Cassava Starch Edible Film with Addition of Gelatin or Modified Cassava Starch

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Abstract. This research aimed to improve the quality of cassava starch edible film by addition of gelatin or modified cassava starch. Modified cassava starch was obtained by precipitation of gelatinised cassava starch. First experiment was carried out using a completely randomized design (CRD) with six treatments of addition of gelatin (0%, 1%, 1.5%, 2%, 2.5% and 3% (w/w). Second experiment was carried out by using the addition of modified cassava starch (15% w/w). The results showed that the addition of 3% gelatin produced edible film with highest compressive strength but did not improve its water vapor transmission rate (WVTR). WVTR of cassava starch edible film, however, can be improved by using 15% modified cassava starch.

Keywords: Cassava Starch, Edible Film, Gelatin, Modified Cassava Starch

1. Introduction
The environmental problem caused by the use of synthetic plastic has encouraged researchers to be able to produce high quality bioplastic. Edible film is one type of bioplastic which can be produced from biopolymer such as starch, protein and hydrocolloids. Cassava starch is easily produced with low cost, hence become a cheap source for edible film. However, edible film from cassava starch has low quality due to its low strength and high water vapor transmission rate. Some studies used gelatin for its ability to increase the strength of film [1] and its oxygen and aroma barrier properties [2]. Gelatin is a protein obtained from natural collagen in animal skin or bone [3]. It forms thin, elastic and strong film and decreases gas transmission rate in edible film [4]. However, gelatin has polar properties that allow edible film to have high water vapor transmission rate and water solubility. Starch particles of smaller size produced from modification of starch using precipitation method is known to have ability to decrease water vapor transmission rate of edible film [5]. These small particles fill the empty spaces in the film structure which further inhibit the flow of water vapor in and out the film. The objectives of this research were to determine the effect of addition of gelatin in the quality of cassava starch edible film and to investigate whether the use of modified cassava starch in the film forming solution be able to decrease water vapor transmission rate of edible film.
2. Methods

2.1. Material
Cassava starch was obtained by extraction of cassava tuber bought at Jambi City. Gelatin of cow origin was in form of coarse material. Glycerol, Calcium Chloride, Magnesium Nitrate, Sodium Chloride and absolute Ethanol were analytical grade produced by Merck. Instruments used were digital balance, blender, 200 mesh filter, desiccator, petridish, oven dryer, texture analyzer, micrometer secrup and spectrofotometer.

2.2. Methods
This experiments was carried out at Laboratory of Agricultural Technology Faculty, University of Jambi, Energy and Nano-material Study Centre, LP2M University of Jambi and Analytical Laboratory FMIPA University of Sriwijaya. First experiment used Complete Random Design with 5 levels of gelatin concentration and 4 repetitions. The gelatin concentration were 0%, 1%, 1.5%, 2%, 2.5% and 3% calculated from total film forming solution. The resulted films were analysed for their transparency, thickness, water vapour transmission rate (WVTR), compressive strenght and water solubility.

2.2.1 Modification of Cassava Starch
1% of cassava starch (w/w, in distilled water) was gelatinised at 100°C for 30 minutes, followed by slow precipitation using anti-solvent ethanol 96%. The amount of ethanol 96% was ten folds for every volume starch solution. Modified starch was recovered by centrifugation at 2500g for 15 min, washed 3 times using absolute ethanol and cold dried.

2.2.2 Edible Film Preparation with Addition of Gelatin
Total film forming solution was made for 150 gram. Based on this number, the amount of starch, gelatin, and glycerol was calculated and distilled water was used to adjust the weigh to 150 gram. An exact amount 4.5 gram of cassava starch were weighed and dissolved using distilled water. This mixture was mixed using magnetic stirrer without heat for 10 minutes. Three grams of glycerol and certain amount of gelatin (0, 1.5, 2.25, 3, 3.75 and 4.5 grams) was added to the solution while agitation still continued. This solution was heated at 80°C for 30 minutes with continous stirring. 25 grams of film solution was placed in petridish (ϕ 9.2 cm) and dried in the oven at 50°C for a day. The films were further equilibrated in desiccator at room temperature and RH 52% using saturated solution of Mg(NO₃)₂ salt for 2 days before analysed [6].

2.2.3 Edible Film Preparation with Addition of Modified Cassava Starch
3.5 gram of cassava starch were weighed and dissolved using 100 ml distilled water. 1.75 gram of glycerol was added to this solution and stirred for 10 minutes. This mixture was heated at 70°C for 30 minutes and agitated continously using magnetic stirrer. 0.52 gram modified cassava starch was added afterward, followed by mixing using vortex for 10 minutes. This film solution was reheated at 70°C for 5 minutes, taken out and placed in petridish. The solution was dried in the oven at 60°C for a day and equilibrated in desiccator at room temperature and RH 52% using saturated solution of Mg(NO₃)₂ salt for 2 days before analysed [6].

2.2.4 Quality of Edible Film
Quality of edible film was measured by its film thickness [7], transparency [8], water vapor transmission rate/WVTR [8], and compressive strenght.
   a) Film thickness was measured at 5 points in the film using micrometer.
   b) Measurement of transmittance of edible film (50x10mm) using UV-Vis spectrophotometer at wavelength 600 nm, was used to calculate transparency of edible film. Where Transparency = \log T/ Thickness.
   c) WVTR was calculated using formula below:
\[
W_{TR} = \frac{S}{A}
\]

Where \( A \) = The area of the edible film (m²).

A tube containing Calcium Chloride was sealed using samples of edible film. The sealed tube was weighed and placed inside a desiccator which saturated using saturated Sodium Chloride solution (RH 75%). The changes of the sealed tube weight over time was plotted as a function of time.

d) Compressive strength was measured using LFRA Brookfield Texture Analyzer. The probe was TA 7 60 mm, trigger 2 g, distance 2 mm, and speed 2 mm/s. Film sample (5 x 2 cm) was placed under the probe. The probe press the film and the strength can be read on the screen.

2.3. Statistical Analysis
Analysis of variance was conducted to determine the effect of gelatin concentration on the quality of edible film. Duncan new multiple range test was used to determine the mean difference. The effect of modified cassava starch was investigated by comparing the mean values of each quality parameter.

3. Result and Discussion

3.1. Edible Films
Cassava starch edible films have clear appearance. The addition of gelatin has slightly changed the colour to more yellowish with the increasing concentration of gelatin (Figure 1). The addition of modified cassava starch did not change the appearance of cassava edible film which remained clear and colourless (Figure 2). Dried films were easily removed from the mould after equilibrated for 2 days and possess sticky surface.

Figure 1. Cassava starch edible film with different level of gelatin concentration: (a) 0%, (b) 1%, (c) 1.5%, (d) 2%, (e) 2.5% and (f) 3%

Figure 2. Cassava starch edible film (left) and cassava starch edible film with addition of modified cassava starch (right)
3.2. Quality of Edible Film
Addition of gelatin increased total soluble solid of film forming solution and gave rise to the increased in film thickness (Table 1). The addition of gelatin 1 to 3% did not influence water vapour transmission rate of cassava edible film. Whether water vapor can move in and out the film, depend on the relative polarity of the polymer used in film forming solution. The more cationik and hydrophylic the polymer, the higher water vapor transmission rate of the film [9]. Gelatin has hydrophobic nature due to some hydrophobic amino acid present in its structure [9]. The increase in gelatin concentration in film forming solution decreased transparency of cassava edible film. On the other hand, the increase in gelatin concentration in film forming solution increased compressive strength of cassava edible film. This is similar to what has been shown by Khodaei that gelatin had the ability to increase mechanical properties of edible film [10].

Table 1. Quality of cassava starch edible film with several concentration of gelatin

| Gelatin (%) | Thickness (mm) | WVTR (g/m².hour) | Transparency (%/mm) | Compressive Strength (N/m²) |
|-------------|----------------|------------------|---------------------|----------------------------|
| 0           | 0.188 ± 0.05a  | 6.16a            | 3.46b               | 27.66 ± 2.34a              |
|             | 0.265 ±        | 49.13            | 6.46                |                            |
| 1           | 0.06ab         | 24.83a           | 2.13a               | 27.73 ± 0.97a              |
|             | 0.268 ±        | 62.36            | 6.01                |                            |
| 1.5         | 0.03ab         | 16.35a           | 0.63a               | 30.86 ± 2.87a              |
|             |                | 43.16            | 5.41                |                            |
| 2           | 0.285 ± 0.04b  | 3.79a            | 1.31a               | 32.36 ± 3.14ab             |
|             |                | 32.63            | 4.92                |                            |
| 2.5         | 0.329 ± 0.02b  | 24.75a           | 0.73a               | 33.36 ± 3.98ab             |
| 3           | 0.414 ± 0.03c  | 43.86 ±7.16a     | 0.21a               | 37.50 ± 4.85b              |

Note: Means with same superscript in the same column were not significantly different (p>5%)

Modified cassava starch had smaller granule size than native cassava starch. Gelatinisation followed by precipitation had destroyed intramolecular bond in the starch granules and changed morphology of granules (Figure 3). The addition of this modified cassava starch had improved WVTR and transparency of cassava starch edible film (Table 2). Similar results showed by Dularia et al [11] that the addition of water chestnut starch nanoparticles decreased water vapour transmission rate of film. The decrease in water vapour transmission rate may due to the increase ratio of surface to volume in modified starch which cause the increase in compactness of the film [3]. Study by Garcia et al [12] and Gonzales et al [13] showed that the addition of modified starch with decreased granules size increased mechanical property of the film. However, both studies showed different effect on barrier property.

Figure 3. SEM Image of native cassava starch (a) and modified cassava starch (b)
Table 2. Quality of cassava starch edible film with addition of 15% modified cassava starch

| Quality of Edible Film | Cassava starch | Cassava starch + modified cassava starch |
|------------------------|----------------|----------------------------------------|
| Thickness (mm)         | 0.153 ± 0.009  | 0.227 ± 0.011                          |
| WVTR (g/m²/hour)       | 59.064 ± 7.609 | 22.632 ± 0.744                         |
| Transparency (%/mm)    | 12.537 ± 0.108 | 8.339 ± 0.121                          |

4. Conclusion
The quality of cassava starch edible films can be improved by using 3% gelatin or 15% modified cassava starch. Gelatin increased compressive strength of the film while modified cassava starch increased water vapour transmission rate, and transparency of the film.

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