Modification of *Dioscorea alata* L starch with propylene oxide to make edible film

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**ABSTRACT**

The research about modification uwi starch (*Dioscorea alata* L) by using propylene oxide has been done. Concentration of propylene oxide were 6%(v/w), 8%(v/w), and 10%(v/w). The amylograph parameter after modification were characteristic breakdown viscosity 43 BU and setback viscosity 975 BU. The modification starch has edible properties according to FDA (food and drug administration) which have degree of modification < 7%, degree of substitution < 0,1 and propylene oxide concentration < 10%(v/w). The best propylene oxide in making of edible film was 8%(v/w). The starch control can be made into edible film with thickness 0,136 mm, tensile strength 20,4605 Mpa and elongation 22%. Modification starch of uwi can be made into edible film with thickness 0,146 mm, tensile strength 25,3521 Mpa, elongation 30% and water vapor transmission 7,2651 g/m²/24 hours. FTIR characterization of uwi starch showed the occurrence of hydroxypropylation. The peak spectrum at 2900 cm⁻¹ showed bonding of C-H from methyl group, which is characteristic for modification starch with hydroxypropil. Characterization with scanning electron microscopy showed that modification of uwi starch has turned the granule of starch to be fully swollen.

**Keywords:** Modification starch, uwi starch (*Dioscorea alata* L), propylene oxide, edible film

**1. INTRODUCTION**

Polysaccharides from tuber starch can be used as raw material for edible film making. Starch is often used in the food industry as a biodegradable plastic polymer film to replace undegradable plastic, because it is cheap, easily available, renewable and can provide good physical characteristics. Edible films made of polysaccharides have several advantages, namely either to protect the product against oxygen, carbon dioxide and lipids but very low water vapor resistance (Bourtoom, 2008). Uwi starch has the potential to be modified because the functional properties of this starch are acceptable as the film. Edible film from uwi starch has low resistance to water vapor. The chemical properties of uwi starch needs to be improved by modification.

Modified starch is mostly done in various ways to obtain starch with certain characteristics. Modifications can be carried out by crosslinking (Munarso et al, 2004), hydroxypropylation (Febby et al, 2012), etherification (Doulkely et al, 2007), and etherification (Aziz et al, 2004; Choi and Kerr, 2003; Lawal, 2009). In this research modified uwi starch was conducted using propylene oxide to produce a lower gelatinization temperature, the optimum swollen of starch granule and resistant to retrogradation (Lawal, 2009). Uwi tuber is one food starch that has not been utilized in maximum way (Richana and Sunarti, 2004). This tuber contains starch that include of amylose and Amylopectin which can be used to create a thin layer film, to serve as an alternative material of edible filmmaking.

**2. EXPERIMENTAL SECTION**

**2.1. Modification of Uwi Starch**

Concentration of propylene oxide (C₅H₈O) that was used were 0%, 6%, 8% and 10%. Modification procedures of uwi tuber starch were made in accordance with Lingfeng and Ya-Jane procedures (2000). 15 g of sodium sulfate (15% of the dry weight of uwi starch) was dissolved in 186 mL of deionized water in a 300 mL at room temperature, forming a solution of sodium sulfate. Uwi starch was weighed 100 g (dry weight) and then put in a solution of sodium sulfate with a magnetic stirrer to form a suspension. pH was set at 11.5 by the addition of 1% NaOH solution and stirred for 10 minutes.

Propylene oxide was added with variation 0%, 6%, 8% and 10%(v/w) of the dry weight of starch into the suspension. Flask was closed and the solution was stirred at room temperature for 1 hour before the temperature rose to 45 °C. Stirring was continued constantly using a dry incubator at a speed of 150 rpm for 24 hours and the pH was lowered to 5,5 using HCl 1 N. Suspension temperature was lowered to 30 °C. The suspension was filtered using whatman paper no. 4, while washed with distilled water for 5 times. Drying is carried out at temperature of 40 °C in an oven for 18 hours. Parameters observed for uwi starch modification are pattern of amylograph, modification levels and degree of substitution.
2.2. Modification levels JECFA 2009

Levels of modified starch with propylene oxide performed using ninhydrin reagent. Ninhydrin reagent prepared from 3% solution of 1,2,3-triketohidrin crystals in a solution of 5% sodium bisulfite. Modified starch samples were weighed as much as 50-100 mg and put in a 100 mL volumetric flask, and were added 1 N sulfuric acid at 25 mL. Then unmodified starch samples were treated in the same way as the above treatment. The flask was placed into a water bath and then heated until the sample is solved, after that it was cooled and diluted with water to a volume of 100 mL samples as well as unmodified starch.

Solution of 1 mL were taken and put into a 25 mL test tube lids. The test tube immersed in cold water and then was dropped with 8 mL of concentrated sulfuric acid. The solution was mixed until homogeneous and the reaction tube is placed into the water bath for 3 minutes. After that it was transferred to an ice bath until the solution became cool. Ninhydrin was added by 0.6 mL through the tube and stirred. After that the tube was placed into a water bath at temperature of 25 °C for 100 min. Each test tube concentrated sulfuric acid is added, until the volume reaches 25 mL and mix for several times.

3 mL of solution measured with spectrophotometer. Unmodified starch used as a reference and the absorbance was measured at 591 nm. Curve of calibration was made with standard solutions containing 10; 20; 30; 40 and 50 μg propylene glycol each mL. The calculation of hydrokxipropil as follows.

\[
\%\text{HP} = \frac{K \times 0.7763 \times F}{w} \times 100
\]

Where HP is hydroxypropyl, W is weight of sample (mg), F is force, and K is concentration of propylene glycol

2.3. Determination of the substitution degree (Wurzburg 1989)

Determination of the substitution degree of the modified starch can be calculated by using the calculation as shown below.

\[
\text{DS} = \frac{162x\%\text{hydroxypropyl}/38}{100 - \left(\frac{37\,\text{g}}{57\,\text{g}}\times\%\text{hydroxypropyl}\right)}
\]

Where 162 is the molecular weight of glucose, 58 is the molecular weight of propylene oxide, and 57 is the molecular weight of propylene-1 atom H

2.4. Pattern Amilograf of Ravid Visco Analyzer

Analysis of the rheological properties of samples performed by using RVA Newport Scientific Pty Master Tec. Ltd., Warriewood, Australia. RVA tool set using a modified standard 2 with basis

| Concentration of propylene oxide (%) | Gelatinization Temperature | Viscosity |
|-------------------------------------|----------------------------|-----------|
|                                     | Initial (°C) | Maximum (°C) | Maximum (BU) | Breakdown (BU) | Set back (BU) |
|-------------------------------------|--------------|--------------|--------------|----------------|---------------|
| 0                                   | 88 ± 0.36    | 90.7 ± 0.16  | 1946.5 ± 0.38 | 547 ± 0.41     | 977.5 ± 0.42  |
| 6                                   | 82.75 ± 0.27 | 90 ± 0.22    | 4197 ± 0.11  | 1407.5 ± 0.36  | 1608 ± 0.16   |
| 8                                   | 77.5 ± 0.15  | 82 ± 0.46    | 2407.5 ± 0.20| 43 ± 0.28      | 975 ± 0.25    |
| 10                                  | 76.5 ± 0.21  | 85.5 ± 0.12  | 4379.5 ± 0.43| 2377.5 ± 0.12  | 834 ± 0.43    |
The cup was weighed to the nearest 0.0001 g, and the difference in weight gain (mg) and time (hours). Water vapor transmission rate value was calculated with the following equation: Moisture absorbing material was placed in the cup so that the surface is 3 mm of the film to be tested. The cup was placed part facing up. Film were put into the cup until cover all of the cup.

\[
LTUA = 4.8 \times \frac{m}{t} \text{ (g/m}^2/24 \text{ hours)}
\]

Where \( m \) is weight gain (mg per hour), \( t \) is time last weighing between 2 (hour).

\( \Delta J \) is the distance difference before and after drawn (cm), \( J_0 \) is the distance between the two end clamps of the film before the drawn (cm).

### 3. RESULT AND DISCUSSION

#### 3.1. Pattern of Amilograf

Amilograf starch pattern is determined from the ability of starch granules to swell and rupture, which causes swelling of the starch granules and increasing the viscosity of the suspension. Modified uwi starch amilograf have a different pattern with uwi natural starch. Retrogradation the starch could be seen from the decrease in the temperature gelatinization faster compared by the control starch. The decrease in the temperature gelatinization of this starch will also influence the physical characteristics of the breakdown of the film and percent of elongation. Films from starch that has a low gelatinization temperature will produce the film with tensile strength and elongation percent better than the films of starch that has a high gelatinization temperature (Table 4). This happens because of the low gelatinization temperature will result in a more stable starch granules so that when made into a film will produce the film ediable with compact and robust properties (Bourtloom, 2008). The increase in the viscosity after modification of the natural starch (the Table 1) was caused by the modification of the starch. This process facilitates penetration of water in the granule of the starch and weakened the structure of the granule of the starch. (Han et al, 2005) reported that the modification of the rice starch with propylene oxide showed the increase in the viscosity. Breakdown values obtained from starch amilograf results granule stability in the heating process. The stability of paste viscosity values calculated from the difference between the maximum value of viscosity at 95 °C.

The higher the level difference paste viscosity during the process shows that the starch is increasingly unstable. Table 1 shows that the higher of the maximum viscosity the value breakdown (stability pasta) greater. Choi and Kerr (2005) said that the modification of the starch with propylene the oxide also could reduce retrogradation the starch. Retrogradation the starch could be seen from the value setback. The table 1 showed that thought setback the modification starch with propylene the oxide was smaller compared by the natural starch.

Increasing in the concentration propylene the oxide 6% did

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**Table 2. Modification levels and degree of substitution**

| Concentration of Propylene Oxide (%) | Modification Levels (%) | Degree of Substitution |
|-------------------------------------|-------------------------|------------------------|
| 0                                   | 0                       | 0                      |
| 6                                   | 1.118±0.30              | 0.031±0.27             |
| 8                                   | 1.800 ±0.21             | 0.051±0.30             |
| 10                                  | 3.100 ±0.31             | 0.089±0.28             |

**Fig 1.** IR spectrum of natural uwi starch and modification of uwi starch with the addition of Propylene Oxide 8%

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- IR spectrum of uwi starch before modification
- IR spectrum of uwi starch after modification

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Elongation (\%) = \( \frac{\Delta J \text{ (cm)}}{J_0 \text{ (cm)}} \times 100\% \)
Characterization edible film needs to be done in order to know the quality of edible film to apply as a food wrap. Characterization had been done to edible film of natural and modified starch with the addition of propylene oxide 8% (v/w). Parameters that can be used to see the quality of the food packaging is among others thickness, tensile strength and percent elongation of the film edible also water vapor transmission.

The parameter is formed from the natural starch uwi broke because amylose content of the starch is not too high is only ± 22%. While the film of starch modification produces films that are not broken and has better characteristics by increasing thickness, tensile strength, percent elongation and reduction of water vapor transmission. Amylose is one of the compiler molecules of the starch where it can be used in the making of the film and a strong gel. High amylose will make the film becomes more compact because amylose is responsible for the formation of the film matrix. According to Bourtoom (2008) that making an edible film of the high amylose corn starch (75%) would be better than making edible film of normal corn starch (25%).

3.5. Thickness of Edible Film

Thickness of edible film is a physical trait which is affected by the concentration of dissolved solids in the solution of the film and the size of the glass plate.

Table 3 shows that the modification edible film of the starch has higher thickness that hydroxpropyl edible film where 0.136 mm becomes 0.146 mm; 0.172 mm and 0.139 mm with variation thickness, tensile strength and percent elongation of the film edible not broken and has better characteristics by increasing thickness, because amylose content of the starch is not too high is only ± 22%. While the film of starch modification produces films that are not broken and has better characteristics by increasing thickness, tensile strength, percent elongation and reduction of water vapor transmission.

Table 4 shows that an increase in the tensile strength of the film edible disconnected. Percent elongation showed the film’s ability to stretch to the maximum. Edible films with low elongation values indicate that the film is less well used as packaging for its physical characteristics are less robust and easily broken.

3.6. Tensile Strength and Percent Elongation of Edible Film

Tensile strength is the maximum tensile force which can be held on the film until disconnected. Great tensile strength value means quality packaging films as well as good. Film edible with small tensile strength values indicate that the film is less well used as packaging for its physical characteristics are less robust and easily broken.

3.7. Water Vapor Transmission of Films Edible

Permeability is one important factor in food packaging, because it is closely related to the shelf life of food products. Permeability values serve to estimate the shelf life of products packaged and to determine the appropriate foodstuffs packaged.

Table 5 shows a decline in water vapor transmission films made from natural uwi starch than films made from modified uwi starch.
starch of 100 g / m² / 24 hours to 7.2651 g / m² / 24 hours. Edible films made from natural uwi starch have water vapor transmission of 100 g / m² / 24 hours. Water vapor transmission of this film was large, indicates the film is very easy to absorb moisture.

Water vapor transmission of edible film from modification starch was smaller than the natural starch films due to the replacement of OH groups on the glucose units with a group hydroxypropyl ether leads to reduced the ability to bind water. Detduangchan N et al (2014) stated that due to the hydrophilic nature of the chemical structure of starch is widely available with hydroxyl group (OH) which has the ability to bind water. In replacing, the hydroxyl group with Hydroxypropyl ether made polymer matrix become denser due the increase in molecular weight of Hydroxypropyl ether. Yuliasih et al (2007) suggest that modification of starch can make the arrangement polymer matrix denser so that the water vapor transmission rate is lowered.

### 3.8. Morphology of Edible Film From Natural and Modified Uwi Starch by SEM

Film edible from natural and modified uwi starch was carried out through process of gelatinization. Gelatinization temperature recorded 77 °C. Based on the results of the scanning electron microscopy (SEM) the film control shows still have starch granules. At this temperature natural starch have not swollen completely. Edible film from modified starch look smooth and no longer contain starch granules. This indicates that at temperature of 77 °C all modified starch granule completely swollen. This phenomenon is supported by the data of tensile strength and percent elongation of the film. Control starch films have tensile strength values 20.40 N / mm² while the modified starch film has a tensile strength of 25.30 N / mm². In natural starch film, gelatinization process is incomplete and caused polysaccharide chain still wrapped tightly in starch granules so the tensile strength becomes weaker than modified starch films. It is also strengthened by the data of percent elongation from modified starch films. It has greater elongation than natural starch film. Based on morphology form SEM, it can be explained that water vapor transmission rate of the control starch film (100 g / m² / 24 h) is greater than the modified starch films (7.26 g / m² / 24 h). The natural starch granules were pack in film randomly causing a gap between starch granules and it is easy to absorb water molecule.

### 4. CONCLUSION

Natural Uwi starch has the characteristics with initial gelatinization temperature 88°C, maximum Gelatinization temperature 90°C, maximum viscosity 1946.5, viscosity of breakdown 547, and viscosity of setback 971.5. Uwi starch which has been modified by the addition of propylene oxide with various concentration of 6%, 8% and 10% showed decrease in gelatinization temperature and increase of maximum viscosity. Modified starch by the addition of propylene oxide 8% (v / w) has the effect that can improve characteristics of edible film where an increase in mechanical properties such as the thickness from 0.136 mm to 0.146 mm, tensile strength from 25.3251 to 20.4605 MPa, percent elongation from 22% to 31% and decreased permeability of water vapor transmission from 100 g / m² / 24 hours to 7.2651 g / m² / 24 h compared to unmodified starch.

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