Process design of acetylated sago starch-based edible film

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Abstract. Starch has potential as a material of edible film packaging. However, the use of native starch has a limitation due to the hydrophilic character. Native starch produces brittle edible film and low physical, mechanical properties. This research modified the sago starch with acetylation to produce more hydrophobic starch and improve the film characteristics. The experiments investigated the effect of sago acetylated starch (3%, 4%, and 5%) on the physical and mechanical properties of edible film. The acetylated starch films showed improved physical-mechanical properties compared to the edible film made from native starch. Edible film made by 4% acetylated starch presented lower thickness (0.14 mm), moisture content (7.43%), solubility (26.891 %) and water vapor transmission rate (0.87 g/hour.mm²). This edible film also had higher transparency and tensile strength (87.84%, 1.99 MPa). Characteristics of the edible film were improved and affected by the acetylated starch that used.

Keywords: acetylated starch, edible film, physical-mechanical properties, sago starch

1. Introduction

Edible film is a thin layer used to coat food that has a function to protect the product. Edible films have the potential to increase shelf life and improve the quality of the product. Starch is an essential polysaccharide in films process. Several studies on polysaccharides such as starch have been studying because they have potential as edible film packaging materials [1]. Starch is a natural polysaccharide that is abundant, inexpensive, and renewable [2]. As raw material starch film coating must contain amyllose content quite high [3]. Sago starch was included starch group with high amyllose content (28.84% amyllose and 71.16% amylopectin) [4], and have good film formation ability so that it can be used as a raw material in produce edible film.

However, the use of native starch has a limitation due to the hydrophilic character. Native starch produces brittle film and low physical-mechanical properties [5] and produces a brittle film [6]. Therefore, to improve its characteristics, sago starch can be modified to produce more hydrophobic starch. A Chemical modification that can use to modify the starch is acetylation using acetic anhydride. Acetylation modification is a chemical modification to produce starch acetate by substituting acetyl groups into starch molecules [7]. Modified starches with lower levels of chemical modification can significantly improve their hydrophobicity [8]. Other research [9] reported that acetylation can be used to decrease the hydrophilic character of native starch. Plasticizers can be added to increase the flexibility of edible film. The most common plasticizers used in starch-based edible films are sorbitol and glycerol.
This work focuses on the suitability acetylated sago starch as materials for making edible films, with the best physicochemical properties. The experiments investigated the effect of sago acetylated starch (3%, 4%, and 5%) to the physical-mechanical properties of edible film.

2. Materials and methods

2.1. Material
The material used in this study were sago starch (Metroxylon sp.) supplied by SME in Bogor West Java, acetate starch, aquadest, and glycerol.

2.2. Preparation of starch edible film
The Native and acetylated starch film were prepared by suspended five grams of starch were mixed with distilled water (100 mL) and 2 mL glycerol (40%, v/w) and different starch concentrations (3, 4, 5%) at room temperature (25 °C) for 5 min. This suspension was transferred to a water bath at 90 °C for 30 min and agitated by magnetic stirrer (500 rpm). After cooling, about 50 mL of the sample was poured into a teflon casting tray and then dried at 60 °C in an oven to cast the films [5].

2.3. Physicochemical properties
For the characterization of films, the methodology proposed by Hu et al. [10].

Film thickness. Film thickness was measured using a micrometer. The final value represented the average of 5 measurements taken at different parts of the film.

Moisture content. Measurement of the water content of film using the oven method. A total of 2–10 g of the sample were weighed in a cup that was known for its weight, then dried in an oven at 105 °C for 5 hours. The sample is then cooled in a desiccator and weighed until the weight is constant.

\[
\text{Moisture content} \, (\%) = \frac{a - b}{a} \times 100\%
\]

(1)

Water vapor transmission rate. The film specimens to be tested are cut to an area of 10x10 mm. Then the place of silica gel in the desiccator is replaced with distilled water, and silica gel is put in a plastic jar (film testing place) as much as ¾ of the volume jar. Before that, silica gel was dried at 105 °C for a minimum of 3 hours. The film specimens which have been cut and then made into a jar lid, are stored in a desiccator containing distilled water. The weight of jar containing silica gel and covered film specimen is measured at 0, 1, 2, 3, 4, and 5 hours. Water vapor transmission rate is calculated using equation (2).

\[
WVTR = \frac{\Delta W}{t \times A}
\]

(2)

Where,
\[
\Delta W = \text{change in weight of silica gel after 5 hours (g)}
\]
\[
t = \text{time (5 hours)}
\]
\[
A = \text{film surface area (mm)}
\]

Transparency. The transparency value of the films was obtained by measuring its transmittance in a spectrophotometer, at a wavelength of 600 nm. Samples were tested in duplo.

Mechanical properties. The tensile strength and elongation at break were determined using (ASTM D 3039, 2012).

Solubility film. Samples with a size of 4 x 2 cm for each film were dried up to 40°C until reach constant weight (Wo), submerged in a beaker with 50 mL of distilled water, and the covered vessels staged at 27°C with some agitation for 24 h. After this time, samples were released and dried up to 40°C until reach constant weight (W2). Percentage of water solubility (% WS) was calculated as follows:
\[ WS = \frac{(W_0 - W_2)}{W_0} \times 100 \]  

**Statistical analysis.** Data were analyzed by one-way analysis of variance (ANOVA). Duncan test at a confidence level of 95% was used to observe differences among the edible film.

3. **Results and discussion**

The edible film made by native sago starch and acetate sago starch with glycerol as plasticizer. Based on research [11], the concentration of sago starch used in films is 4% (b/b solution). However, it is necessary to determine the appropriate concentration formulation in addition of starch acetate as edible film raw material. The concentrations of starch acetate tested were 3% (P1), 4% (P2), and 5% (P3). In addition, this study also tested edible film with 4% native sago starch as a comparison. While the concentration of glycerol used refers to the other study that used 40% (b/b starch) [5]. Edible films produced are transparent with different thicknesses.

Figure 1 showed visually of native and acetate edible films. Native starches produced edible films that are slightly transparent but more opaque while edible acetate films have more transparent appearance and bright colors. This is caused by the modification of acetylation, which increases the clarity of starch paste so that the resulting film is more transparent. At the concentration of 3% starch acetate, the film formed is thinner so that it has the most transparent appearance, but the film is easily break.

![Figure 1](image1.png)

**Figure 1.** Edible film (a) native starch 4% (b) acetate starch 3% (c) acetate starch 4% (d) acetate starch 5%.

3.1. **Characteristics of the starch used in the film preparation**

Acetate starch was obtained with a low degree of substitution (DS) value (0.01 - 0.2). In the range of DS values, starch has the ability to form films [12]. The acetate starch produced in this study had an acetyl content of 2.30% and a DS value of 0.09. One of the factors that influence the DS value is
In this study, the acetylation reaction temperature is 30°C, and the resulting DS value is low. Other research [13] reported that acetylation temperature of 100°C produced a high DS value of 2.43 [13].

Based on proximate analysis data, native starch and acetate starch contain low minor components. Minor components in acetate starch are 0.38% and 0.12% for fat and protein content, while native starch has value 1.68% and 0.48%. The presence of high fat and protein components will provide hydrophobic properties around the granules, causing inhibition of binding of water by starch granules. The results of the functional properties of starch showed that the value of swelling power and solubility at a temperature of 70°C was 62.48 and 30.45% (native starch), 42.69 and 15.00% (acetate starch). The percentage value of the two parameters has decreased in starch acetate. The acetylation reaction makes it difficult for water to enter the starch granules, so that swelling power decreases but also causes bonds in the starch molecules to be stronger. The presence of acetyl groups entering so that the starch dissolves less [14]. Substitution of acetyl groups in starch can change the nature of starch from hydrophilic to hydrophobic, thereby reducing the level of solubility of starch acetate in water [15].

3.2. Thickness of film

The higher the percentage of sago starch used, the more edible film produced will be thicker. Thickness is one of the essential characteristics because it affects the barrier (barrier) of water vapor and affects the shelf life of the product to be packaged. The graph of the relationship between thickness and WVTR is presented in figure 2. The thickness of edible acetate film has a value between 0.125 mm to 0.175 mm. Native edible films have a higher thickness than edible acetate film but lower than 5% acetate film. The thickness of edible film had increased with increasing concentration of starch acetate. The thickness value increases due to the concentration of raw material was increase, while the volume of the solution has the same size [16].

![Figure 2. Tensile strength, elongation, WVTR, and transparency value.](image-url)

Based on the analysis of variance showed a significant effect on each treatment between the concentration of starch acetate and the thickness of the edible film. The smallest edible film thickness was the edible film with 3% starch acetate (0.125 mm). The edible film with 5% acetylation starch as a raw material has the highest thickness of 0.175 mm. This can be caused by the presence of an acetyl...
group which makes the distance between starch chains so that thickness increases [14]. The higher the concentration of a component added to the solution, the thicker the film produced will be. The thickness is influenced by several factors such as the thickness of the solution, the volume of the solution, the area of the mold, and the high solution [3].

3.3. The moisture content of the film
Water content is one of the important parameters in edible film. The graph in figure 3 shows, the value of water content has decreased with increasing concentration of acetate starch, but at 5% acetate starch, the value of water content has increased with a value of 9.445%. This can be caused by too much starch so that the solution is not homogeneously dispersed, which results in the presence of cavities, so the film absorbed much water.

![Figure 3. Moisture content and thickness value of edible film.](image)

The average moisture content value of 4% acetate starch film is lower than the results of the Larasati et al. (2017) [17], which has a value of ± 10%. It can be caused by the acetate starch that used in this research affected on increased the hydrophobicity of starch.

3.4. Solubility film
Solubility is an important factor in determining the degradability of the film produced. The solubility of the films decreased with increasing concentration of starch acetate. The solubility of the film is between 26.15% - 40.28%. This value is lower than the results of Larasati, which has a value of 54.9% - 74.9% [17]. This can be caused by the presence of the fillers used in the research. Solubility value influenced by covalent bonds between modified starch molecules are stronger than natural starches so they are not easily released when immersed in water. Decreasing solubility is also caused by increased hydrophobicity of starch due to the modification process of acetylation [8].

3.5. Water vapor transmission rates of film
WVTR is important to measure the film's ability to maintain water vapor coordination. Film has function to control air, both from the product to the environment or from the environment to the product [18]. WVTR discusses the amount of water that can pass through a film in a specific area in a specific time unit. Low WVTR values indicate films that have compatibility that enters the vapor in packaged...
products. Based on the results of a variety of fingerprint analysis which showed real on each interaction between the factors of starch acetate concentration on the value of WVTR edible film. The results of the analysis of WVTR values on edible films were between 0.876 - 1.271 g/hour.mm². figure 2 show that there is a decrease in WVTR along with the increase in film thickness, while at certain concentrations WVTR values increase. In edible film with the highest thickness of 0.175 mm, there is an increase in WVTR value (1.271 g/hour.mm²). The amount added to the amount added is too much and overlaps with each other and does not bind well in the film, which causes the water to enter easily. These results are lower than the results of Larasati’s research which is between 1.8 - 1.9 g/hour.mm² [17]. This indicates that edible film with starch acetate has the ability to prevent high water migration.

3.6. Transparency of film
Transparency plays an important role when the edible film will be applied because it will affect the appearance of the product. In the graph figure 2 can be seen that increasing the thickness of the film, the transparency of the film does not change significantly, it is also supported by the results of statistical analysis that is not significantly different (F count < F table). The transparency value of edible films ranges between 87.848% - 90.698%. Edible films with 5% acetate starch have the highest transparency value. This is consistent with the other research [9], reported that films with raw starch acetate had the highest transparency [9]. Starch increases water retention capacity, thereby facilitating light exchange.

3.7. Physicochemical properties of the film
This study also analyzed mechanical properties of film include tensile strength and elongation. Tensile strength is the maximum tensile received by the film before breaking [19]. The value of high tensile strength indicates that the edible film produced is getting stronger, while the value of low tensile strength indicates that the edible film is more flexible. The strength of the edible film is essential because it relates to its application to package a product. The results of the analysis of the tensile strength of edible films showed an increase with increasing film thickness (figure 2). The value of tensile strength of edible films ranges from 0.66 - 2.39 MPa. The average value of tensile strength in this study is greater than the results of other research [17] which is around 0.43 - 1.75 MPa. This is caused by the acetylation process in this study which has an effect on increasing the hydrophobicity of starch so that the film is not easily brittle. The highest tensile strength value was produced on 5% acetate starch edible film. The results of ANOVA showed that there were significant differences in the tensile strength of the edible film produced. However, Duncan's further test results showed edible film 4% starch acetate concentration was not significantly different from 5% edible film.

Elongation shows the flexibility of the film when given mechanical pressure and stress. Edible films with high elongation values show a high degree of plasticity. A high level of plasticity will be better when applied to the product, which is easier to adjust to the product and not easily cracked or broken. Based on the results of the analysis of variance showed a significant effect on each treatment between the factors of starch acetate concentration on the value of elongation of edible film. The elongation value of edible film with the raw material of starch acetate is 28.2-56.48%. Similar to the value of tensile strength, elongation also increases with increasing thickness of edible film (figure 2). Elongation can be influenced by plasticizers which results in more flexible films.

Acetate starch edible films have lower elongation values than native starches. This can be caused by the chemical modification of starch can reduce the value of elongation by the interaction between various components of the film [8]. In addition, the decrease in elongation value can be caused by the presence of molecules that fill the space between the polymer chains resulting in a decrease in the intermolecular forces of polymer chains and decreasing the ability of chains to hold each other so that film elongation decreases.
4. Conclusion
The edible film made by 4% acetylated starch suitable as raw material to produce the edible film with the best physicochemical characteristics. Edible film (4% acetylated starch) presented lower thickness (0.14 mm), moisture content (7.43%), solubility (26.891%) and water vapor transmission rate (0.87 g/hour.mm2). This edible film also had higher transparency and tensile strength (87.84%, 1.99 MPa). Characteristics of the edible film were improved and affected by the acetylated starch that used.

References
[1] Siracusa V, Rocculi P, Romani S and Rosa M D 2008 Biodegradable polymers for food packaging: a review J. Trends. Food. Sci. Technol. 19 (12) 634–43
[2] Nouri L and Naﬁchi A M 2014 Antibacterial, mechanical, and barrier properties of sago starch film incorporated with betel leaves extract Int. J. Biol. Macromol. 66 254–59
[3] Bae H J, Cha D S, Whiteside W S, and Park H J 2008 Film and pharmaceutical hard capsule formation properties of mungbean, waterchestnut, and sweet potato starches J. Food. Chem. 106 96–105
[4] Jading A, Eduard T, Payung P and Gultom S 2011 Karakteristik fisikokimia pati sagu hasil pengegerangan secara fluidisasi menggunakan alat pengegerangan Cross Flow Fluidized Bed bertenaga surya dan biomassa J. Univ. Neg. Papua 13 155–64
[5] Ghanbarzadeh B, Almasi H, and Entezami A A 2011 Improving the barrier and mechanical properties of corn starch-based edible films: Effect of citric acid and carboxymethyl cellulose J. Ind. Crops Prod. 33 229–35
[6] Mali S, Sakanaka L S, Yamashita F and M V E Grossmann 2005 Water sorption and mechanical properties of cassava starch films and their relation to plasticizing effect J. Carbohydr. Polym 60 283–89
[7] Phillips D L, Liu H, Pan D, and Corke H 1999 General application of Raman spectroscopy for the determination of level of acetylation in modified starches J. Cereal. Chem. 76 439–43
[8] Zamudio-Flores P B, Torres A V, Salgado-Delgado R and Bello-Pe’ez L A 2010 Inﬂuence of the oxidation and acetylation of banana starch on the mechanical and water barrier properties of modiﬁed starch and modiﬁed starch/chitosan blend ﬁlms J. Appl. Polym. Sci. 115 991–98
[9] Medina V O J, Pardo O H C and Ortiz C A 2012 Modiﬁed arracacha starch ﬁlms characterization and its potential utilization as food packaging J. Vitae. 19 186–96
[10] Hu G, Chen J and Gao J 2009 preparation and characteristics of oxidized potato starch films J. Carbohydr. Polym 76 291–98
[11] Naﬁchi A M, Cheng L H and Karim A A 2011 Effects of plasticizers on thermal properties and heat sealability of sago starch ﬁlms, J. Food Hydrocoll. 25 56–60
[12] Luo Z G and Shi Y C 2012 Preparation of acetylated waxy, normal, and high-amyllose maize starches with intermediate degrees of substitution in aqueous solution and their properties J. Agric. Food Chem. 60 9468–75
[13] Singh A V, Nath L K and Guha M 2011 synthesis and characterization of highly acetylated sago starch J Starch/Stärke 63 523–27
[14] Colussi R, Pinto V Z, El Halal SL et al 2014 structural, morphological, and physicochemical properties of acetylated high-, medium-, and low-amyllose rice starches Carbohydr. Polym. 103 405–13
[15] Yulisiah I and Sunarti T C 2014 Pati Sagu Termodifikasi Sebagai Bahan Starch-based Plastics Pros. Semin Nas Kulit, Karet, dan Plast 29th October Yogyakarta 3 67–83
[16] Nugroho A, Basito and Katri R B A 2013 Kajian pembuatan edible film tapioka dengan pengaruh penambahan pektin beberapa jenis kulit pisang terhadap karakteristik ﬁsik dan mekanik J. Teknosains Pangan 2 73–79
[17] Larasati D A, Yulisiah I and Sunarti T C 2017 Desain proses pembuatan coating film berbasis pati sagu (Metroxyylon Sp) ikat silangasam sitrat J. Teknol. Ind. Pertan. 27 318–27
[18] Gontard N, Guilbert S and Jean-Louis C 1993 Water and glycerol as plasticizer affect mechanical and water vapor barrier properties of an edible wheat gluten film J. food Sci. 58 206–11

[19] Wattimena D, Ega L and Polnaya F J 2016 Karakteristik edible film pati sagu alami dan pati sagu fosfat dengan penambahan gliserol J. Agritech. 36 247–52

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