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Physico-chemical properties of cross-linked tuber starches

(Ciri fizikokimia kanji umbisi rangkaian silang)

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Key words: tapioca, sweet potato, starch, cross-linked, properties

Abstrak

Kanji ubi kayu dan ubi keledek (varieti Bukit Naga dan Gendut) diubahsuai untuk meluaskan penggunaannya. Pengubahsuaian dijalankan secara mengikat silang dengan menggunakan natrium trimetafosfat. Ciri fizikokimia kanji rangkaian silang ditentukan. Ciri pes dan ciri cair sejuk beku kanji rangkaian silang didapati serupa dengan ciri kanji jagung terubahsuai komersial yang disyorkan untuk sos. Kandungan sisa fosforus dan fosfat adalah di bawah tahap yang dibenarkan oleh FAO/WHO dan EEC.

Kanji ubi keledek (Bukit Naga) terubahsuai mempunyai daya penggembungan yang terendah manakala kanji ubi kayu terubahsuai mempunyai daya penggembungan yang tertinggi. Bagi kanji ubi keledek terubahsuai, penurunan kelikatan berlaku pada pH 3.7. Sementara penurunan kelikatan kanji ubi kayu terubahsuai berlaku pada pH 3.5. Dengan itu, kanji ubi keledek terubahsuai sesuai untuk makanan yang mempunyai pH ≥3.7 manakala kanji ubi kayu terubahsuai sesuai untuk makanan yang mempunyai pH ≥3.5.

Abstract

The tapioca and sweet potato (var. Bukit Naga and Gendut) starches were modified to widen their uses. Modification was done by cross-linking the starches with sodium trimetaphosphate. The physico-chemical properties of the cross-linked starches were determined. The pasting characteristic and freeze-thaw properties of the cross-linked starches were similar to that of the commercial modified corn starch recommended for sauces. The residual phosphorus and phosphate contents were lower than the permitted levels specified by FAO/WHO and EEC.

The modified sweet potato (Bukit Naga) starch had the least swelling power while the tapioca starch had the highest swelling power. For the modified sweet potato starches, a viscosity drop in the pasting cycle occurred at pH 3.7. In the case of modified tapioca starch, the viscosity drop was at pH 3.5. This indicates that the modified sweet potato starches are suitable for foods with pH ≥3.7 while the modified tapioca starch is suitable for foods with pH ≥3.5.

Introduction

Tapioca *(Manihot esculenta)* and sweet potato *(Ipomoea batatas)* are two popular local tuber crops grown for food. Most of the tapioca tubers produced are used by the starch processing industry while the rest is for fresh consumption and dried chips production. The tapioca starch is used in the

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production of seasoning, sweetener and vermicelli. Unlike tapioca, sweet potato tubers are mainly consumed fresh; only a small amount is used by the extruded snack industry and for livestock feed.

One of the ways to widen the industrial usage of these tubers is to modify the starch produced. Modified starch is promising due to its high demand, extensive usage and good market. Starch has to be modified to tailor made its functional characteristics to desired applications. It has to be more versatile and modifications are performed to achieve a desired texture under conditions of high temperature, high shear, freeze-thaw cycles, or low pH.

Several techniques can be applied to produce starch derivatives. One of the techniques is cross-linking. In this technique, starch in the intact unswollen granule form is reacted with di- or poly-functional reagents capable of reacting with at least two of the hydroxyl groups in neighbouring molecules *(Figure 1).*

The study was initiated to extend the scope of usage of tapioca and sweet potato in foods. The objectives were to modify tapioca and sweet potato starches by cross-linking with sodium trimetaphosphate, and to determine their physico-chemical properties and hence their suitability for use in foods.

Materials and methods

Starch extraction

Tapioca starch was obtained commercially from a starch processing factory. Two varieties of sweet potato were used to produce starch. The Bukit Naga variety was obtained commercially from a farm while the Gendut variety was obtained from MARDI, Serdang. The sweet potato starches were prepared from the tubers by peeling, chopping, grinding, washing several times with water, drying in an oven at 45–50 °C and grinding to 150 µm in size.

Starch modification

The modified or cross-linked starch was prepared by reacting the native starch with

$$2StOH + Na_3P_3O_9 \xrightarrow{Catalyst} StO\text{-}P(=O)(ONa)\text{-}OSt + Na_2H_2PO_7$$

Starch (Sodium trimeta-phosphate) (Phosphate di-starch ester)

Figure 1. Cross-linking of starch with sodium trimetaphosphate

50% (w/v) aqueous starch suspension
↓
Stir
↓
Heat to 45 °C
↓
Add sodium trimetaphosphate (0.4% dry weight of starch)
↓
Adjust to pH 10.0 with 1*N* sodium hydroxide
↓
Continue stirring for 8 h
↓
Adjust to pH 6.5 with 1*N* hydrochloric acid
↓
Filter
↓
Wash with distilled water
↓
Filter
↓
Wash with distilled water
↓
Dry at 50 °C
↓
Grind and sieve
↓
Cross-linked starch

Figure 2. Preparation of cross-linked starch

sodium trimetaphosphate (0.4% dry weight of native starch) for 8 h at 45 °C and at pH 10.0 *(Figure 2).*

Analysis

The colour of the native and modified starches was measured by Chroma Meter CR200 (Minolta Camera Co.) based on 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 of the starches were determined according to the AOAC methods (1984). The amylose content was determined using a simplified assay for milled rice amylose (Juliano 1971).

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, a holding period at 95 °C for 30 min followed by a cooling period to 50 °C. In the determination of pasting characteristic of starches at different pH, the pH of the starch paste was initially adjusted to the desired pH before it was measured by the amylograph.

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 starches was determined as described by Wu and Seib (1990). The starch paste (6% d.b., pH 6.5) which had undergone the heating-cooling cycle in the amylograph, was used in the determination. The cooked starches in sealed tubes were held first at 4 °C for 24 h and then subjected to freeze-thaw cycles (–18 °C for 48 h and thawed at 30 °C in a water-bath for 2 h).

Results and discussion

The tapioca and sweet potato (Bukit Naga and Gendut) starches exhibited high degree of whiteness *(Table 1)*. However, the colour of cross-linked tapioca starch was not as white as its native starch. The cross-linked sweet potato starches had slightly higher degree of whiteness than their native starches. Both the native tapioca and sweet potato starches had low moisture, protein, fat, ash and crude fibre contents *(Table 2)*. The native tapioca starch had lower amylose content than the sweet potato starches. However, the amylose contents of these starches are comparatively higher than those reported by Lii and Chang (1991) in Taiwan (19.4–22.8% in three sweet potato varieties grown for starch) and Takeda et al. (1986) in Japan (17.2–19.0% in three sweet potato varieties).

The pasting viscosities of native tapioca and sweet potato (Bukit Naga and Gendut) starches were lower than that of their derivatives *(Figure 3)*. Generally, the

Table 1. Colour of tapioca and sweet potato starches

Crop	Starch	*L* value	*a* value	*b* value	Chroma
Tapioca	Native	96.50	–0.38	3.64	3.66
	Cross-linked	94.64	0.19	5.52	5.52
Sweet potato (Bukit Naga)	Native	94.49	–0.83	4.65	4.72
	Cross-linked	94.66	–0.84	3.81	3.90
Sweet potato (Gendut)	Native	96.16	–0.43	3.06	3.09
	Cross-linked	97.66	–0.36	2.60	2.62

The higher *a* value denotes its tendency towards pinkish colour while the higher *b* value indicates its tendency towards yellowish colour

Table 2. Composition of native tapioca and sweet potato starches

Starch	Moisture (%)	Protein (%)	Fat (%)	Ash (%)	Crude fibre (%)	Starch (%)	Amylose* (%)
Tapioca	10.8	1.0	0.1	0.1	0.2	81.9	33.1
Bukit Naga	7.3	–	0.1	0.5	0.6	80.7	34.3
Gendut	7.3	2.6	0.2	0.5	0.4	81.8	34.5

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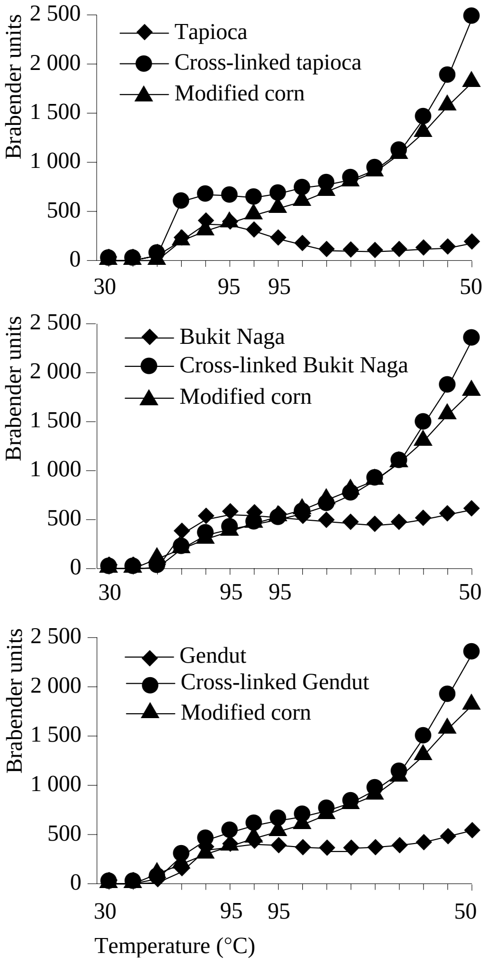

Figure 3. Pasting characteristics of tapioca, sweet potato (Bukit Naga and Gendut) and modified corn starches (6% d.b.)

three native starches exhibited a single stage gelatinisation process indicating uniform distribution of forces within the granules. However, there were differences in the pasting characteristics of the three native starches *(Table 3)*. The Bukit Naga starch had the highest gelatinisation temperature (78.8 °C), pasting peak (550 B.U.), viscosity at the end of holding period (450 B.U.), viscosity at 50 °C (610 B.U.) and consistency (160 B.U.) than the tapioca and Gendut starches. A higher pasting peak viscosity corresponds to a higher thickening power of the starch. The tapioca starch had the highest breakdown value (280 B.U.)

Table 3. Pasting characteristics of 6% (d.b.) native tapioca and sweet potato (Bukit Naga and Gendut) starches

Starch	Gelatinisation temp. (°C)	Time taken to gel (min)	Peak viscosity (B.U.)	Time taken to reach peak viscosity (min)	Viscosity at the end of holding period (B.U.)	Viscosity at 50 °C (B.U.)	Set back (B.U.)	Consistency (B.U.)	Breakdown (B.U.)
Tapioca	5.3	23.5	370	30.0	90	168	–202	78	280
Bukit Naga	78.8	32.5	550	44.0	450	610	60	160	100
Gendut	78.0	32.0	400	44.5	362	520	120	158	8

Set back = viscosity at 50 °C – peak viscosity
Consistency = viscosity at 50 °C – viscosity at the end of holding period
Breakdown = peak viscosity – viscosity at the end of holding period

indicating comparatively the lowest starch stability. The lower set back value of tapioca starch also denotes the degree of softness of the gel when cooled.

The mechanism of water absorption and gelatinisation of sweet potato starch had been studied by Valetudie et al. (1995). They reported that the gelatinisation temperature of sweet potato starch by differential scanning calorimetry (DSC) was T_o 67.3, T_p 72.7 and T_e 79.6 °C. Another report from Venezuela stated that the gelatinisation temperature of sweet potato starch by Brabender amylograph was initially at 60.8 °C and finally at 70.5 °C (Perez-Sira and Gonzalez-Parada 1997).

The pasting characteristic of the cross-linked starches differed from that of their native starches *(Figure 3* and *Figure 4)*. The peak viscosity was absent in the cross-linked starches and their pasting characteristic curves were similar to that of the commercial modified corn starch. The gelatinisation temperature of the modified Gendut starch (75.8 °C) was lower than that of its native starch (78.0 °C) while there was no difference in the gelatinisation temperature between the native and modified Bukit Naga and tapioca starches. The gelatinisation temperature of the modified tapioca and corn starches was similar (65.3 °C). During the heating, holding and initial cooling cycle, the viscosity of modified tapioca starch was highest among the starches. The viscosities of the modified tapioca, Bukit Naga and Gendut starches at 50 °C were higher than that of the modified corn starch.

The residual phosphorus and phosphate contents of the prepared cross-linked tapioca, Bukit Naga and Gendut starches *(Table 4)* were found to be lower than the permitted levels, i.e. 0.04% phosphorus or 0.11% phosphate, as specified by FAO/WHO and EEC (Trimble 1983; Wurzburg 1986).

The cross-linked starch granules are usually more resistant to swelling than their native starches. The cross-linked Bukit Naga starch had comparatively the least swelling power while the native tapioca starch had the highest swelling power *(Figure 5)*.

Syneresis or water separation was observed throughout the freeze-thaw cycles *(Figure 6)*. The increase in water separation was more gradual in the cross-linked Gendut starch than in the cross-linked Bukit Naga

Table 4. Phosphorus and phosphate residues in the cross-linked tapioca and sweet potato (Bukit Naga and Gendut) starches

Starch	Residual phosphorus (%)	Residual phosphate (%)
Tapioca	0.007 ± 0	0.021 ± 0
Bukit Naga	0.024 ± 0.002	0.071 ± 0.0003
Gendut	0.022 ± 0.001	0.066 ± 0.0003

Values are means of 3 replicates ± SD

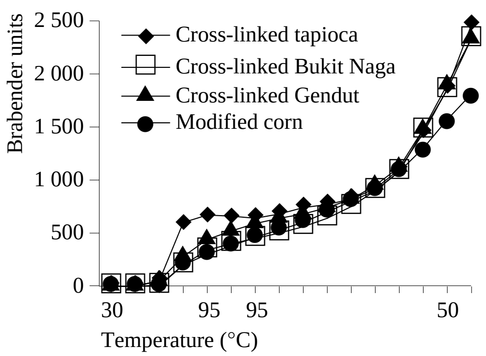

Figure 4. Pasting characteristics of modified tapioca, sweet potato and corn starches (6%)

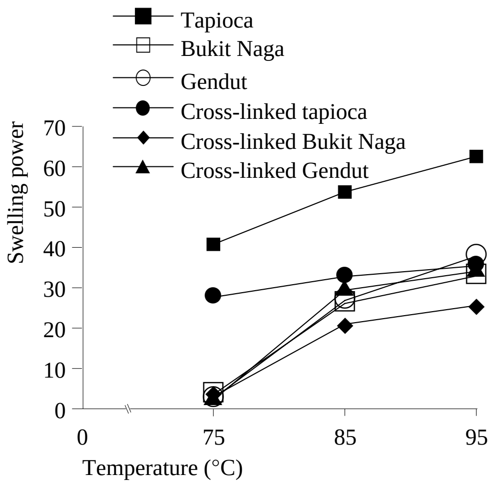

Figure 5. Swelling power of tapioca and sweet potato starch granules

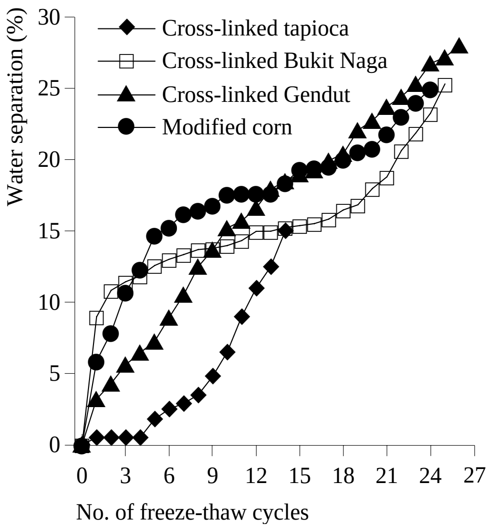

Figure 6. Freeze-thaw cycle of modified starches

starch. The syneresis curves for modified Bukit Naga and corn starches were quite similar. The cross-linked tapioca starch was comparatively more stable initially but after the fourth freeze-thaw cycle, syneresis increased sharply.

The viscosities of modified tapioca, Bukit Naga and Gendut starches decreased with a decrease in pH *(Figure 7)*. For both the sweet potato starches, there was a viscosity drop at pH 3.7, whereas in the case of modified tapioca starch the viscosity drop was at pH 3.5. Thus, modified sweet potato starches are more suitable for foods with pH ≥3.7 while the modified tapioca starch is suitable for foods with pH ≥3.5.

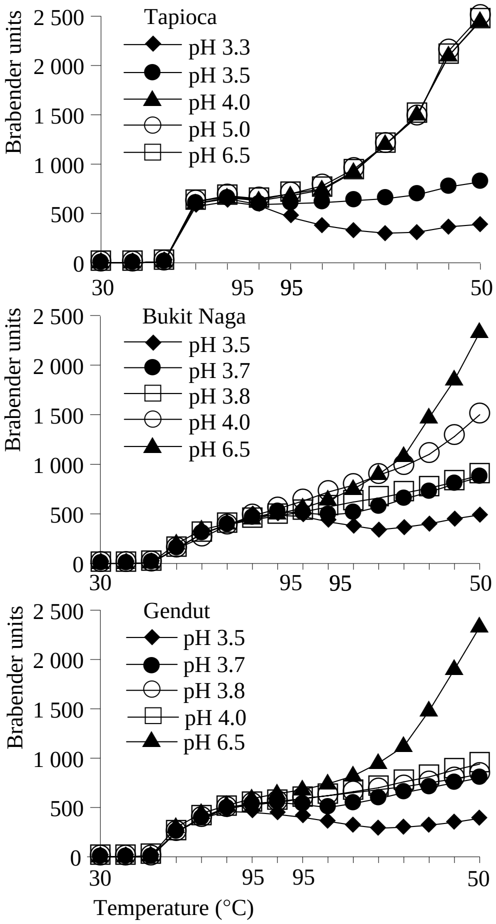

Figure 7. Pasting characteristics of cross-linked tapioca and sweet potato (Bukit Naga and Gendut) starches

Conclusion

Cross-linking resulted in better starch stability towards pH, shear and temperature. Cross-linked tapioca and sweet potato starches had similar properties as that of commercially recommended modified corn starch for sauces. Hence, the possible usage of these starches in foods such as sauces widens the scope of use of local starches.

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