

Hydroxypropylation and Acetylation of Sago Starch

**Azronnizan Aziz, *Rusli Daik, Maaruf Abd. Ghani, Nik Ismail Nik Daud,
and Bohari M. Yamin.**

School of Chemical Sciences and Food Technology, Faculty of Science and Technology
Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor

*corresponding author

Abstract: Sago starch was chemically modified by etherification and esterification reaction with propylene oxide followed by a mixture of 2% sodium trimetaphosphate (STMP) and 5% sodium tripolyphosphate (STPP), and acetic anhydride, respectively. Etherification or hydroxypropylation reaction was done using 5% sodium sulphate and adjusting the pH to 10.5 by adding aqueous sodium hydroxide or hydrochloric acid to the pre-reaction slurries containing propylene oxide. Esterification or acetylation reaction was done using glacial acetic acid as solvent and concentrated sulphuric acid as catalyst. FTIR spectroscopy was used to examine the chemically modified sago starch. The degree of substitution was relatively low with 0.044 (1.5%) and 0.342 (11.4%) for hydroxypropylation and acetylation respectively. Thermal analysis showed that acetylation increases the gelatinization temperature (T_p) but reduces the enthalpy (ΔH) while hydroxypropylation cross-linking reduces both the T_p and ΔH .

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Introduction

The development of new starch-based packaging material includes the chemical modification of starch or the addition of hydrophobic groups or components in the formulation [1]. Chemical modification has been used to introduce new properties of starch for different applications [2]. Acetylation, hydroxypropylation and cross-linking are widely used methods to prepare modified starches. The benefits from this modification are that cross-linking will reinforce the granule of starch to be more resistant towards acidic medium, heat and shearing while hydroxypropylation will improve their freeze-thaw or cold-storage stability [3,4,5]. Yeh and Yeh (1993) reported that the preparation procedure for dual-modified starch affects the product properties. Cross-linking reduces the degree of subsequent hydroxypropylation, and hydroxypropylation increases the degree of subsequent cross-linking. Acetylation of starch provides sol stability and functional properties such as hydrophobic, cationic or anionic character at relatively low cost [6]. Clarity, viscosity and stability of acetylated starches are of value in food, paper and textile applications [7].

Chemical modifications on starches have markedly altered physicochemical properties compared with their parent starches [6]. The introduction of acetyl group reduces the interaction between starch molecules and thereby increases the swelling power and solubility of the starch granule, decreases the coagulation of the starch and gives improved clarity and freeze-thaw stability.

Shogren reported that acetylation of starch was found to increase hydrophobicity and thus is a useful approach towards increasing the water resistance of starch [8]. Derivatization of starch hydroxyl groups

may also reduce the tendency of starch to form strongly hydrogen-bonded networks and increase film flexibility.

Starch acetate was reported to be considerably more hydrophobic than is native starch and has been shown to have better tensile property retention in an aqueous medium, improved solubility compared to native starch and is easily cast into films from common solvents. The degree of acetylation is easily controlled by transesterification [9].

In this paper, attempts to modify physicochemical properties of sago starch by etherification and esterification were described. Properties studied include gelatinization temperature, thermal behaviour, solubility or hydrophobicity and degree of substitution (D.S).

Experimental

Materials

Sago starch was obtained from Nee Seng Ngeng & Sons Sago Industries Sdn. Bhd., Sarawak in powder form with an average particle size of 31.59 μ m. Propylene oxide and sodium trimetaphosphate (STMP) were purchased from Fluka Chemika, GmbH, Switzerland. Sodium tripolyphosphate was supplied by Sigma Chemical, St. Louis, MO. Glacial acetic acid, acetic anhydride and all chemicals used were analytical grade.

Analytical Methods

The particle size was determined using Mastersizer S, laser beam apparatus (Malvern Instruments Ltd., Malvern, U.K.). Acetyl content was determined according to method of Wurzburg [10]; phosphorus content was determined based on the

Mission's reaction [11] and hydroxypropyl content was determined by spectrophotometric method of Johnson [12]. The degree of substitution (DS) and molar substitution (MS) were calculated in the usual manner [6].

Acetylation of Starch

Acetylated starch was prepared according to the procedure modified from Surdia *et al.* [13]. Sago starch (5 g) was suspended in glacial acetic acid (25 mL). Then, concentrated sulphuric acid (0.2 mL in 5 mL glacial acetic acid) was added. The starch slurry was then stirred in shaking incubator at 37°C with shaking rate at 200 rpm and held for 1 hour. Acetic anhydride (16.5 mL) was added to the mixture. The reaction was allowed to proceed for 44 hours in incubator shaker. After that, isopropanol (200 mL) was added gradually with stirring. The starch slurry was filtered, washed with hot distilled water to remove the excess acetic anhydride and then dried at 40°C for 8 hours.

Hydroxypropylation cross-linking of sago starch

Dual modification of starch was carried out by first reacting starch with propylene oxide followed by a mixture of phosphate salt (2% STPM and 5% STPP) according to the method of Saowakon Suwanliwong [14]. The etherification reaction was done at 40±2°C for 24 h using 12% propylene oxide in a 40% starch slurry at pH 10.5 containing 15% sodium sulfate (dsb) and 5% sodium hydroxide. Following etherification, the modified starch was cross-linked for 2 h using 2% STMP and 5% STPP.

Sodium sulfate (30 g, 15% dry starch basis, dsb) was added into water (300 mL) and stirred. When the salt was dissolved, sago starch (200g dsb, equivalent to 40% starch solid in slurry) was added and the mixture was stirred to make up uniform slurry. Then sodium hydroxide solution (5%) was added with vigorous stirring to maintain the slurry pH at 10.5. The propylene oxide (12% v/w of starch solid) was added and the slurry, which was at room temperature, was stirred for 30 min. The slurry was then transferred to plastic bottles and contained in shaking incubator at the temperature of 40 ± 2°C with shaking rate at 200 rpm and held for 24 hours. The slurry was then transferred into mixing container at room temperature. The pH of that slurry was recorded and then the cross-linking reagent was added with vigorous stirring for 30 min. After that, the slurry was again transferred to the previous plastic bottles and the reaction was allowed to proceed for 120 minutes at 40 ± 2°C in incubator shaker with a shaking rate of 200 rpm. The starch slurry was then adjusted to pH 5.5 with 10% HCl solution to terminate the reaction. The starch was recovered by vacuum filtering through Whatman filter paper No.4, and the filter cake was washed with five volumes of distilled

water. The starch was dried at 40°C to reach moisture content of 10-12% for about 8 hours.

Differential Scanning Calorimetry (DSC)

Thermal analysis was performed with a Mettler Toledo Star^e System. Sample preparation was done as described by Liu *et al.* [15]. Starch and modified starch (2.5 mg dsb) were weighed directly into a 40 µL aluminium standard pan and then 7.5 mg of deionized water was added into the pan by a microsyringe. After sealing, the pan was left for 1 hour to allow the sample to mix and equilibrate. Then the sample was scanned from 30°C to 150°C at a heating rate of 10°C/min. Onset temperature (T_o), intermediate temperature (T_p), completion temperature (T_c) and gelatinization enthalpy (ΔH) were recorded.

FTIR Spectroscopy

FTIR spectra were obtained on a FTIR spectrometer (Perkin Elmer model Spectrum GX) using a KBr disc. The equipment was operated with a resolution of 4cm⁻¹ and scanning range from 4000 to 370 cm⁻¹.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis of native and modified starches was performed with Shimadzu TGA-500. This apparatus provides a continuous measurement of sample weight at a range of temperatures between ambient and 600°C. Samples of approximately 5-10 mg were heated in an alumina cell to 600°C at heating rate of 10°C/min with air as the circulating gas.

Results and Discussion

The degree of substitution (DS) for hydroxypropylated cross-linked and acetylated starches was found to be 0.044 (1.5%) and 0.342 (11.4%) out of three possible substitutions for every D-glucopyranosyl unit, respectively. The effect of modification on hydrophilic nature of sago starch was not significant. Hydroxypropylated cross-linked and acetylated sago starches were insoluble in acetone and THF, and soluble in hot water and this characteristic is probably due to low DS of both of modified starches. According to Rutenberg and Solarek [6], solubility characteristics of starch acetates are dependent upon DS. Whole starch acetates of up to 15% acetyl are soluble in water at 50-100°C and are insoluble in organic solvent. At high cross-linking levels, granules no longer gelatinize in boiling water or even under autoclave condition [6].

FTIR spectroscopy was used to confirm the formation of the hydroxypropylation cross-linking and acetylation reaction (Fig. 1). The typical stretching vibrations of P=O or P-O bonds (at about

1200-1100 cm^{-1}) were observed in the spectrum of the hydroxypropylated cross-linked starch (Fig.2,b). FTIR spectrum of acetylated starch showed the

presence of carbonyl group at 1754 cm^{-1} (Fig.1,c) indicating that the ester group is present in starch structure.

Table 1 : Effect of modification on the phosphorus, hydroxypropyl, and acetyl content, degree of substitution (DS) and molar substitution (MS) of sago starch*

Starch	Molar substitution (MS)	Degree of substitution (DS)	hydroxypropyl content (%)	phosphorus content (%)	acetyl content (%)
Native starch	-	0.026±0.001	-	0.494±0.002	-
Hydroxypropylated cross-linked starch	0.002±0.001	0.044±0.001	0.055±0.001	0.819±0.002	-
Acetylated starch	-	0.342±0.001	-	-	8.330±0.004

* data of triplicates for a single experiments

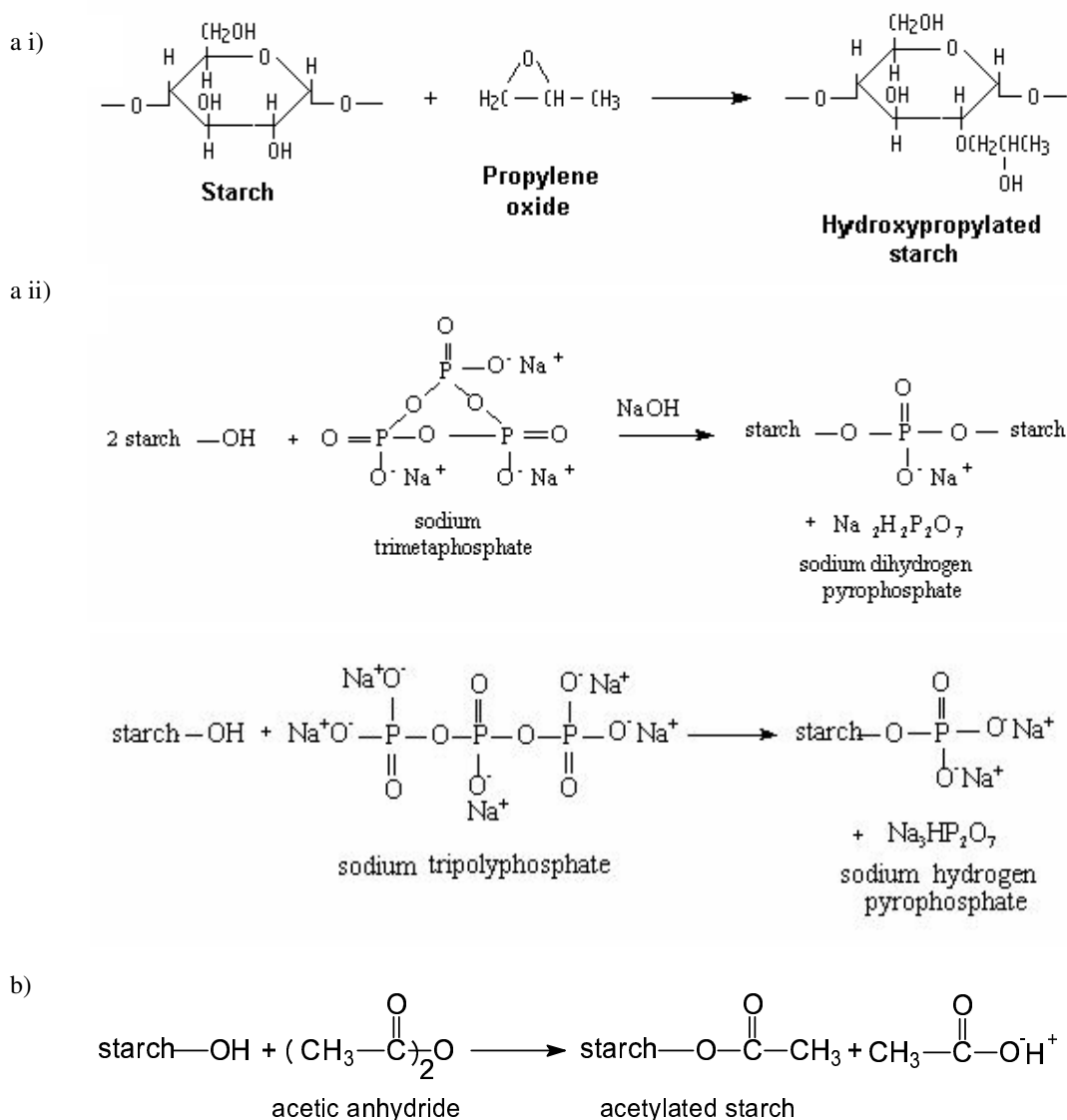


Figure 1 : Suggested possible structures of a i) hydroxypropylated starch, a ii) crosslinked hydroxypropylated starch and b) acetylated starch

Figure 3 showed the TGA thermogram of native and modified sago starches. The thermogram of native starch showed a single step decomposition with a maximum weight lost occurred at around 319°C and the on-set decomposition at about 250°C. The decomposition was completed at about 380°C. The thermogram of hydroxypropylated cross-linked starch was very much similar to that of the native starch indicating that the limited hydroxypropylation

achieved was not sufficient to affect the thermal property of the modified starch. TGA thermogram of the acetylated sago starch exhibited two thermal decomposition steps at 301°C and 383°C, which represented about 36% and 27% weight lost, respectively. Furthermore, the decomposition was not completed until the temperature reached 425°C. This clearly showed that acetylation has increased the thermal stability of native starch.

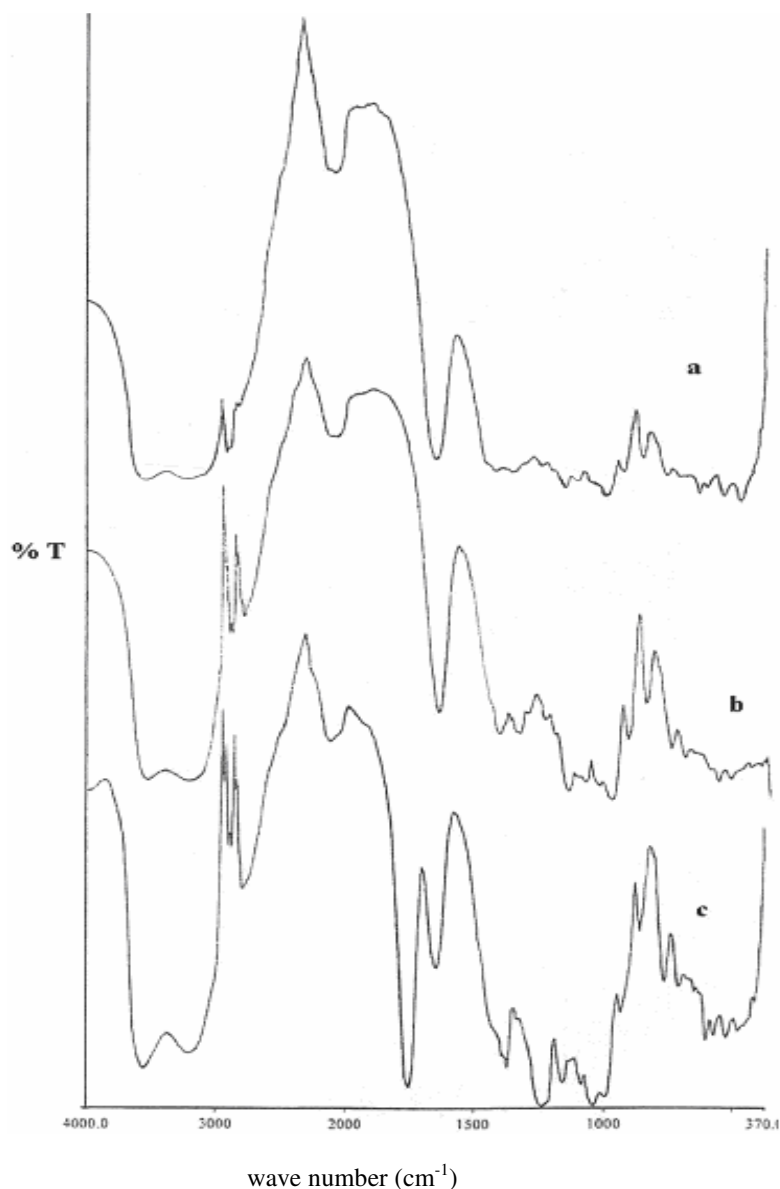


Figure 2 : FTIR spectra (KBr disc) of (a) native, (b) hydroxypropylated cross-linked and (c) acetylated sago starches

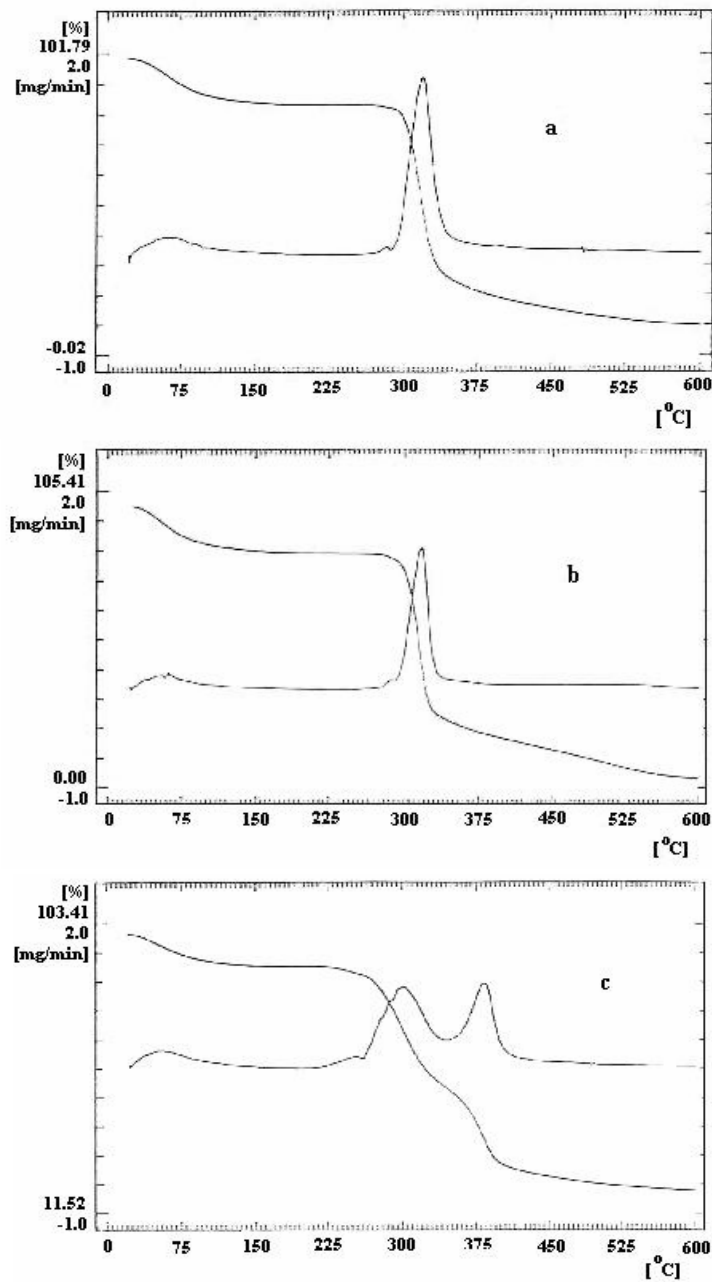


Figure 3 : Thermograms of (a) native, (b) hydroxypropylated cross-linked and (c) acetylated sago starches

DSC results of native, hydroxypropylated cross-linked, and acetylated sago starches are given in Table 2. Hydroxypropylation cross-linking caused a reduction in T_o , T_p , T_c and ΔH while acetylation caused a further reduction in ΔH but increase in T_o , T_p , T_c . Gelatinization enthalpy reflects the energy required for disrupting the granule structure [15]. Rutenberg and Solarek reported that the formation of cross-linkages retains the integrity of starch granules [6]. Thus, more heat was needed for gelatinization. However, ΔH found for hydroxypropylated cross-linked and acetylated starches in this study were

smaller than that of the native starch. This is similar to observation by Morikawa and Nishinari [16], and Liu *et al.* [15]. Morikawa and Nishinari described that the modification (especially cross-linking) prevents gelatinization and some loss of structural order during the process of chemical modification may occur. However, since the degree of cross-linkage was low (1.5%) in this investigation, T_p was not significantly affected. This result is in agreement with the reports of Yeh and Yeh [5], and Wootton and Bamunuarachchi [17].

Table 2 : Gelatinization (Onset, T_o ; peak, T_p ; and completion, T_c) temperature ($^{\circ}\text{C}$) and gelatinization enthalpy (ΔH) of native and modified sago starches

Starch	T_o ($^{\circ}\text{C}$)	T_p ($^{\circ}\text{C}$)	T_c ($^{\circ}\text{C}$)	ΔH (J/g)
Native starch	68.42	73.43	78.20	-3.50
Hydroxypropylated cross-linked starch	68.32	73.27	77.93	-3.36
Acetylated starch	70.00	73.61	77.05	-1.27

According to Yeh and Yeh [5], starch granules could have been swollen or damaged due to alkali treatment or heating during the cross-linking preparation. Hydroxypropylation loosened the granular structures and thus lowered T_p and ΔH , whereas acetylation has been shown to slightly increase the T_p and this is probably due to the level of acetylation achieved in this study was high enough to strengthen the integrity of starch granules.

Conclusions

Results obtained showed that chemical modification improves the physicochemical properties of sago starch. The modification of starch by hydroxypropylation and acetylation reactions was monitored by FTIR spectroscopy. DSC results showed that acetylation increases the gelatinization temperature (T_p) but reduces the enthalpy (ΔH) while hydroxypropylation cross-linking reduces both the T_p and ΔH , indicating that hydroxypropylation cross-linking and acetylation loosen the structure of starch granules, thus requires less heat for gelatinization. It has also been shown that acetylation has increased the thermal stability of sago starch. The solubility or hydrophobicity of modified starches is not significantly changed because of low degree of substitution (DS). Further study to increase the degree of substitution is required to improve the hydrophobicity nature and thermal properties of sago starch.

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