Synthesis of Dual Modification Breadfruit Starch 
(*Artocarpus communis*) with Hydroxypropylation and Cross-Link

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**Abstract.** The use of starch is currently very widespread in the food and non-food industries, but this is not supported by the natural starches which have weaknesses in their application so that modification of natural starch is needed. Dual modification of starch by hydroxypropylation and crosslinking is expected to be a solution to overcome the weaknesses of the nature starches, especially in food sector. Dual modification starch is synthesized by reacting breadfruit stach with the addition of 12% propylene oxide and STMP : STPP (1:4; 2:5; and 3:6). From the results of tests that have been carried out on IR spectroscopy testing are marked POC vibrations appear in the region of the wave number 1050-995 cm\(^{-1}\) and vibration P=O or P-O bonding in the area of 1149-1157 cm\(^{-1}\). The degree of substitutions obtained ranged 0.18 – 0.30. Dual modification starch has a gelatinization temperature (81.16 – 82.32°C), peak viscosity (4750 – 8000cP), setback viscosity (1090 – 2583cP), and breakdown viscosity (620 – 1090cP). The result dual modification of breadfruit starch has stable properties when heating and stirring.

1. Introduction

The current food problem in Indonesia is people's dependence on a single food source such as wheat which is not a native plant of Indonesia. Indonesia is currently the second largest wheat importer in the world after Egypt. According to a report from AsosiasiProdusenTepungTerigu Indonesia (Aptindo) indicates that imports of wheat from July 2015 until May 2016 had reached a total of 8.2 million tons. While throughout 2016 it reached 8.71 million tons. This number increased rapidly during Ramadhan up to 10%.

Flour is a solid particle in the form of fine grains and even very fine depending on the use which is usually made from various types of vegetable matter, such as from grains, tubers, roots, or vegetables that have starch content. In addition to these materials, one of the food commodities in Indonesia that can also be processed into flour and not yet utilized optimally is breadfruit plants (Triyani, et al. 2013). Breadfruit (*Artocarpus altilis*) has a fairly high carbohydrate content (28.2%), so it has the opportunity to be processed into flour. Utilization of breadfruit flour into processed food can substitute up to 75% use of wheat flour. The use of starch is very wide in the industry, both food and non-food because of the ease of getting raw materials and the price is relatively cheap. However, natural starch is an obstacle when used as industrial raw materials, including the nature of starch which is easily damaged by heat, acid and stirring, so modifications are needed to correct this deficiency.
One chemically modified starch is a double modified starch. Double modification is a modification of starch by hydroxypropylation and crosslinking which will produce type 4 resistant starch. Research on the modification of the modified double starch has been carried out by several researchers: on tapioca starch [2], sago starch[3], Tuber and Root starches [4], rice starch(Shen et al. 2019; Woggum et al. 2014), danpotato starch[7]. The dual modification can serve as a food thickener and stabilizer, as stated in the CODEX Standard (1995) with INS No.1442 as hydroxypropylstarch-phosphate. This research is expected to provide information related to the characteristics of double modified breadfruit starch by hydroxypropylation and crosslinking, and can be the basis for the development of functional food ingredients made from breadfruit raw materials to increase the added value of breadfruit fruit.

2. Materials and Methods

2.1. Materials

The materials used in this study include: Breadfruit, 10% Na$_2$SO$_4$, propylene oxide, 5% NaOH, Aquadest, 10% HCl, STMP, STPP, KH$_2$PO$_4$ anhydrous, and Vanadate-molybdate.

2.2. Methods

2.2.1. Isolations of starch from Breadfruit. Isolation of starch from breadfruit using the method used by Zuhra et al. (2016). Ripe breadfruit is peeled, then washed clean until the gum disappears. Then cut the breadfruit into small pieces and mashed using a blender. Breadfruit that has been mashed, filtered using a filter cloth to separate from the pulp. Starch extract is left to form a precipitate on beaker glass. The precipitate is washed several times with water until the solvent above becomes clear. The obtained starch is dried in an oven at 45°C for 24 hours. The dried starch is then mashed, sieved and weighed.

2.2.2. Production dual modification Breadfruit starch. The making of dual modified starch using the method that has been done by Wattanachant et al. (2003) and Aziz et al. (2004) in Maulani et al. (2013). 10 g of breadfruit starch dissolved in 25 mL of 10% sodium sulfate solution to form a 40% suspension (w/v). while stirring the pH is increased to 10 by adding 5% NaOH. Propylene oxide is added at a concentration of 12% (v/w). The suspension is stirred for 90 minutes at room temperature (25°C), then the suspension is placed in a shake incubator (temperature 40 °C; 200 rpm) for 24 hours. After that, a mixture of STMP and STPP was added with a concentration ratio of 1%; 4%; 2%; 5%; and 3%; 6% (w/w). The suspension is stirred again for 30 minutes at room temperature and then the pH of the suspension is lowered to 5 by adding 10% HCl. The suspension is placed back on the incubator shake (temperature 40 °C; 200 rpm) for 24 hours. Then the suspension was centrifuged (2000xg, 5 minutes), washed using aquadest 5 times. The precipitate is dried at 40 °C for 24 hours and mashed.

2.2.3. Analysis of functional groups of natural Breadfruit starch and dual modified Breadfruit starch FT-IR Spectrum of Natural Breadfruit Starch and Double Modified Breadfruit Starch determined by FT-IR instruments using the method stated by Singh et al. (2004)in Polnaya et al. (2009). Starch was weighed ± 3 mg, then each pounded with 800 mg KBr. The sample mixture and KBr are then pressed, to form pellets with a diameter of ± 1 cm. The pellets are placed in the FT-IR, and the scanning is carried out starting from 4000 – 400cm$^{-1}$ wave numbers. The measurement spectrum is then interpreted to identify functional groups in starch.

2.2.4. Determination of substitution level. The level of substitution is calculated based on the equation described in Matoz and Pérez (2003) as follows:
DS = \frac{162P}{(3100 - 102P)} \tag{1}

where P is the level of phosphorus (% dry basis) in the modified starch.

2.2.5. Determination of starch amylography. Determination of amylographic properties of double modified starch was carried out in accordance with the method used by Bao et al. (2004) in Shen et al. (2019), using Rapid Visco Analyzer (RVA) to show peak viscosity (PV), hold viscosity (HV), final viscosity (FV), final viscosity (FV), seatback (SB), and breakdown (BD) in starch.

3. Results and Discussion

3.1. Breadfruit starch isolation
Starch obtained from 2 kg of breadfruit isolation (Artocarpus altilis) is 200 g of breadfruit starch (10%). Breadfruit starch is then tested qualitatively by adding iodine reagents, producing a purple color that shows positive results from the polysaccharide carbohydrate chain.

3.2. Analysis of functional groups of natural Breadfruit starch and dual modified Breadfruit starch
IR spectrum on breadfruit starch can be seen in Figure 1 which shows the spectrum with vibration peaks in the region of wave number 3425 cm\(^{-1}\) showing -OH group. Absorption at wave number 2931 cm\(^{-1}\) shows the stretching vibration of the alkane group C-H (-CH\(_3\)) and absorption at the wave number 1635 cm\(^{-1}\) indicates the presence of group C=O which is a stretching vibration of the ester group. The absorption band at the wave number 1157 cm\(^{-1}\) indicates the presence of the C-O ester function group. In the absorption band at wave number 1018 cm\(^{-1}\) shows the glycosidic C-O function group [14].

Figure 1. Spectrum of FT-IR Breadfruit Starch

FTIR spectroscopy results of dual modified starch (in figure 2) are marked with absorption bands in the region of wave numbers 1050 - 995 cm\(^{-1}\) indicating there is a P-O-C streching group and P=O vibrations or P-O bonds in the region 1149 – 1157 cm\(^{-1}\). The vibrational region of 1635 cm\(^{-1}\) shows the intramolecular hydrogen bonds. This peak breadfruit starch appear higher than this double modification starch upon the hydrogen bond has been broken so that the OH group is converted to phosphate starch [15].
3.3. Degree of substitution

Phosphate starch (dual modification starch) was produced from the continued modification of hydroxypropyl starch with the addition of variations of STMP: STPP degree of substitution calculated using a UV-VIS spectrophotometer. The results of the degree of substitution from variations of STMP: STPP levels in Table 1. Tests of phosphate levels and the degree of substitution are used to find more phosphate groups substituted into dual modification breadfruit starch. According to Lim and Seib (1993), the maximum acceptable phosphorus level in commercial starch modification is 0.4% (U.S. Regulations). The results of the degree of substitution of double modified starch with 12% propylene oxide and variations in the addition of STMP: STPP are <0.4.

3.4. Amylographic properties of starch

The temperature of starch gelatinization is the temperature at which the starch forms a completely transparent gel. Gelatinization is a change that occurs in starch granules when experiencing extraordinary swelling and cannot return to its original shape [17]. The thickening and gelling properties of starch are important properties and can provide better product sensory characteristics. In the test results obtained gelatinization temperatures ranging from 81-82 °C. The characteristics of amylography dual modified breadfruit can be seen in Table 2 and Figure 3.
Table 2. Amylographic Properties of Dual Modified Breadfruit Starch

| Variations STMP : STPP | Peak Viscosity (cP) | Hold Viscosity (cP) | Final Viscosity (cP) | Breakdown (cP) | Setback (cP) | Pasting Temperature (°C) |
|------------------------|---------------------|---------------------|---------------------|---------------|-------------|--------------------------|
| 1 : 4                  | 6037               | 5417               | 8000               | 620            | 2583        | 81.16                    |
| 2 : 5                  | 4750               | 4386               | 6737               | 364            | 2351        | 82.32                    |
| 3 : 6                  | 8000               | 6910               | 8000               | 1090           | 1090        | 81.63                    |

Paste viscosity is an important characteristic of starch, during heating of starch and water suspension, this is considered as the basis of food application, as well as identification of starch variability (Meares et al., 2004). On the increase in DS, the double modification of breadfruit starch decreased the value of hold viscosity, breakdown and final viscosity, and experienced the opposite when DS decreased. The results reported by Shen et al. (2019) also stated the same thing, hold viscosity, breakdown and final viscosity decreased occurred on DS which had a high value.

Figure 3. Graph of Dual Modified Amylographic Starch of Breadfruit Starch

The breakdown value indicates how easily the structure of the starch granule breaks or cracks during processing [18] and high amylose content in starch[19]. A high breakdown value will produce cohesive properties on the paste which is highly undesirable while a low breakdown value indicates stable starch when heating or stirring.

4. Conclusion
Based on the results of research that has been done, dual modified breadfruit starch can be synthesized by reacting breadfruit starch with propylene oxide (12%) and the addition of STMP: STPP (1:4; 2:5; and 3:6). From the results of tests have been performed on IR spectroscopy is characterized by appearing vibrations of P-O-C in the wave number region 1050 – 995 cm\(^{-1}\) and vibration P=O or P-O bonding at 1149-1157 cm\(^{-1}\) region. The best result of dual modification of breadfruit starch is the variation of the addition of 2% STMP: 5% STPP with characterization: degree of substitution is 0.3; gelatinization temperature 82.32 °C: peak viscosity 4750cP; setback 2351cP; and a breakdown of 364cP. The double modification of breadfruit starch produced has stable properties when heating and stirring.

5. References
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