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Effect of pH on phosphorylation of sago starch

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Abstract

Sago starch, in a semidry state was phosphorylated with 2% sodium trimetaphosphate (STMP), 5% sodium tripolyphosphate (STPP) singly, and in combination at pH levels between 6 and 11. As the reaction pH was increased from 6 to 11, the degree of phosphorylation was observed to decrease from 0.186 to 0.083% P with STPP, except at pH 9 where the degree of phosphorylation was increased to 0.224% P. In the case of STMP, the degree of phosphorylation increased from 0.066 to 0.119% P as reaction pH was increased from 6 to 10. In the reactions using a mixture of STPP and STMP, the P content decreased from 0.320 to 0.115% when a similar range of pH was employed. At the reaction pH of 9, a starch phosphate obtained using STPP exhibited low hot paste viscosity but high cold paste viscosity and shear stability when cooked at 95°C. Treatment of sago starch with a mixture of STPP and STMP yielded the best starch phosphate at the reaction pH of 9.5 which showed lower hot paste viscosity and much higher cold paste viscosity than that of sago starch phosphates prepared at pH 9 using STPP. Paste clarity measurements of the phosphorylated starches indicated that cross-linking accelerated rapidly above pH 8 with STMP, above pH 9 with STPP, and above pH 6 with a mixture of the two. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Sago starch; Phosphorylation; Starch phosphates

1. Introduction

Starch phosphates are ester derivatives of phosphoric acid (Solarek, 1986). They include simple (monostarch) and cross-linked (distarch) phosphate esters. In general, monoesters are introduced at a much higher level of substitution on starch than are diesters because even very few cross-links can drastically alter the paste and gel properties of starch. The formation of distarch phosphates however is generally considered the most important reaction used to prepare modified food starches (Lim & Seib, 1993). Starch phosphate esters that are cross-linked have unusual properties that make them suitable for a number of industrial uses. They are more resistant to gelatinization, and pastes made from them display increased thermal stability compared to unmodified starch. In fact, depending upon the degree of cross-linking, starch esters may be prepared which are non-gelatinizable in boiling water. The few processes describing starch phosphates production all emphasize preparing starch phosphates having nearly the maximum P (0.4%) allowed by US Code of Federal Regulations (CFR, 1991), as well as high paste consistency, short paste texture, and good shear stability upon cooking at atmospheric pressure (Lim & Seib, 1993). The properties of starch phosphates depend to a great extent on the degree of modification. Therefore, parameters that affect modification such as pH will in turn affect the type and quality of the starch phosphates produced.

Starch produced from tropical sago palm is a useful resource for foodstuffs and industrial raw materials, but a large portion of it has not yet sufficiently been utilized (Arai, Kaneko & Ito, 1981; Nagato, 1967). Since 1976 the quality of sago starch in Malaysia has improved tremendously due to the development of more effective and efficient refining processes. As a result, sago starch has replaced other starches in a number of applications (Fong, 1991).

The starches commonly used internationally for commercial derivatization however are corn, waxy maize, tapioca, and potato (Langan, 1986). Since sago starch is available in large quantities in Malaysia and has potential market as locally produced starch phosphates, the general aim of the present study was to produce sago distarch phosphates with low hot paste viscosity but high cold paste viscosity, good shear stability upon cooking and containing P not exceeding 0.4% as specified by US regulations. This paper reports the production of starch phosphates up to a DS of 0.02 and the effect of various levels of reaction pH on the phosphorylation process.

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Table 1
Physicochemical properties of sago starch employed in this study

Property	SIRIM[a]	Sago starch[b]
Moisture (% w/w)	13.0	12.4 ± 0.04
Total ash (on dry basis) (% w/w)	0.20	0.02 ± 0.01
pH of aqueous extract	4.5–6.5	5.34 ± 0.04
Crude fibre (on dry basis) (% w/w)	0.1	0.05 ± 0.01
Viscosity (6% dry basis suspension)	600	670 ± 15
Colour (*L* value)	90	90 ± 2
Sulphur dioxide (ppm)	30	20 ± 2
Particle size (% through 125 mm or 120 mesh sieve)	99	99.4 ± 0.2
Starch damage (%)	–	0.1 ± 0.002
Amylose content (%)	–	25 ± 0.2
Phosphorus content (%)	–	0.009 ± 0.02

[a] Malaysian Standard MS 470:1992 (SIRIM, 1992).
[b] Data are mean and standard deviation of three determinations.

2. Materials and methods

2.1. Materials

Sago starch was obtained from Refined Sago Starch Sarawak Chemicals Industries, Malaysia. The sago starch quality was determined according to the methods prescribed in the Malaysian standard for edible sago starch (SIRIM, 1992). Pentasodium tripolyphosphate (STPP) (BDH Laboratory Supplies, Poole, UK) and trisodium trimetaphosphate (STMP) (Sigma Chemical Co., St. Louis, USA) were used as phosphorylation agents. All other chemicals were reagent grade unless specified.

2.2. Phosphorylation of starch

To study the effect of pH on the phoshorylation of sago starch, the starch was phosphorylated according to the method described by Lim and Seib (1993). Sago starch was phosphorylated at various pH levels (from 6 to 11) with 5% dry starch basis (dsb) STPP and/or 2% dsb STMP in the presence of 5% (dsb) sodium sulphate. The phosphorylation was carried out for 1 h at 27°C and heating was performed for 2 h at 130°C. The degree of starch damage observed after phosphorylation was minimal. The method employed for starch damage measurement was in accordance to that of Karkalas, Tester and Morrison (1992).

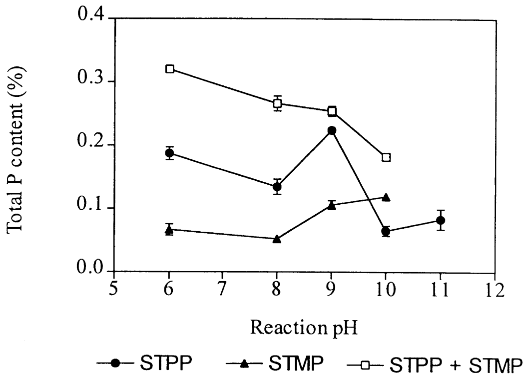

Fig. 1. Effect of various initial reaction pH on the total phosphorus content of sago starch phosphates prepared using 2% sodium trimetaphosphate (STMP), 5% sodium tripolyphosphate (STPP), and a mixture of the two. Data are mean of three determinations using three different modified samples.

2.3. Phosphorus content of starch

Phosphorus was determined by the procedure of Egan, Kirk and Sawyer (1981). P levels are the sum of endogenous P in a starch plus that incorporated by chemical treatment. The endogenous P in sago starch was 0.009 ± 0.02%.

2.4. Pasting profiles

The pasting behaviour of native and modified starches was examined in a Brabender Amylograph (Brabender GmbH, Duisburg, Germany) using a torque of 700 cm g equivalent to 1000 BU and 75 rpm. The starch slurry (400 ml at 6% 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 30 to 95°C, held at 95°C for 30 min, cooled from 95 to 50°C, and held at 50°C for 30 min. The following parameters were determined from the amylograph curve: initial pasting temperature, peak viscosity temperature, shear stability at 95°C and average slope at 95°C. The shear stability of a paste was defined as the difference between the peak viscosity and the viscosity after holding for 30 min at 95°C (Dengate, 1984), and the average slope was calculated as average slope of curves at 95°C holding (Yeh & Yeh, 1993).

2.5. Paste clarity

The clarity of starch paste was determined according to the method described by Craig, Maningat, Seib and Hoseney (1989). One percent by weight of starch in water at pH 6.5 was heated in a boiling water bath for 30 min. The tube was thoroughly shaken for every 5 min. Then the sample was cooled to 25°C and evaluated using percent transmittance (%*T*) at 650 nm against a water blank in a Perkin–Elmer Lamda 3 UV/VIS spectrophotometer.

3. Results and discussion

The results of the analysis on the quality of sago starch and degree of starch damage are shown in Table 1. The sago starch met the Malaysian Standards for edible sago starch.

3.1. Phosphorus content of phosphorylated sago starches

The phosphorus content of sago starch phosphorylated with 2% STMP, 5% STPP, and a mixture of the two are shown in Fig. 1. Native sago starch contained 0.009 ±

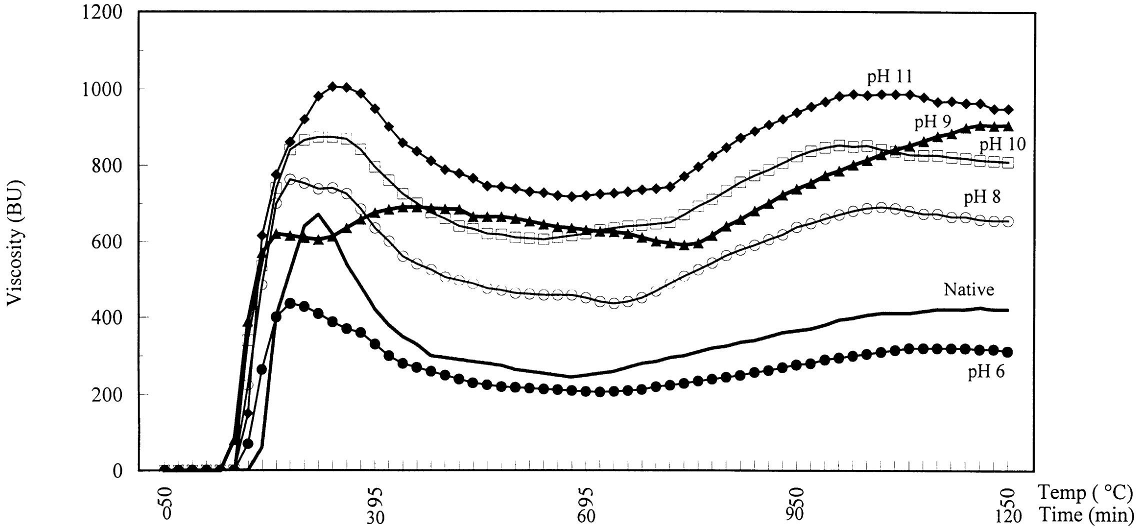

Fig. 2. Amylograms of sago starch and sago starch phosphates prepared by reacting starch at various initial pH levels with 5% sodium tripolyphosphate (STPP) based on dry starch. All amylograms were obtained at pH 6.5 and 6% starch solids.

0.02% P (dsb). Reaction of semidry sago starch with 5% STPP in the presence of 5% sodium sulphate (swelling inhibitor) (Na_2SO_4) at pH 6–11 and 130°C for 2 h gave starch phosphates that contained 0.186–0.083% P. At pH 10, sago starch showed the lowest incorporation of P (0.065%), which was roughly one-third to one-fourth the incorporation at pH 9. These results are at variance with those of Lim and Seib (1993), who reported that the degree of phosphorylation of corn and wheat starches decreased gradually as the initial reaction pH was raised from 6 to 10, and decreased rapidly between pH 10 and 11. However, the results with the modified sago starch phosphates showed almost similar patterns to those reported by Nierle (1969), who found that the degree of phosphorylation of corn starch increased from 0.12% P at pH 7.5 to 0.36% P at pH 9.5 upon reaction with STPP at 130°C for 2 h. The incorporation of P into sago starch showed an increase between pH 8 and 9 (0.134 and 0.224%, respectively) under identical conditions. The highest degree of phosphorylation of sago starch was obtained at pH 9 (0.224%). After correcting for the P content of native sago starch (0.009% P), the sago starch phosphate prepared at pH 9 contained 0.215% P, which is equivalent to the degree of substitution (DS) 0.011 as monophosphate ester or 11 mmol of P per anhydroglucose unit (AGU). As the starch was reacted with 66 mmol of P per AGU (Lim & Seib, 1993), the P incorporated into the sago starch phosphates at pH 9 amounted to 17% of that in the reagent. Since none of these reaction pH levels resulted in P levels exceeding the maximum level (0.4%) specified by CFR, the sago starch phosphates produced using 5% STPP can be applied in food products.

Sago starch was also reacted with 2% STMP in the presence of 5% sodium sulphate at pH 6–10 and 130°C for 2 h. As the initial pH was raised from 6 to 8, the P level decreased gradually, but at pH 8 and above, STMP phosphorylation increased rapidly. Adjusting the pH from 8 to 10 increased total P levels in the products by more than 100% (from 0.052 to 0.119%). Phosphorylation with STMP at pH 10 showed the highest incorporation of P (0.119%). After correction for endogenous P, sago starch phosphate prepared at pH 10 contained 0.106% P which amounted to 18% of that in the reagent. The 2% STMP present was equal to DS 0.033 or 33 mmol of P per anhydroglucose unit (AGU). Thus, the incorporation of P in starch using STMP (18% of that in the reagent at pH 10) was slightly higher than that using STPP (17%) at pH 9. It is conceivable that STMP gave more P-substitution because it had more polyphosphate groups on the starch chain as reported by Lim and Seib (1993). The authors also mentioned that the first attack of starch on the cyclic STMP would yield starch tripolyphosphate, as opposed to starch mono- and diphosphate with STPP. The maximum level of P permitted by CFR is 0.04% when using only STMP, thus all the pH levels tested gave starch products that cannot be used in food application.

In the reactions using a mixture of 2% STMP and 5% STPP, as the initial reaction pH was increased from 6 to 10, the P content decreased gradually from pH 6 to 9 (0.320–0.254%), and decreased drastically from pH 9 to 10 (0.254–0.115%). The total P content of these products was approximately equal to the sum of P incorporated using each of the two reagents singly and was within the limit (0.4%) specified for food starches by the US Code of Federal Regulations (CFR, 1991).

3.2. Pasting profiles of phosphorylated sago starches

The amylograms of sago starch phosphates prepared at various initial reaction pHs using 5% STPP are presented in Fig. 2. The initial pasting temperature of sago starch

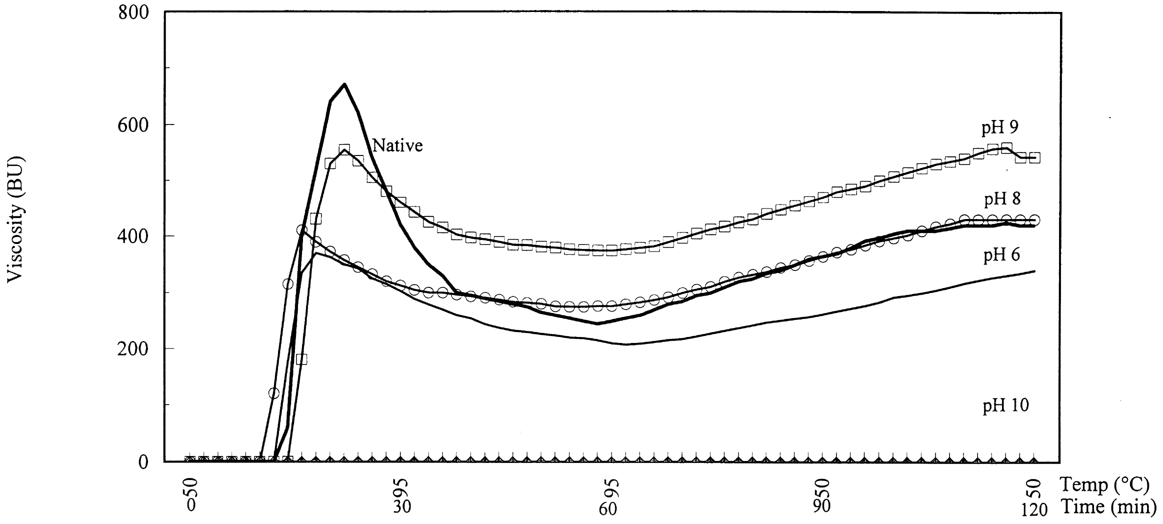

Fig. 3. Amylograms of sago starch and sago starch phosphates prepared by reacting starch at various initial pH levels with 2% sodium trimetaphosphate (STMP) based on dry starch. All amylograms were obtained at pH 6.5 and 6% starch solids.

phosphates was lower than that of native starch. As the reaction pH was increased from 8 to 11, peak viscosity increased relative to that of the native starch. According to Lim and Seib (1993), a reduction in initial pasting temperature and an increase in peak viscosity indicates the presence of monostarch phosphates. Sago starch phosphate prepared at pH 9 was relatively stable to shearing at 95°C in the amylograph, which indicated cross-linking in the starch. However, pastes from sago starches phosphorylated at pH 6, 8, 10 and 11 were susceptible to shear at 95°C. The double pasting peaks observed for sago starch phosphate prepared at pH 9 may have been due to non-uniform phosphorylation. The hot paste viscosity of the starches phosphorylated at pH 10 and 11 was higher than that of paste prepared at pH 9; but the cold paste viscosity of the latter would approach that of the paste prepared at pH 11 as cooling goes beyond 50°C. To achieve the proper balance of high cold paste viscosity, low hot paste viscosity and shear stability upon cooking, initial reaction pH of 9 using 5% STPP is recommended for the phosphorylation process.

Fig. 3 shows the amylograms of sago starch phosphates prepared by reacting starch with 2% STMP at 130°C for 2 h at various pH levels. As initial reaction pH was increased from 6 to 9, peak viscosity increased but the viscosity was lower than that of native starch. Sago starch phosphates prepared at pH 8 and below exhibited a lower initial pasting temperature, but that prepared at pH 9 showed a higher pasting temperature than the unmodified starch. When

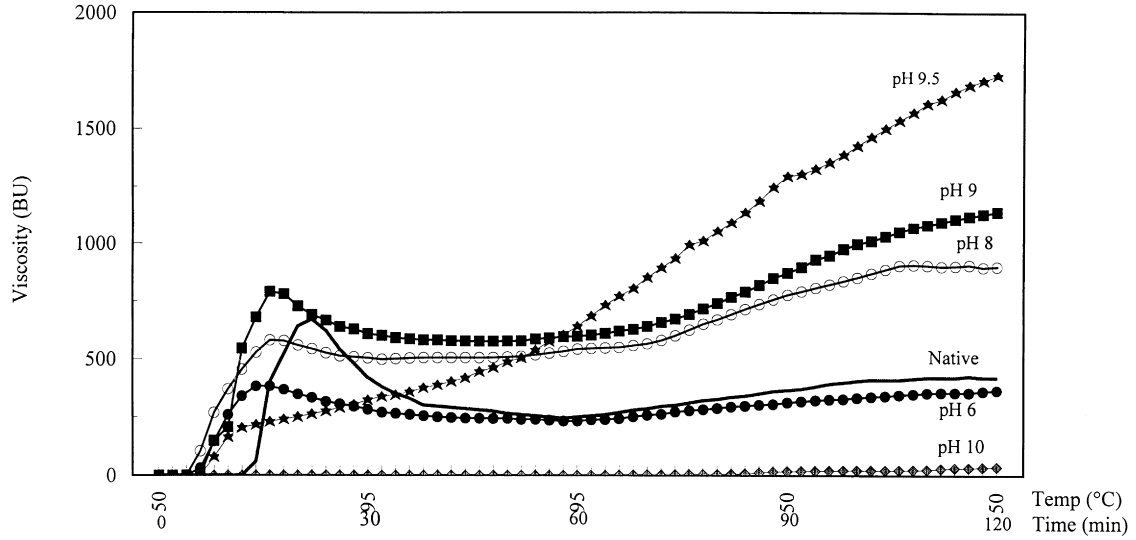

Fig. 4. Amylograms of sago starch and sago starch phosphates prepared by reacting starch at various initial pH levels with a mixture of 5% sodium sulphate, 5% sodium tripolyphosphate, and 2% sodium trimetaphosphate based on dry starch. All amylograms were obtained at pH 6.5 and 6% starch solids.

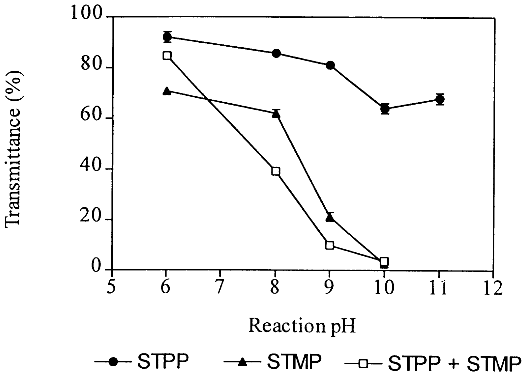

Fig. 5. Paste clarity of sago starch phosphates prepared using 5% sodium tripolyphosphate (STPP), 2% sodium trimetaphosphate (STMP), and a mixture of the two at various pH levels. Data are mean of three determinations using three different modified samples.

reacted at pH 10, the phosphorylated sago starch (containing 0.119% P) showed no pasting curve at 6% starch solids indicative of excessive cross-linking. The decreased peak viscosity and increased initial pasting temperature suggest that formation of distarch phosphate esters was dominant at pH 9 and above when STMP was used, whereas conditions at pH levels of 8 and below were suboptimal for cross-linking as manifested by the shear thinning of the hot pastes.

Fig. 4 shows the amylograms of unmodified sago starch and sago starch phosphorylated by reacting with 5% sodium sulphate and a mixture of 2% STMP and 5% STPP at various reaction pH levels. Sago starch phosphate prepared at pH 6 exhibited a viscosity increase at 57°C and attained a peak (382 BU) at 71°C. Its paste consistency decreased during the holding period at 95°C. STMP and STPP formed mainly monostarch phosphates at lower pH values and the degree of phosphorylation when both salts were used at pH 6 was DS 0.320 compared to DS 0.066 with STMP alone and DS 0.186 with STPP alone. The increase in degree of monosubstitution in the reaction with the mixed phosphate salts allowed starch granules to swell at a lower pasting temperature. Sago starch phosphorylated with 5% STPP at pH 6 in the presence of 5% sodium sulphate exhibited initial pasting temperature of 64°C whereas the starch treated with 2% STMP, under the same condition had a pasting temperature of 68°C. As the reaction pH was increased to 9.5, the paste became resistant to heat and shearing and gave a high consistency after cooling. The excellent pasting characteristics of sago starch phosphate prepared at pH 9.5 indicated that the ratio of cross-linking to monosubstitution is higher. However, phosphorylation at pH 10 gave phosphorylated sago starch with virtually no thickening power indicating excessive cross-linking. Thus, phosphorylation with a combination of STMP and STPP, like that with STMP alone gave very rapid increases in cross-linking above pH 9.5. Shear stability of sago starch was improved after phosphorylation. Stability seemed to increase at all reaction pH levels. At pH 9.5 the average slope value was positive and the highest (10.28) among all of the phosphorylated starches. This indicated that no breakdown occurred at all when the starch was cooked at 95°C. Cross-linking treatment imparts strength to the granule and restricts swelling to the point viscosity development is suppressed during the holding period (Swinkels, 1992). The amylose does not leach out from the granule because the phosphate groups have strengthened the granule and prevented it from swelling.

3.3. Clarity of phosphorylated sago starch pastes

The paste clarity of sago starch phosphorylated with STMP, STPP, and a combination of the two is shown in Fig. 5. Phosphorylation pH had a pronounced effect on the paste clarity of the resulting starch pastes. Unmodified sago starch produced a translucent paste and showed 64.5 ± 0.2% light transmittance. In general, phosphorylation with STMP and/or STPP at neutral or acidic conditions increased light transmittance of starch pastes than observed for unmodified starch. According to Lim and Seib (1993) the repulsion between adjacent starch molecules caused by the negatively charged phosphate groups apparently reduced interchain associations and gave increased levels of hydrated molecules. These highly swollen phosphorylated starches formed starch pastes with high light transmittance. With increased reaction pH, paste transmittance of the resulting phosphorylated starches decreased. When sago starch is phosphorylated using STPP alone, an increase in reaction pH from 6 to 9 resulted in a slight decrease in the clarity of starch paste. However, at a reaction pH of 9–11, the paste clarity dropped by about 14–17% in light transmittance. Cross-linking is known to reduce paste clarity. Thus these results indicate that cross-linking with STPP accelerated at pH above 9. For starches phosphorylated with STMP, the change in paste clarity indicated that cross-linking began to accelerate when the initial reaction pH was greater than 8. At pH above 8 the paste clarity dropped drastically from 60 to almost 3%*T*. The observed pattern was similar to that described by Lim and Seib (1993). In the reaction with a mixture of STPP and STMP, as the reaction pH increased the paste clarity dropped drastically from 85%*T* at pH 6 to 6.5%*T* at pH 10. The cross-linking actually started to occur at pH above 6. When compared to the light transmittance of phosphorylated wheat and corn starches reported by Lim and Seib (1993), in which their threshold pH was 8, it can be seen that the effect of the reaction pH on phosphorylation of sago starch is very significant.

4. Conclusions

In conclusion, phosphorylation of starch with 2% STMP alone is not recommended because the cross-linking reaction is difficult to control above pH 9 and because at all reaction pH levels, sago starch phosphates exceeded the level of substitution allowed by US Code of Federal

Regulations (0.04% P). When 5% STPP is used to phosphorylate sago starch, it should be reacted at pH 9. At that pH level the phosphorylated starch produced contains less than 0.4% P, exhibits low hot paste viscosity but high cold paste viscosity, and is shear stable during cooking. With a mixture of 2% STMP and 5% STPP pH above 9.5 for phosphorylation of sago starch is not recommended because of the extreme sensitivity of the cross-linking reaction under those conditions. A reaction pH of 9.0–9.5 appears to be optimal. The phosphorylated sago starch produced contain less than 0.4% P. Its hot paste viscosity is lower and cold paste viscosity higher than that of sago starch phosphates prepared at pH 9 using 5% STPP.

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