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Synthesis of Phosphorylated Sugar Palm (Aren) Starch Using Low Level Sodium Tripolyphosphate (STPP)

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Abstract

Sugar palm or aren (Arenga pinnata) is a traditional source of starch widely cultivated throughout Indonesia. Despite its potentiality to be used as feedstock for food industries, there has been very little research reported on sugar palm starch characterization and modification. This paper describes a preliminary experimental study on the chemical modification, i.e. phosphorylation of sago palm starch using low level of Sodium tripolyphosphate (STPP), and characterization of some important physicochemical and functional properties of the modified products. Starch phosphate synthesis was conducted at an initial pH of 9, reaction temperatures of 120-140 ºC, and STPP intakes of 0.5-1.5%-weight based on dry starch. The experimental result shows that Degree of Substitution (DS) of the obtained products is accessible in the range of 0.0013 – 0.0068. An increase in reaction temperature as well as STPP intake leads to products with higher DS values. The modified starch products exhibit higher swelling power (16.57-24.81 g/g) and solubility (9.12-22.79 %-w/w) compared to native sugar palm starch (swelling power and solubility of 14.50 g/g and 7.91 %-w/w, respectively). Phosphorylated starch products also have significantly improved paste clarity clarity and water/ oil absorption capacity compared to native sugar palm starch. The result suggests that phosphorylation is a promising method to enhance the properties of sugar palm starch.

INTRODUCTION

Aren/ enau, also known as sugar palm or dryland sago (Arenga pinnata) (Wina et al., 1986) is a natural forest species of humid tropical regions of Asia. Compared to other multiple purpose trees (MPTs) of palm family, aren has the widest range of use, involving virtually all parts of the plant (root, stem, fibers, leaves, sap, and fruit) (Mogea et al., 1991). Sugar palm starch is an important product of aren collected from the pith of trees that are no longer productive in terms of sugar and fruit production (Adawiyah et al., 2013). Sugar palm starch commands a premium over swamp sago (Metroxylon sago) flour (Wina et al., 1986), and is used in the preparation of various traditional food products such as wet noodle, soun, cendol, dodol, and kerupuk opak (Mogea et al., 1991). Despite its potentiality to be used as a feedstock for industrial applications, there has been very little research reported on sugar palm starch characterization (Wina et al., 1986; Adawiyah et al., 2013) or modification.

Starch has extensive potential uses in food as well as non-food industries. Native starch, however, has inferior properties that limit its applications. Hence, in most cases, the physicochemical and functional characteristics of starch must be upgraded through physical or chemical modification (Chiu & Solarek, 2009). Phosphorylation is a potential chemical modification technique commonly applied to increase the hydrophilicity of starch, resulting in products suitable for food, paper, adhesive, textile,

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as well as pharmaceutical industries (Solarek, 1986). Results from previous researches showed that phosphorylation technique has been successfully applied to improve the properties of rice, corn, wheat, sago, and mung bean starch (Lin et al., 2009; Lim & Seib, 1993; Muhammad et al., 2000; Nathania et al., 2017). Nevertheless, to the best of our knowledge, no study has been reported on the phosphorylation of sago palm starch.

The aim of this research is to explore the potentiality of using low level sodium tripolyphosphate (STPP) as a reagent for sugar palm starch phosphorylation. In particular, the effect of STPP intake and reaction temperature on P-content and Degree of Substitution (DS) of the products was investigated. Several functional properties of the phosphorylated products (swelling power, solubility, water/ oil absorption capacity, and paste clarity) were characterized and compared to native sago palm starch.

RESEARCH METHODOLOGY

Materials

Sugar palm starch was obtained from local market in Bogor, West Java, and used without further purification. Proximate analysis revealed that this starch contains 0.20 %-w/w ash, 0.24 %-w/w lipid, 0.26%-w/w protein, and 99.30% carbohydrate (dry basis). Phosphorylation reaction was conducted using Sodium tripolyphosphate (STPP) reagent (technical grade) obtained from Sigma Aldrich, Singapore and sodium sulfate (analytical grade, Merck, Jakarta). The pH of the suspensions was adjusted using hydrochloric acid and sodium hydroxide (analytical grade, Merck, Jakarta). Reagents used for phosphate content determination (Vanadate Molybdate, potassium hydrogenphosphate, and sodium carbonate) were all of analytical grade and obtained from Merck, Jakarta. All chemicals were used without further purification.

Methods

Preparation of Phosphorylated Starch Products

Phosphorylated sugar palm starch products were prepared according to a previously reported method for wheat and corn starch phosphorylation (Lim & Seib, 1993) with slight modification. A solution containing 0.5-1.5 %-w STPP/ w of starch (dry weight basis), 12 ml of water, and 1 gram of sodium sulfate was prepared, and pH of the solution is adjusted to 9 using HCl or NaOH solution (10%-mol/ mol). Sugar palm starch (10 gram, dry weight basis) was added into the solution, and pH was adjusted back to 9. The resulting starch suspension was stirred for one hour at room temperature, before subsequently dried in a tray dryer at 45 °C. When water content of the starch mixture reached 10-15 %-w/ w, the temperature of the drier was increased to 120-140 °C, and reaction was carried out for two more hours. The resulted phosphorylated starch products were cooled to room temperature and washed for three times (using 25 ml of RO water, pH of the suspension was adjusted at pH 9). Each time, the solid product was separated from the washing solution by centrifuging the mixture at 1500g for 10 minutes. Phosphorylated starch products were finally dried in a tray dryer at 45 °C until constant weight. Each experiment was performed in duplicate.

Product Characterization: Determination of DS and P-content

Phosphorus content and Degree of Substitution (DS) of the phosphorylated starch products were determined spectrophotometrically at $\lambda = 385$ nm according to a previously reported procedure (Passauer et al., 2010). DS is calculated as mol P/ mol of anhydroglucose (AHG) units of sugar palm starch molecules.

Product Characterization: Swelling Power and Solubility

Swelling power and solubility of native and phosphorylated sugar palm starch products were determined according to a published method (Li & Corke, 1999). Starch sample was mixed with RO water (3.33 %-w/ v) at 85 °C for 30 minutes. The mixture was subsequently centrifuged (3000 rpm, 15 minutes) to separate starch paste from supernatant containing soluble starch. Collected supernatant was dried at 100 °C until constant weight. Swelling Power (g/ g) and Solubility (%-w/ w) of the samples were calculated by using Eq. (1).

$$Swelling\ Power = \frac{weight\ of\ sediment\ paste\ (g)}{weight\ of\ initial\ sample(g) \times \left(1 - \frac{Solubility}{100}\right)} \tag{1}$$

$$Solubility = \frac{weight\ of\ soluble\ starch\ (g)}{weight\ of\ initial\ sample\ (g)} \times 100\% \tag{2}$$

Table 1. Phosphorus Content and Degree of Substitution of Phosphorylated Starch Products

Reaction Temperature (°C)	**P-Content (%-w/ w)**			**Degree of Substitution**		
	STPP Intake (%-w/ w of Dry Starch)			**STPP Intake (%-w/ w of Dry Starch)**		
	0.5	**1**	**1.5**	**0.5**	**1**	**1.5**
120	0.025	0.061	0.091	0.0013	0.0032	0.0049
130	0.043	0.078	0.097	0.0023	0.0041	0.0051
140	0.055	0.089	0.129	0.0029	0.0046	0.0068

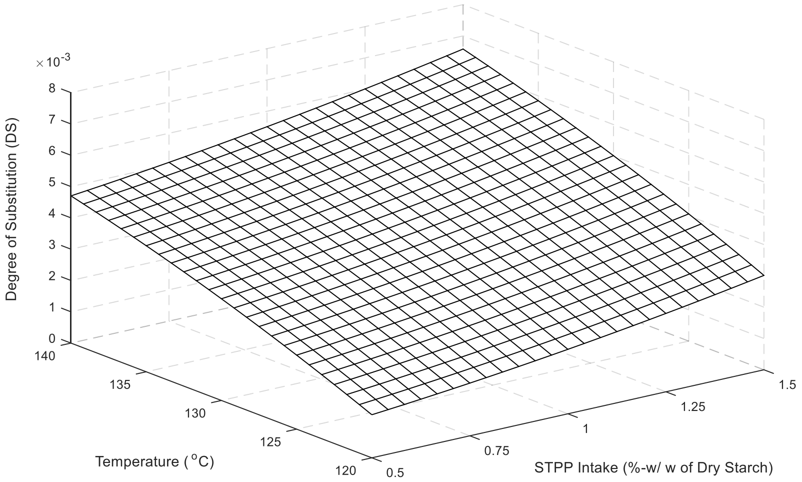

Figure 1. Degree of Substitution (DS) of Phosphorylated Starch Products (Based on Multivariable Regression Model).

Product Characterization: Water and Oil Absorption Capacity

Water and oil absorption capacity were determined based on a reported procedure (Mishra & Rai, 2006) with a slight modification. Starch sample was mixed in RO water or palm cooking oil (10 %-w/ v) in a centrifuge tube and kept at room temperature (1 hour). The suspension was subsequently centrifuged (3000 rpm, 30 min), and the separated sediment paste was collected and weighed. The absorption capacity was calculated as mass of water or oil (in g) absorbed per g of the initial starch sample.

Product Characterization: Paste Clarity

Paste clarity of gelatinized starch suspensions was measured spectrophotometrically based on the procedure suggested by Stahl et al. (2007) with a slight modification. Paste clarity is defined as the percentage of transmittance (at λ = 650 nm) of starch suspensions in RO water (1 %-w/ v, pH = 7), heated at 85 °C for 30 mins and subsequently cooled to 25 °C for 60 minutes before the measurement.

RESULT AND DISCUSSION

Phosphorylation of sugar palm starch was conducted at temperatures of 120, 130, and 140 °C, with an intake of 0.5-1.5%-w STPP/ w of dry starch. During the reaction, hydroxyl groups available at anhydroglucose (AHG) units of starch molecules attacked phosphate groups from STPP, and became substituted with mono- or di-phosphates (Lim & Seib, 1993). After isolation and drying steps, the phosphorylated starch product was obtained as white powder.

P-Content and Degree of Substitution of Phosphorylated Starch Products

Phosphorus content and DS of the phosphorylated sugar palm starch was determined spectrophotometrically, and the result is given in Table 1. The P-content of the products ranges from 0.025-0.129%, while the DS values are accessible in the range of 0.0013-0.0068. Apart from the slightly lower P-content values obtained for products synthesized at lowest STPP intake (0.5 %-w/ w of dry starch), most of the P-content values are still comparable with the results reported previously for

Table 2. Swelling Power and Solubility of Native and Phosphorylated Sugar Palm Starch Products

Temperature (°C)	Swelling Power (g/ g)			Solubility (%-w/ w)		
	STPP Intake (%-w/ w of Dry Starch)			STPP Intake (%-w/ w of Dry Starch)		
	0.5	1	1.5	0.5	1	1.5
Native		14.50			7.91	
120	16.57	18.82	21.49	9.12	13.70	17.38
130	17.53	19.62	23.45	11.87	15.62	19.24
140	18.75	22.03	24.81	13.66	18.25	22.79

Table 3. Water Absorption Capacity (WAC) and Oil Absorption Capacity (OAC) of Native and Phosphorylated Sugar Palm Starch Products

Temperature (°C)	Water Absorption Capacity (g/ g)			Oil Absorption Capacity (g /g)		
	STPP Intake (%-w/ w of Dry Starch)			STPP Intake (%-w/ w of Dry Starch)		
	0.5	1	1.5	0.5	1	1.5
Native		0.73			0.55	
120	0.86	0.90	0.96	0.62	0.64	0.67
130	0.89	0.94	1.00	0.63	0.66	0.69
140	0.92	0.98	1.25	0.65	0.68	0.72

Table 4. Paste Clarity of Native and Phosphorylated Sugar Palm Starch Products

Temperature (°C)	Paste Clarity (%-T)		
	STPP Intake (%-w/ w of Dry Starch)		
	0.5	1	1.5
Native		37.65	
120	58.60	62.15	65.65
130	60.80	63.95	67.95
140	62.00	65.40	70.25

phosphorylated sago starch (P content =0.05-0.32%) (Muhammad et al., 2000), corn/ wheat starch (P content =0.06-0.29%) (Lim & Seib, 1993), and our previous results on mung bean and arrowroot starch (P content =0.045-0.250%) (Nathania et al., 2017; Sugih, et al., 2015). The P-content of phosphorylated sugar palm starch products are still far below Food Chemical Codex (FCC) permitted level for food purposes (0.4%) (Committee on Food Chemical Codex, 2003), suggesting that the products are safe for human consumption.

In order to observe the dependence of the DS values on the experimental variables (reaction temperature and STPP intake), a simple non-linear multivariable regression model (R^2 = 0.9996) has been developed and the result is shown graphically in Figure 1. The use of higher STPP intakes provides starch with more available phosphate groups during the reaction, causing more replacement of starch hydroxyl groups (higher DS). This result shares a similar trend with our previous result on the phosphorylation of arrowroot starch (Sugih et al., 2015). Phosphorylation reaction rate will also be faster at higher temperature, resulting in products with increased DS values. This temperature effect is in agreement with previous observations on the phosphorylation of rice, sago, and arrowroot starch (Lin et al., 2009; Sugih et al., 2015; Sugih et al., 2013).

Characterization of Phosphorylated Sugar Palm Starch Products

Several functional properties of native and phosphorylated sugar palm starch (i.e. swelling power and solubility, water and oil absorption capacity, and paste clarity) were determined, and the results are shown in Tables 2-4. Swelling power and solubility of starch products were determined by mixing and heating starch/water suspension.

Starch paste was subsequently isolated from the suspension after centrifugation. Swelling power of native sugar palm starch (14.50 g/ g) is higher compared to reported values for arrowroot, mung bean, sweet potato, and corn starch (4.87-11.42 g/g) (Nathania et al., 2017; Stahl et al., 2007; Sugih et al., 2015; Sugih et al., 2016), but lower than swelling power of pinhao starch (26.02 g/ g) (Stahl et al., 2007). Its solubility (7.91 %-w/ w) is again relatively high compared to arrowroot, mung bean, sweet potato, and corn starch (1.669-7.26 %-w/ w) but rather low compared to pinhao starch (22.07 %-w/ w) (Nathania et al., 2017; Stahl et al., 2007; Sugih et al., 2015; Sugih et al., 2016). Substitution of starch hydroxyl groups with phosphate significantly improves the swelling power and solubility of sugar palm starch. Sitohy et al. (2000) hypothesized that introduction of phosphate groups reduces strong hydrogen bonds present in starch granules. As the result, water is allowed to penetrate into starch structure more easily, and swelling power and solubility of the products increases. Phosphorylated product with highest DS (0.0068) also has the highest swelling power (24.81 g/ g) and solubility (22.79 %-w/ w), or about 170% and 290% of native sugar palm starch, respectively. These achieved values are much higher compared to reported swelling power and solubility values for other phosphorylated starches (the maximum values are 12.82 g/ g and 14.10 %-w/ w, respectively) (Nathania et al., 2017; Sugih et al., 2015; Sugih et al., 2016), and only slightly lower compared to phosphorylated corn and pinhao starch with significantly higher DS of 0.15 (25.16-25.45 g/ g and 24.21-27.20%-w/ w, respectively) (Stahl et al., 2007).

Water and oil absorption capacity (WAC and OAC) of native and phosphorylated starch products were measured by weighing starch pastes collected after centrifugation of starch/ water or starch/ oil mixtures prepared at room temperature. Native sugar palm starch has the lowest WAC (0.73 g/g) and OAC (0.55 g/ g) compared to reported values of other types of starch (0.847-10.4 g/ g and 0.572-1.40 g/ g, respectively) (Nathania et al., 2017; Mishra & Rai, 2006; Sugih et al., 2015; Sugih et al., 2016). The presence of phosphate groups significantly increases WAC as well as OAC of sugar palm starch. Similar trend is also observed when phosphorylation was performed on other types of starch (Lim & Seib, 1993; Nathania et al., 2017; Sugih et al., 2015; Sugih et al., 2016). The substitution of hydroxyl groups of starch with more polar phosphate groups resulted in attraction of more water molecules, resulting in higher WAC of the products. It is also hypothesized that at the same time, the presence of negatively charged phosphate reduces the strength of hydrogen bonds between anhydroglucose units of starch (Sitohy et al., 2000), providing more spaces inside the molecules that can be filled with more water or oil.

Paste clarity was determined spectrophotometrically after heating and subsequently cooling starch pastes. Native sugar palm starch has rather high paste clarity (37.65%) compared to corn, wheat, sweet potato, or mung bean starch (15.30-34%) (Lim & Seib, 1993; Nathania et al., 2017; Sugih et al., 2016). Phosphorylation significantly improves sugar palm starch paste clarity to 58.60-70.25%. Similar results were observed for other types of starch (Lim & Seib, 1993; Nathania et al., 2017; Li & Corke, 1999; Stahl et al., 2007; Sitohy et al., 2000). It is suggested that negatively charged phosphate groups induces repulsion between neighboring starch molecules. As the result, starch hydration level increases and highly swollen particles with high light transmittance is formed (Lim & Seib, 1993).

CONCLUSION

A preliminary study on the synthesis of phosphorylated sugar palm starch has been reported. Phosphorylation is successfully performed using STPP reagent (with intakes of 0.5 - 1.5 %w/ w of dry starch) at 110-130 °C. Modified products with DS = 0.0013-0.0068 (corresponding to P content of 0.025-0.129%, far below the permitted safe level for food application) have been obtained. Phosphorylation significantly improves swelling power and solubility, water/ oil absorption capacity, and paste clarity of sugar palm starch. In particular, sugar palm starch phosphate products exhibit very high swelling power and solubility compared to phosphorylated products from other types of starch. The obtained result suggests that phosphorylation is a potential method to improve functional properties of sugar palm starch. Further research is currently carried out to examine physicochemical and functional properties of phosphorylated sugar palm starch synthesized using different STPP and STMP intake ranges, and the result will be reported in forthcoming papers.

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