SYNTHESIS OF BREAD FRUIT (*Artocarpus communis*)-BASED HYDROXYPROPYL STARCH THROUGH ETHERIFICATION USING PROPYLENE OXIDE

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ABSTRACT

Hydroxypropyl starch was synthesized from bread fruit (*Artocarpus altilis*) starch that modified with the variation of propylene oxide, i.e. 8, 10 and 12%; and reaction time, i.e. 30, 60 and 90 min, in alkaline condition. The optimum condition to prepare hydroxypropyl starch was found at 12% of propylene oxide concentration and 90 min of reaction. As an ether starch modification, the obtained hydroxypropyl starch was confirmed by the presence of FT-IR band at 1149-1157 cm⁻¹ that assigned as the C-O-C vibration. The ¹H-NMR confirmed the ether starch modification was successfully synthesized with the disappearance of the peak at 4.5-5.5 ppm, and the appeared of a new doublet peak at 3-4 ppm that confirmed the presence of hydroxypropyl group. The highest substitution degree of hydroxypropyl was 1.8 that found a variation of 12% propylene oxide and 90 min of reaction. The obtained hydroxypropyl starch showed swelling power of 12.05, the solubility of 9.42%, and water content of 4.16%.

Keywords: Hydroxypropyl Starch, Bread Fruit (*Artocarpus altilis*) Starch, Propylene Oxide

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INTRODUCTION

Food issue in this era is caused by the limited food supply and the dependency of people to consume specific food. As an example, Indonesia has a huge variety of food crops, i.e. cassava, potato, taro, etc, but still, rice is the main food consumed by Indonesian. The studies about finding new material for substituting the current functional food is urgently needed. One kind of raw material of food product is flour, that known as a solid particle that appears as a fine powder and is commonly made by grinding process of grains, roots, beans, nuts, or seeds that contained starch. Other than those materials, there is one commodity that has not been utilized yet, i.e. bread fruit (*Artocarpus altilis*).¹

Starch is the main component of bread fruit, but there are several disadvantages if this crop is utilized as a food commodity, e.g. it would be swelling easily and has low viscosity during heating and mechanical stirring treatments. Due to that issue, chemically structure modification is needed to improve the properties of bread fruit starch.² One kind of chemical modification that is commonly used for this purpose is by introducing hydroxypropyl group into starch backbone through etherification using propylene oxide in alkaline conditions. This modified starch can be classified as resistant starch type 4, which is a kind of starch that cannot be hydrolyzed by amylase as well as ester or ether starch and crosslinked starch.^{3,4}

Researches that focused on the preparation of hydroxypropyl starch have been conducted by several researchers, e.g. sago starch⁵, rice, wheat⁶, potato⁷, banana, cassava^{8,9}, corn and amaranth starch.¹⁰ Wogum¹¹ also performed a study that focused on the characteristic and biodegradable properties of hydroxypropylyed rice-starch film. The study revealed the gelatinous and enthalpy of modified starch was lower than unmodified starch, equivalent to the propylene oxide concentration, with a lower gel strength and opacity. In the utilization of the biodegradable film, the elongation, permeability, mechanical strength

and opacity of modified starch was highest than a neat starch. This result revealed that the hydroxypropyl starch showed good properties and suitable for food commodity.

The objective of the current study was to evaluate the potency of bread fruit starch modified by introducing hydroxypropyl group to improve the starch properties. The etherification was conducted by varying the concentration of propylene oxide and the reaction time. This variation is believed can be used as a representative to determine the optimum condition for obtaining the etherified starch which has a high yield and superior properties.

EXPERIMENTAL

Material

Materials used in this study were: bread fruit, 10% Na₂SO₄, propylene oxide, 5% NaOH, distillate water, 10% HCl.

Bread Fruit Starch

Bread fruit starch was isolated using the previous method developed by Zuhra et al.¹². The obtained starch was then characterized using a spectrophotometer FT-IR.

Synthesis of Etherified Starch

The etherified starch was synthesized as per the method developed by Hung¹³. About 10 g of bread fruit starch was dispersed in 10wt% of sodium sulphate until the starch solution concentration was 40% (w/v). The pH of the solution was adjusted to 10 by adding 5% NaOH and continued by the addition of propylene oxide (8, 10 and 12% (w/v)) into the starch solution⁹. The obtained suspension was stirred for 30 min in the room temperature (25°C) and then placed it on shake incubator using the following condition T = 40°C and ν = 200 rpm. After 24 h, the pH of the suspension was adjusted to 6 by adding 10% HCl, centrifuged (3000xg for 5 min) and washed 4 times. The obtained precipitate was dried at 40°C for 24 h and ground. The hydroxypropylyed starch then was characterized using spectrophotometer FT-IR and ¹H-NMR. This procedure was repeated with the different stirring time, i.e. 60 and 90 min.

Determination of Degree Substitution

The substitution degree of etherified starch was determined using the equation of De Graaf *et al.*¹⁵:

$$MS = \frac{I_A}{3I_{AGU}}$$

Where:

I_A = Specific signal of hydroxypropyl in ¹H-NMR

I_{AGU} = Specific signal of anhydrous starch that confirmed by three peaks in ¹H-NMR

Water Content

The water content of the neat and modified starch was determined using a drying method of AOAC¹⁶. About 5 g of starch was placed in the petri dish that has been dried for 2 h and weighed. The starch and petri dish then placed in an oven at 110°C for 24 h or until the weight was constant. The water content was calculated using the following equation:

$$\text{Water Content}(\%wt) = \frac{(x - y)}{(x - a)} \times 100\%$$

Where:

x = Weight of sample and petri dish before the drying process (g)

y = Weight of sample and petri dish after the drying process(g)

a = Weigh of petri dish (g)

Swelling Power and Solubility

The swelling power and solubility of starch were determined using the following method^{6,17}. The starch was suspended in distillate water (1wt%). The suspension was heated in a water bath at 95°C for 30 min and cooled until the temperature was $\pm 27^\circ\text{C}$. The starch suspension was centrifuged at 5000 rpm for 15 min. The 10 mL of supernatant was dried at 110°C until the constant weight was obtained. The residue

obtained from dried supernatant showed the amount of soluble starch. The solubility of starch can be calculated using the following equation:

$$\text{Solubility} = \frac{W \text{ dried supernatant}}{\text{starch}} \times 100\%$$

The residue and water that retained after centrifugation was weighed and the swelling power was determined using the following equation:

$$\text{Swelling Power} = \frac{\text{Residue} + \text{water}}{\text{Starch}}$$

RESULTS AND DISCUSSION

The starch that was prepared using a method from the previous study¹² has a yield percentage of 10 wt%. That value was obtained by using the following method, about 200 g of starch was produced from 2 kg of bread fruit (*Artocarpus altilis*) fine powder. A qualitative method using iodine reagent was performed to determine the presence of starch on the isolated material of bread fruits. The formation of purple color during the reaction between iodine and isolated material of bread fruit confirmed the amyllum or starch was successfully isolated.

Fig.-1: FT-IR Spectrum of Bread Fruit Starch

FT-IR spectrum of bread fruit starch is displayed in Fig.-1, which shows the band of specific vibration at 3425; 2931; 1635; and 1157,29 cm^{-1} . The presence of hydroxyl group (-OH) was confirmed at 3425 cm^{-1} . In the previous research, hydroxyl functional group was found at 3377-3387 cm^{-1} . The stretching vibration of C-H from methyl or methylene group and C=O from ester was found at 2931 and 1635 cm^{-1} , respectively. This result was supported by the¹⁸, it appeared at 1645 cm^{-1} . The band that appeared at 1157 cm^{-1} was assigned as C-O bonding from ether group. The previous research conducted by Muljana¹⁹ reported that C-O of ether group was found at 1242 cm^{-1} . The presence of C-O from glycosidic bond was found at 1018 cm^{-1} , this number has slightly different in number that obtained by Muljana^{19,20}, it was 1028 cm^{-1} .

Hydroxypropyl Starch

The obtained hydroxypropyl starch has a white color in the powder. The yield of etherification was 88.30%. The mechanism reaction of introducing hydroxypropyl into starch backbone is predicted as in (Fig.-2): As in the previous research, Yuniar²¹ stated that the reaction between starch and propylene oxide will be more effective if starch contained high amylose. This is due to amylose has a straight chain with the presence of hydroxyl group in the C2. This position is more reactive than other atom carbon positions

because it is placed in an open position and easy to reach by the propylene oxide, compared to amylopectin. Van de Burgt et al.²², in their research, claimed the hydroxyl group that presents in C2 (60-65%) is more reactive than in C3 (20%) and C6 (15-20%). The substitution of hydroxyl group in the region of amylose is 1.6-1.9 higher than in the region of amylopectin. Amylose region is also called an amorphous region. The substitution of hydroxyl group in this amorphous region can be easily performed.

1. Reaction between starch and NaOH

2. Reaction of Starch-ONa with Propylene Oxide

Fig.-2 : Mechanism Reaction of Hydroxypropyl Starch²³

FT-IR Analysis of Hydroxypropyl Starch

The FT-IR spectrum of hydroxypropyl starch showed a not significant change on the wavenumber, this is due to the ether group actually can also be found in the neat starch. The hydroxypropyl starch was confirmed by the presence of a band around 1480-1375 cm^{-1} that assigned as methyl ($-\text{CH}_3$) group. This band indicated the hydroxypropyl group was successfully substituted in the starch and this methyl group will not be found in neat starch.²⁴ Based on the FT-IR spectrum can be concluded that the chemical modification was not broke the starch's chemical structure. FT-IR data of the variation of propylene oxide concentration and reaction time can be seen in (Fig.-3 and Fig.-4), respectively.

Fig.-3: FT-IR Spectra of Hydroxypropyl Starch – A Variation of Propylene Oxide Concentration

¹H-NMR Analysis

The ¹H-NMR analysis (Fig.-5 – 10) of modified starch shows a doublet signal at 3-4 ppm. This chemical shift indicated the presence of hydroxypropyl group, and there were three signals between 4.5 and 5.5 ppm that assigned to anhydroglucose (-OH) starch.

Fig.-4: FT-IR Spectra of Hydroxypropyl Starch – A Variation of Reaction Time and Propylene Oxide 12%

Fig.-5: ¹H-NMR of Bread Fruit Starch

Fig.-6: ¹H-NMR of Hydroxypropyl Starch that prepared using Propylene Oxide 8% and Reaction Time of 30 min

Fig.-7: ^1H -NMR of Hydroxypropyl Starch that prepared using Propylene Oxide 10% and Reaction Time of 30 min

Fig.-8: ^1H -NMR of Hydroxypropyl Starch that prepared using Propylene Oxide 12% and Reaction Time of 30 min

Fig.-9: ^1H -NMR of Hydroxypropyl Starch that prepared using Propylene Oxide 12% and Reaction Time of 60 min. The optimum condition to performed starch modification was obtained at the variation of 12% of propylene oxide and 60 min of reaction time. This optimum condition was decided based on the absence of three

signals at 4.5-5.5 ppm that indicated the hydroxyl group in the neat starch has been successfully substituted. The maximum yield was obtained at the variation of 12% of propylene oxide and 90 min of reaction time, where the doublet signal gave a value of 1.8. The ^1H -NMR analysis of neat starch using DMSO as the solvent showed the hydroxyl group's proton of C6, C3, and C2 at 4.5-6 ppm²⁵. Substitution molar was determined by calculating the ratio between peak area of substituted hydroxypropyl (indicated as doublet peak) at 3-4 ppm and peak area of anhydroglucose unit at 4.5-5.5 ppm. This equation can be used to determine the number of hydroxyl groups attached to the bread fruit starch during etherification. In the current study, the substitution molar will increase with the increase of propylene oxide concentration. Krishnan et al¹⁰ obtained a similar correlation between the concentration of hydroxypropyl and the substitution molar on corn starch and amaranth.

Fig.-10: ^1H -NMR of Hydroxypropyl Starch that prepared using Propylene Oxide 12% and Reaction Time of 90 min

Characterization of Hydroxypropyl Starch

Substitution Degree

The substitution degree of modified starch that was prepared using various propylene oxide concentrations and reaction time can be seen in Tables-1 and 2.

Table-1: Substitution Degree of Modified Starch that reacted for 30 min

Propylene Oxide Concentration (%)	Substitution Degree
8	0.47
10	0.66
12	0.77

Table-2: Substitution Degree of Modified Starch that prepared using 12% of Propylene Oxide

Reaction Time (min)	Substitution Degree
30	0.77
60	1.2
90	1.8

The substitution degree showed a linear correlation to the propylene oxide concentration, as well as reaction time. The increase of hydroxypropyl group and MS was caused by the starch granules swollen easily at the alkaline condition during the etherification. As the impact, hydroxypropyl group can easily change the hydroxyl group of neat starch.⁶

Water Content

The water content analysis of bread fruit starch can be seen in Table 3. On other hand, the water content of modified starch as per concentration and reaction time variation can be seen in Tables 4 and 5.

Table-3 : Water Content of Bread Fruit Starch

Starch	Water Content (%)
Bread fruit	4.28

Table-4 : Water Content of Modified Starch that reacted for 30 min

Propylene Oxide Concentration (%)	Water Content (%)
8	5.48
10	4.91
12	5.33

Tabel-5 : Water Content of Modified Starch that prepared using 12% of Propylene Oxide

Reaction Time (min)	Water Content (%)
30	5.33
60	4.60
90	4.16

The water content of modified starch was easily influenced by the process condition, especially during the drying process. The oven temperature used in this research was 40°C for 8 h.

Swelling Power and Solubility of Starch

The swelling power and solubility of bread fruit starch can be seen in Table-6 and the hydroxypropyl starch with concentration and reaction time variation can be seen in Table-7 and 8, respectively.

Table-6: Swelling Power and Solubility of Bread Fruit Starch

Starch	Swelling Power	Solubility (%)
Bread fruit starch	8.023	3.10

Table-7: Swelling Power and Solubility of Modified Starch that reacted for 30 min

Propylene Oxide Concentration (%)	Swelling Power	Solubility (%)
8	8.72	4.10
10	9.22	5.18
12	9.75	6.30

Table-8: Swelling Power and Solubility of Modified Starch that prepared using 12% of Propylene Oxide

Reaction time (min)	Swelling Power	Solubility (%)
30	9.75	6.30
60	11.66	8.16
90	12.05	9.42

Fig.-11: Morphological of (a) Bread Fruit Starch, (b) + Propylene Oxide 8%, (c) + Propylene Oxide 10%, (d) + Propylene Oxide 12% - 30 min, (e) + Propylene Oxide 12% - 60 min, (f) + Propylene Oxide 12% - 90 min

A linear correlation was found between propylene oxide concentration and swelling power, as well as solubility of starch. With the increase of propylene oxide, the amylose content of modified starch will decrease, as the impact of the swelling power and solubility will increase.

Swelling power is influenced by the ability of starch molecules to bind water through hydrogen bonding. In the gelatinization, the hydrogen bonding among starch molecules is replaced by hydrogen bonding between starch and water molecules. During this process, the starch will swell into its maximum capacity.²⁶ The difference in maximum capacity and solubility indicated the difference in bonding force of granule's starch.²⁷ This strong interaction will reduce the water inhibition into the granule and will implicate the swelling power and solubility.²⁸ The increase of substitution molar will improve the solubility of starch.²⁹ This is due to the modification process of starch caused the change in the structure of starch, become more stretch. These changes reduce the intermolecular strength but improve the hydrophilicity of starch.^{5,30}

Morphological of Hydroxypropyl Starch

The SEM analysis of modified starch can be seen in Fig.-11. The morphological of neat and modified starch showed almost similar particle-shaped, granules.³¹ This indicated the addition of propylene oxide was not have a significant influence on the morphological of modified starch.

CONCLUSION

The starch modification that was prepared using propylene oxide showed a chemical shift at the wavenumber of 1149-1157 cm^{-1} that assigned to C-O-C vibration. The $^1\text{H-NMR}$ also supported the FT-IR spectrum with the presence of a doublet signal at 3-4 ppm that indicated as hydroxypropyl group. The optimum variation to synthesis hydroxypropyl starch was at 12% of propylene oxide and 90 min of reaction time. The other properties of the optimum starch were 1.8 of substitution degree; 12.05 of swelling power; 9.42% of solubility in water; and 4.16% of water content; and the morphological showed insignificance changed between the neat and modified starch.

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