Physical characteristics of edible film from modified breadfruit starch (*Artocarpus altilis* F.) with glycerol

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**Abstract.** Along with the increasing public awareness of environmental sustainability, the use of packaging that is environmentally friendly also increases. One of the research that supports it is the development of packaging such as edible film which is biodegradable from breadfruit starch. Utilization of breadfruit starch as the basic material for making an edible film is an effort in diversifying food processing. Edible films from modified breadfruit starch are considered to provide better physical characteristics of the film. The method used was an experimental method that was analyzed by the explorative description. This research consisted of 4 treatments with two repetitions and calculated the standard deviation. The results showed that the modified treatment of breadfruit starch had an influence on film color characteristics (L*, a*, b*), film thickness, and film solubility. The highest L* film color was owned by native starch treatment. The most reddish color a* film was owned by the heat-moisture treatment (HMT). The lowest color value b* is owned by the microwave heat treatment (MHT). The thinnest film thickness was owned by heat-moisture treatment and microwave heat treatment. The highest solubility was owned by microwave heat treatment.

**Keywords:** Breadfruit starch, modified starch, edible film, glycerol

1. **Introduction**

The edible packaging industry has had remarkable growth in recent years and is expected to have an important impact on the food market in the following years. Recently, consumers’ demand for higher-quality and safe foods with extended shelf lives and also their desire for natural and biodegradable materials instead of synthetic and non-biodegradable materials. The use of edible, biodegradable, and renewable materials to replace (partially or totally) petroleum-based packaging materials has increased the interest of the global market for edible packaging solutions.

One of the research that supports it is the development of edible packaging such as edible film which is biodegradable from breadfruit starch. Utilization of breadfruit starch as the basic material for making an edible film is an effort in diversifying food processing. Edible films from modified breadfruit starch are considered to provide better physical characteristics of the film. According to [1] a package is defined as “a metal can, glass bottle, plastic bag, or pouch which serves the functions of containing and protecting the product, as well as providing convenience and communicating to the consumer”. Edible packaging can be included in the presented packaging definition; however, in this case, all the materials...
used should be edible according to the legislation, both in the initial (packaging ingredients) and in the final (packaging) forms [2].

Starch films are odorless, tasteless, colorless, nontoxic, and semipermeable to carbon dioxide, moisture, oxygen, as well as lipid and flavor components [3]. Starch is composed of anhydroglucose residues and it is a naturally existent carbohydrate polymer [4]. Starch edible films suffer physical aging by crystallization and retrogradation, which alter film matrix structure and hence film physicochemical properties. This phenomenon, which consists of the rearrangement of amylose and linear parts of amyllopectin to form a more crystalline structure stabilized by hydrogen bonds, usually occurs together with plasticizer migrations to the surface and has been related to elongation capacity losses and embrittlement [5]. Film aging or its effects on film properties may be alleviated by employing different plasticizers or their mixtures, developing composite edible films made from different polymers, or tailoring the polymer properties by chemical or pH modifications [6].

Breadfruit (Artocarpus altilis) found in Indonesia which is a plant species that is spread in Polynesia, the Pacific and Southeast Asia. Breadfruit is usually harvested twice in January-February and August-September. Ripe breadfruit cannot be stored for long time because it decays quickly [7]. Therefore, efforts should be made to utilize it to become more diverse products and have a longer shelf life such as flour and breadfruit starch production. The high carbohydrate content of breadfruit makes it a valuable source of starch. Native starches have been used since ancient times as raw material to prepare different products. They are employed in foods because of their good thickening and gelling properties.

Physical modification of starch such as giving heat, creating conditions of water content, and a certain time in starch so that it changes the D-glucopyranosyl unit in the polymer molecule. This physical treatment generally changes the external arrangement of the starch polymer molecules that are inside the granules and the whole structure of the starch granules [8]. The physical modification is more acceptable in food products since it is an environmentally friendly and low-cost method [9]. These changes will change the nature of starch, especially the properties of starch paste and gel. Examples of physical modification of starch are heat-moisture treatment (HMT), microwave heat treatment (MHT), and annealing. However, the semi-crystalline (20% to 45%) nature of native starch results in some undesirable drawbacks, such as its hydrophilic character, poor solubility, poor mechanical properties, uncontrollable paste consistency, and low freeze-thaw stability during film formation [10]. Modified starch has grabbed much attention, both at the academic as well as at the industrial level, because these films exhibit dramatic improvement in filming properties without involving any significant increase in cost of production [3].

Plasticizer is one of the basic ingredients for making edible films that serves to overcome the fragile nature of the film layer. Glycerol is a plasticizer that is widely used because it is quite effective in reducing internal hydrogen bonds so that it will increase intermolecular distances. Theoretically, plasticizer can reduce the internal force between the polymer chains, so that it will reduce the level of agility and increase the permeability to water vapor [11]. Rodriguez added that glycerol is a plasticizer that is hydrophilic, making it suitable for forming a film which is hydrophilic like starch [12].

Previous studies have shown that the thickness, the tensile strength, and the elongation of the modified SPS edible films were higher while the WVP and the solubility were lower than those of the native SPS edible films. The film surfaces of modified SPS edible films appeared to be denser and compact than those of native SPS edible films. The crystallinity and the thermal properties of the modified SPS edible films showed a higher increase than those of the native SPS edible films [9].

Some previous studies about recent physical modifications of starch for film preparation show that microwave radiation can increased water solubility, reduced crystallinity, reduced viscosities of pasting, decreased enzyme susceptibility, gel clarity, and gel transparency [13]. Moist heat treatments can Low swelling, high thermal stability and pasting viscosity, increased gel hardness [14]. Annealing can enhance enzyme susceptibility and color change [15].

Based on the explanation above, research on edible films with starch modification is still rarely done. Therefore, it is important to conduct research on physical characteristics of edible film from modified breadfruit starch (Artocarpus altilis F.) with glycerol.
2. Materials and methods

2.1. Materials
The main ingredient used was breadfruit (*Artocarpus altilis* F.) obtained from Bandung, Indonesia. Glycerol obtained from Bratachem which was used as a plasticizer in making edible films.

2.2. Starch extraction
Mature unripe breadfruit was bought from Bandung, Indonesia. Starch from breadfruit was extracted based on the method described by [7] with slight modifications. Briefly, the breadfruit was peeled, sliced and washed thoroughly with water. Next, the breadfruit was blended with water at 1:4 ratio (w/v), and sieved using a filter cloth. The filtrate was precipitated for 12 h. Precipitated starch was washed with water, and centrifuged (Becman, model TJ-6) at 3,500 rpm for 30 min. The resulting precipitate was oven-dried (Shel Lab FX-14-2) at 50°C for 24 h, milled (FCT-Z300) and sieved (80 mesh).

2.3. Preparation of modified breadfruit starches
HMT modification, the method described by [16] was followed. Firstly, the moisture content of starch was adjusted to 30%, equilibrated at 4°C for 24 h, and heated at 100°C for 16 h in an oven (Memmert UNB 300). The HMT-starch was further oven-dried (Shel Lab FX-14-2) at 50°C for another 12 h. MHT modification, the process of making breadfruit modified starch by microwave heating refers to [17]. Natural starch is adjusted to the water content in accordance with the procedure of regulating the water content in the previous heat-moisture treatment method. A 100 grams of sample was put into an airtight polypropylene container then heated in the microwave for 5 minutes with a power level of 180 W. The starch was then dried using a cabinet oven at 50°C for 12 hours. Annealing modification, the process of making annealing modified breadfruit starch refers to [18]. Breadfruit starch was weighed, then made starch suspend with excess water content of about 65%, heating in a water bath (T = 55°C, t = 12 hours). Furthermore, centrifugation of 3000 rpm (t = 30 minutes) was carried out to produce precipitates (separated from the supernatant), then drying (T = 50°C, t = 24 hours), then grinding (grinder), and then sieving (100 mesh).

2.4. Edible films preparation
Weighed 5 g of breadfruit starch and glycerol with certain variations. Breadfruit starch was dissolved in 100 ml of distilled water and then heated using a magnetic stirrer until the gelatinization starch temperature was 73.98 °C. After 25 minutes of heating, the mixture was added to glycerol and stirred for 5 minutes. Furthermore, the solution was cooled and air bubbles or impurities were mixed in the solution (degassing). Then ± 150 gram solution was poured into a glass mold (14 × 2.5) cm and the mold was put into the oven at T = 70 °C for ± 4 hours using an oven blower/cabinet dryer. Then the mold was removed and cooled for ± 20 minutes. The next process of edible film was released from its mold and ready to be analyzed with various characterizations [19].

2.5. Film color characteristics (*L*<sup>*</sup>, *a*<sup>*</sup>, *b*<sup>*</sup>)
The color test was done using a chromameter, by measuring the values of *L*<sup>*</sup>, *a*<sup>*</sup>, *b*<sup>*</sup>.

2.6. Film thickness
Film thickness was measured using a micrometer (Digimatic Model Mitutoyo Micrometer, JP), as stated by [20]. The trick was to place the film between the micrometer jaws. Thickness was measured at seven different places, for each sample shape (circle, squares and dimensions l), then the average was calculated.

2.7. Film solubility
The solubility test as states by [11] the sample was cut to size 2 x 2 cm. Samples with filter paper were dried at 105°C, for 24 hour. Weigh filter paper and sample separately, determine the weight as initial
weight \((W_1)\). Insert the sample into 50 mL of water containing solution sodium azide 0.02%. The addition of sodium azide solution was intended to prevent the growth of microorganisms. Soaking was done for 24 hours, stirring slowly periodically. Filter, then paper filter and insoluble film were dried 105°C for 24 hours, after that the sample was weighed \((W_2)\) to determine a dry matter that was insoluble in water. The solubility was calculated by equation (1).

\[
\% \text{Solubility} = \frac{W_1 - W_2}{W_1} \times 100\%
\]

(1)

2.8. Statistical analysis
The analysis was performed with an explorative descriptive method and the standard deviation was calculated [21]. This research consisted of 4 treatments with 2 repetitions.

3. Results and discussion

3.1. Edible film colors
The color of an edible film was observed using chromameter.

3.1.1. \(L^*\) value (brightness). The degree of brightness material was an ability of a material to reflect light that hits its surface. Soaking and extraction processes during breadfruit starch preparation can have an influence on the brightness degree of breadfruit flour. The brightness value of this starch will affect edible film products. If the color of the starch is used more white, the color of the edible film produced will be more transparent.

![Figure 1](image1.png)

**Figure 1.** Color value of \(L^*\) edible films from various starch modifications.

The results of color value of \(L^*\) edible films from various starch modifications can be seen in figure 1. Edible films made from native breadfruit starch were almost as bright as HMT modified breadfruit starch. While the brightness of edible film in the MHT treatment was at a rather bright value. HMT modifications had the least brightness compared to the others. This is probably due to the high temperature heating treatment using the oven. The brightness of edible film was influenced by the white degree of breadfruit starch. The HMT treatment had the smallest white degree than native, MHT, and annealing which was used for long-term use of high temperatures. During heating there was a non-enzymatic browning that reduced the value of the white degree. The non-enzymatic browning reaction is known as the Maillard reaction, where the hydroxyl group of reducing sugars reacts with an amino group of protein peptides/aminos acids and produces a brown polymer (melanoidin) [22]. Heat-moisture treatment of breadfruit starch affected the color of starch, consequently altered color values \((L^*, a^* and
$b^*$ parameter) of produced starch films. The $L^*$ value was decreased following hydrothermal modification.

3.1.2. $a^*$ value (chromatic green-red color). The results of color value of $a^*$ edible films from various starch modifications can be seen in figure 2. Edible films from HMT modified breadfruit starch was the most reddish in color from the others, then followed by MHT, Annealing, and Native treatments. This was probably due to the HMT process there was heating at high temperatures so that the colored starch is more brownish red than the others.

![Figure 2](image)

**Figure 2.** Color value of $a^*$ edible films from various starch modifications.

3.1.3. $b^*$ value (chromatic blue-yellow color). The results of color value of $b^*$ edible films from various starch modifications can be seen in figure 3, the value of $b^*$ edible film in the MHT treatment has the smallest value. This was probably due to the MHT process did not warm up with the oven but uses the microwave to cause the flour to remain white.

![Figure 3](image)

**Figure 3.** Color value of $b^*$ edible films from various starch modifications.

3.2. Thickness of edible film

The thickness of edible film was observed using micrometer.
Figure 4. The thickness of edible films from modified starches.

The result of thickness of edible films from modified starches can be seen in figure 4, edible films from native treatment and annealing treatment had the same thickness and the highest value, while edible films in the MHT and HMT treatments had the same value. The thickness of the film would affect the characteristics of the mechanical film produced. Film thickness affected the tensile strength and elongation properties of the film. At starch concentrations that were too high will produce films with properties that were brittle (stiff, brittle) and not elastic. This will be an obstacle in the application of edible film as packaging. Edible films that were too thick can had a detrimental effect. The high modification temperature treatment damages the structure of the starch molecule which causes damage to molecular hydrogen bonds in starch granules so that amylose was very easy to escape [7]. Thickness of film was another important factor affecting water vapour permeability and lower thickness of films of heat-moisture treated starch could be the grounds for lower water vapour permeability of starch films than native buckwheat starch film [23].

3.3. Solubility of edible film

Film solubility can be used to show film integrity in a liquid environment. High solubility films show that the film’s resistance to water is lower, whereas if the solubility is low it shows that the resistance of the film to water is high. Besides that, solubility can show the hydrophilicity of the film.

Figure 5. The solubility of edible films from various starch modifications.

The result of solubility of edible films from various starch modifications can be seen in figure 5, the highest solubility value was found in the MHT treatment and then followed by the treatment of
annealing, native, and HMT respectively. The solubility of the film was affected by the bonding of the hydrogen. The increasing hydrogen bond causes the structure of the mutual starch molecules to bind to form a compact network, thereby reducing the solubility of the film. The three-dimensional network structure can inhibit starch bubbles and increase cohesion forces in starch granules that not much dissolves when starch dissolves. Whereas according to [24] states that the lower amylose content causes the weaker gel structure formed. The weak structure of the starch causes the dissolved solids to be greater so that the solubility gets bigger. This was the same opinion with [3] that MHT treatment could increase water solubility. HMT produced a stronger crystalline structure to prevent granular swelling starch granules resulting in a decrease of the solubility of edible film [9].

4. Conclusion
The results showed that the most appropriate amount of glycerol in making edible films was as much as 2% because it had a texture that was not easily torn and not brittle. In addition, the modified treatment of breadfruit starch had an influence on film color characteristics ($L^*$, $a^*$, $b^*$), film thickness, and film solubility. The highest $L^*$ film color was owned by native starch treatment. The most reddish color $a^*$ film was owned by the HMT treatment. The lowest color value $b^*$ is owned by the MHT treatment. The thinnest film thickness was owned by the HMT and MHT treatments. The highest solubility was owned by MHT treatment.

References
[1] Zepf P 2009 Glossary of Packaging Terminology and Definition The Wiley Encyclopedia of Packaging Technology vol 3 ed K L Yam (New Jersey: John Wiley & Sons, Inc) pp 1287–304
[2] Angelo M, Teixeira C and Augusto A 2016 Edible Packaging Today Edible Food Packaging: Materials and Processing Technologies, ed M. P. Angelo, R. Nuno, et al (Boca Raton, Florida: CRC Press) p 1
[3] Shah U, Naqash F, A Gani and F A Masoodi 2016 Art and Science behind Modified Starch Edible Films and Coatings : A Review Food Sci. Food Saf. 15 568–80
[4] Sondari D, Aspiyanto and Amanda A 2018 Characterization edible coating made from native and modification cassava starch Characterization Edible Coating Made From Native and Modification Cassava Starch AIP Conference Proceedings 2049 030013
[5] Van Soest J J G and N Knooren 1997 Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging, J. Appl. Polym. Sci. 64(7) 1411–22
[6] Nuria B and Joaquin G-E 2016 Production and Processing of Edible Packaging: Stability and Applications Edible Food Packaging : Materials and Processing Technologies ed M P Angelo, R Nuno (Boca Raton, Florida: CRC Press) pp 153–72
[7] Adebowale K O, Olu-Owolabi B I, Olawumi and O S Lawal E K 2005 Functional properties of native, physically and chemically modified breadfruit (Artocarpus artilis) starch Ind. Crops Prod. 21(3) 343–51
[8] J N Be Miller and K C Huber 2015 Physical Modification of Food Starch Functionalities Annu. Rev. Food Sci. Technol. 6(1) 19–69
[9] Indrianti N, Pranoto and A Abbas Y 2018 Preparation and Characterization of Edible Films Made from Modified Sweet Potato Starch through Heat Moisture Treatment IJC 18(4) 679–87
[10] Sabetzadeh M, Bagheri and M Masoomi R 2015 Study on ternary low density polyethylene/linear low density polyethylene/thermoplastic starch blend films Carbohydr. Polym. 119 126–33
[11] Gontard N, Guilbert and Cuq J -L S 1992 Edible Wheat Gluten Films: Influence of the Main Process Variables on Film Properties using Response Surface Methodology J. Food Sci. 57(1) 190–5
[12] Rodríguez M, Osés J, Ziani K and Maté J I 2006 Combined effect of plasticizers and surfactants on the physical properties of starch based edible films Food Res. Int. 39(8) 840–6
[13] Bertolini A C, Mestres C, Colonna P and Raf J 2001 Free radical formation in UV- and gamma-irradiated cassava starch J. Agric. Food Chem. 44 269–71
[14] Klein B et al 2013 Effect of single and dual heat–moisture treatments on properties of rice, cassava and pinhao starches Carbohydr. Polym. 98(2) 1578–84
[15] Chung H, Liu Q and Hoover R 2009 Impact of annealing and heat-moisture treatment on rapidly digestible, slowly digestible and resistant starch levels in native and gelatinized corn, pea and lentil starches Carbohydr. Polym. 75(3) 436–47
[16] Sui Z, Yao T, Zhao Y, Ye X, Kong X and Ai L 2015 Effects of heat-moisture treatment reaction conditions on the physicochemical and structural properties of maize starch: Moisture and length of heating Food Chem. 173 1125–32
[17] Deka D and Sit N 2016 Dual modification of taro starch by microwave and other heat moisture treatments Int. J. Biol. Macromol. 92 416–22
[18] Hoove R and Vasanthan T 1993 the Effect of Annealing on the Physicochemical Properties of Wheat, Oat, Potato and Lentil Starches, J. Food Biochem. 17(5) 303–25
[19] Setiani W, Sudiarti T and Rahmidar L 2013 Preparation and Characterization of Edible Films from Polunlend Pati Sukun-Kitosan Jurnal Kimia Valensi 3(2)
[20] Kim K W, Ko C J and Park H J 2002 Mechanical properties water vapor permeabilities and solubilities of highly carboxymethylated starch-based edible films J. Food Sci. 67(1) 218–22
[21] Wahyudi D and Djamaris A R A 2018 Statistical Methods for Food Science and Technology
[22] John M 1999 Principles of Food Chemistry Third Edition (New York: Aspen Publishers Inc.)
[23] Sindhu R and Khatkar B S 2018 Development of Edible Films from Native and Modified Starches of Common Buckwheat IARJSET 5(3) 9–12
[24] Lii C and Chang S 1981 J. Food Sci. 46 78–81

Acknowledgments
The present work was financially supported by Internal Grant of Universitas Padjadjaran, Indonesia.