

Characteristics of Hydroxypropylated and Acetylated Sago Starches

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Abstract: Sago starch was chemically modified with propylene oxide followed by acetic anhydride. Hydroxypropyl sago starch was prepared at 40°C using 0.0-7.5 ml propylene oxide in alkaline condition for 24 h. Acetyl sago starch was prepared at room temperature using 0.0-9.0 ml acetic anhydride in medium alkaline condition. The objective of this study was to determine the effects of molar substitution (MS) and degree of substitution (DS) on the properties of modified sago starch, characterized for swelling power, solubility and paste clarity (%T). The results showed that MS hydroxypropyl sago starch (HPSS) was 0.021-0.058 and DS hydroxypropyl-acetyl sago starch (HP-ASS) was 0.029-0.051 and 0.047-0.061 at acetic anhydride of 6.5 ml and 9 ml, respectively, while DS acetyl sago starch (ASS) was 0.051 and 0.057. DS HP-ASS was the lowest compared to ASS, as MS HP-ASS was 0.021 and 0.044. Swelling power, solubility and paste clarity of HPSS, ASS and HP-ASS were the highest compared to native sago starch (NSS).

Key words: native sago starch, hydroxypropyl, acetyl, swelling power, solubility, paste clarity

ヒドロキシプロピル化およびアセチル化したサゴデンプンの特徴

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要約: サゴデンプンを酸化プロピレン、ついで無水酢酸を用いて化学的に修飾した。ヒドロキシプロピル化サゴデンプンはアルカリ条件下で24時間、40°Cで0-7.5mlの酸化プロピレンを用いて調整した。アセチル化サゴデンプンは中程度のアルカリ条件下で室温、0-9mlの無水酢酸を用いて調整した。この研究の目的は化学修飾を受けたサゴデンプンの諸性質（膨潤力、溶解度、糊液の透明性(%T)）に及ぼす置換の程度の影響を決めることであった。ヒドロキシプロピル化したサゴデンプン (HP-S) のモル数 (MS値) は0.021-0.058であり、ヒドロキシプロピル-アセチル化したサゴデンプン (HP-ASS) の置換度 (DS値) は無水酢酸6.5mlでは0.029-0.051、9mlでは0.047-0.061となった。一方、アセチル化したサゴデンプン (ASS) のDS値は0.051と0.057であった。HP-ASSのDS値はASSと比較して低く、HP-ASSのMS値は0.021と0.044であった。HPSS、ASS、およびHP-ASSの膨潤力、溶解度、糊液の透明性は修飾前のサゴデンプンと比べて高い値を示した。

キーワード: サゴデンプン、ヒドロキシプロピル化、アセチル化、膨潤力、溶解度、糊液の透明性

Introduction

Starch is the major carbohydrate reserved in plant tuber and seed endosperm where it is found as granules. As natural biopolymers, starch has received more attention because of its low cost and availability. However, starch has some disadvantages such as hydrophilicity, poor mechanical properties and dimensional stability, especially in presence of water and humid environments (Xu et al. 2005). Similar to other native starches, sago starch needs to be modified to improve its quality. The viscosity of sago starch is highly reduced during heating and shearing and this breakdown is further increased under acidic conditions. Furthermore, the native starches exhibit a higher retrogradation which will result in the formation of a long cohesive gel with increasing syneresis (Wattanachant et al. 2003). Starch is often chemically modified by introducing a different functional group in order to obtain products with desired properties for certain applications. Starch is widely used in food industries as a thickening, stabilizing, and gelling agent.

Sago starch consists of oval granules with diameters of 20-40 μm and C-crystalline type (Ahmad et al. 1999), which allows a potential for sago starch modification. Preparation of modification starch from sago starch such as hydroxypropyl-cross-linked sago starch (Haryadi and Kuswanto 1996, Wattanachant et al. 2002a, 2002b, 2003) and acetylated sago starch (Haryadi and Kuswanto 1997) has been reported.

Hydroxypropylated and acetylated starches are commonly added to food products to control retrogradation and to increase the viscosity and smoothness of starch pastes (Jane 1997). Propylene oxide and acetic anhydride have often been used to prepare starch derivatives because they can reduce the gelatinization temperature and enhance the stability of the starch paste (Liu et al. 1997, Wattanachant et al. 2003).

The objective of this study was to determine the effects of molar substitution (MS) and degree of

substitution (DS) on the swelling power, solubility and paste clarity (%T) properties of native sago starch (NSS), hydroxypropyl sago starch (HPSS), acetyl sago starch (ASS) and hydroxypropyl-acetyl sago starch (HP-ASS).

Materials and Methods

Materials

Sago starch (*Metroxylon rumphii* Mart.) used was extracted by a farmer of Saparua Island, Province of Mollucas, Indonesia. The sample was collected from the farmer on October 2004, and taken to the laboratory. The sample was washed and filtered through a 100 mesh sieve and the slurry was then collected and settled. After sedimentation, water was decanted and the starch cake was washed three times by suspending the starch in distilled water. Finally, the starch was dried at 40°C in a hot air oven (Memmert, Germany) for about 12 h and stored in a high-density polyethylene (HDPE) bag before analyzing. Propylene oxide and acetic anhydride (Merck), propylene glycol (Nacalai Tesque), 1,2,3,-triketohydrindene crystals (Merck) and all chemicals used were analytical grade.

Proximate analysis

Standard AOAC methods (Association of Official Analytical Chemist 1984) were used for the measurement of moisture and ash. Moisture content (% w/w) was assayed by loss in weight on drying at 105°C for 5 h in a hot air oven (Memmert, Germany). The ash (% w/w) was determined by incinerating of known sample weights in a muffle furnace (Lenton Furnaces). Starch was burned in a furnace overnight (12 h) at 550°C, and cooled down in a desiccator.

Determination of amylose

Amylose in the starch samples was determined according to the colourimetric procedure of AOAC methods (Association of Official Analytical Chemist 1984). Starch (0.1 g, dry basis) was accurately

weighed and dissolved by heating in 1 ml 95% ethanol and 9 ml 1 N NaOH for 10 min in a water bath at 100°C to reach gelatinization. After the solution had dissolved, it was diluted to 100 ml in a volumetric flask with distilled water. An aliquot (5 ml) of this solution was diluted to 100 ml by distilled water. Acetic acid (1 ml) 1 N and 0.2% iodine (2 ml) were added and mixed and the absorbance of this solution was placed in a 1cm path length glass cell and read at 620 nm using a UV-Vis 1601 (Shimadzu, Kyoto, Japan). Standard amylose was purchased from Merck, and different concentrations of solutions were prepared. The amylose content in the starch samples was determined by using the prepared standard amylose graph.

Sago starch dual-modification

Hydroxypropyl starch was prepared from sago starch using the method as described by Leegwater and Luten (1971). Sago starch (80 g) was dispersed in 200 ml alkaline solution (0.25 M NaOH in 0.86 M Na₂SO₄) at room temperature. The mixture was heated at 40°C in a water bath, and propylene oxide (0.0, 2.5, 5.0 and 7.5 ml) was added and kept in an orbital shaking water bath at 40°C for 24 h. The starch slurry was then adjusted to pH 7.0 with 1% sulfuric acid solution to terminate the reaction. The starch cake was washed several times by suspending the starch in distilled water, followed by centrifugation at 4500 rpm for 5 min until the starch was free of sulfuric acid. Finally, the starch was dried at 40°C in the cabinet dryer.

Acetylated and hydroxypropyl-acetylated starches were prepared from sago starch as described by Phillips et al. (1999). Sago starch (100 g) was dispersed in 225 ml of distilled water and stirred using a magnetic bar at 25°C for 60 min to obtain a uniform suspension. The pH of the slurry was adjusted to 8.0 by adding 3.0% NaOH and acetic anhydride (0.0, 6.5 and 9.0 ml) was slowly added into the slurry. The mixture was constantly stirred and the pH of the slurry was maintained between 8.0-8.4 using 3.0%

NaOH solutions. The mixture was let stand for 10 min to allow the reaction to proceed after completing the addition of acetic anhydride. The slurry was then adjusted to pH 4.5 with 0.5 N HCl. After sedimentation, it was washed twice with distilled water until free of acid and once with 95% ethanol, and then oven-dried at 40°C.

Determination of MS of HPSS and DS of ASS and HP-ASS

MS was determined by the following method of WHO and FAO (2001). Accurately weigh 50 - 100 mg of the sample into a 100 ml volumetric flask and add 25 ml of 1 N sulfuric acid. Prepare a sample of unmodified starch of the same source in the same manner. Place the flasks in a boiling water bath and heat until the samples are in solution. Cool and dilute the contents to 100 ml with water. If necessary, dilute the sample further to assure the presence of no more than 4 mg of hydroxypropyl group per 100 ml, and then dilute the blank starch in the same proportion. Pipet 1 ml of the solutions into 25 ml graduated test tubes with glass stoppers and, with the tubes immersed in cold water, add drop-wise 8 ml of concentrated sulfuric acid to each. Mix well and place the tubes in a boiling water bath for exactly 3 min, then immediately transfer the tubes to an ice bath until the solution is chilled. Add 0.6 ml of ninhydrin reagent (a 3% solution of 1,2,3,-triketohydrindene crystals in 5% aqueous sodium bisulfite solution), carefully allowing the reagent to run down the walls of the test tubes. Immediately shake well, and place the tubes in a 25°C water bath for 100 min. Adjust the volume in each tube to 25 ml with concentrated sulfuric acid and mix by inverting the tubes several times. (Do not shake.) Immediately transfer portions of the solutions to 1cm cells and after exactly 5 min, measure the absorption (A) at 590 nm (UV-Vis 1601, Shimadzu, Kyoto, Japan), using the starch blank as the reference. Prepare a calibration curve with 1 ml aliquots of standard aqueous solutions, containing 10, 20, 30, 40 and 50 µg of propylene glycol per ml.

Calculations:

$$\text{Hydroxypropyl (HP) groups (\%)} = \frac{C \times 0.7763 \times 10 \times F}{W}$$

where C = amount of propylene glycol in the sample solution read from the calibration curve ($\mu\text{g/ml}$); F = dilution factor (if a further dilution has been necessary); W = weight of sample (mg).

$$\text{MS} = \frac{\% \text{ HP}}{59.08} \times \frac{162.14}{(100 - \% \text{ HP})}$$

where 59.08 and 162.14 are molecular weights of hydroxypropyl groups and anhydroglucose unit, respectively.

DS of modified sago starch was determined by following the method of Wurzburg (1978). Acetylated starch (1.0 g) was placed in a 250 ml flask and 50 ml of 75% ethanol in distilled water was added. The loosely stoppered flask was agitated, warmed to 50°C for 30 min and cooled, and 40 ml of 0.5 M KOH was added. The excess alkali was back-titrated with 0.5 M HCl using phenolphthalein as an indicator. The solution was let stand for 2 h, and then any additional alkali, which may have leached from the sample, was titrated. A blank, using the original unmodified starch, was also used.

$$\text{Acetyl\%} = \frac{([\text{Blank} - \text{Sample}] \times \text{Molarity of HCl} + 0.043 \times 100)}{\text{Sample weight}}$$

Blank and sample were titration volumes in ml; sample weight was in g. DS is defined as the average number of sites per glucose unit that possess a substituent group (Whistler and Daniel 1995).

$$\text{DS} = \frac{(162 \times \text{Acetyl\%})}{(4300 - [42 \times \text{Acetyl\%}])}$$

FT-IR (Fourier Transform Infrared) spectroscopy

FT-IR spectra analysis of native and modified starches was obtained on a FT-IR spectrometer IRPrestige-21 (Shimadzu, Kyoto, Japan) using a KBr disc. The equipment was operated with a scanning range from 4000 to 400 cm^{-1} (Singh et al. 2004).

Properties of sago starch modification

Swelling power and solubility

Swelling power and solubility of modified sago starch

were determined by following the method of Adebowale et al. (2002). A starch sample (1.0 g) was accurately weighed and quantitatively transferred into a clean dried test tube and reweighed (W_1). The starch was then dispersed in 50 cm^3 of distilled water. The resultant slurry was heated at 95°C for 30 min in a water bath. The mixture was cooled to 30°C and centrifuged (500 rpm, 15 min). Aliquots (5 ml) of the supernatant were dried to a constant weight at 110°C. The residue obtained after drying the supernatant represented the amount of starch solubilized in water. Solubility was calculated as g per 100 g of starch on a dry-weight basis. The residue obtained from the above experiment (after centrifugation) with the water it retained was quantitatively transferred to the clean dried test tube used earlier and weighed (W_2).

Swelling of starch = $(W_2 - W_1) / \text{weight of starch}$

Paste clarity

The value of light transmittance (%T) was measured using the method as described by Craig et al. (1989). An aqueous suspension of starch (2% w/v) was heated in a water bath at 90°C for 30 min with constant stirring. The suspension was cooled to 30°C and stored at 4°C for 5 days and the percentage of light transmittance at 650 nm was determined against water blank in UV-Vis. 1601 spectrophotometer (Shimadzu, Kyoto, Japan).

Statistical analyses

The data obtained from the study were analyzed using analysis of variance at a 95% confidence level and comparisons significant for all treatments against a control used Dunnett's t tests. SAS 9.0 software (SAS Inc.) was used to analyze the data.

Results and Discussion

Composition of native sago starch used in this study is shown in Table 1. The composition is relatively similar to sago starch from different sources and varieties as reported by Ahmad et al. (1999), Cui and Oates (1999), Muhammad et al. (2000), Pomeranz (1991) and Wattanachant et al. (2002b).

Table 1. Composition of native sago starch (NSS)

Property	Research result	Ahmad et al. (1999)	Cui and Oates (1999)	Wattanachant et al. (2002b)
Moisture (% w/w)	12.54	20.00	9.00	12.54
Amylose content (%)	27.64	24.00	27.20	27.00 ^a
Ash (% w/w)	0.18	0.15	0.17	0.21

^a Pomeranz (1991)

Table 2. Hydroxypropyl group and molar substitution (MS) of hydroxypropyl sago starch (HPSS)

Propylene oxide (ml)	HPSS	
	Hydroxypropyl group (%)	MS
Native starch	0.00	0.000
2.5	0.75 ^{***}	0.021 ^{***}
5.0	1.58 ^{***}	0.044 ^{***}
7.5	2.06 ^{***}	0.058 ^{***}

Comparisons significant at the 0.05 level are indicated by *** for all treatments against a control using Dunnett's t tests.

Hydroxypropyl group and Molar Substitution (MS) HPSS

The efficiency of reaction of hydroxypropylation sago starch was indicated by molar substitution (MS) of the hydroxypropyl group into the granular starches. Native sago starch was presented as zero MS since it was used as a blank treated starch (Table 2). The hydroxypropyl group of HPSS was 0.75 to 2.06% at different levels of propylene oxide, which is similar to hydroxypropyl tapioca starch found by Haryadi et al. (1994). The MS was 0.021, 0.044 and 0.058 for propylene oxide 2.5, 5.0 and 7.5 ml per 80 g starch, respectively. The increasing of propylene oxide used in hydroxypropylation showed a significant increase in the hydroxypropyl group.

FT-IR spectroscopy was used to confirm the formation of the hydroxypropyl group. The peak at wave number of 1508.2 cm⁻¹ (Fig. 1b) was a methyl-stretching band indicating the presence of hydroxypropyl group in HPSS, but no peaks at wave number 1508.2 cm⁻¹ were observed for NSS (Fig. 1a).

Acetyl group and DS ASS and HP-ASS

Starch modification using hydroxypropylation forms the new hydroxyl group in chain sides, and this new hydroxyl group can also react with other

modification groups (Wootton and Haryadi 1991; Wootton and Haryadi 1992).

The level of acetylation of sago starch was indicated by the degree of substitution (DS) of the acetyl group into the granular starches (Table 3). ASS showed that the DS was 0.051 and 0.057 for 6.5 and 9 ml acetic anhydride, respectively, which is similar to DS 0.06 and 0.07 obtained by Haryadi and Kuswanto (1997). DS for HP-ASS with MS HP-ASS of 0.021, 0.044 and 0.058 was 0.029, 0.038 and 0.051 for 6.5 ml acetic anhydride, and was 0.047, 0.051 and 0.061 for 9 ml acetic anhydride, respectively. The results showed that

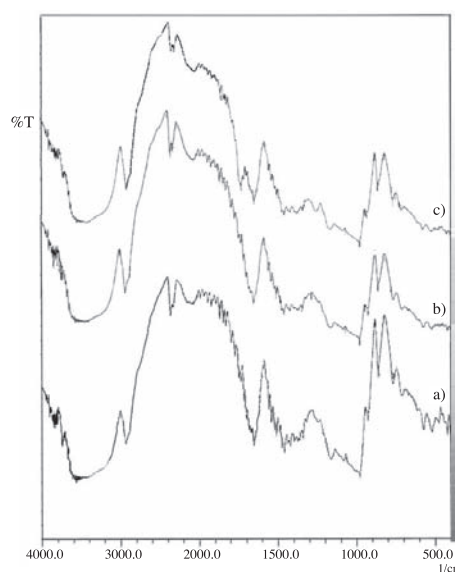


Fig. 1. FT-IR spectra of: a) NSS; b) HPSS; and c) HP-ASS

Table 3. Acetyl group and degree of substitution (DS) of acetyl sago starch (ASS) and hydroxypropyl- acetyl sago starch (HP-ASS)

MS HPSS	Acetic anhydride (ml)	ASS and HP-ASS	
		Acetyl group (%)	DS
0.000	0.0	0.000	0.000
	6.5	1.323 ***	0.051 ***
	9.0	1.481 ***	0.057 ***
0.021	0.0	0.000	0.000
	6.5	0.752 ***	0.029 ***
	9.0	1.236 ***	0.047 ***
0.044	0.0	0.000	0.000
	6.5	1.010 ***	0.038 ***
	9.0	1.334 ***	0.051 ***
0.058	0.0	0.000	0.000
	6.5	1.321 ***	0.051 ***
	9.0	1.593 ***	0.061 ***

Comparisons significant at the 0.05 level are indicated by *** for all treatments against a control using Dunnett's t tests.

MS HPSS and DS HP-ASS increased at the same concentrations of added acetic anhydride. This suggested that the hydroxyl group at chain side of the hydroxypropyl group had facilitated the substitution of the acetic group into granular structure, or the efficiency of sago starch reaction was determined by molar substitution of hydroxypropyl starch.

Yeh and Yeh (1993) found that hydroxypropylation increases the degree of subsequent cross-linking. On the other hand, Wattanachant et al. (2003) have reported that dual-modification sago starch with hydroxypropyl-cross-linking has improved the degree of substitution cross-linked by increasing of MS hydroxypropyl sago starch.

FT-IR spectroscopy was used to confirm the formation of the hydroxypropyl and hydroxypropyl-acetyl groups (Fig. 1). These spectra were characterized by the presence of methyl band at 1508.2 cm⁻¹, while carbonyl-stretching band at 1735.8 cm⁻¹ indicated the presence of hydroxypropyl and acetyl groups in starch structure (Fig. 1b and 1c, respectively). The presence of acetyl group (%) for

acetyl potato starch was at 1733.25 cm⁻¹ and acetyl corn starch was at 1733-1734 cm⁻¹ (Singh et al. 2004) and sago starch was at 1754 cm⁻¹ (Daik et al. 2004). The result confirmed that FT-IR spectroscopy was a quick and reliable method to evaluate the presence of hydroxypropyl and acetyl groups in starch structure.

Properties of modified sago starch

The effects of MS-DS HP-ASS at different levels influenced swelling power, solubility and paste clarity of sago starch, as shown by Table 4.

The increased of hydroxypropyl group and MS produced easy swelling sago starch granules (Haryadi et al. 1994). This means that the changes of crystalline granule have caused propylene oxide to be more readily present in starch granules.

Swelling power and solubility

The swelling power of NSS (19.27 g g⁻¹) decreased compared to the modified starch (27.38-36.76 g g⁻¹), while Dunnett's t test showed a significant difference for modified starch against NSS (Table 4). The substitution of hydroxypropyl group produced swelling power of HPSS (MS 0.058) ranging from

Table 4. Swelling power, solubility and paste clarity of native and modified sago starch

Level of modification		Swelling power (g g ⁻¹)	Solubility (%)	Paste clarity (%T)	Paste clarity (%T), after 5 days, at 4°C
MS	DS				
0.000	0.000	19.27	14.81	25.35	19.22
0.00	0.051	27.38 ***	19.85 ***	35.26 ***	33.27 ***
0.044	0.000	33.01 ***	22.04 ***	45.05 ***	43.35 ***
0.044	0.051	32.35 ***	21.79 ***	45.29 ***	44.29 ***
0.058	0.000	36.76 ***	23.79 ***	52.14 ***	50.94 ***
0.058	0.051	36.23 ***	23.20 ***	51.32 ***	50.38 ***

Comparisons significant at the 0.05 level are indicated by *** for all treatments against a control using Dunnett's t tests.

19.27 to 36.76 g g⁻¹, while ASS (DS 0.051) was 27.38 g g⁻¹. The higher MS and DS increased the swelling power and this was probably related to the weakening of hydrogen bonding between starch molecules due to substitution of the hydroxypropyl group. Moreover, the result showed that hydroxypropylation produced a higher swelling power than acetylation. This can be linked to the ability of hydroxypropylation to form the new hydroxyl group in chain side (Wootton and Haryadi 1991; Wootton and Haryadi 1992).

The increasing of swelling power was shown by the hydroxypropyl banana starch (MS 0.017) from 8.7 g g⁻¹ to 13.8 g g⁻¹ (Waliszewski et al. 2003). Liu et al. (1997) also showed a similar result for acetyl maize starch. On the other hand, Betancur et al. (1997) indicated that swelling power of acetyl starch was 15.51 g g⁻¹ compared to 14.40 g g⁻¹ for the native starch.

The increasing of swelling of starch granules was expected as the result of more rapid hydration permitted by acetylation (Liu et al. 1997). The changes observed in swelling by acetylation may be attributed to the introduction of hydrophilic substituting groups that retained water molecules to form hydrogen bonds in the starch granules (Betancur et al. 1997).

The swelling power parameter of the ASS was higher than the NSS but lower than HP-ASS. This indicated that the improvement of swelling power is more influenced by hydroxypropylation than acetylation. The substitution of acetyl group on HPSS tends to decrease the swelling power of starch as indicated by HP-ASS. These conditions may be caused by the introduction of acetyl groups into the polymer chain resulting in destabilization of granular structure and causing an increase in swelling, while dual-modification gave more effects.

The high DS may change the starch granules to become hydrophobic. This means that the water absorption by granule will decrease and then influence the swelling power of HP-ASS. Fringant et al. (1996) have indicated that when the DS increases, the acetyl group is associated and is not available to

interact with water molecules, thereby increasing the hydrophobicity of the product.

The solubility of HPSS (MS 0.058) was 23.79% and that of ASS (DS 0.051) was 19.85%, while NSS was 14.81%. The higher MS and DS will increase sago starch solubility (Table 4). These conditions caused by that modification group tend to make the molecules of starch loosen from one another and degrade the strength of the intermolecular bond, facilitating the water access of the amorphous region, and also increasing the starch hydrophilicity.

Sitohy et al. (2000) showed that the tendency of starch molecules to be loosened among the positively charged group modification of starch molecules was caused by the substitution of the hydroxypropyl group, degrading the strength of intermolecular bond. Cardinali et al. (2002) explain that hydroxypropylation can yield high aqueous stability, improve solubility and produce softer texture in solution. The hydrophobic group can be substituted at the starch to alter the solubility, yielding better bonding and repairing the stream characteristic.

The solubility of ASS was higher compared to the NSS. This possibly caused the weakness of hydrogen bond between the starch molecules and water molecules in the starch granules. Adebowale et al. (2002) showed that this increased the solubility of acetyl bambarra starch relative to its native starch. This probably is due to the weakening of starch granules. Starch solubility depends on DS, with higher DS showing an increase in level of solubility.

Acetylation treatment increased the solubility of starches from all rice cultivars. Solubility of acetyl starch was 17.01% compared to the native starch at 15.95%. The changes observed in solubility by acetylation may be attributed to the introduction of hydrophilic substituting groups that retained water molecules to form hydrogen bonds in the starch granules (Betancur et al. 1997). The substitution of acetyl group on the starch granules could facilitate the water access in the amorphous region. Liu et al. (1997) showed that the increasing of starch solubility

was influenced by starch hydrophylicity, especially amylose molecules more than amylopectin.

Solubility of starch dual-modification was shown to be lower than HPSS but higher than ASS. Starch solubility was more influenced by hydroxypropylation.

Paste clarity

Paste clarity related directly to the circumstances of dispersal suspension of starch and the tendency of the starch retrogradation. According to Phillips and Williams (2000), native sago starches give an opaque gel.

Starch modification improved the clarity of HPSS (MS 0.058) to become 52.14%, while ASS (DS 0.051) was 35.26% compared to NSS at 25.35%, and based on the result of Dunnett's t test, the modified sago starch showed significant difference against NSS. The higher MS and DS produced the increased clarity of starch paste (Table 4).

Hydroxypropyl starch granules tend to estrange among nearby starch granules and obviously lessened interchange association, which facilitated the increase of transmittance percentage. Increased hydroxypropylation or acetylation starch paste clarity was shown by Craig et al. (1989) for the hydroxypropyl starch; Lawal (2004) for acetyl new cocoyam starch; Liu et al. (1997) for acetyl maize starch; Singh et al. (2004) for maize and potato acetylation starch; and Yook et al. (1993) for rice hydroxypropyl starch.

Craig et al. (1989) showed that changes in starch granules and molecular structure by hydroxypropylation could facilitate the water penetration and absorption, thereby causing the starch to be easy to swell and increasing the paste clarity. Therefore, we can say that, with the substitution of hydroxypropyl and acetyl groups into starch granules, this group can then pursue the occurrence of the retrogradation that has significant influence on paste clarity.

Betancur et al. (1997) showed that increasing of starch paste clarity was caused by the entry of the hydrophilic substitution group, which detained water

molecules to form the hydrogen bond. The tendency of paste clarity for the HP-ASS is equal to the swelling power and solubility. HPSS gives the super ordinate score compared to the HP-ASS.

Clarity of sago starch paste was measured after the starch paste was stored for five days in a cool room (4°C), to observe the tendencies of retrogradation, which happened to the sago starch paste. If starch paste was allowed to become cold, eventually it becomes opaque, because the retrogradation process will be quickened at low temperatures.

The measurement of paste clarity showed that paste of modified sago starch stored after five days (4°C) decreased by $\pm 1-2\%$. The NSS, on the other hand, decreased from 25.35% to 19.22% ($\pm 6\%$), as a result of tendencies of retrogradation. The retrogradation effect decreased for HPSS, ASS and HP-ASS because bonding strength in the retrogradation decreased in the modified group substitution.

The acetylation of starches gave the same results for measurement of clarity of cocoyam starch paste, after storage in a cool room (4°C) for ten days. Paste clarity on the first day was $38.98 \pm 0.44\%$, decreasing to 36.87 ± 0.84 (Lawal 2004). The change of granule and molecule structure induced by hydroxypropylation, facilitating water penetration and absorption in starch granule, facilitating swelling and improving the transmutation scores (Craig et al. 1989). Yook et al. (1993) showed that resilience to the occurrence of retrogradation was higher in the rice starch that was modified by hydroxypropylation using 5% propylene oxide.

The clarity of acetylated starch remained higher than its counterpart native starches during storage. The clarity of acetyl starch (DS 0.18) decreased from 47.8 to 40.7% compared to the native starches at 34.8 to 25.8% (Singh et al. 2004).

This research result indicates that treatment modification by hydroxypropylation and acetylation can depress the retrogradation of starch. This retrogradation was described as a crystal core forming on the addition of starch molecule segment, which

situated slowly to form the growing crystal line area (D'Appolonia et al. 1971). If the starch suspension is allowed without stirring, inter-molecular bonding formed between the granules of starch and pieces of starch granules, resulting in blur starch sol and obstinacy in character (Hodge and Osman 1976). The problem was in retrogradation of food processing which formed a flimsy coat on the surface of starch pasta and thickened on refrigeration and cannot be distributed again with warm-up and squealer (Howling 1974).

Conclusions

The research shows that hydroxypropylation and acetylation can change the physical properties of NSS. The level of hydroxypropyl and acetyl groups can be shown with the measurement of MS and DS and supported by FT-IR spectra at typical methyl (-CH₃) for the hydroxypropyl group and carbonyl (-C=O) for the acetyl group. Hydroxypropyl groups provide internal plasticization of starch in amorphous regions. The swelling power, solubility and paste clarity parameters of the HPSS, ASS and HP-ASS were shown to be higher than those of NSS. The highest swelling power, paste clarity and solubility parameters were shown by HPSS (MS 0.058).

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