results obtained in the study manufacture of bioplastics with skin matrix material cassava and shrimp shell waste as an amplifier can be concluded as follows:

- Bioplastics from skin starch cassava (M. utilisima) and reinforcement of chitosan can be developed as wrap packaging direct consumption (sausage) with the addition of chitosan composition 5% w. Bioplastics produced is safe for consumption because it does not contain heavy metals, but contains useful minerals for the body.
- Packaging in the form of a bag can also be developed with the addition of 7% w chitosan composition. Wherein the composition has the physical and mechanical properties are better than other compositions as well as nearly approaching the tensile strength and elongation value of commercial plastic.
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