Characterization edible films of sago with glycerol as a plasticizer

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Abstract. Sago is one of the local food districts of Sangihe archipelago, but its use is still limited to traditional products. Edible film of sago starch is one of the alternative products for increasing the added value of this commodity as well as an environmentally friendly packaging material. The research aims to obtain edible film from sago starch using CMC and glycerol. Edible film processing was carried out by mixing 5% sago starch, and CMC 0.5% w/v and glycerol variation 1; 1.25; 1.5; 1.75; 2; 3.75; (%v/v) at 65-70°C, molded and heated with oven at 60°C. Sago-based edible film can be made with the use of CMC and glycerol as plasticizers in various concentrations. Use of variation glycerol concentrations at CMC concentrations of 0.5% in edible film making significantly influenced properties of sago’s edible film such as thickness, WVTR value, tensile strength, and elongation. The increasing amounts of glycerol concentration tend to increase WVTR values, decrease tensile strength value, and decrease elongation values of sago’s edible film.

1. Introduction
Sago is one of the regional foods of the Sangihe archipelago district, but its use is still limited to traditional products. Actually, sago starch was produced from the trunk of the true sago palm (Metroxylon sago) has the potential to be developed [1]. Each sago tree can contain more than 400 kg of dry starch, and its starch production can be up to 25 MT/ha, several times higher than rice and wheat and 10 times higher than potatoes and cassava [2].

Sago starch as a source of starch for industry (food and non-food) is different from ordinary starches such as cereals (rice, corn), tubers (potatoes), tubers ( tapioca), and beans (peas, green beans). [3]. Starch has the potential to be used in the production of prebiotics, composite film formulation, nanoparticle formation, pharmaceutical and medical applications, lactic acid and pullulanase production, electrolyte formation, environmental cleaning agents, as a food and aqua food thickener, ceramic foam filler, and emulsion [1].

Starch is the most popular plant polysaccharide for edible film and coating due to its abundance, cost-effectiveness, and excellent film-forming capability. Starch-based films have advantages, including excellent optical properties (transparent, colorless), organoleptic (tasteless, tasteless, odorless), and barrier properties (O2 and CO2 permeability) [4]. Amongst the starches, cheap sago
starch extracted from the palm *Metroxylon sago* has been used in a limited capacity in developing edible films [5].

Edible packaging comes from materials that can be consumed by humans. Edible coatings can be eaten with the food/drink they contain, so waste disposal problems are almost non-existent [6]. Due to the nature of the packaging material safe for human consumption, the transmission of packaged molecules into food does not cause health problems. Due to these advantages, edible packaging has undoubtedly attracted a lot of attention to replacing synthetic and biodegradable plastic packaging in food packaging applications [7]. Edible active packaging offers several additional advantages, including edibility, aesthetic appearance, and protection from contamination microbiology, biocompatibility, biodegradability, gas barrier properties, non-toxicity, and cost-effectiveness [8]. Bio-based edible packaging materials not only offer physical protection to the packaged foods but also serve as mass-transfer barriers for oxygen, moisture, lipids, flavors, carbon dioxide, and aromas between the atmosphere and food products.

Plasticizers are materials with a low molecular weight that increase the strength and flexibility of a material [9]. Plasticizer added to edible film making to overcome fragile, fragile, and low properties elasticity [10]. One of the plasticizers that are often used for biofilm-based on its film-forming capabilities is glycerol. Glycerol is a simple, colorless, odorless, viscous polyol compound that is boiled at a high point and freezes to form pasta [11]. Among the plasticizers, glycerol has often been used as a plasticizer for starch films due to its compatibility with amylose, which promotes better mechanical properties with interfering with amylose packing, thereby decreases the intermolecular forces between the starch molecules [12,13].

Besides the plasticizer, stabilizers are one of the additional ingredients in the making process of edible film. The stabilizer is an additional material of food that use is limited. Generally, the stabilizer is used to stabilize the food and make them become more concentrated or viscous. Stabilizers that often use are Carboxymethyl Cellulose (CMC), gelatin, and carrageenan [14]. CMC, an anionic linear polysaccharide derived from cellulose, is used as a viscosity modifier (thickener) for the stabilization of various food product emulsions. It absorbs water and moisture formation, and the hydrogel has a wide range of applications because of its excellent properties, such as high water content and superior biodegradability [15]. Research on sago film edible using CMC and glycerol has been conducted at varying levels of CMC and glycerol concentrations [16], however based on authors’s knowledge, research on making an edible film with a concentration of CMC 0.5% has not been conducted. Therefore, the research aims to characterize edible film from sago starch using CMC (0.5% w/v) and glycerol.

2. Method

2.1. Tools and material

The materials used in the study were sago, carboxyl methylecellulose, glycerol, and distilled water. The tools used are a digital scale, beaker glass, measuring cup, hot plate stirrer, magnetic stirrer, water bath, thermometer, glass plate measuring 8 x 7 x 2 cm, oven, Lloyd Instrument, micrometer, and other auxiliary equipment.

2.2. Edible Film Making

5% (w/v) solution of sago starch is stirred until homogeneous for approximately 10 minutes and then filtered using a filter cloth. The starch suspension is put in a 1,000 ml cup glass and heated in a water bath solution temperature of 65-70°C while stirring (30-40 rpm) for 10 minutes, then added CMC (0.5% w/v) little by little while continuing to heat and stir until the starch suspense thickens. After that, add glycerol according to treatment 1; 1.25; 1.5; 1.75; 2; 3.75; (%v/v), and the solution is cooled. The solution is then poured into a glass plate mold measuring 8 x 7 x 2 cm (length x width x
thickness), dried at 60 C for 10-12 hours. The film was removed from the mold and stored in a plastic container filled with silica gel for 12 hours. Relative humidity in a plastic container is around 40-50%.

The film is then cut into pieces according to the parameters to be tested. Tensile strength and elongation tests were 3 x10cm, while for WVTR, a circle was made with a diameter of 7 cm. The solubility is 2 cm x 2 cm. Before taking measurements, the film was conditioned for 24 hours in a plastic container containing silica gel.

2.3. Data analysis and collection procedures
Testing tensile strength and elongation were measured using a Universal Testing Machine (Lloyd Instrument), while film thickness was measured using a micrometer (accuracy 0.001 mm). The water vapor transmission rate (WVTR) using the gravimetric method was determined using the ASTM procedure. The film to be tested is glued to a bowl made of acrylic with an outer diameter of 8 cm, an inner diameter of 7 cm, and a thickness of 2 cm, then filled with 50 ml of water. The acrylic bowl is then stored in a jar containing silica gel with a relative humidity of 20%. The water vapor that diffuses through the film will be absorbed by the silica gel, the amount of which can be found by calculating the reduced weight of the bowl filled with water at the time of measurement. All tests were carried out twice. Changes in bowl weight and time are then plotted on a graph where the y-axis is the weight of the plate (g) when weighed, and the x-axis is time (from this graph, a regression line equation will be generated where the resulting slope is the rate of weight gain per unit (g / hour). WVTR is calculated by dividing the slope by the area of the film so that the WVTR unit is g / m²h.

3. Result and Discussion
The performance of edible films is typically evaluated by some important film characteristics, such as mechanical strength (TS – tensile strength, YM - Young’s modulus, and EAB - elongation at break), water vapor transmission rate (WVTR), and film color. Mechanical strength is essential for protecting the contained food from the external loads [6]

3.1. Thickness
The thickness is one of the characteristics of the edible film. Table 1 shows the thickness of the edible film at different glycerol concentrations.

| Treatment   | Thickness | Notation |
|-------------|-----------|----------|
| Glycerol 1 %| 0.200     | Ab       |
| Glycerol 1.25 %| 0.212 | Ab       |
| Glycerol 1.5 %| 0.183 | A        |
| Glycerol 1.75 %| 0.144 | A        |
| Glycerol 2%  | 0.269     | Be       |
| Glycerol 3.75 %| 0.328 | Be       |

Notes: Means within a column with the same letter are not significantly different at the 5% level of probability.

Table 1 shows that the edible thickness of sago film with the addition of CMC and glycerol from the results of the study ranged from 0.200 - 0.328 cm. The research results presented in Table 1 also showed that the addition of glycerol could decrease the thickness of the edible film at concentrations of 1.5% and 1.75% and increase thickness with the addition of glycerol. The treatment of glycerol 1.5% and 1.75% didn’t differ markedly from the addition of glycerol 1%, 1.25%, but differed markedly with the addition of glycerol 2% and 3.75%.

The result edible film tends to get thicker with increasing glycerol concentration; this is due to the greater mass in the solution. The highest film thickness is indicated by the glycerol concentration of 3.75%. Plasticizers glycerol can penetrate the network of starch quickly and easily to form a stronger
and thicker film than the unplasticized film [3]. The film with a larger thickness is easier to remove from the film plate. The thicker the film, the higher the hydrogen bonding with the amyllose molecule. This condition will cause an increase in the crystallinity of the polymer so that the water vapor transmission rate will be lower [16].

Glycerol can help retaining water in the film matrix due to its hydrophilic nature. Addition of glycerol increased the moisture content of films compared with other plasticizers and therefore increases film thickness to a greater extent. Because of its characteristic glycerol’s small molecular size, so the number of hydroxyl groups was higher [17]

3.2. Mechanical strength characteristic

Characteristic sago-based edible films with variations in glycerol concentrations, especially WVTR, tensile strength, and elongation shown in table 2

Table 2. Characteristics of sago-based edible films with variations in glycerol concentrations

| Treatment      | WVTR (g/m2/h) | Tensile Strength (Mpa) | Elongation (%) |
|----------------|---------------|------------------------|----------------|
| Glycerol 1 %   | 5.08950± 0.011 a | 2.27800± 0.191 b | 28.57700±0.081 a |
| Glycerol 1.25 %| 6.20400± 0.933 ab | 4.06350± 0.855 d a | 25.23000±0.534 ab |
| Glycerol 1.5 % | 10.35450± 0.137 abc | 4.26650± 0.302 d a | 23.05000±1.852 b |
| Glycerol 1.75 %| 14.91100± 3.961 cd | 3.17400± 0.025 c a | 24.82500±0.700 b |
| Glycerol 2 %   | 13.46300± 4.302 bc | 2.11900± 0.373 b c | 17.01750±2.095 c |
| Glycerol 3.75% | 22.05800± 4.849 d | 0.95000±0.096 a d | 14.01950±2.626 e |

Notes: Means within a column with the same letter are not significantly different at the 5% level of probability.

The data in Table 2 shows that treatment of glycerol concentrations statistically affects the mechanical strength characteristic of edible sago film.

3.2.1 Water Vapour Transmission Rate. Water vapor transmission rate (WVTR) is the speed at which water vapor transfers every unit permeation cell area. WVTR can be calculated from the slope graph of cell weight changes of each unit of time divided by the area of mass displacement [18]. Based on the results of statistical analysis, the WVTR value in the treatment of glycerol addition of 1.5% was no different from the additional treatment of glycerol 1%, 1.25%, 1.75%, and 2% but differed markedly from the treatment of the addition of glycerol 3.75%. While the WVTR value in the treatment of glycerol addition of 3.75% was no different from the treatment of glycerol 1.75%, but differed markedly with the treatment of the addition of glycerol 1%, 1.25%, 1.5%, and 2%. This means that the ability to withstand sago film edible water vapor produced using glycerol is 1.75% and 3.75% more likely to be the same compared to other treatments.

Table 2 shows that the value of WVTR increases with the addition of glycerol. The lowest WVTR value was found in the 1% glycerol addition treatment of 5.08950±0.011 g/m2/h, and the highest at 3.75% glycerol increase of 22.05800±4.849 g/m2/h. Barrier properties are essential for preventing the transmission of liquids/gases between the contained food and the environment [6].

Based on the results of statistical analysis, the WVTR value in the treatment of glycerol additions of 1%, 1.25%, 1.5% did not differ markedly from each other, while the WVTR value in the treatment of glycerol addition of 1.75% was no different from the treatment of glycerol additions of 1.5%, 2%, and 3.75%.

Glycerol as hydrophilic plasticizers is known to enhance the water vapor permeability of hydrocolloid-based films [19]. The plasticizer effectively reduced internal hydrogen bonding while increasing intermolecular spacing, thereby decreasing brittleness and increasing permeability of the film materials [3]. The film’s WVP is a steady-state property that describes the rate of water, based on differences in RH, which can move through the film. This means that the lower the WVP, the higher the water can hold with the film [11]. Plasticizers can modify the protein network structure and increase the water vapor permeability (WVP) of edible water-soluble when both plasticizers sorbitol.
and glycerol increased from 25% to 75%. Plasticizers modify the molecular organization of the protein network and increase the free volume resulting in a less dense network that results in more films that are permeable to water. The hydrophilicity nature of plasticizer molecules could be the cause of permeability increase with an increase in plasticizer. The addition of plasticizers on coating or film helps to increase permeability to gases and water due to the capacity for reduction of intermolecular forces in a polymer.

3.2.2. Tensile Strength (TS). The data in Table 2 shows that tensile strength tends to decrease with the addition of glycerol. The lowest tensile strength value is found in the treatment of glycerol addition 3.75% with a value of 0.95000+0.096 Mpa and the highest in the treatment of glycerol addition 1.5% with a value of 4.26650+0.302 Mpa.

The results presented in Table 2 indicate that an increase in glycerol content tends to reduce tensile strength. It is due to the plasticizing effect of glycerol can be attributed to the reduction in the tensile strength films. The films without a plasticizer were relatively brittle, and the seal separated instantly after application of force without the films being ruptured [3].

The additional treatment of glycerol 1% did not differ markedly from the treatment of glycerol 2% to the tensile strength value but differed markedly from other treatments, while the additional treatment of glycerol 1.25% and 1.5% did not differ markedly but differed markedly from other treatments. While the tensile strength value of glycerol addition treatment was 1.75%, and the treatment of 3.75% was significantly different from other treatments.

The use of glycerol in starch-based edible film making is because of the good compatibility of glycerol with starch, which enables glycerol to interfere in between amylose packing in the starch matrix through hydrogen bonding [20]. The number of glycerol causes the mobility of the polymer chains to increase, thus reduced the tensile strength. This consequently reduced the intramolecular attractions between starch chains, thereby promoting glycerol-starch attraction [21]. Based on the research on other research, at a fixed glycerol concentration, the tensile strength value increased, and the creep ability decreased with increasing CMC concentration [16].

3.2.3. Elongation. The results of the study in table 2 showed that the treatment of increased concentrations of glycerol tended to decrease the elongation value of the resulting sago film edible. The highest elongation value is found in the treatment of glycerol concentration of 1%, which is 28.57700+0.081%, and the lowest elongation value is found in the treatment of glycerol concentration of 3.75%, which is 14.01950+2.626%. It indicated that increased glycerol concentrations tend to decrease the elongation value of the edible film.

Based on the results of statistical analysis, the elongation value of glycerol concentration treatment of 2% and 3.75% did not differ markedly from each other, but the two treatments differed markedly from the treatment of glycerol concentrations of 1%, 1.25%, 1.5%, and 1.75%.

The results of this study are in line with the statement of Souza et al., which reported a significant decrease in the value of film elongation when glycerol was used. This fact is caused by the anti-plasticization effect caused by the high content of plasticizers. The anti-plasticization development at higher plasticizer concentration is associated with stronger interactions between plasticizer and starch molecules that inhibit a macromolecular movement, thus resulting in a decrease in elongation values.

The research is by the results of other research [16]. At the same CMC concentration, increasing the glycerol concentration resulted in a biodegradable film with a decreasing creep ability value. This is due to the influence of the CMC in the solution mixture, which functions as a thickener.

The use of glycerol can help the appearance of sago-based film edible with CMC composites. The price of glycerol is quite affordable, so sago-based edible processing can be done on a home industry scale, thereby increasing the benefit of sago as a local food commodity.
4. Conclusion
A sago-based edible film can be created with the use of CMC and glycerol as plasticizers in various concentrations. Use of variation glycerol concentrations at CMC concentrations of 0.5% in edible film making significantly influenced properties of sago edible film such as thickness, WVTR value, tensile strength, and elongation. The increasing amounts of glycerol concentration tend to increase WVTR values, decrease tensile strength value, and decrease elongation values of sago’s edible film.

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