ORIGINAL ARTICLE

Suitability of sago starch as a base for dual-modification

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Abstract

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The quality and physicochemical properties of native sago starch were studied in order to evaluate the suitability of sago starch as a base for dual-modification, hydroxypropylation and crosslinking. The properties of starch derivatives obtained from dual-modification are different depending upon the kind of starch bases used and their basic properties. Therefore, the properties of several starches including waxy maize, waxy barley, tapioca, wheat, corn and rice and properties of their derivatives were investigated comparatively. The data obtained elucidates that the swelling power of a starch base is the most important factor which influences the dual-modification. The native sago starch had higher swelling power and bigger average granule size when compared to that of other starch bases. Its gelatinization temperature was in the same range as that of waxy maize while its pasting characteristic was similar to that of tapioca starch. It can be inferred that sago starch is suitable as a starch base for hydroxypropylation and crosslinking.

Key words : sago starch, dual-modification, hydroxypropylation, crosslinking,
starch properties, modified starch

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ความเหมาะสมของแป้งสาคูสำหรับใช้เป็นแป้งพื้นฐานในกระบวนการทำแป้งดัดแปรแบบสองครั้ง

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การศึกษาครั้งนี้ได้ทำการวิเคราะห์คุณสมบัติทางเคมีและกายภาพของแป้งสาคูที่ได้จากธรรมชาติในเชิงเปรียบเทียบ เพื่อประเมินความเหมาะสมของการใช้แป้งสาคูเป็นวัตถุดิบพื้นฐานในการทำแป้งดัดแปรแบบสองครั้งโดยกระบวนการไฮดรอกซีโพรพิลเลชั่นและครอสริงค์ แป้งอนุพันธ์ที่ได้จากกระบวนการทำแป้งดัดแปรแบบสองครั้งมีคุณสมบัติแตกต่างกันขึ้นอยู่กับชนิดและคุณสมบัติของแป้งพื้นฐานที่ใช้ ดังนั้นในการศึกษานี้จึงได้ทำการเปรียบเทียบคุณสมบัติของแป้งสาคูกับแป้งธรรมชาติชนิดอื่น ๆ ได้แก่ แวกซีเมส (waxy maize) แวกซีบาร์เลย์ (waxy barley) แป้งมันสำปะหลัง แป้งสาลี แป้งข้าวโพด และ แป้งข้าว ที่ใช้เป็นวัตถุดิบพื้นฐานในการทำแป้งดัดแปร เพื่อเปรียบเทียบถึงผลกระทบต่อคุณสมบัติของอนุพันธ์จากแป้งเหล่านี้ที่ได้จากกระบวนการทำแป้งดัดแปรแบบสองครั้ง ข้อมูลที่ได้ชี้ให้เห็นว่ากำลังการพองตัวของแป้งพื้นฐานเป็นปัจจัยที่สำคัญที่สุดที่มีผลกระทบต่อกระบวนการทำแป้งดัดแปรแบบสองครั้ง แป้งสาคูจากธรรมชาติมีกำลังการพองตัวและค่าเฉลี่ยของขนาดเม็ดแป้งสูงกว่าวัตถุดิบแป้งชนิดอื่น ๆ อุณหภูมิในการเกิดเจลาติไนเซชันของแป้งสาคูอยู่ในช่วงเดียวกับแป้งแวกซีเมส ขณะที่การเปลี่ยนแปลงของความหนืดมีลักษณะคล้ายคลึงกับแป้งมันสำปะหลัง จากผลการศึกษาสรุปได้ว่าแป้งสาคูมีคุณสมบัติเหมาะสมในการใช้เป็นวัตถุดิบแป้งพื้นฐานในการทำแป้งดัดแปรโดยกระบวนการไฮดรอกซีโพรพิลเลชันและครอสริงค์

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Commercial sago starches have variable quality depending upon the production process and sources. Some physical and chemical properties of commercial sago starches with various viscosities have been reviewed (Yatsugi, 1986; Takeda *et al*., 1989). Results of various studies on chemical modification illustrated that the properties of starch derivatives obtained were different depending upon the kind of starch base used and their basic properties. Waxy corn and tapioca starches are mostly used as bases for commercial modification since the most desirable properties are obtained from their derivatives but not those from rice, wheat or high amylose corn starch. Therefore, the important properties of a starch base which may have an influence on the dual-modification should be elucidated. This study was designed to document on the properties of several starches such as waxy corn, waxy barley, tapioca, wheat, corn, and rice (Pomeranz, 1991; Yeh and Yeh, 1993; Lim and Seib, 1993; Wu and Seib, 1990; Takahashi *et al*., 1989) in order to compare and determine the suitability of sago starch as a base for dual-modification.

Materials and Methods

Native sago and tapioca starches were obtained from Ajinomoto Co., Ltd., and Longcoh Industries (M) Sdn. Bdh., respectively.

Proximate analyses

The proximate analyses of sago starch including moisture, ash, crude fibre, colour and particle size was determined as specified by SIRIM (1992).

Pasting characteristics

The pasting properties of starch samples were examined in a Brabender Amylograph using 75 rpm and a torque of 700 cm-g equivalent to 1,000 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 to 50 °C at the rate of 1.5 °C/min, and finally held at 50 °C for 30 min. The following measurements 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.

Swelling power

Swelling power was determined as described by Schoch (1964). Starch was accurately weighed (2 g, dbs) into a dry tarred pre-weighed 250 ml centrifugal bottle. Distilled water was added to give a total volume of water equivalent to 180 g. The starch was completely suspended by stirring at 200 rpm using a magnetic stirrer. After taking out the stirrer, the bottle was immediately placed in a temperature-controlled water bath at 85 °C ± 0.2 with continuously shaking at 200 rpm for 30 minutes. The centrifugal bottle was then dried and placed on a balance followed by the addition of distilled water to bring to a total weight of 200 g. After capping, the bottle was centrifuged for 15 minutes at 1000xg for 15 minutes. To measure solubility, 50 ml of the supernatant was then pipetted and transferred into an evaporating petri dish and dried overnight in a hot air oven at 105 °C. The dried residue was then cooled in a desiccator and weighed for soluble starch. To measure the swelling power, the residual supernatant was carefully removed and discarded. The bottle with the sediment paste was then weighed to give the weight of swollen starch granules. The result was expressed by the calculation :

$$\text{Swelling power} = \frac{\text{Weight of sediment paste} \times 100}{\text{Weight of sample on dry basis} \times (100 - \%\text{solubility})}$$

Paste clarity

The clarity (transmittance % at 650 nm) of sago and tapioca starch paste was measured using the procedure of Kerr and Cleveland (1959) cited by Lim and Seib (1993). A 1% aqueous suspension of starch near neutral pH was heated in a boiling water bath for 30 min with intermittent shaking. After the suspension was cooled for 1 hr at 25 °C, the light transmittance at 650 nm was read against a water blank.

Results and Discussion

Quality of native sago starch

The content of moisture, total ash, and crude fibre in the native sago starch were 12.54%, 0.21%, and 0.08%, respectively. All characteristics of the native sago starch were in accordance to the SIRIM specifications (1992) except that the colour quality was slightly lower as shown in Table 1. It has been known that commercial sago starches have the lowest whiteness among industrial starches, which accounts for the lower price (Yatsugi, 1986). Its viscosity characteristic as shown in Figure 1 exhibited a high viscosity during gelatinization. The peak viscosity at 6.0% starch solid (dsb) was 640 BU. According to Takeda *et al.* (1989), native sago starch is defined as a high-viscous starch, which is thought to be of good quality (Azudin and Lim, 1991).

Physicochemical properties of native sago starch

The properties of native sago and other starches are shown in Table 2. Sago starch has a high amylose content as compared with the other native starches. It had been postulated that starch containing high amylose would inhibit its swelling (Wu and Seib, 1990). However, the swelling power of native sago starch was very high (70.2 at 85 °C) as compared with the lower amylose starches such as rice, tapioca, waxy maize and waxy barley. This is probably due to its average

Table 1. Quality of native sago starch compared with SIRIM standard (1992)

Characteristic	Requirement*	Native sago**
Moisture (%m/m), max.	13.0	12.5
Total ash (%m/m, on dry basis), max.	0.20	0.21
pH aqueous extract	4.5 - 6.5	5.2
Crude fibre (%m/m, on dry basis), max.	0.1	0.08
Viscosity (BU, 6% dry basis suspension), min	600	640
Colour (L value), min.	90	88
Particle size (% through 125 or 120 mm mesh sieve), min.	99	99

*** SIRIM standard MS 470 : 1992 ; ** Mean of duplicate determinations**

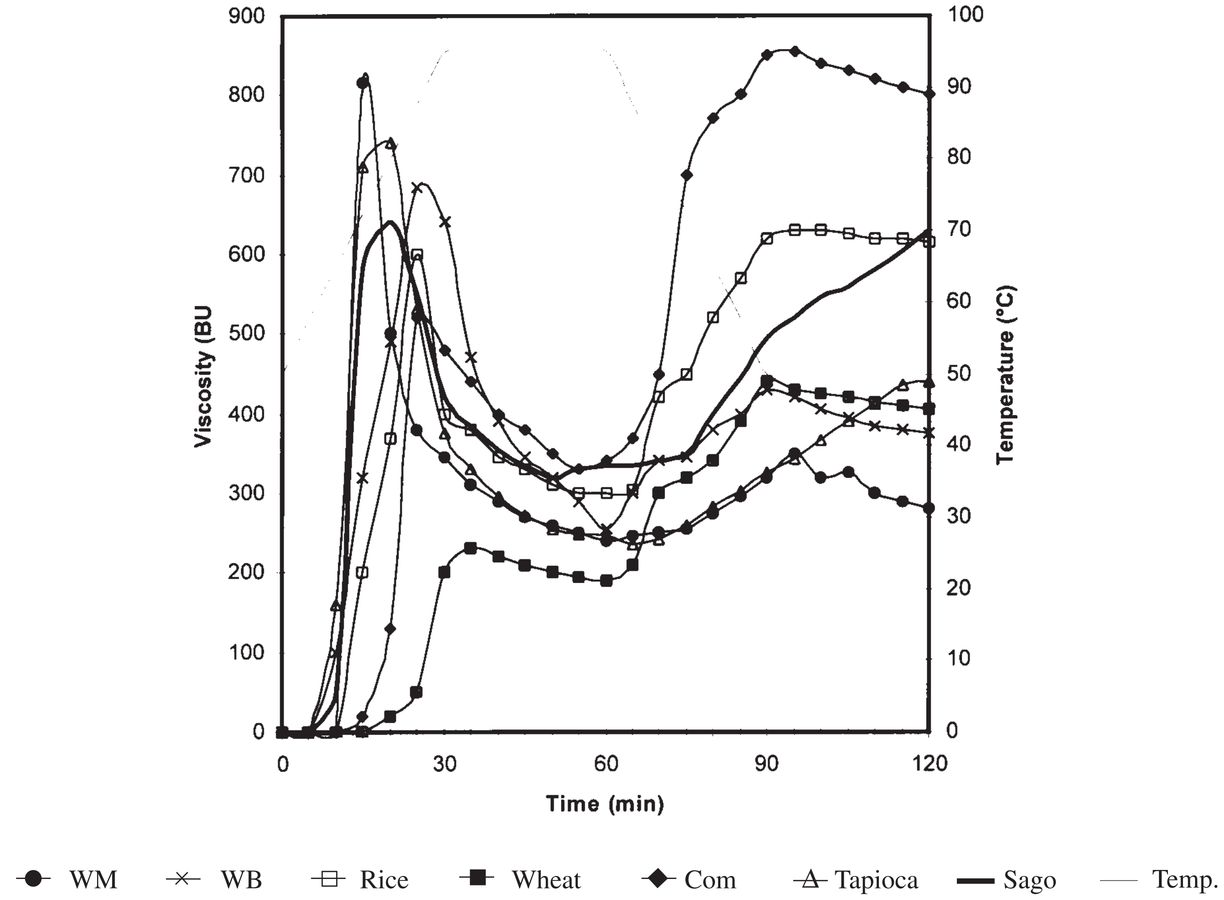

Figure 1. Pasting characteristics of native starches obtained using Brabender Amylograph (6.25% of WM = waxy maize and WB = Waxy barley adapted from Wu and Seib (1990), 8% of rice adapted from Yeh and Yeh (1993), 7.5% of wheat and corn adapted from Lim and Seib (1993), 6.0% of tapioca and sago starch, rechecked)

Table 2. Physicochemical properties of native starches

Starch	Average Granule Size (μm)	Amylose content (%)	Swelling power at 95ºC (or 85ºC)	Gelatinization Range (ºC)	Paste Clarity (%T_{650})
Rice	5	17	19	61-80	Slightly opaque
Wheat	15	25	21	53-72	24.0**
Corn	15	26	24	62-80	34.0**
Waxy maize	15	~1	64/(28.1)*	63-74	65.0*
Waxy barley	20	~5	(22.3)*	56-62	65.2*
Tapioca	20	17	71	52-64	58.3
Sago	25	27	97/(70.2)	60-74	54.2

Note: Adapted from Pomeranz (1991) ; * Wu and Seib (1990) ; **Lim and Seib (1993)

granule size which is bigger than that of the other starches. The intermolecular hydrogen bonds between hydroxyl groups on the adjacent chains of bigger size starch granule were more easily broken during heating, resulting in a higher expansion and an increased swelling rate of granules when compared to the smaller size granules. It is also illustrated by the high swelling big tapioca granules when compared to a smaller size rice starch granules although both contained the same amount of amylose content (17%). However, the property of high swelling in starches such as sago, tapioca, waxy corn and waxy barley resulted in a high peak viscosity during the heating period (Figure 1) which was undesirable for application in some food products that need a low hot paste viscosity. The gelatinization temperature of native sago is nearly of the same range as that of waxy maize but higher than that of tapioca, waxy barley and wheat. Rice and corn starches, however, gelatinised at a relatively higher temperature (Table 2). Each starch gelatinises at different temperature caused by the difference in the molecular organisation within the granule (Pomeranz, 1991). Paste clarity of sago starch was clear and translucent (Pomeranz, 1991) with a high light transmittance of 54.2%. This is an attractive property to the food industry which is similar to that of tapioca, waxy maize and waxy barley (Radley, 1976).

Pasting characteristics of native sago starch

The pasting temperature of sago starch started at 66.0 ºC and progressed rapidly up to 81.0 ºC. After reaching peak viscosity at 640 BU, its viscosity was broken down rapidly during the heating cycle followed by a medium high setback during cooling period. This pasting behaviour was similar to that of tapioca and differed from those of wheat, corn, and rice (Figure 1). Wu and Seib (1990) reported that the high peak viscosity and rapid breakdown during the heating cycle are also typical of waxy starches such as waxy corn and waxy barley except that the waxy starches have a low setback during cooling cycle.

Tapioca and waxy corn starches reached their peak viscosity at a lower temperature and exhibited a higher peak viscosity than sago starch due to the difference in the amylose contents. The amylose content of sago starch was 27% (Pomeranz, 1991) compared with (2% of waxy corn (Wu and Seib, 1990) and 17% of tapioca (Takeda *et al*., 1989), in which amylose controls pasting by intermolecular hydrogen bonding between other amylose or amylopectin.

Also referred to as setback or retrogradation is the precipitation or crystallisation of the amylose fraction. According to Takeda *et al.* (1989), the retrogradation tendency of the high viscosity sago starch is similar to that of tapioca starch. Its retrogradation rate is faster than that of tapioca starch. Therefore, it could be obviously seen that the increase in viscosity during holding at 50 °C of sago starch paste was higher than that of tapioca (Figure 1).

The pasting characteristics show that all of the native starches discussed have an unstable viscosity during heating and some exhibited high retrogradation which will cause undesirable gel texture or high syneresis and low freeze-thaw stability thereafter (Pomeranz, 1991). For these reasons, the dual-modification, hydroxypropylation and crosslinking has been carried out to produce modified starches with high stability.

Starch base properties influencing the dual-modification

The effect of starch base properties on dual-modification had been observed in the study performed by Takahashi *et al.* (1989) who found that corn starches always showed higher consistency than wheat starches when comparing their native or similarly modified forms. Results obtained by other researchers, also illustrated the same phenomena (Yeh and Yeh, 1993; Wu and Seib, 1990; Takahashi *et al.*, 1989). The data obtained from these studies (Table 3) show that the pasting temperature and peak viscosity temperature of all starch derivatives were reduced by hydroxypropylation (Luallen, 1985). However, the derivatives from waxy maize, waxy barley and tapioca had a very high molar substitution (MS) followed by those from wheat and corn starches whereas a very low MS value was obtained with rice starch. This suggests that it is more difficult for hydroxypropylation to take place inside the granules of rice, wheat and corn, than in the granules of waxy and tapioca starches. When considering at the properties of these native starches (Table 2), it was found that their amylose content, swelling power and the average granule size are different. The swelling power had a major influence on the hydroxypropylation reaction since the order of MS value of those starch derivatives has a close relation with the swelling

Table 3. Properties of hydroxypropylated crosslinked starch from general starch bases

Starch base	MS	Pasting Temp. (°C)		Peak Temp. (°C)		Peak Viscosity (BU)		Stability at 95°C[a]		Consistency at 50°C[b]		Ref.
		native	modified	native	modified	native	modified	native	modified	native	modified	
Rice	0.04	71.4	69.0	84.6	81.0	600	700	-300	-325	570	950	c
Wheat	0.10	no data	no data	no data	no data	200	400	-20	50	500	750	d
Corn	0.10	no data	no data	no data	no data	550	1000	-150	-120	900	1450	d
Waxy maize	0.14	67.0	58.0	75.0	70.0	815	>815	-600	-200	320	1440	e
Waxy barley	0.13	61.0	51.0	90.0	80.0	685	>685	-490	-190	430	1480	e
Tapioca	0.13	63.0	57.0	76.5	70.0	795	1150	-552	-100	325	1750	d

Remark : a = peak viscosity - viscosity after holding at 95°C ; b = consistency when paste was cooled to 50°C
Ref.: c = Yeh and Yeh (1993), d = Takahashi *et al.* (1989) ; e = Wu and Seib (1990)

power of their native starch bases. When the granules of starches are easy to swell in the warm alkaline condition of hydroxypropylation, it resulted in a large number of hydroxypropyl groups being substituted at the hydroxyl groups inside the granule.

The peak viscosity of the starches increased after hydroxypropylation and crosslinking. Crosslinking is known to improve the heat stability and consistency of starch products (Wurzburg, 1986). Results of various studies have shown that the stability at 95ºC of tapioca, waxy maize and waxy barley was improved tremendously, but the same procedure was not effective in increasing the stability of rice starch. The native tapioca, waxy maize and waxy barley had lower consistency when compared to native corn, rice and wheat. This is due to the fact that they have a different pattern of swelling (Pomeranz, 1991). During pasting, the former starches swell much more rapidly than the latter starches and thus cannot retain their granule integrity, resulting in the lower consistency when heated (see Figure 1). However, their consistency was increased to a large extent after dual-modification (Table 3). From these results it can be concluded that the hydroxypropylation and crosslinking processes were more effective for the starches with high swelling power. For this reason, waxy and tapioca starches are usually selected to be used as bases for commercially modified starch.

The amylose content in native starches can affect their swelling power, which will in turn affect the dual-modification. For example, high amylose corn starch containing more than 50% amylose has a very low swelling power (6 at 95 ºC) (Pomeranz, 1991). It has been suggested that the granular high amylose starch must be hydroxypropylated with a high amount of propylene oxide to an MS of between 0.10 and 0.30 and inhibited by a reaction with the crosslinking reagent to obtain an advantageous result (Tessler, 1975). Rice starch, however, behaves in a different manner. It has a low amylose content but its small average granule size affects its swelling. This may be the reason for the difference in the results obtained with rice when compared with other starches. Sago starch has a higher amylose content than rice starch but because of its bigger granule size, it has a higher swelling power.

Conclusions

The native sago starch used in this study was of good quality when compared to SIRIM standard except in its colour. The native sago starch had higher swelling power and bigger average granule size when compared to that of other starch bases that can be employed for dual-modification. Its gelatinization temperature was in the same range as that of waxy maize while its pasting characteristic was similar to that of tapioca starch. The swelling power of a starch base is the most important factor which influences the dual-modification. Starch bases which have high swelling power such as waxy starches and tapioca perform better than the others after dual-modification. It can thus be deduced that sago starch is suitable as a starch base for hydroxypropylation and crosslinking since it has a high ability to swell.

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