## Physico-chemical properties of cross-linked sago starch

(Ciri fizikokimia kanji sagu rangkaian silang)

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Key words: starch, sago, cross-linked, properties

#### Abstrak

Kanji sagu diubahsuai secara perangkaian silang dengan menggunakan natrium trimetafosfat untuk meluaskan penggunaannya dalam pemprosesan makanan. Keadaan optimum untuk proses rangkaian silang kanji sagu ialah pH 10.0, suhu  $45 \pm 2$  °C, 0.4% natrium trimetafosfat dan tempoh tindakbalas selama 8 jam. Kandungan sisa fosforus kanji yang dihasilkan lebih rendah daripada tahap yang dibenarkan oleh FAO/WHO dan EEC. Ciri kanji rangkaian silang ini berbeza daripada kanji aslinya.

Kanji sagu rangkaian silang didapati mempunyai daya penggembungan yang kurang daripada kanji aslinya. Walau bagaimanapun, kelikatannya tinggi dan stabil pada pH 3.6. Kestabilan ini menunjukkan bahawa kanji sagu rangkaian silang sesuai digunakan dalam makanan yang mempunyai pH  $\geq$ 3.6 seperti sos.

#### Abstract

Sago starch was modified by cross-linking with sodium trimetaphosphate to widen its use in food processing. The optimum conditions required for cross-linking were pH 10.0, temperature  $45 \pm 2$  °C, 0.4% sodium trimetaphosphate and a reaction time of 8 h. The residual phosphorus content of the resulting starch was lower than the level specified by FAO/WHO and EEC. The characteristics of the cross-linked starch differed from its native form.

The cross-linked starch had lower swelling power than its native starch. However, it had high viscosity stability even at pH 3.6. This indicates its suitability to be used in foods with pH  $\geq$ 3.6 such as sauces.

#### Introduction

Modified starches have widened their usage in food industries. They are more flexible and have the functional properties required by food processors. They can provide a wider peak viscosity range, improve tolerance to rigorous processing conditions, desirable texture and prolonged stability.

Major work on starch modification has been done on corn, wheat and potato. Recently, there is an upsurge of interest in modifying starches from new conventional starch varieties and also from other sources such as tapioca, sweet potato, yam, rice, barley and amaranth grains (Von Koch et al. 1982; Azemi and Wootton 1985; Osunsami et al. 1989; Wu and Seib 1990; De Boer 1991; Maneepun and Sirirojana 1992; Perez et al. 1993; Azemi et al. 1995).

Several techniques can be applied to produce starch derivatives which are used as additives to thicken, stabilise or provide textural characteristics to a wide variety of food systems. Various starch derivatives

\*Food Technology Centre, MARDI Headquarters, P. O. Box 12301, 50774 Kuala Lumpur, Malaysia Authors' full names: Khatijah Idris and Patimah Hasim ©Malaysian Agricultural Research and Development Institute 1998 have been approved for food applications and classified as GRAS (generally regarded as safe). One of the techniques used is cross-linking. In this process, starch in the intact unswollen granule form is reacted with di- or polyfunctional reagents capable of reacting with at least two of the hydroxyl groups in neighbouring molecules (*Figure* 1). Several cross-linking agents, such as sodium trimetaphosphate, epichlorohydrin, linear dicarboxylic acid anhydrides, phosphorus oxychloride and acrolein, can also be used.

Realising the potential of local starches, this study which is part of a comprehensive study on the use of local starches in foods, was initiated. This paper reports on the optimum conditions required in the preparation of cross-linked sago starch and the physico-chemical properties of the modified sago starch. This study focussed on the usage of sodium trimetaphosphate as a cross-linking agent.

# Materials and methods *Sample*

Sago starch was obtained commercially from a sago starch processing factory.

## Starch modification

The modified or cross-linked starch was prepared by reacting the native starch with sodium trimetaphosphate at various conditions. Three temperatures  $(40 \pm 2, 45 \pm 2 \text{ and } 50 \pm 2 \text{ °C})$ , three pH values (10.0, 10.5 and 11.0), eight sodium trimetaphosphate concentrations ranging from 0.2% to 2.0% (dry weight of native starch) and four reaction times (2, 8, 16 and 24 h) were used (*Figure 2*).

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$2$ StOH + Na <sub>3</sub> P <sub>3</sub> O <sub>9</sub> $\xrightarrow{Catalyst}$ StO-P-OSt + Na <sub>2</sub> H <sub>2</sub> PC					
	(Sodium				
	trimeta-	ONa			
	phosphate)	(Phosphate			
		di-starch ester)			

Figure 1. Cross-linking of starch with sodium trimetaphosphate

## Analysis

Colour was measured by Chroma Meter CR200 (Minolta Camera Co.) which measures colour according to the Hunter's system (*L*, *a* and *b* values). The standard white plate used has the *L*, *a* and *b* values of 97.83, -0.38 and +1.94 respectively. Chroma was calculated using the formula,  $C = \sqrt{[a^2 + b^2]}$  where *a* and *b* are colour values from the Chroma Meter CR200.

The moisture, protein, fat, ash, crude fibre and starch contents were determined according to the AOAC methods (1984). The amylose content was determined using Rapid Flow Analyser (Alpken 300).

The starch pasting characteristic was measured using a Brabender amylograph (700 cm-g and at 75 rpm). A 6% (d.b.) starch suspension was used and the cycle involved a heating period from 30 °C to 95 °C, holding period at 95 °C for 30 min followed by a cooling period to 50 °C.

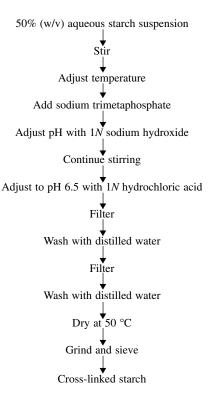


Figure 2. Preparation of cross-linked starch

The phosphorus or phosphate residue was determined spectrophotometrically using the Smith and Caruso method (1964). The swelling power of the starch granules at 75, 85 and 95 °C was determined as described by Petersen (1975).

The freeze-thaw cycle of the gelatinised starch was determined as described by Wu and Seib (1990). The starch paste (6% d.b., pH 6.5) which had undergone drastic treatment in the heating-cooling cycle in the Brabender amylograph (heated to 95 °C, held at 95 °C for 30 min and cooled to 50 °C), was used in the freeze-thaw cycle determination (-18 °C for 48 h and thawed at 30 °C in a water-bath for 2 h).

### Results and discussion Starch modification

The pasting characteristics of the crosslinked sago starches prepared at three temperatures and three pH had different peak viscosities (*Figure 3* and *Figure 4*). The highest pasting peak was obtained when the starch was prepared at the optimum temperature of  $45 \pm 2$  °C and pH 10.0. The modification or degree of cross-linking increased with an increase in sodium trimetaphosphate concentration and reaction time (*Figure 5*). The viscosity of the starch paste became more stable with the increase in cross-linking (*Table 1*). The greatest viscosity drop was achieved at 0.6% sodium trimetaphosphate and a reaction time of 8 h.

Further determination of the optimum level of sodium trimetaphosphate to yield an optimum amount of cross-linked starch and most stable starch paste viscosity was carried out at an 8 h reaction time. A reaction time of more than 8 h was avoided as it would not have considerable advantage and would be uneconomical. The highest starch paste viscosity and stability without a viscosity drop during the heating cycle was obtained using 0.4% sodium trimetaphosphate (*Table 2* and *Figure 6*).

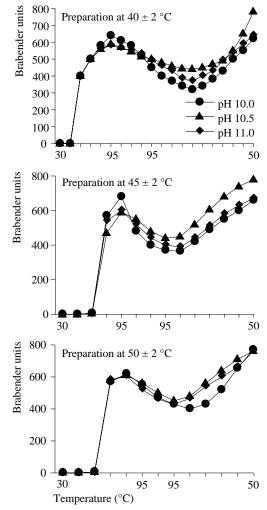


Figure 3. Pasting characteristics of cross-linked sago starch (6% d.b.) prepared at three temperatures

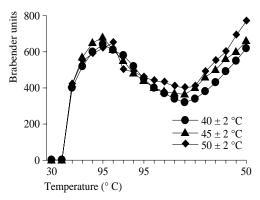


Figure 4. Pasting characteristics of cross-linked sago starch (6% d.b.) prepared at pH 10.0

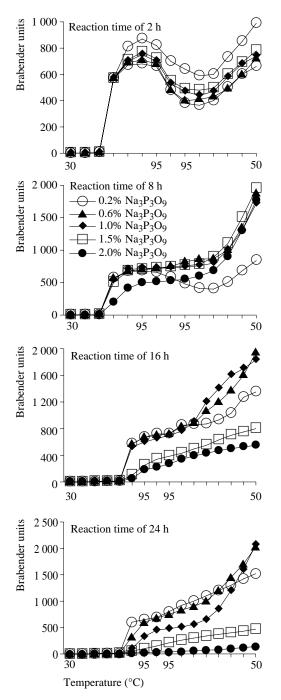


Figure 5. Pasting characteristics of cross-linked sago starch (6% d.b.) prepared at four reaction times

Table 1. Effect of sodium trimetaphosphate level on the viscosity stability of cross-linked sago starch (6% d.b.) during heating cycle at four reaction times

Na <sub>3</sub> P <sub>3</sub> O <sub>9</sub> level (%)	Viscosity stability* (B.U.) at 4 reaction times				
	2 h	8 h	16 h	24 h	
0.2	300	160	-130	-310	
0.6	300	-170	-130	n	
1.0	280	-130	n	n	
1.5	260	n	n	n	
2.0	280	n	n	n	

\*Difference between the highest viscosity peak and the viscosity at the end of a holding period (30 min at 95  $^{\circ}$ C)

B.U. = Brabender units

n = none due to absence of pasting peak

Table 2. Effect of sodium trimetaphosphate level on the viscosity stability of cross-linked sago starch (6% d.b.) during heating cycle at 8 h reaction time

Na <sub>3</sub> P <sub>3</sub> O <sub>9</sub> level (%)	Viscosity stability* (B.U.)
0.3	- 35
0.4	-145
0.5	-170

\*Difference between the highest viscosity peak and the viscosity at the end of a holding period (30 min at 95 °C)

B.U. = Brabender units

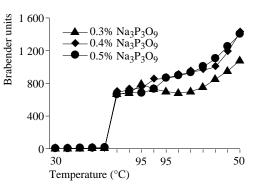


Figure 6. Pasting characteristics of cross-linked sago starch (6% d.b.) prepared with a reaction time of 8 h

#### **Physico-chemical properties**

The cross-linked starch prepared by using 0.4% (dry weight of starch) sodium trimetaphosphate, at pH 10.0,  $45 \pm 2$  °C and with a reaction time of 8 h, was then analysed for its properties. Its colour was found to be not as white as its native starch (*Table 3*). However, both of them exhibited high degree of whiteness. The higher *a* value denotes its tendency towards pinkish colour while the higher *b* value indicates its tendency towards yellowish colour.

The protein, ash and crude fibre contents of the native starch were expectedly low. It contained a considerable amount of starch which consisted of 44.7% amylose. The high amount of amylose is usually related to the high gelatinisation temperature of 72  $^{\circ}$ C of the starch.

The residual phosphorus content of the cross-linked starch was 0.02% which is lower than the permitted level of 0.04% as specified by FAO/WHO and EEC (Trimble 1983; Wurzburg 1986).

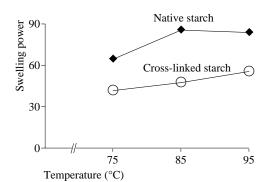
The cross-linked starch was more resistant than its native starch and it did not swell as easily as its native starch (*Figure* 7). Syneresis or water separation in the

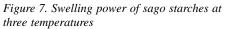
Table 3. Colour and composition of sago starches

Colour/ composition	Native starch	Cross-linked starch
Colour		
L value	92.2	90.4
a value	0.7	1.2
b value	7.1	8.9
Chroma	7.1	9.0
Moisture (%)	11.9	
Protein (%)	0.6	
Ash (%)	0.1	
Crude fibre (%)	0	
Starch (%)	74.6	
Amylose (%)	44.7*	

Higher *a* value denotes its tendency towards pinkish colour while higher *b* value indicates its tendency towards yellowish colour \*Ajimilah, N. H., Food Technology Centre, MARDI, Serdang, pers. comm. (1995) cross-linked starch was observed after the second freeze-thaw cycle (*Figure 8*).

The pasting viscosity of the crosslinked starch decreased with a decrease in pH (*Figure 9*). The pasting viscosity at pH 3.5 was much lower than those at pH  $\geq$ 3.6. This indicates the suitability of the starch for use in foods with pH  $\geq$ 3.6 such as sauces.





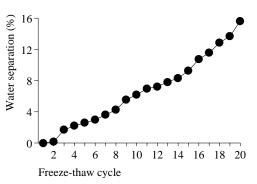


Figure 8. Freeze-thaw cycle of cross-linked sago starch

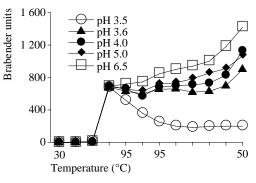


Figure 9. Pasting characteristics of cross-linked sago starch at five pH

## Conclusion

Cross-linked sago starch can be prepared by reacting its native starch with sodium trimetaphosphate. The optimum conditions being pH 10.0,  $45 \pm 2$  °C, 0.4% (starch dry weight) sodium trimetaphosphate and with a reaction time of 8 h. Its residual phosphorus content was lower than the restricted level set by FAO/WHO and EEC, and hence regarded as GRAS. The characteristics of the cross-linked starch differed from its native form.

The swelling power of the cross-linked starch was lesser than its native starch. However, it had high viscosity stability even at pH 3.6. Thus, it is suitable to be used in foods with pH  $\geq$ 3.6 such as sauces.

This study had shown the potential use of sago starch in its modified form. This value-added product can thus widen the scope of use of local starches.

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