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Food Chemistry 80 (2003) 463–471

Food Chemistry

www.elsevier.com/locate/foodchem

Effect of crosslinking reagents and hydroxypropylation levels on dual-modified sago starch properties

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Received 25 October 2001; received in revised form 2 July 2002; accepted 2 July 2002

Abstract

Chemical modification is usually carried out to overcome the unstable properties of native sago starch and improve its physical properties during processing. In this study, dual-modification of sago starch was carried out. The first stage of modification was hydroxypropylation, using propylene oxide at levels ranging from 6 to 12%. This was followed by crosslinking, using three different types of crosslinking agents: a mixture of sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP), phosphorus oxychloride and epichlorohydrin. Through hydroxypropylation, it was found that there was a significant increase in molar substitution which in turn induces an increase in crosslinking and this was seen from the marked increase in phosphorus content and degree of substitution. This was accompanied by a significant decrease in paste clarity, swelling power and solubility compared to that of the native starch. Starch that was hydroxypropylated with 10–12% propylene oxide and crosslinked by a mixture of 2% STMP and 5% STPP produced modified starch with the most desirable properties in that it exhibited no viscosity breakdown, high acid resistance, high freeze-thaw stability and improved gel texture.

Keywords: Sago starch; Hydroxypropylation; Crosslinking; Dual-modification; Dual-modified starch; Starch properties

1. Introduction

Like other native starches, sago starch needs to be modified to improve its quality. Sago starch undergoes a high viscosity reduction during heating and shearing and this breakdown is further increased under acidic conditions. Furthermore, the native starch exhibits a higher retrogradation, which will result in the formation of a long cohesive gel with increased syneresis. In order to overcome the inherent deficiencies of native starches, a dual-modification, hydroxypropylation and crosslinking, is commercially carried out (Lopez, 1987; Tessler, 1975; Tuschhoff, 1986; Wurzburg, 1986; Yeh & Yeh, 1993). Starches with high amylose content can be stabilised by initially reacting them with propylene oxide and this reaction is inhibited by adding crosslinking agents to yield modified starches having outstanding high temperature and short time retort properties (Tessler, 1975). Phosphorus oxychloride, sodium trimetaphosphate, and epichlorohydrin were reported to be generally used as crosslinking reagents by several authors (Luallen, 1985; Smolka & Alexander, 1985; Takahashi, Maningat, & Seib, 1989; Tessler, 1975; Valle, Tuschoff, & Streaty,1 978; Wu & Seib, 1990; Yeh & Yeh, 1993; Yook, Pek, & Park, 1993). Lim & Seib (1993) investigated the preparation of starch phosphates and showed that a mixture of phosphate salts (sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP)) gave better results than using STMP alone to prepare distarch phosphate (crosslinked starch).

The reaction conditions for preparing dual-modified starches with the above crosslinking reagents in several starch bases such as corn, tapioca, wheat, waxy corn, waxy barley and rice starch have been studied (Takahashi et al., 1989; Tessler, 1975; Wu & Seib, 1990; Yeh & Yeh, 1993; Yook et al., 1993). The amount of crosslinking reagent necessary to give starch products with desirable properties will vary, depending on the starch base used, the crosslinking reagent, the reaction efficiency of the crosslinking reagent, the level of hydroxypropyl ether substitution on the starch base and a

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0308-8146/03/$ - see front matter
PII: S0308-8146(02)00314-X

specified range of final modified starch properties. Several previous studies have investigated the effects of the different reaction conditions such as starch base concentration, temperature, pH, and concentration of catalyst salt for preparing hydroxypropylated cross-linked starch (Lim & Seib, 1993; Smolka & Alexander, 1985; Tessler, 1975; Wu & Seib, 1990; Yeh & Yeh, 1993). However, the comparison in the efficiency of different crosslinking reagents and added propylene oxide levels for preparing hydroxypropylated crosslinked sago starch has not been reported.

The objective of this study was to establish the suitable crosslinking reagent and propylene oxide levels for preparation of hydroxypropylated crosslinked sago starch with good thickening power which is non-gelling, resistant to heat, acid and shear, and which exhibits good stability at low temperatures.

2. Materials and methods

Sago starch was contributed by Ajinomoto Co., Ltd. Its quality was in accordance with that specified by the Malaysian Standard for sago starch (SIRIM, 1992). All chemicals and reagents used in this study were of analytical grade.

2.1. Preparation of dual-modified sago starch

Sago starch was stabilised by reacting with propylene oxide, and crosslinked by crosslinking reagent following the procedures modified from Smolka and Alexander (1985), Tessler (1975), Wu and Seib (1990), Yeh and Yeh (1993), and Lim and Seib (1993). Thirty grammes of sodium sulphate (15% based on dry wt. of starch) were added to 300 ml of water and stirred. When the salt was dissolved, 200 g of sago starch (dbs, equivalent to 40% starch solid in slurry) were added and the mixture stirred to make up a uniform slurry. Then a 5% sodium hydroxide solution was added with vigorous stirring to prevent starch gelatinization and to adjust the slurry to pH 10.5. The propylene oxide 6–12% (vol. by weight of starch solid) was then added and the slurry, which was at room temperature, was stirred for half an hour. The slurry was then transferred to centrifugal bottles and placed in a shaking incubator at 40 °C ± 2 °C, with shaking rate at 200 rpm, and held for 24 h. After completing step one of substitution, the slurry was transferred into a mixing container at room temperature. The pH of that slurry was recorded and then the crosslinking reagent was added with vigorous stirring for half an hour. After that, the slurry was again transferred to the previous centrifugal bottles and the reaction was allowed to proceed for 120 min at 40 °C ± 2 °C in an incubator shaker with a shaking rate of 200 rpm. The starch slurry was then adjusted to pH 5.5 with 10% hydrochloric acid 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 moisture content of 10–12% for about 8 h.

2.2. Types of crosslinking reagents

The experiment was carried out by using complete randomised design (CRD) in duplicate runs to produce dual-modified sago starches from different types of crosslinking reagents. The propylene oxide at 8%, based on dry weight of sago starch, was used for hydroxypropylation and then the crosslinking was conducted with three types of crosslinking reagents, using appropriate amounts recommended by previous studies: 0.075% phosphorus oxychloride ($POCl_3$); 0.075% epichlorohydrin; the mixture of 2% sodium trimetaphosphate (STMP) and 5% sodium tripolyphosphate (STPP) (Lim & Seib, 1993; Takahashi et al., 1989; Valle et al., 1978; Yeh & Yah, 1993; Yook et al., 1993).

2.3. Levels of hydroxypropylation

The dual-modified sago starch was prepared using a CRD experimental design by hydroxypropylation with four levels of propylene oxide, which vary from 6% to 12%, and reaction was inhibited by the same crosslinking reagent, the mixture of 2% STMP and 5% STPP.

2.4. Degree of hyxypropylation and crosslinking

Phosphorus and hydroxypropyl contents were determined by the method of Egan, Kirk, and Sawyer (1981) and Johnson (1969). The degree of substitution (DS) and the molar substitution (MS) were calculated in the normal fashion (Rutenberg & Solarek, 1984).

2.5. Paste properties

Swelling power and solubility were measured as described by Schoch (1964). The procedure of Kerr and Cleveland (1959) was followed for analysis of paste clarity.

2.6. Pasting characteristics

The pasting of starch sample was examined in a Brabender Amylograph using 75 rpm and a torque of 700 cm-g, equivalent to 1000 BU. The starch slurry (400 ml at 6.0% starch solids) was adjusted to pH 6.5 with a few drops of 5% HCl or 5% NaOH solution, pasted at a heating rate of 1.5 °C/min from 50 to 95 °C, held at 95 °C for 30 min, cooled from 95 °C to 50 °C, and finally held at 50 °C for 30 min. The following mea-

surements were taken from the Amylograph curve: the pasting temperature, the peak consistency during the heating stage, the consistency after being held for 30 min at 95 °C and the consistency after cooling to 50 °C. To determine the acid resistance on starch paste, a few drops of 30% acetic acid solution was used to adjust the pH of starch slurry to 3.5 to simulate pasting of starch equivalent to nearly the same pH of high-acid food.

2.7. Freeze-thaw stability

The procedure was modified from Takahashi et al. (1989) and Wu and Seib (1990). A starch solution (8% starch solid) was adjusted to pH 6.5 and heated to 95 °C, holding at 95 °C for 30 min, and cooled to 50 °C in shaking water bath. After cooling at 50 °C, starch paste was weighed (accurately 20 g each) into known weight 50 ml conical centrifugal tubes which were sealed tightly with screw caps. The tubes were shelved for 24 h at 4 °C, followed by freezing at −20 °C for 48 h and thawing for 4 h at 25 °C. Then the freeze-thaw stability was measured as percentage of water separated on alternate freezing and thawing of the pastes, followed by centrifugation at 3000 rpm for 15 min. The percentage of syneresis was the ratio of the weight of the separated water to the weight of the paste. In this study, six freeze-thaw cycles were conducted.

2.8. Gel properties

The texture of the starch gel (8% starch solid) was determined using a Stable Micro Systems TAXT-2 Texture Analyser. To prepare the gels, the procedure described by Takahashi et al. (1989) was used. All starches were adjusted to pH 6.5 by using 5% NaOH or 5% HCl solution before cooking from 30 to 95 °C, held at 95 °C for 30 min, and then cooled to 50 °C. The hot paste was poured to a height of 2.7 cm in a cylindrical plastic container (diam. = 4.0 cm, height 5.5 cm) and stored for 24 h at 25 °C and 4 °C before measurement. For gel strength measurements, the gels were compressed at a speed 2.0 mm/s to a distance of 15 mm using a cylindrical plunger (diam. = 10 mm). For gels, the maximum force during compression was considered as the gel strength and for non-gelling pastes, the maximum force of deformation at 15 mm compression was regarded as 'gel strength'. The paste and gel characteristics were recorded by visual evidence.

2.9. Statistical analyses

The data obtained from the study were analysed using analysis of variance (ANOVA) and the means were separated by Duncan's New Multiple Range Test or the least significant difference (Steel & Torie, 1980).

3. Results and discussion

3.1. Effects of crosslinking reagents

The reaction efficiencies of hydroxypropylation and crosslinking were indicated by molar substitution of the hydroxypropyl group and the degree of substitution of the phosphate group into granular starches. Native sago was presented as zero MS since it was used as a blank for treated starches (Table 1). In this study, different MS values were found although all the sago starches were hydroxypropylated with the same amount of propylene oxide (8%). The different MS values obtained were due to the influence of the different crosslinking reagents. As can be seen in Table 1, phosphorus oxychloride and epichlorohydrin were more efficient in inhibiting hydroxypropylation than the mixture of phosphate salts, resulting in significantly lower MS value ($P < 0.05$). Phosphorus oxychloride and the mixture of phosphate salts enabled phosphate groups to produce the distarch phosphate derivative. Therefore, sago starch crosslinked with phosphorus oxychloride (HPPO) and the mixture of phosphate salts (HPST) showed a significantly higher phosphorus content ($P < 0.05$) than the native starch. In consideration of P content and DS, the HPST was more efficient for crosslinking than HPPO since it resulted in the highest P content and significantly increased DS value ($P < 0.01$). Epichlorohydrin was used in crosslinking to give a distarch glycerol derivative; thus P content could not be used to indicate the degree of substitution in sago starch crosslinked with epichlorohydrin (HPEP). Because of the very low degree of crosslinking reaction with epichlorohydrin to obtain a very appreciable effect, the analysis of DS is also difficult to determine directly. Therefore, the characterisation of crosslinked starch and its quality control are dependent on the measurement of physical properties (Radley, 1976; Rutenberg & Solarek, 1984).

The crosslinking of starch can be confirmed by the reduction of paste clarity (Kerr & Cleveland, 1959; Lim & Seib, 1993; Wu & Seib, 1990). In this study, therefore, paste clarity was used to compare the efficiencies of the crosslinking reagents. The high clarity of native sago starch paste at 52.6%T_{650} was decreased significantly ($P < 0.01$) after dual-modification, as presented in Table 1. Paste clarities of 22.5, 21.9, and 20.0% were obtained from crosslinking with phosphorus oxychloride, epichlorohydrin and the mixture of phosphate salts, respectively. Although the influence of the reagents on paste clarity was not significantly different ($P > 0.01$), HPST exhibited the lowest paste clarity.

The results obtained are shown in Table 1 which illustrates that the viscosity of all the modified starches increased significantly ($P < 0.05$) as compared to that of the native starch. The starches which were dual-mod-

ified with 8% propylene oxide, and those from crosslinking reagents, did not show any significant differences ($P > 0.05$) in their pasting temperature or peak viscosity temperature. However, crosslinking of the sago starch with a mixture of phosphate salts, after hydroxypropylation with 8% propylene oxide, reduced the pasting temperature and delayed the temperature of peak viscosity.

The peak viscosity and viscosity at 95 °C, after holding at 95 °C for 30 min, and the viscosity at 50 °C, were used to compare the efficiency of crosslinking reagents. The results for peak viscosity in Table 1 did not show any significant difference ($P > 0.05$) when different crosslinking reagents were used. However, the mixture of phosphate salts affected the highest peak viscosity among the samples. The viscosity of HPPO at 95 °C and after holding for 30 min at 95 °C was the lowest but did not differ significantly ($P > 0.05$) from that of HPEP, whereas that of HPST was the highest. The cold paste viscosities at 50 °C, of all the dual-modified starches, were significantly higher ($P < 0.05$) than that of the native starch. HPST had the highest cold paste viscosity that was significantly different ($P < 0.05$) from the others.

It has been postulated that viscosity breakdown can be reduced through crosslinking (Rutenburg & Solarek, 1984). Therefore, the decrease in viscosity breakdown as seen in HPEP and HPST (Table 1) can be indicative that crosslinking has taken place. However, the breakdown in HPPO was not significantly different from that of the native starch ($P > 0.05$) and this is probably due to less crosslinking occurring. This confirms that the mixture of phosphate salts is the most effective of the crosslinking agents used in this study, since it showed the lowest viscosity breakdown ($P < 0.05$).

The setback was related to the rate of retrogradation and was calculated as the viscosity of paste when cooled to 50 °C minus the peak viscosity. It was found to decrease when starches were hydroxypropylated (Yook et al., 1993). In this study, on the other hand, the sago starch that underwent dual-modification using propylene oxide and the various crosslinking reagents showed increased setback. This cannot be attributed to the retrogradation since the setback for native starch was very much lower. The most probable explanation for this is that, since the level of hydroxypropyl substitution is low, the consequent crosslinking is not uniformly distributed throughout the starch granules. Granules that are not crosslinked, or have experienced only hydroxypropylation, would exhibit a higher breakdown after reaching the peak viscosity temperature. Meanwhile, the crosslinked granular starches would retain their granule integrity under the heat and shear conditions applied in the Amylograph and would consequently show a higher viscosity development during the cooling period, resulting in a higher setback. As shown in Table 1, the HPST, being a more efficient crosslinking reagent, had the highest viscosity setback, which was significantly different from that of the native starch ($P < 0.05$).

The consistency during the cooling period (Table 1) for native and all the dual-modified starches were not significantly different ($P > 0.05$). However, the cold paste viscosities of all the dual-modified starches tended to stabilise during the holding at 50 °C.

Thinning viscosity of the native starch, caused by acid hydrolysis, is undesirable for starch thickener when applied in low pH food products. Therefore, crosslinking can be employed to strengthen starch granules and to improve their acid resistance. Native sago starch had low acid resistance and exhibited thin viscosity after cooking at pH 3.5, adjusted using acetic acid solution. Its viscosity showed a sharp breakdown when compared to that of the starch in neutral condition (figure not shown). Under the same acidic conditions, hydroxypropylation and crosslinking with the different agents significantly ($P < 0.01$) increased the cold paste viscosity of sago starch when compared to that of the native sago starch and it tended to stabilise during holding at 50 °C.

Table 1
Effects of crosslinking reagents on physicochemical properties of native and hydroxypropylated crosslinked sago starches

Sample	Pasting temp. (°C)	Peak viscosity temp. (°C)	Viscosity (BU)				Breakdown (BU) (P-H)	Setback (BU) (C-P)	Consistency (BU) (C-H)	MS	P content (%)	Clarity (%T_{650})
			Peak (P)	95 °C	after 30 min (H)	50 °C^{ns} (C)						
NT	66.0	81.0	635.0	435.0	332.5	480.0	302.5	−155.0	147.5	0.000	0.022	52.6
HPPO	66.8	81.8	1047.5	905.0	740.0	910.0	307.5	−137.5	170.0	0.005	0.025	22.5
HPEP	66.0	84.0	1022.5	930.0	775.0	917.5	247.5	−105.0	142.5	0.004	0.022	21.9
HPST	64.5	89.5	1170.0	1155.0	1025.0	1160.0	145.0	−10.0	135.0	0.014	0.053	20.0
$LSD_{0.05}$	ns	ns	205.8	243.4	92.7	326.0	126.7	135.7	ns	0.001	0.002	2.3

NT = native sago starch, HPPO = hydroxypropylated, crosslinked with 0.075% $POCl_3$, HPEP = hydroxypropylated crosslinked with 0.075% epichlorohydrin, HPST = hydroxypropylated, crosslinked with the mixture of 2% STMP and 5% STPP. All data represent the means of duplicate and four replicate determinations for pasting characteristics and paste properties. $LSD_{0.05}$ = least significant difference at 95%. ns = mean of sample is not significantly different ($P > 0.05$).

HPST showed the highest viscosity among the various modified starches. The viscosities of all the dual-modified sago starches were lower and exhibited more breakdown at pH 3.5 than at pH 6.5. However, HPST exhibited the lowest viscosity breakdown and was significantly different ($P<0.05$) from that of the native starch. Because some molecular chains of dissolved amylose were acid-hydrolysed, the native and all the dual-modified starches decreased their setback viscosity when compared to that at pH 6.5. Crosslinking with all the reagents studied imparted more strength to the starch granules than did the native. Therefore, the setback viscosities and consistencies of all the dual-modified starches were significantly ($P<0.01$) higher than that of the native starch. By comparison of the viscosity characteristics, breakdown and setback, the HPST was considered to have higher acid resistance than the other samples.

It has been known that native sago starch is very poor in freeze-thaw stability. The syneresis of native sago increased as freeze-thaw cycles were increased. Fig. 1 illustrates the significant effects of hydroxypropylation and crosslinking, with different crosslinking reagents, for improving freeze-thaw stability ($P<0.01$). HPST had the lowest syneresis but the value was not significantly different ($P>0.05$) from that of HPPO. HPEP exhibited a slow increase in syneresis which was at the same rate as HPPO until four freeze-thaw cycles but lost its stability thereafter. This implies that the mixture of phosphate salts was the best reagent for improving freeze-thaw stability of dual-modified sago starch. However, crosslinking alone did not result in substantial

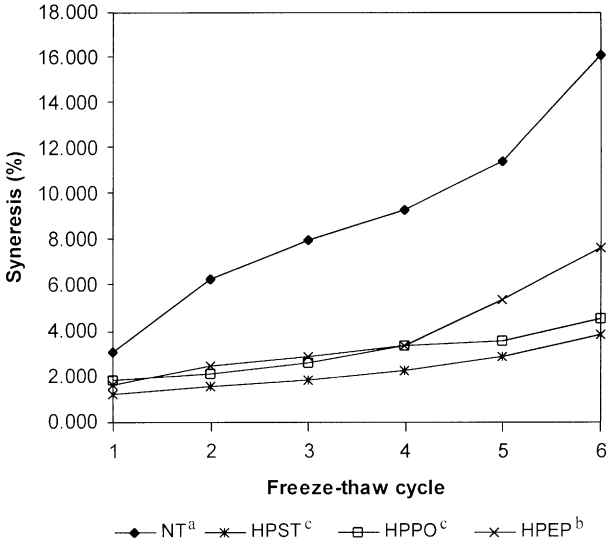

Fig. 1. Freeze-thaw stability of native and dual-modified sago starches. Native sago (NT), hydroxypropylated crosslinked with the mixture of phosphate salts (HPST), hydroxypropylated crosslinked with phosphorus oxychloride (HPPO), and hydroxypropylated crosslinked with epichlorohydrin (HPEP). The same superscript letters are not significantly different ($P>0.01$).

freeze-thaw stability (Luallen, 1985) and it would be very much dependent on hydroxypropylation. This is clearly shown by the MS value shown in Table 1 where HPST had the highest MS value, followed subsequently by HPPO and HPEP. The order of freeze-thaw stability of the dual-modified sago starches has a close relation with increasing MS value in each treatment. Hydroxypropylation introduces mono functional hydroxypropyl groups to the hydroxyl group of the starch molecule, thus preventing dissolved linear starch molecules from associating closely by reduction of the attractive forces between hydroxyl groups on adjacent chains during cooling or freezing. Therefore, the higher the hydroxypropyl content in terms of MS value, the lower the syneresis.

From the results of syneresis, viscosity characteristics and paste clarity, it seems that the mixture of phosphate salts least inhibits hydroxypropylation and is the most efficient crosslinking reagent for dual-modification of sago starch.

3.2. Effects of hydroxypropylation levels

The physicochemical properties of native and dual-modified sago starches with different levels of hydroxypropylation are shown in Table 2. The level of hydroxypropylation was varied by adding different amounts of propylene oxide and the MS value ranged from 0.010 to 0.033. This study found that the level of hydroxypropylation during the first stage of the dual-modification process enhanced the subsequent crosslinking and this was indicated by a marked increase in the phosphorus content and DS value. The accompanying paste clarity, swelling power and solubility decreased significantly compared to that of the native starch ($P<0.01$). This observation is in agreement with an earlier investigation on hydroxypropylated crosslinked rice starch (Yeh & Yeh, 1993). It is believed that hydroxypropylation will weaken the bonding between starch molecules, thus allowing more crosslinking reagents to react with the starch molecules.

The swelling power was reduced very significantly ($P<0.01$), while the solubility and paste clarity showed no significant decrease ($P>0.01$), when a higher level of propylene oxide was employed. Hence, the correlation between the propylene oxide level and the swelling power of dual-modified sago starch is important. There was a strong linear correlation ($R^2=0.98$) between the levels of propylene oxide and the swelling power of dual-modified sago starch, as presented in Fig. 2 and the regression equation given below:

$$Y = -4.808X + 71.267 \; R^2 = 0.98 (P < 0.01)$$

where Y = swelling power of hydroxypropylated crosslinked sago starch, and X = propylene oxide used in

Table 2
Physicochemical properties of native and dual-modified sago starches hydroxypropylated with different levels of propylene oxide, crosslinked with the mixture of phosphate salts

Sample	MS	DS	P content (%)	Clarity (%T650)	Swelling power	Solubility (%)
NT	0.000±0.000	0.001±0.000	0.023±0.001	55.78±5.42	69.08±3.55	54.92±5.31
6HPST	0.010±0.004	0.002±0.001	0.045±0.005	8.18±0.49	43.37±0.14	15.62±0.34
8HPST	0.016±0.001	0.003±0.000	0.052±0.004	8.15±0.00	32.43±1.85	13.72±0.93
10HPST	0.021±0.004	0.003±0.001	0.060±0.016	5.13±0.14	21.08±0.82	10.43±0.52
12HPST	0.033±0.001	0.004±0.001	0.069±0.020	4.48±0.14	15.10±1.46	8.50±0.32
$LSD_{0.05}$	0.004	0.001	0.013	3.68	4.99	6.25
$LSD_{0.01}$	0.005	0.001	0.018	5.09	7.83	9.80

NT = native sago starch, 6HPST, 8HPST, 10HPST and 12HPST = hydroxypropylated with 6, 8, 10 and 12% of propylene oxide, respectively, crosslinked with the mixture of 2% STMP and 5% STPP. Data presented are the means of four replicate determinations with the standard deviation of the mean. $LSD_{0.05}$ = least significant difference at 95%. $LSD_{0.01}$ = least significant difference at 99%.

hydroxypropylation followed by crosslinking with a mixture of 2% STMP and 5% STPP.

From this correlation, it would be possible to predict the different levels of propylene oxide used from the swelling power. This is further confirmed from the swelling power at zero percent propylene oxide, which is 69.1, very close to the value of 71.3 obtained from a linear regression fit of the data. The swelling power of 71.3 was presented at zero percent of propylene oxide, which was in the range of the swelling power of the native sago (see Table 2). As discussed here, without hydroxypropylation (0% propylene oxide), the crosslinking with the mixture of STMP and STPP could not occur at the low temperature of 40 °C (Kerr & Cleveland, 1959). Therefore, the calculated swelling power was possible since there was no crosslinking influence.

The regression could predict the maximum level of propylene oxide to be 14.8%, based on sago starch solid. If this predicted maximum level of propylene oxide was used, it would enhance a very high degree of crosslinking, until no swelling of hydroxypropylated crosslinked sago starch was obtained. Based on visual evidence, however, the starch granules became swollen or pasted when over 14% of propylene oxide was employed, resulting in a product which was difficult to filter and wash and consequently impossible to remove undesirable by-products.

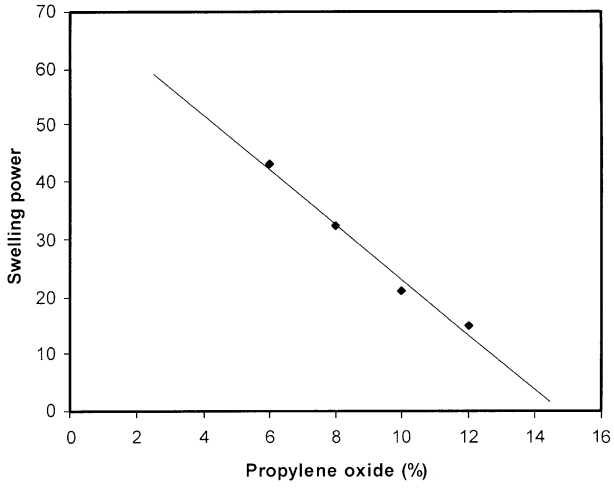

Fig. 2. Linear regression of swelling power of dual-modified sago starches hydroxypropylated with different levels of propylene oxide crosslinking with the mixture of phosphate salts.

The advantage of this linear regression was to countercheck the propylene oxide level employed, or to estimate the swelling power at the level of propylene oxide used in the production of hydroxypropylated distarch phosphate.

The pasting characteristics of the starches were taken into consideration in selecting the optimum level of propylene oxide to encourage the appropriate crosslinking level so that the most desirable dual-modified sago starch properties were obtained. The Brabender amylograms of native and dual-modified sago starches with different levels of hydroxypropylation are shown in Fig. 3. All dual-modified treatments altered sago starch properties until no viscosity breakdown was achieved and they possessed higher viscosities than the native starch. The result obtained at 8% propylene oxide, used in this experiment, was different from the result shown in Table 1, even though the sago starch underwent crosslinking with the same amount of phosphate salts and same reaction conditions. This is probably because, in the former experiment, the crosslinking agents might not have penetrated well enough to react inside the granule, resulting in less crosslinking. These results suggest that a continuous reactor should be considered in further studies to achieve good reproducibility. In this experiment, however, it was observed that thin to thick viscosities of starches were obtained when 10 and 12% propylene oxide were used. These propylene oxide levels induce high crosslinking in starch granules. This type of pasting characteristic is appropriate for starch thickener used in retorted canned food since it would not interrupt heat penetration of product (Tessler, 1975; Valle et al., 1978).

The effects of different levels of propylene oxide on reduction of pasting temperatures of dual-modified

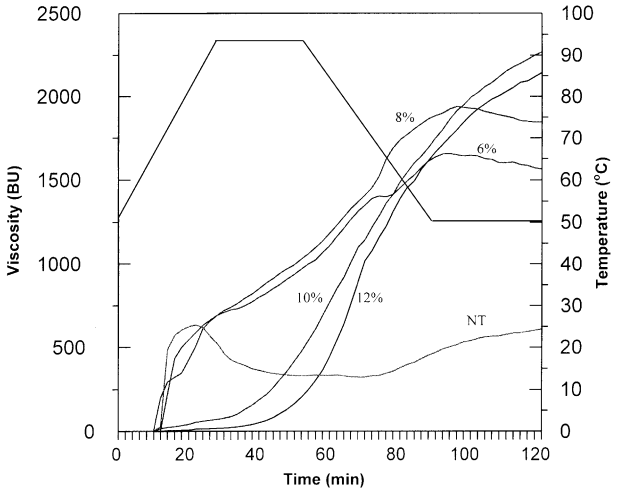

Fig. 3. Amylographs of native (NT) and dual-modified sago at 6% starch solid, pH 6.5, hydroxypropylation with 6, 8, 10 and 12% propylene oxide, crosslinking with the mixture of 2% STMP and 5% STPP.

starches, compared to that of the native starch ($P<0.01$), are presented in Table 3. At higher levels of propylene oxide, the pasting temperature tended to increase. This was another indication that crosslinking had taken place inside the starch granules. Therefore, the treatments increased resistance to heat and shear as applied in the Brabender Amylograph, by the crosslinking. This was elucidated by the absence in peak viscosity, viscosity breakdown and viscosity setback. However, two different characteristics of the hydroxypropylated crosslinked sago starch were obtained from the various levels of propylene oxide employed. Lower propylene oxide levels (6 and 8%) imparted higher viscosities than that obtained with the native starch ($P<0.01$), while at higher levels (10 and 12%), a lower hot paste viscosity at 95 °C was obtained ($P<0.01$). Eventually, however, all levels of propylene oxide used increased cold paste viscosity at 50 °C as compared to that of the native starch ($P<0.01$) but were not significantly different among those levels ($P>0.05$). The consistency of the hydroxypropylated crosslinked sago paste was another important criterion to determine the extent of crosslinking. As illustrated in Table 3, the paste consistency of all the dual-modified sago starches increased as the level of propylene oxide was increased. From the results obtained, the crosslinking was mostly found to occur at 12% of propylene oxide, since the associated modified starch had the highest paste consistency ($P<0.01$).

The effect of acid conditions (pH 3.5) on the starch pastes, studied in a Brabender Amylograph, are presented in Fig. 4 and Table 4. The results showed that the crosslinking obtained was sufficient to resist the acid condition by initial hydroxypropylation with 10 to 12% of propylene oxide. This was clearly shown in that no viscosity breakdown was found at these levels of propylene oxide used for preparation of dual-modified sago starches. However, as the starch granules were weakened by the acid, the pasting temperatures and viscosities of all the starches were decreased as compared to those of the starches at pH 6.5 (Tables 3 and 4). The pasting characteristics, at pH 3.5, of the dual-modified sago starches that were hydroxypropylated with 10% and 12% of propylene oxide, did not differ significantly when compared to each other.

The gel property of a starch thickener is important. Native sago starch exhibits long cohesive gels with very high gel strengths that are undesirable for application in canned foods. However, this undesirable property could be counteracted by hydroxypropylation and crosslinking (Kim & Eliasson, 1993; Takahashi et al., 1989; Tuschhoff, 1986; Wurzburg, 1986). Gel strengths of starches from all treatments were determined and

Table 3
Pasting characteristics, at 6% starch solid, pH 6.5, of native and dual-modified sago starches hydroxypropylated with different levels of propylene oxide, crosslinked with the mixture of phosphate salts

Sample	Pasting temp.(°C)	Peak viscosity temp. (°C)	Viscosity (BU)				Breakdown (BU) (P-H)	Setback (BU) (C-P)	Consistency (BU) (C-H)
			Peak (P)	95 °C	after 30 min (H)	50 °C (C)			
NT	66.0	81.0	635.0	435.0	332.5	480.0	302.5	−155.0	147.5
6HPST	58.5	–	–	772.5	1292.5	1645.0	–	–	352.5
8HPST	59.2	–	–	720.0	1185.0	1885.0	–	–	700.0
10HPST	59.2	–	–	132.5	965.0	1887.5	–	–	922.5
12HPST	60.0	–	–	34.0	697.5	1777.5	–	–	1080.0
$LSD_{0.05}$	1.7	–	–	135.4	285.7	530.0	–	–	573.1
$LSD_{0.01}$	2.7	–	–	212.3	448.0	831.2	–	–	898.8

NT = native sago starch, 6HPST, 8HPST, 10HPST, and 12HPST = hydroxypropylated with 6, 8, 10, and 12% of PO, respectively, followed by crosslinking with the mixture of 2% STMP and 5% STPP. Data presented are the means of duplicate determinations. $LSD_{0.05}$ = least significant difference at 95%. $LSD_{0.01}$ = least significant difference at 99%.

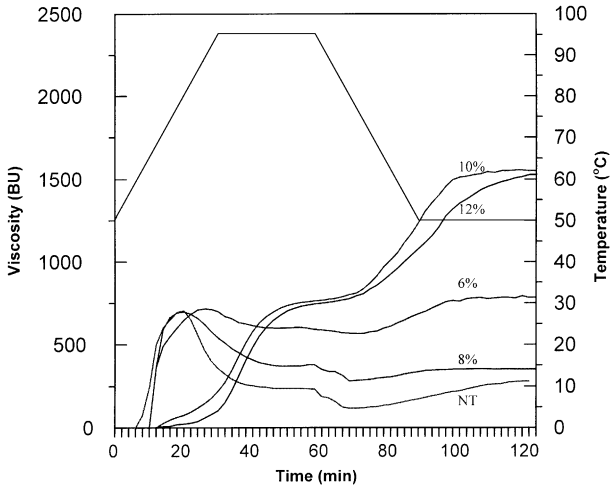

Fig. 4. Amylographs of native (NT) and dual-modified sago at 6% starch solid, pH 3.5, hydroxypropylation with 6, 8, 10 and 12% propylene oxide, crosslinking with the mixture of 2% STMP and 5% STPP.

analysed statistically in a factorial experimental design, using ANOVA and Duncan's multiple range test to separate the mean of response variables. Fig. 5 illustrates the effect of propylene oxide level and storage temperature on gel strength of hydroxypropylated crosslinked sago starches. Zero percent propylene oxide was represented by the gel strength of the native sago starch which was not significantly different ($P > 0.05$) from that of the dual-modified sago starch prepared using 6% propylene oxide. At higher levels of propylene oxide (more than 6%), the gel strength of the dual-modified sago starch was reduced ($P < 0.01$). It was observed that, at 10 and 12% propylene oxide, the dual-modified sago starches gave non-gelling pastes, which did not differ significantly ($P > 0.05$).

Cold storage is optimum for promoting retrogradation or to encourage close alignment of starch chains to form a three-dimensional network, resulting in a higher gel strength (Pomeranz, 1991). Hence, gel strengths of starches from all treatments were significantly increased ($P < 0.01$) after cold storage at 4 °C. The increase in hydroxypropylation, as a result of an increase in the propylene oxide level, produced starch gels which were more stable when stored at 4 °C. As illustrated in Fig. 5, each line represents the storage temperature studied and they tended to align close to each other as the propylene oxide level was increased.

The results of the study on the effects of freezing and thawing on the starch paste can serve as a guide for selecting a starch thickener which is to be applied in frozen foods. Freezing temperature influences the retrogradation of starch pastes for the same reason as cold storage. Retrogradation is responsible for the shrinkage and syneresis of starch pastes and gels when held for a long period of time and the effect is highly magnified when gel is frozen and thawed in many cycles (Pomeranz, 1991; Radley, 1976). Nevertheless, many researchers found that starch which had undergone hydroxypropylation could overcome the problem of syneresis (Kim & Eliasson, 1993; Takahashi et al., 1989; Wu & Seib, 1990; Yeh & Yeh, 1993).

In dual-modification of sago starch, an increase in the propylene oxide level resulted in a reduction in the syneresis of starch gels and pastes ($P < 0.01$) (see Fig. 6). The freeze-thaw stability of starches hydroxypropylated with 8–12% propylene oxide did not differ significantly. However, sago starch, which was dual-modified using 12% propylene oxide (12HPST), showed the highest freeze-thaw stability whereby its syneresis did not increase significantly ($P > 0.05$) as freeze-thaw cycle increased. 8HPST and 10HPST did not exhibit syneresis ($P > 0.05$) up to five freeze-thaw cycles but beyond this the percent syneresis increased slightly ($P < 0.05$).

Table 4
Pasting characteristics at 6% starch solid pH 3.5, of native and dual-modified sago starches hydroxypropylated with different levels of propylene oxide, crosslinked with the mixture of phosphate salts

Sample	Pasting temp. (°C)	Peak viscosity temp. (°C)	Viscosity (BU)				Breakdown (BU) (P-H)	Setback (BU) (C-P)	Consistency (BU) (C-H)
			Peak (P)	95 °C	after 30 min (H)	50 °C (C)			
NT	65.2	81.0	705.0	360.0	210.0	177.5	517.5	−525.0	−32.5
6HPST	57.8	81.8	735.7	632.5	572.5	747.5	165.0	10.0	175.0
8HPST	57.8	78.5	700.0	540.0	350.0	342.5	350.0	175.0	−7.5
10HPST	57.8	–	–	510.0	792.5	1477.5	–	–	685.0
12HPST	58.5	–	–	315.0	763.5	1240.0	–	–	476.5
$LSD_{0.05}$	2.4	–	–	194.0	122.9	334.5	–	–	234.4
$LSD_{0.01}$	3.8	–	–	304.2	192.8	524.6	–	–	367.6

NT = native sago starch, 6HPST, 8HPST, 10HPST, and 12HPST = hydroxypropylated with 6, 8, 10, and 12% of PO, respectively, followed by crosslinking with the mixture of 2% STMP and 5% STPP. Data presented are the means of duplicate determinations. $LSD_{0.05}$ = least significant difference at 95%. $LSD_{0.01}$ = least significant difference at 99%.

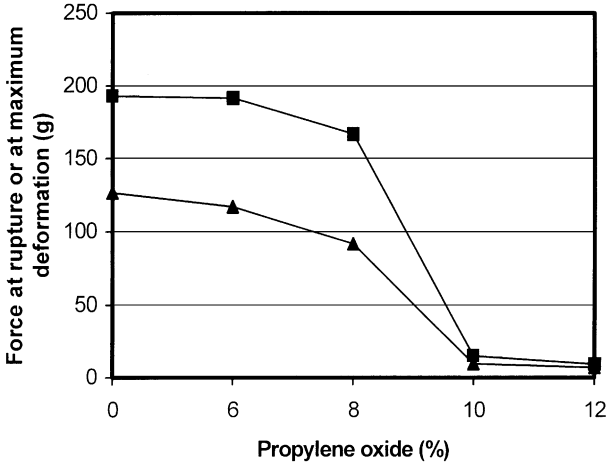

Fig. 5. Effects of propylene oxide levels on gel strength of dual-modified sago starches hydroxypropylated with 6–12% propylene oxide followed by crosslinking with the mixture of 2% STMP and 5% STPP. Cooking was done at 8% starch solid in water pH 6.5, aging for 24 h at 25 (▲) and 4 °C (■). The maximum force of deformation was noted for non-gelling pastes at 10–12% propylene oxide.

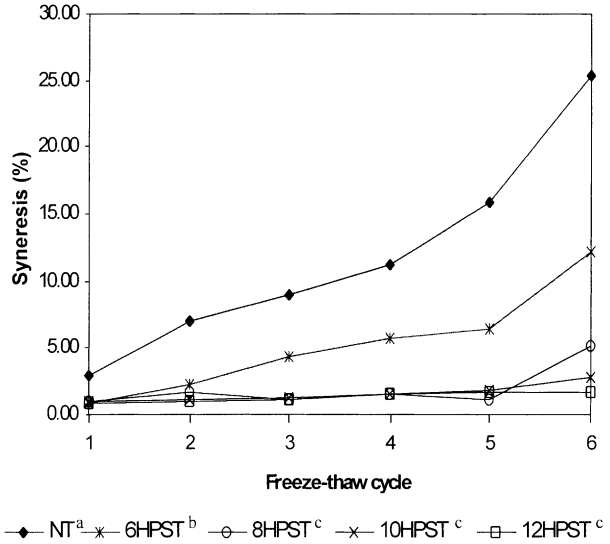

Fig. 6. Freeze-thaw stability of native and dual-modified sago starches. Native starch (NT), hydroxypropylated with 6, 8, 10 and 12% propylene oxide crosslinked with the mixture of phosphate salts (6HPST), (8HPST), (10HPST), (12HPST), respectively. The same superscript letters are not significantly different ($P > 0.01$).

4. Conclusions

The study on preparation of dual-modified sago starch which was done under selected conditions, found that the mixture of phosphate salts at 2% STMP and 5% STPP was more efficient in crosslinking than phosphorus oxychloride or epichlorohydrin for preparing the hydroxypropylation-crosslinked sago starch. Greatly altered sago starch was obtained by hydroxypropylation with 10–12% propylene oxide, followed by crosslinking with a mixture of 2% STMP and 5% STPP. Under those conditions of dual-modification, undesirable starch properties were counteracted.

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