



## Characterization of Chemical and Physical Properties of Hydroxypropylated and Cross-linked Arrowroot (*Marantha arundinacea*) Starch

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**Abstract.** The modern food industry and a variety of food products require tolerant starch as raw material for processing in a broad range of techniques, from preparation to storage and distribution. Dual modification of arrowroot starch using hydroxypropylation and cross-linking was carried out to overcome the lack of native arrowroot starch in food processing application. The modifications applied were: combined propylene oxide (8%, 10%, and 12%); sodium tri meta phosphate/STMP (1%, 2%, and 3%); and sodium tri poly phosphate/STPP (4%, 5%, and 6%). These modifications significantly affected the composition of the amylose and amylopectin and the amount of phosphorus in the granules. Higher amounts of phosphate salt gave a higher phosphorus content, which increased the degree of substitution (DS) and the degree of cross-link. Arrowroot starch that was modified using a concentration of 8-10% propylene oxide and 1-2% STMP : 3-5% STPP produced a starch with < 0.4% phosphorus content. A higher concentration of propylene oxide provided a higher degree of hydroxypropyl. The changed physical properties of the modified granular arrowroot starch were examined through SEM testing, and its changed crystalline patterns through X-ray diffraction measurements. Especially, provision of a high concentration of propylene oxide (12%) combined with 3% STMP : 6% STPP affected the granular morphology and the crystallinity.

**Keywords:** *arrowroot starch; cross-linking; dual modification; hydroxypropylation; modified starch.*

### 1 Introduction

Arrowroot starch derived from tuber of *Marantha arundinacea*. Like other starches, arrowroot starch can be widely used in the food and non-food industry,

but its use is limited by its native properties. Some disadvantages of the native starch are: susceptible to shear, susceptible to acidic conditions, lack of stability, inconsistent viscosity, and low solubility. This encourages modification of arrowroot starch in order to improve it or add certain functional properties that are not found in its native starch, so that broad application in industry becomes feasible. Functional properties include improving solubility in cold water, gelatinization properties, lowering the level of retrogradation and syneresis, gel formation, film formation, acidic conditions stability, and so forth.

Improving the quality of arrowroot starch needs to be done so it can serve as a raw material for food and non-food industry, that is derived from local sources. Arrowroot starch production as a raw-material industry is still underdeveloped compared to waxy maize starch (waxy corn) and tapioca starch production [1], especially in Indonesia. Arrowroot starch has a specific composition of physical and chemical properties, such as a relatively high content of amylose, so it is widely used for various food products. Chemical modification of native starches can alter both the chemical and physical properties of starch.

Starches can be chemically modified by hydroxypropylation through a reaction between the starches with propylene oxide by etherification under alkaline conditions. Etherification with a low degree of substitution causes hydroxypropyl groups ( $-\text{OCH}_2\text{CH}_2\text{CH}_3$ ) to take the place of hydroxyl groups. This method is commonly used in the food industry. Hydroxypropylation can improve durability, freeze-thaw stability, stability of storage at low temperatures, clarity and texture of paste, reduce temperature of gelatinization [2-7], and increase the swelling power [8] of starches.

Cross-linking is a treatment in which a small number of compounds that can react with more than one hydroxyl group is added to the starch polymer. The cross-link reaction involves the replacement of the hydrogen bonds between the starch chains with the phosphate group from STMP and STPP reagent, forming a cross-link bridge through covalent bonds that are stronger and more permanent. Cross-linked starch can maintain a higher viscosity and shows low changes in viscosity [9]. Cross-linking can also modify the properties of granule swelling, improve texture and the rheological properties of the paste [10], and is useful for improving the film formation properties of the paste [11]. The goal is to preserve the dispersion texture of the cooked starch and resistance to processing conditions such as temperature, acid, and shear [12]. Next, the hydroxypropylated starch is reacted with cross-linked reagent to produce dual-modified starch, further improving the quality of the native starch. Dual-modified starch can swell but the starch granules remain intact [7].

The purpose of this study was to determine the changes in the chemical and physical properties of arrowroot starch when it is modified with a combination of hydroxypropylation and cross-linking to obtain a modified arrowroot starch with appropriate characteristics for use in the food industry.

## **2 Materials and Methods**

### **2.1 Materials**

The starch used in this study was derived by extraction from arrowroot tuber (harvest age 10 months). Materials for the modification of the starch were: STMP, STPP, and propylene oxide, purchased from Sigma-Aldrich Chemical Company. Analytic grade sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), hydrochloride acid (HCl), sodium hydroxide (NaOH), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), methanol, sodium carbonate, propylene glycol, sodium dihydroxy phosphate ( $\text{Na}_2\text{H}_2\text{PO}_4$ ), and vanadate-molybdate reagen were purchased from a local chemical supplier.

### **2.2 Hydroxypropylation and Cross-linking**

Hydroxypropylation was conducted according to what was previously described [1, 13-17], with some modifications. Arrowroot starch (100 g, db) was dissolved in 10% sodium sulphate solution to obtain a suspension with a concentration of 40%. While stirring, the pH was increased to 10.5 by adding NaOH 5%. Propylene oxide was added with concentrations of 8%, 10%, and 12% by weight of starch used, respectively. The suspension was stirred for 30 min at room temperature. The suspension was then placed on a shaking incubator for 24 h (40°C; 200 rpm). Mixtures of STMP and STPP were added with a ratio of 1% : 4%, 2% : 5%, and 3% : 6% by weight of starch used, respectively. Each suspension was stirred for 30 min at room temperature and the pH was lowered to 5.5 by adding HCl 1M. The suspension was placed back on the shaking incubator for 24 h (40°C; 200 rpm). The next step was separation of starch and precipitated solvent by centrifugation at 2500 rpm for 15 min, after which the precipitate was washed with distilled water five times. The precipitated starch was then dried at a temperature of 40°C for 12 h (moisture content 10-12%) and then crushed and sieved with 100 mesh size.

### **2.3 Analysis of Chemical Properties**

#### **2.3.1 Amylose and Amylopectin Content**

The method used was developed by Takeda [18]. The starch (10 mg) was suspended in 0.2 ml ethanol 99% and 1 ml of distilled water, then heated at 100°C for 5 min. After the solution was cooled at room temperature, a total of 0.5 ml NaOH 1M was added, and the mixture was placed into a shaking water bath for 10 min in order to dissolve the suspension. A pH of 6.5 was established

by adding HCl 1M, after which the solution was diluted with 10 ml of distilled water. A total of 0.4 ml solution was taken and added with 0.4 ml iodine 0.2% solution, and then added with distilled water until the volume reached 10 ml. The mixture was left at room temperature for 2 h. The absorbance value of the mixture (blue value) was tested using a spectrophotometer at 620 nm wavelength. The amylose content was obtained from a standard curve created by the same method using pure amylose materials at various concentrations. The standard curve was created by plotting the concentration of amylose to its absorbants, with concentration as abscissa and absorbance as ordinate. The amylopectin content was calculated as the result of 100% minus content of amylose (%).

### 2.3.2 Phosphorus Content

Sodium carbonate (1.5 g) was dissolved in 5 ml of distilled water and then starch sample (2.5 g) was added. The mixture was stirred well and then burned at a temperature of 550°C for 12 h. The final product was cooled to room temperature and added with 2 ml of HCl 25% and 10 ml of distilled water. The solution was transferred to a beaker glass containing 20 ml of distilled water and added to reach a volume of 50 ml, stirred, and then filtered using filter paper. The solution was transferred into a 250-ml volume flask and distilled water was added again to reach a volume of 250 ml. Then 10 ml of solution was pipetted and 2 ml vanadate-molybdate reagent was added, after which the solution was stored at room temperature for 45 min. The absorbance of the samples was measured at 435 nm with a spectrophotometer. The phosphorus content was compared to the standard curve. Preparation of the standard curve was done by dissolving 2.2275 g of  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  made up to 100 ml of solution in a flask, after which the solution was prepared with a concentration in sequence. 2 ml of HCl 25% was added to each concentration of the solution and each was made up to 10 ml by adding distilled water. The absorbance values were plotted to obtain the standard curve [19].

### 2.3.3 Degree of Hydroxypropylation

Measurement of the degree of hydroxypropylation was performed using the method of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) [20]. A total of 50-100 mg samples of hydroxypropylated starch was put into a 100-ml volumetric flask and mixed with 25 ml of 0.5 M sulphuric acid, the tube was placed onto a heater until a clear mixture was obtained. Subsequently the sample was cooled and then diluted with 100 ml of water. A total of 1 ml of the mixture was pipetted into 25-ml test tubes, dipped in cold water, and concentrated sulphuric acid (8 ml) was added drop-wise. Subsequently, the tube was shaken, and then placed back onto the heater for 3 min, and immediately cooled again in an ice bath. A total of 0.6 ml ninhydrin reagent was added

carefully through the wall of the tube and the mixture was shaken and then heated at a temperature of 25°C for 100 min. A matching volume of 25 ml with concentrated sulphuric acid was added and mixed by inverting the tube several times. Part of the solution was immediately transferred into a 1-cm cell, and after 5 min the absorbance was read at 590 nm, using the starch blank as reference. A calibration curve was prepared using 1 ml of propylene glycol standards (10, 20, 30, 40, and 50 µg per ml) using the same procedure. The hydroxypropyl group (%) was calculated using the following equation:

$$\% \text{ Hydroxypropyl groups} = (C * 0.7763 * 10 * F) / W \quad (1)$$

C = amount of propylene glycol in the sample was read from the calibration curve (µg/ml)

F = dilution factor

W = sample (mg)

### 2.3.4 Degree of Substitution

The degree of substitution was calculated based on the equation previously described in [21] as follows:

$$DS = 162P / (3100 - 102P) \quad (2)$$

where P is phosphorus content (% dry basis) in modified starch.

### 2.3.5 Degree of Cross-link

Measurement of the starch amylograph was performed using a Rapid Visco Analyzer (RVA) to obtain the peak viscosity (cP) of the starch pastes. The degree of cross-link can be determined using the equation developed by Kaur, *et al.* [22], as follows:

$$\text{Degree of cross - link (\%)} = \frac{(B-A)}{A} \times 100\% \quad (3)$$

A = value of peak viscosity of starch without cross-link (cP)

B = value of peak viscosity of cross-linked starch (cP)

## 2.4 Analysis of Physical Properties

### 2.4.1 Birefringence Properties

The birefringence properties of the starch granules were observed using a polarizing microscope. The starch sample was diluted with distilled water, after which a solution of iodine was added to increase the contrast. Subsequently, the suspension was dripped onto an object glass and carefully covered with a glass

cover. The preparations were tested by passing light through a polarizer and observing the results. The resulting image was photographed using a camera [23].

#### **2.4.2 Scanning Electron Microscopy (SEM)**

Measurement of the physical properties of the starch granules was performed using a scanning electron microscope (JEOL JSM-6510LA) with the method previously described in [21]. The starch sample was sprayed onto the surface of a metal plate covered with double-sided tape, put into a vacuum chamber and coated with platinum. The samples were observed in a tool-coated SEM with an accelerating voltage of 20 kV.

#### **2.4.3 X-ray Diffraction**

The crystallinity of starch granules can be detected through X-ray diffraction [24]. The instrument used was a Philips diffractometer using monochromatic radiation of cobalt, 31 kV, 26 mA, a 4-second time constant and a paper speed of 1 cm/min. The diffractogram was recorded at  $2\theta = 4-30^\circ$  with a scan speed of  $1^\circ/\text{min}$ .

### **2.5 Statistical Analysis**

Statistical analysis was performed on nine treatments consisting of nine different combinations of concentrations of propylene oxide and phosphate salts. Each treatment was replicated three times. Each treatment was analyzed with an analysis of variance, and diversity of treatment was analyzed using the Duncan Multiple Range Test ( $\alpha = 0.05$ ) with SPSS 16.0 for Windows.

## **3 Result and Discussion**

### **3.1 Chemical Properties**

#### **3.1.1 Amylose and Amylopectin Content**

Starch consists of two fractions, namely amylose and amylopectin. Both macromolecules greatly contribute to the physical, chemical, and functional properties of the starch. Amylopectin has a branched chain of properties and is easily degraded by digestive enzymes, whereas amylose is not easily degraded by enzymes [25]. Based on our observations (Table 1), the amylose and amylopectin contents of the modified starch had various values. The amylose levels ranged between 15.33 and 33.49%, while the levels of amylopectin ranged between 66.51 and 84.67%. The high amylose levels of arrowroot starch are considered to provide good opportunities for modification of the starch.

Native arrowroot starch has elevated levels of amylose (29.41%) and amylopectin (70.59%).

Differences in concentration of propylene oxide and phosphate salts gave real effect to changes in the composition of amylose and amylopectin in the starch granules (Table 1). The tendency observed was that amylose content measured higher than its native form when a concentration of phosphate salt with a ratio of 2% STMP : 5% STPP was provided. This is comparable with what was reported by Singh, *et al.* [26], *i.e.* the presence of certain chemical groups (such as the acetyl group or other groups) can lead to increased estimated levels of amylose.

### 3.1.2 Phosphorus Content

Measurement of the phosphorus content was performed to prove occurrence of phosphate bridges on the amylose chains. Table 1 shows that the modified starch contained phosphorus in the range of 0.272 to 0.886%. There was a tendency of a higher phosphorus content with a higher concentration of phosphate salts provided. This is in accordance with the standards issued by CFR [27] that the maximum allowable phosphorus level in commercial modified starches is 0.4% (U.S. Regulation). In the process of dual modification it was shown in this study that the use of a phosphate salt concentration with a ratio of 1-2% STMP : 4-6% STPP combined with a propylene oxide concentration of 8-10%, resulted in starch phosphate levels < 0.4%.

**Table 1** Levels of amylose, amylopectin, and phosphorus of dual-modified arrowroot starch.

Treatments	Levels of amylose (%)	Levels of amylopectin (%)	Level of phosphorus (%)
Native	29.413 ± 0.752 e	70.587 ± 0.094 d	nd
PO 8%; STMP 1%:STPP 4%	20.940 ± 0.151 b	79.060 ± 0.151 g	0.359 ± 0.007 b
PO 8%; STMP 2%:STPP 5%	33.300 ± 0.277 h	66.700 ± 0.277 a	0.362 ± 0.020 b
PO 8%; STMP 3%:STPP 6%	31.190 ± 0.231 f	68.810 ± 0.231 c	0.514 ± 0.049 c
PO 10%; STMP 1%:STPP 4%	24.347 ± 0.525 c	75.653 ± 0.525 f	0.272 ± 0.019 a
PO 10%; STMP 2%:STPP 5%	32.310 ± 0.594 g	67.690 ± 0.594 b	0.304 ± 0.003 a
PO 10%; STMP 3%:STPP 6%	28.010 ± 0.141 d	71.990 ± 0.141 e	0.365 ± 0.007 b
PO 12%; STMP 1%:STPP 4%	33.240 ± 0.256 h	66.760 ± 0.256 a	0.670 ± 0.019 d
PO 12%; STMP 2%:STPP 5%	33.490 ± 0.380 h	66.510 ± 0.380 a	0.738 ± 0.020 e
PO 12%; STMP 3%:STPP 6%	15.330 ± 0.974 a	84.670 ± 0.974 h	0.886 ± 0.026 f

Notes: Figures followed by the same letter are not significant according to Duncan's multiple range test ( $\alpha = 0.05$ ). PO = propylene oxide; STMP = sodium tri meta phosphate; STPP = sodium tro poly phosphate; nd = not detected

### 3.1.3 Degree of Hydroxypropylation and Degree of Substitution (DS)

The efficiency of the hydroxypropylation and cross-linking reactions on the starch modification process is characterized by the degree of hydroxypropylation of the hydroxypropyl groups and the degree of substitution of the phosphate groups in the starch granule. The degree of hydroxypropylation value (% hydroxyl groups) expresses the percentage of hydroxypropyl groups substituting hydroxyl groups on amylose chains. The DS value indicates what percentage of phosphate groups form the cross-link bridge in the amylose chain, which is closely related to the phosphorus levels in the granule. Table 2 shows that the degree of hydroxypropylation on the dual-modified arrowroot starch ranged between 0.037 and 0.261%. There is a tendency of higher concentrations of propylene oxide was awarded the higher the degree of hydroxypropylation.

The DS values ranged between 0.014 and 0.048. The higher the concentration of phosphate salts, the higher the DS value at every level of propylene oxide concentration. For comparison, results of previous research on sago starch [17] showed that the DS of hydroxypropylated and cross-linked modified starch with a concentration of propylene oxide of 12% and 2% STMP : 5% STPP was 0.044 with a degree of hydroxypropylation of 0.055%. These results are similar to those previously reported in [1], where a similar modification of sago starch was performed. The reported degree of hydroxypropylation during the early stages led to a subsequent cross-link reaction. This is characterized by a similar trend, where an increase in value of the degree of hydroxypropylation is in line with higher levels of phosphorus and higher DS values.

**Table 2** Degree of hydroxypropylation, degree of substitution, and degree of crosslink of dual-modified arrowroot starch.

Treatments	Degree of hydroxypropylation (%)	Degree of substitution (DS)	Degree of crosslink (%)
Native	nd	nd	nd
PO 8%; STMP 1%:STPP 4%	0.127 ± 0.021 b	0.019 ± 0.000 b	47.358 ± 0.896 a
PO 8%; STMP 2%:STPP 5%	0.169 ± 0.044 bc	0.019 ± 0.003 b	55.281 ± 0.280 b
PO 8%; STMP 3%:STPP 6%	0.261 ± 0.012 e	0.027 ± 0.001 c	67.822 ± 0.174 c
PO 10%; STMP 1%:STPP 4%	0.109 ± 0.003 b	0.014 ± 0.001 a	76.948 ± 0.349 e
PO 10%; STMP 2%:STPP 5%	0.130 ± 0.062 b	0.016 ± 0.000 a	78.962 ± 0.067 f
PO 10%; STMP 3%:STPP 6%	0.258 ± 0.058 de	0.019 ± 0.000 b	82.620 ± 0.558 h
PO 12%; STMP 1%:STPP 4%	0.037 ± 0.005 a	0.036 ± 0.001 d	68.498 ± 0.183 c
PO 12%; STMP 2%:STPP 5%	0.196 ± 0.012 cd	0.040 ± 0.001 e	74.043 ± 0.164 d
PO 12%; STMP 3%:STPP 6%	0.213 ± 0.025 cde	0.048 ± 0.001 f	81.463 ± 0.489 g

Notes: Figures followed by the same letter are not significant according to Duncan's multiple range test ( $\alpha = 0.05$ ); PO = propylene oxide; STMP = sodium tri meta phosphate; STPP = sodium tro poly phosphate; nd = not detected

### 3.1.4 Degree of Cross-link

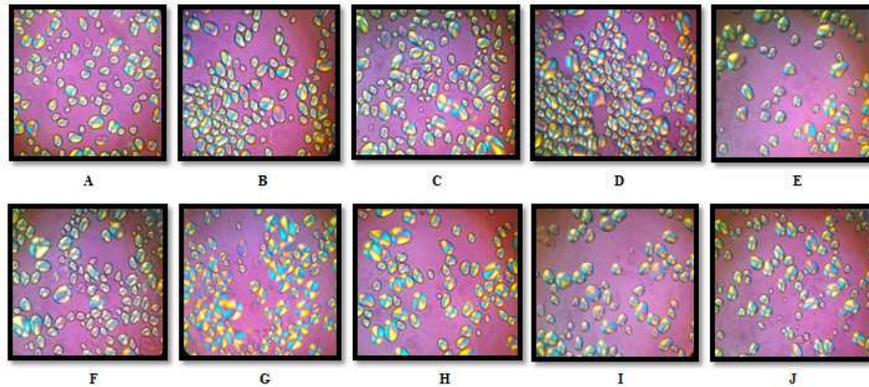
Data about the degrees of cross-link are shown in Table 2, where the values range from 47.358 to 82.620%. Heightening the concentration of phosphate salts (STMP/STPP) will increase the degree of cross-linking at various concentration levels of propylene oxide. The modified starch granules showed a high number of cross-links of amylose chains. This is similar with the results of the research by Koo, *et al.* [28], who reported that any increase in the concentration of phosphate salts as much as 10% will increase the degree of cross-linking in proportion to the maximum phosphate salt concentration of 10-12%.

## 3.2 Physical Properties

### 3.2.1 Birefringence Properties

Starch granules have birefringence properties, *i.e.* the ability to refract polarized light. The birefringence properties of starch can be lost by heating above the gelatinization temperature, caused by rupture of molecular bonds so that the hydrogen bonds bind more water molecules [29]. Observation using a polarizing microscope showed that the modified arrowroot starch granules demonstrated a clear blue-yellow color, which means they still had the same refractive index as native starch granules (Figure 1). This indicates that the process of modification at various concentration levels of propylene oxide and phosphate salts did not cause starch gelatinization changes, that the granule shapes were still intact and that the granules had kept their birefringence properties. This can be understood, because during the modification process the maximum temperature used was 40°C, a temperature lower than the starch gelatinization temperature.

The components that cause the crystallinity and the birefringence properties are amylopectin and amylose. French [30] has reported that the birefringence properties, a blue-yellow color on the surface of the starch granules, are due to a difference in the refractive index of the starch granules. The refractive index of the starch granules is affected by the molecular structure of the amylose in the starch. The helical form of amylose can absorb some of the light that passes through the starch granule. If the direction of the light waves is parallel to the axis of the helical amylose, there is intensive light absorption. If the direction of the light waves is perpendicular to the axis of helical amylose, there is little or no light absorption.

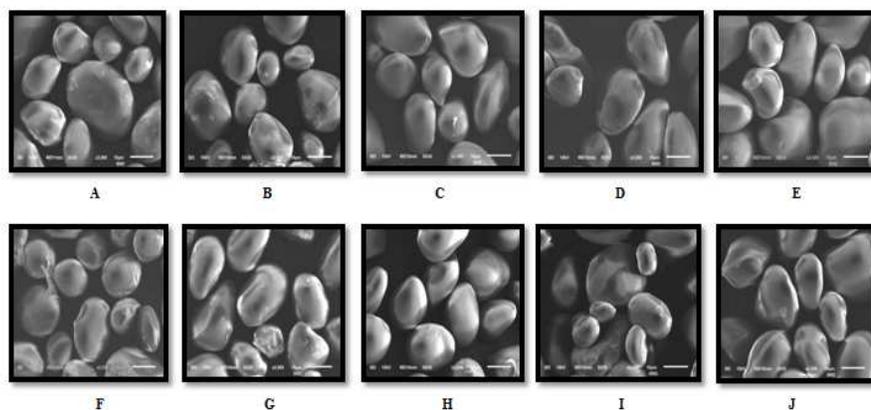


**Figure 1** Birefringence properties of dual-modified arrowroot starch for various reagents concentrations: A = native; B = PO 8%; STMP 1% : STPP 4%, C = PO 8%; STMP 2%: STPP 5%, D = PO 8%; STMP 3% : STPP 6%; E = PO 10%; STMP 1% : STPP 4%, F = PO 10%; STMP 2% : STPP 5%, G = PO 10%; STMP 3% : STPP 6%, H = PO 12%; STMP 1% : STPP 4%, I = PO 12%; STMP 2% : STPP 5%, J = PO 12%; STMP 3% : STPP 6%.

### 3.2.2 Scanning Electron Microscopy (SEM)

The results of the morphology analysis of the modified arrowroot starch granules using SEM are presented in Figure 2. The granules of arrowroot starch are oval-shaped with a smooth surface and a size range of 10-70  $\mu\text{m}$ . Using 2000x magnification, the morphology of the modified starch granules showed an insignificant change when compared with native starch granules. A little damage occurred on the surface of the starch granules with higher concentrations of modified reactants.

Similar with the results of researches pertaining to cross-linking cassava starch [21], hydroxypropylation of *Canna edulis* starch [31], and cross-linking and methylation of corn starch [32], the damage due to the modification process only occurred on the surface of the granules, whereby the surface structure became less porous, or showed fine cracks. In contrast, Kaur, *et al.* [22] reported that the surface and size of potato starch granules treated with 10% propylene oxide showed significant changes when compared with native starch granules.

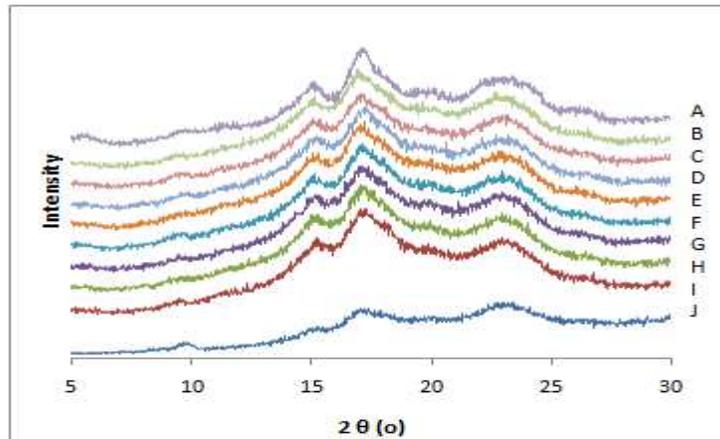


**Figure 2** Scanning electron microscopy (SEM) of dual-modified arrowroot starch for various reagents concentrations: A = native; B = PO 8%; STMP 1% : STPP 4%, C = PO 8%; STMP 2% : STPP 5%, D = PO 8%; STMP 3% : STPP 6%; E = PO 10%; STMP 1% : STPP 4%, F = PO 10%; STMP 2% : STPP 5%, G = PO 10%; STMP 3% : STPP 6%, H = PO 12%; STMP 1% : STPP 4%, I = PO 12%; STMP 2% : STPP 5%, J = PO 12%; STMP 3% : STPP 6%.

### 3.2.3 X-ray Diffraction (XRD)

Figure 3 shows the results of the X-ray diffraction measurements of the dual-modified arrowroot starch compared with its native starch. The X-ray diffraction pattern describes the type of crystallinity of the starch granules. Based on the grouping by Zobel [24], tuber starches have a B-type crystalline pattern (low peak at  $5.6^\circ$ , sharp peak at  $17^\circ$ , and doublet peak at  $22^\circ$  and  $24^\circ$ ), while cereal starches have an A-type crystalline pattern. The diffraction pattern shown by the dual-modified arrowroot starch structure was B-type, similar to its native form, except for the modified starch with a concentration of propylene oxide of 12% and STMP 3% : STPP 6% (J), where the pattern showed significant changes.

Previous studies have mentioned that cross-link modification does not alter the crystalline pattern of cornstarch [32]. Likewise, it was reported by Chuenkamol, *et al.* [31] that heightening the degree of hydroxypropylation of Canna starch did not alter the B-type crystalline pattern of the starch granules. Changes in the crystalline pattern shown by a higher concentration of propylene oxide and STMP/STPP in this study were related to a high DS value and degree of hydroxypropylation. Both variables showed that an amount of hydroxyl groups were substituted and that there was cross-linked bridge formation on the amylose chains, and so affected the granule crystalline structure.



**Figure 3** X-ray diffraction (XRD) of dual-modified arrowroot starch on various reagents concentrations: A = native; B = PO 8%; STMP 1% : STPP 4%, C = PO 8%; STMP 2% : STPP 5%, D = PO 8%; STMP 3% : STPP 6%; E = PO 10%; STMP 1% : STPP 4%, F = PO 10%; STMP 2% : STPP 5%, G = PO 10%; STMP 3% : STPP 6%, H = PO 12%; STMP 1% : STPP 4%, I = PO 12%; STMP 2% : STPP 5%, J = PO 12%; STMP 3% : STPP 6%.

#### 4 Conclusion

Dual modification of arrowroot starch through hydroxypropylation and cross-linking led to changes in the chemical and physical properties of starch granules. Dual modification significantly affected the amylose and amylopectin composition. Addition of phosphate salts reagent (STPP and STMP) as cross-linking agents increased the phosphorus content in the granules in the range of 0.272 to 0.886%; a higher amount of salt gave a higher content of phosphorus. A heightened content of phosphorus in the granules increased the degree of substitution (DS) in the range of 0.014 to 0.048, and the degree of cross-link to a level between 47.358 and 82.620%. Hydroxypropylation was evidenced by the percentage of hydroxypropyl groups, which was in the range of 0.037 to 0.0261%. Changes in the granule morphology of the modified arrowroot starches were shown through SEM testing, and changes in the crystalline patterns through X-ray diffraction measurements. Provision of a propylene oxide concentration of 12% combined with a high salt phosphate content (3% STMP : 6% STPP) makes the surface morphology of the starch granules more porous and fractured, and changes the crystalline pattern of the granules more compared with lower concentrations.

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### References

- [1] Wattanachant, S., Muhammad, S.K.S., Hashim, D.M. & Rahman, R.A. *Effect of Crosslinking Reagents and Hydroxypropylation Levels on Dual-Modified Sago Starch Properties*, Food Chem., **80**, pp. 463-471, 2003.
- [2] Hoover, R., Hannouz, D., & Sosulski, F.W., *Effect of Hydroxypropylation on Thermal Properties, Starch Digestibility and Freeze-Thaw Stability of Field Pea (*Pisum sativum* cv. Trapper) Starch*, Starch/Starke, **40**, pp. 383-387, 1988.
- [3] Kim, H.R. & Eliasson, A.C., *The Influence of Molar Substitution on Thermal Transition Properties of Hydroxypropyl Potato Starches*, Carbohydr. Polym. **22**, pp. 331-335, 1993.
- [4] Perera, C., Hoover, R., & Martin, A.M., *The Effect of Hydroxypropylation on The Structure and Physicochemical Properties of Native, Defatted and Heat-Moisture Treated Potato Starches*, Food Res. Int., **30**, pp. 235-247, 1997.
- [5] Liu, H.J., Ramsden, L., & Corke, H., *Physical Properties and Enzymatic Digestibility of Hydroxypropylated, wx, and Normal Maize Starches*, Carbohydr. Polym., **40**, pp. 175-182, 1999.
- [6] Pal, J., Singhal, P.S., & Kulkarni, P.R., *Physicochemical Properties of Hydroxypropyl Derivative from Corn and Amaranth Starch*, Carbohydr. Polym., **48**, pp. 49-53, 2002.
- [7] Miyazaki, M., van Hung, P., Maeda, T. & Morita, N., *Recent Advances in Application of Modified Starch*, Food Sci. Technol., **17**(11), pp. 591-599, 2006.
- [8] Lee H.L. & Yoo, B., *Effect of Hydroxypropylation on Physical and Rheological Properties of Sweet Potato Starch*, LWT-Food Sci. Technol., **44**, pp. 765-770, 2011.
- [9] Wurzburg, O.B., *Modified Starches: Properties and Uses*, 4<sup>th</sup> printing, CRC Press, Boca Raton, FL, 1989.
- [10] Kim, H.S. & Lee, Y.E., *Physicochemical Properties of Crosslinked Potato Starch*, Korean J. Food Sci. Technol., **28**, pp. 573-579, 1996.
- [11] Rutenberg, M.W., & Solarek, D., *Starch Derivatives: Production and Uses*, Starch Chemistry and Technology, R.L. Whistler, BeMiller, J.N.

- and & Paschall, E.F. (eds.), 2<sup>nd</sup> Ed. Academic Press: Orlando, FL, pp. 311-388, 1984.
- [12] Light, J.M., *Modified Food Starches: Why, What, Where and How*, The Symposium on Modified Food Starches at AACC's 74th Annual Meeting in Washington, DC, 1989.
- [13] Tessler, M.M., *Process for Preparing Cross-Linked Starches*, US Patent 4098997, 1978.
- [14] Smolka, G.E. & Alexander, R.J., *Modified Starch, Its Method of Manufacture and The Salad Dressings Produced Therewith*, US Patent 4562086, 1985.
- [15] Wu, Y. & Seib, P.A., *Acetylated and Hydroxypropylated Distarch Phosphate from Waxy Barley: Paste Properties and Freeze-Thaw Stability*, *Cereal Chem.*, **67**, pp. 202-208, 1990.
- [16] Yeh, A.I. & Yeh, S.L., *Some Characteristics of Hydroxypropilated and Cross-Linked Rice Starch*, *Cereal Chem.*, **70**(5), pp. 596-601, 1993.
- [17] Aziz, A., Daik, R., Ghani, M.A., Daud, N.I.N. & Yamin, B.M., *Hydroxypropylation and Acetylation of Sago Starch*, *Malaysian J. Chem.*, **6**(1), pp. 048-054, 2004.
- [18] Hung, P.V. & Morita, N., *Physicochemical Properties of Hydroxypropilated and Cross-Linked Starches from A-Type and B-Type Wheat Starch Granule*, *Carbohydr. Polym.*, **59**, pp. 239-246, 2004.
- [19] AOAC, *Official Methods of Analysis: Phosphorus in Flour*, Arlington, USA: Association of Official Analytical Chemistry, p. 251, 1984.
- [20] Joint FAO/WHO Expert Committee on Food Additives, *In Compendium of Food Additive Specifications, Hydroxypropyl Starch*, INS No. 1440. FAO Food and Nutrition Paper, **52**, add. 9. Geneva, 2001.
- [21] Matos, M.E. & Pérez, E., *Characterization of Native and Modified Cassava Starches I, Ultrastructural Study by Scanning Electron Microscopy and X-Ray Diffraction Techniques*, *Cereal Food World*, **48**, pp. 78-81, 2003.
- [22] Kaur, L., Singh, J., & Singh, N., *Effect of Cross-Linking on Some Properties of Potato (*Solanum tuberosum* L.) Starches*, *J. Sci. Food Agric.*, **86**, pp. 1945-1954, 2006.
- [23] Wirakartakusumah, M.A., *Kinetics of Starch Gelatinization and Water Absorption in Rice*, Phd Disertation, University of Wisconsin, Madison, United States 1981.
- [24] Zobel, H., *Molecules to Granules: A Compressive Starch Review*, *Starch/Starke*, **40**, pp. 44-50, 1988.
- [25] Ananta, E., *Resistant Starch: Serat Tersembunyi untuk Kesehatan*, *Majalah Food Review Indonesia*, **1**(5), pp. 36-37, 2006.
- [26] Singh, J., Kaur, L. & Singh, N., *Effect of Acetylation on Some Properties of Corn and Potato Starches*, *Starch/Starke*, **56**, pp. 586-601, 2004.

- [27] Lim, S. & Seib, P.A., *Preparation and Pasting Properties of Wheat and Waxy Corn Starch Phosphates*, *Cereal Chem.*, **70**, pp. 137-144, 1993.
- [28] Koo, S.H., Lee, K.Y. & Lee, H.G., *Effect of Cross-Linking on The Physicochemical and Physiological Properties of Corn Starch*, *Food Hydrocolloids*, **24**, pp. 619-625, 2010.
- [29] Fennema, O.R., *Food Chemistry*, Third Edition, Marcel Dekker Inc. New York-Basel-Hongkong, 1996.
- [30] French, D., *Organization of Starch Granules*, *Starch: Chemistry and Technology*, R.L. Whistler, J.N. Bemillerdan, E.F. Paschall (eds.). Academic Press, Inc., New York, 1984.
- [31] Chuenkamol, B., Puttanlek, C., Rungsardthong, V. & Uttapap, D., *Characterization of Low-Substituted Hydroxypropylated Canna Starch*, *Food Hydrocolloids*, **21**, pp. 1123-1132, 2007.
- [32] Sívoli, L., Pérez, E., Lares, M. & Leal, E., *Studies of Conformational Changes, Crystalline and Granular Structures, and In Vitro Digestibility of Cross-Linked and Methylated Corn Starches*, *Interciencia*, **34**(1), pp. 52-56, 2009.