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Physicochemical Properties of Starches from Sri Lankan Rice Varieties

Hetti Arachchige Mangalika Wickramasinghe[1] and Takahiro Noda[2*]

[1] *Department of Agricultural Biology, Faculty of Agriculture, University of Peradeniya, Peradeniya 20400, Sri Lanka*
[2] *National Agricultural Research Center for Hokkaido Region, Shinsei, Memuro, Hokkaido 082-0081, Japan*

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Physico-chemical properties; amylose content, swelling power, pasting properties by Rapid Visco Analyzer (RVA), thermal properties by Differential Scanning Calorimeter (DSC), and enzymatic digestibility of starches isolated from 19 different Sri Lankan rice varieties were analyzed. Significant variation was shown in all the tested properties among tested varieties in which the amylose content varied from 16.0% to 34.7%. Amylose content appears to be the major factor controlling almost all physico-chemical properties of rice starch, as it showed significant correlations to all other properties tested. It correlated negatively to the peak and breakdown viscosities by RVA and enzyme digestibility but positively to all other tested properties. The peak and onset gelatinization temperatures and enzyme digestibility correlated to all properties except enthalpy for starch gelatinization. The peak and onset gelatinization temperatures, as well as the blue value, showed negative correlations to the peak and breakdown viscosities, indicating the importance of low amylose for easy starch pasting. According to our results, low amylose starches started to gelatinize at lower temperatures. During heating and cooling, such starch slurry showed higher peak and breakdown viscosities, but resulted in a softer gel. Low amylose starch was also easily digestible by enzymes. These properties are probably associated with the reduced compactness in the amorphous area of starch granules. Due to lower amylose in the amorphous area, loosely packed starch granules result in higher swelling power and disorganization with heating.

Keywords: rice starch, RVA pasting properties, DSC thermal properties, digestibility

Introduction

Rice is the staple food for million of people in Southeast Asia, and it is the single most important crop in Sri Lanka in terms of area cultivated, production, number of farming families engaged in its production, and political sensitivity (IRRI, Rice Knowledge Bank, 2006). Breeding efforts at the national level have resulted in high-yielding varieties with resistance to different biotic and abiotic stresses. More than 50 rice cultivars have been recommended for Sri Lanka, and the present rice productivity has reached about 3.8 t/ha (IRRI, Rice Knowledge Bank, 2006). The recent increase in per capita income with other development has created a growing consumer demand for physical purity as well as for better intrinsic quality in rice (Kotagama and Kumara, 1996).

Amylose content is the key determinant of the cooking and eating qualities of rice. Furthermore, recent studies have shown that the amylopectin fine structure is also one of the most important factors determining the pasting and gelatinization properties. Generally, high-quality rice is considered to be soft and slightly moist when cooked, and such qualities are provided by starches with intermediate amylose and moderate gelatinization temperatures. Therefore, breeders should give attention to developing varieties with such grain qualities. However, few studies have been conducted to evaluate the cooking and eating qualities of Sri Lankan rice germplasm.

Rice starch has commercial interest as an important ingredient in different industries. Rice starch has the smallest particle size among commercial starches, the whitest powder color, and a neutral state. Therefore, gelatinized rice starch is very smooth and creamy, and does not have any flavor. Furthermore, it provides a texture perception similar to that of fat (Champagne, 1996) and shows potential for replacing fat in some dairy products. Rice is preferably used in producing cosmetic products, such as baby powder, as its native

*To whom correspondence should be addressed.
E-mail: noda@affrc.go.jp

granules are very small. These granules form aggregates thus, pure rice starch is used in pharmaceutical industries as a filling agent (Puchongkavarin *et al.*, 2005).

Sri Lanka has now become self-sufficient in rice production. Therefore, producing quality rice for the international market and increasing rice-based industries are major challenges to breeders and rice researches in the country. Although in a few applications, such as cosmetics and tableting, the type of starch used is not important, the properties of the starch are important for most other applications. The main objective of the present study was to analyze the physico-chemical properties of starches from Sri Lankan rice varieties, which could then be used in different ways in applied studies. Furthermore, this study examines the different physico-chemical properties and their relationships in indica rice varieties with high amylose.

Materials and Methods

Materials Nineteen different Sri Lankan rice varieties, both traditional and popular inbred cultivars, were used in the study. Seed samples of all varieties were collected from the Rice Research and Development Institute (RRDI), Bathalagoda, Sri Lanka. All of them were grown in the "Yala season" (May to August) of 2005 in RDDI fields. Seed samples were dehulled (Satake Dehusking Machine, THU 354), polished (Satake Whitening Machine MC 250), and then ground for starch isolation. Starch isolation was carried out as described by Noda *et al.* (2003). After drying the isolated starch at room temperature for two days, its moisture content was estimated by drying samples in an oven at 115ºC for 3 h. The analysis of starch properties was carried out at Memuro Upland Farming Research Station, National Agricultural Research Center for the Hokkaido Region, Memuro, Hokkaido, Japan.

Amylose content The amylose content was estimated by the blue value method as described by Noda *et al.* (1992) without defatting the starch. A 2% starch suspension was prepared by dissolving starch in dimethyl sulfoxide (DMSO) at 70ºC for 3 h and diluting the mix into a 0.1% starch suspension using distilled water. The absorbance at 680 nm was recorded using a Beckman DU-640 Spectrophotometer (Beckman Coulter, Inc., Fullerton, CA, USA) for a mixture (5 ml) containing 0.2 mg of starch, 0.4 mg of iodine (I2), and 4 mg of potassium iodide (KI) after 30 min after color development. The amylose content was then calculated using an equation developed by Asaoka *et al.* (1994): Amylose content = 99.1 × (blue value) – 5.0.

Pasting properties The pasting properties were analyzed using a Rapid Visco Analyzer (RVA-4, Newport Scientific Pty., Ltd., Australia) as described earlier (Wickramasinghe *et al.*, 2003). The peak viscosity, breakdown, final viscosity, setback, pasting temperature, and peak time were recorded for samples, with two replications. The pasting properties, except the pasting temperature and peak time, were expressed in Rapid Visco Units (RVU).

Thermal properties A 30% starch suspension was heated from 25ºC to 130ºC at the rate of 2ºC/min in a sealed sample cell for the analysis of thermal properties by Differential Scanning Calorimeter (DSC 6100, Seiko Instruments, Inc., Tokyo, Japan), as described by Noda *et al.* (2004). A pan with distilled water was used as the reference, and peak gelatinization temperature, onset gelatinization temperature and enthalpy for the starch gelatinization were measured for each sample, with two replicates.

Swelling power A starch slurry, 200 mg of starch (dry weight basis) in 5 ml of distilled water, was gelatinized at 80ºC for 20 min with frequent mixing to avoid the formation of starch clots. Gels were cooled at 20ºC for 5 min and then centrifuged at 1700 g for 5 min. The swelling power was calculated according to Yasui *et al.* (1999) and was expressed as the weight of swelled starch residue per 1 g of starch (dry weight). The analysis was repeated three times.

Enzyme digestibility One milliliter of 2% raw starch suspension was digested with 3.71 units of crystalline glucoamylase from *Rhizopus* sp. (Oriental Yeast Co., Ltd., Tokyo, Japan) for 4 h at 40ºC according to the modified method of Noda *et al.* (1992). The amount of glucose released during enzyme digestion was estimated by the phenol-sulfuric method (Dubois *et al.*, 1956), and enzyme digestibility was calculated as the percentage of glucose released during incubation with the enzyme to the total amount of sugar in the starch on a weight basis.

Data analysis Data were subjected to statistical analysis using Microsoft Excel 2003 software. The means were compared by the least significant difference (LSD) for each property.

Results and Discussion

Blue value and amylose content The blue value and apparent amylose content of rice starches of tested varieties ranged from 0.212 to 0.400 and 16.0% to 34.7%, respectively, and statistical analysis showed a significant variation in the character among tested varieties (Table 1). The apparent amylose contents were relatively high for most samples and higher than the amylose content previously measured by the iodine affinity test (Juliano, 1971) (data not shown). Asaoka *et al.* (1994) proposed the following equation using 33 rice varieties: amylose content = 99.1 × (blue value) – 5.0. All except one were Japonica rice with low amylose. Their amylose content varied from 8% to 31%. The structures of amy-

Table 1. Blue values, apparent amylose content and thermal properties of starches from different Sri Lankan rice varieties.

Variety	Blue value	Apparent amylose content (%)	DSC Thermal properties Peak gelatinization temperature (ºC)	Onset gelatinization temperature (ºC)	Enthalpy (J/g)
Traditional varieties					
Batapola wee	0.400**a**	34.6*	78.8**c**	73.7**d**	14.9**def**
Uvar Rellai	0.393**abc**	33.9	77.5**gh**	72.6**ef**	15.8**bcd**
Kalu Heenati	0.389**bc**	33.5	76.2**k**	70.5**hi**	14.2**fg**
Dik wee 246	0.379**d**	32.6	79.1**bc**	75.4**ab**	16.9**a**
Dewareddari	0.388**c**	33.4	78.6**d**	74.8**bc**	15.2**cde**
Herath Banda 280	0.398**ab**	34.4	77.1**hij**	72.9**ef**	15.5**cd**
Bandara Hethtanawa	0.304**j**	25.1	76.7**j**	70.8**hi**	14.9**def**
Bata Mawee	0.348**g**	29.5	78.0**efg**	71.5**g**	14.5**efg**
Heenati 662	0.399**a**	34.5	77.3**hi**	72.5**f**	17.0**a**
Martin Samba	0.359**f**	30.6	77.3**hi**	70.3**i**	13.7**g**
Suduru Samba	0.262**k**	21.0	76.8**ij**	70.9**h**	14.0**g**
Improved varieties					
BG 357	0.359**f**	30.6	78.8**c**	74.8**c**	16.0**bc**
BG 358	0.326**h**	27.3	78.2**def**	72.8**ef**	12.0**h**
BG 450	0.368**e**	31.5	77.8**fg**	73.5**e**	16.5**ab**
BG 352	0.379**d**	32.6	79.4**b**	75.1**bc**	15.2**cde**
BG 379-2	0.376**d**	32.3	80.0**a**	75.9**a**	15.7**bcd**
BG 300	0.391**bc**	33.7	79.0**bc**	74.6**c**	17.3**a**
AT 306	0.312**i**	25.9	78. 5**de**	73.9**d**	15.5**cd**
AT 405	0.212**l**	16.0	69.4**l**	64.1**j**	14.2**fg**

Values followed by the same letter in the same column are not significantly different at P<0.05 level.
*Mean comparison was not done for this characteristic, as it is derived from blue values.

Table 2. RVA pasting properties of starches from different Sri Lankan rice varieties.

Rice variety	Pasting properties by RVA Peak viscosity (RVU)	Breakdown viscosity (RVU)	Final viscosity (RVU)	Set back (RVU)	Pasting temperature (ºC)	Peak time (min)
Traditional varieties						
Batapola wee	218**k**	146**k**	305**f**	232**de**	84.0**a**	4.47**c**
Uvar Rellai	292**g**	189**g**	371**bc**	269**b**	79.8**f**	4.33**e**
Kalu Heenati	284**h**	183**gh**	332**e**	230**de**	81.5**d**	4.47**c**
Dik wee 246	348**b**	223**c**	351**d**	226**de**	82.3**c**	4.40**d**
Dewareddari	262**j**	155**j**	331**e**	224**ef**	82.3**c**	4.53**a**
Herath Banda 280	270**i**	171**i**	318**ef**	219**ef**	80.6**e**	4.50**b**
Bandara Hethtanawa	332**d**	238**b**	233**g**	149**i**	80.6**e**	4.47**c**
Bata Mawee	333**d**	209**de**	362**bcd**	235**cde**	80.6**e**	4.44**d**
Heenati 662	272**i**	153**jk**	321**e**	203**g**	80.0**f**	4.40**d**
Martin Samba	423**cd**	190**g**	433**a**	285**a**	80.6**e**	4.33**d**
Improved varieties						
BG 357	322**e**	207**ef**	323**e**	209**fg**	82.3**c**	4.40**d**
BG 358	311**f**	217**cd**	367**bcd**	272**ab**	82.7**c**	4.47**c**
BG 450	325**e**	217**cd**	358**cd**	251**c**	80.7**e**	4.33**e**
BG 352	340**c**	213**de**	375**b**	248**c**	82.3**c**	4.33**e**
BG 379-2	281**h**	175**hi**	333**e**	228**de**	83.1**b**	4.40**d**
BG 300	321**e**	199**f**	363**bcd**	242**cd**	81.5**d**	4.33**e**
AT 306	321**e**	243**b**	243**g**	166**h**	82.3**c**	4.40**d**
AT 405	458**a**	380**a**	177**h**	99**j**	73.5**g**	4.00**f**

Values followed by the same letter in the same column are not significantly different at P<0.05 level.

lose (Takeda and Hizukuri, 1986) and amylopectin (Takeda and Hizukuri, 1987) of indica and japonica rice varieties were analyzed, and only a slight variation in the structures of amylose was identified. However, a significantly higher iodine affinity and blue value were observed in amylopectin of indica rice than in that of japonica. Therefore, these higher blue values could cause higher apparent amylose in indica rice.

Pasting properties by RVA All pasting properties were significantly different among the varieties tested (Table 2). The highest peak viscosity, highest breakdown, lowest setback, lowest final viscosity, lowest pasting temperature, and lowest peak time were recorded for variety AT405, which has the lowest amylose content. The opposite characteristics were shown with some traditional varieties that had a higher amylose content, such as Batapola wee, Martin Samba, and Dewaradderi (Table 2). Han and Hamaker (2000) observed that almost all amylose in the granule is leached out at the level of peak viscosity. Thus, the influence of amylose on the breakdown would be very low, even though the peak viscosity could be affected by both amylose and amylopectin (Han and Hamaker, 2001). Our present data indicated a negative correlation between the blue value and breakdown. Thus, further studies on the amylopectin structures of our samples would be useful to analyze the effect of the molecular structure of amylopectin on different pasting properties. Vandeputte *et al.* (2003b), however, concluded that the amylopectin structure had no correlation to the peak, breakdown, final viscosities, and setback. However, they did show that the starting gel point temperature has an influence on the structure of amylopectin.

Swelling power The swelling power at 80ºC also showed a significant variation among the varieties used (Figure 1) and ranged from 7.33 g for AT 405 and 16.12 g per 1 g of dry starch for a traditional variety, Dik wee. AT 405 was the variety with the lowest amylose content, and Dik wee was among the varieties with higher amylose contents of the samples tested. Previously, Lii *et al.* (1995) explained that amylopectin and the crystal region of the starch granule are responsible for swelling and observed high swelling with low amylose in rice. Tester and Morrison (1990) also demonstrated that amylose and lipids actively inhibited swelling in cereal starches.

Raw starch digestibility As with other properties, the raw starch digestibility by fungal crystalline glucoamylase varied significantly among tested samples (Figure 1). AT 405 gave the highest values for enzyme digestibility, and very high resistance to enzymes was shown by some traditional rice varieties, such as Batapola wee and Dik wee. Our results demonstrated that starch hydrolysis tends to be very quick for low amylose starches in comparison to high amylose starches, which was comparable with previous reports

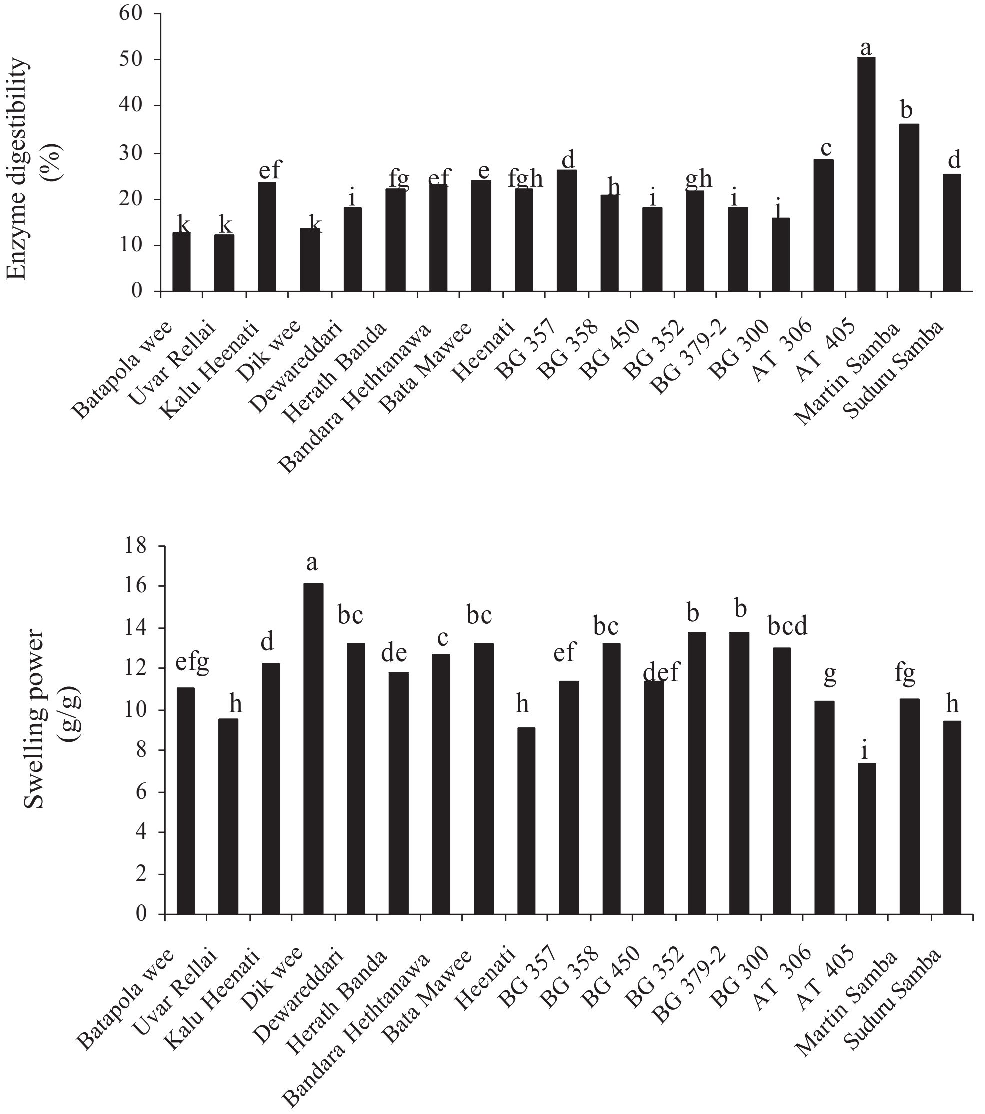

Fig. 1. Swelling power and enzyme digestibility of starches from different Sri Lankan rice varieties. Bars labeled with the same letters are not significantly different at the $P < 0.05$ level.

(Hu *et al.*, 2004; Noda *et al.*, 2003).

Thermal properties by DSC All thermal properties measured by DSC on starch gelatinization had significant variations among the varieties under investigation (Table 1). Starches with low amylose, such as AT 405, gelatinized easily and required low energy for the gelatinization. Some traditional varieties, such as Dik wee, Heenati, and a new improved variety, BG 300, required very high energy for gelatinization. Generally, these varieties had higher amylose in starch. The peak gelatinization temperature and onset gelatinization temperature of our samples ranged from 69.4 to 80.0ºC and 64.1 to 75.9ºC, respectively. The enthalpy for starch gelatinization varied from 12.0 to 17.3 J/g.

Correlation analysis among tested characteristics of rice The blue value of tested varieties showed significant correlations with all other properties, thus again proving the importance of amylose content as a major factor determining starch properties (Table 3). The highest correlation (0.92) was shown with the breakdown at RVA, and the least was shown with the blue value (0.46). The relationships of the blue value with the peak viscosity, breakdown, and enzyme digestibility were negative, while all others were positive. Similar relationships were also found in previous studies, such as negative relationships with peak viscosity and breakdown (Collardo and Corke, 1997; Hu *et al.*, 2004; Vandeputte *et al.*, 2003b; Zeng *et al.*, 1997) and enzyme digestibility (Noda *et al.*, 2003), and positive correlations with thermal properties such as peak gelatinization temperature and enthalpy for starch gelatinization by DSC (Prathepha *et al.*, 2005; Saif *et al.*, 2003).

As for the RVA parameters, very high correlations between the blue value and all RVA parameters have been al-

Table 3. Correlation coefficients among tested starch properties in Sri Lankan rice varieties

Property	Peak viscosity	Breakdown viscosity	Final viscosity	Set back	Pasting temp.	Peak time	Swelling power	Enzyme digestibility	Peak gel. temp	Onset gel. temp.	Enthalpy
Blue value	-0.72**	-0.92**	0.68**	0.71**	0.66**	0.63**	0.46*	-0.87**	0.69**	0.70**	0.47*
Peak viscosity		0.80**	-0.14	-0.30	-0.66**	-0.76**	-0.25	0.69**	-0.58**	-0.62**	-0.23
Breakdown viscosity			-0.61**	-0.67**	-0.74**	0.79**	-0.34	0.80**	-0.75**	-0.67**	-0.21
Final viscosity				0.96**	0.48*	0.32	0.41	-0.63**	0.61**	0.48*	0.01
Set back					0.57*	0.41	0.39	-0.72**	0.64**	0.51*	-0.08
Pasting temperature						0.79**	0.66**	-0.77**	0.93**	0.87**	0.08
Peak time							0.55*	-0.66**	0.70**	0.62**	-0.03
Swelling power								-0.61**	0.67**	0.67**	0.14
Enzyme digestibility									-0.80**	-0.77**	-0.40
Peak gelatinization temperature										0.95**	0.30
Onset gelatinization temperature											0.45

** and * indicate significance at $P < 0.01$ and $P < 0.05$ levels, respectively.

ready described. Apart from significant correlations among some RVA parameters, they all were highly correlated to enzyme digestibility, peak gelatinization temperature, and onset gelatinization temperature at DSC. Furthermore, the pasting temperature and peak time showed significant correlations with the swelling power. No relationships were found between the peak viscosity and the final and setback viscosities or between the setback and the peak time.

According to the correlation coefficients given in Table 3, the swelling power showed significant correlation with the blue value (0.46), peak (0.67) and onset (0.67) gelatinization temperatures by DSC, and pasting temperature (0.66) and peak time (0.55) by RVA, proving the importance of amylopectin, its structure, and relative crystallinity for this property. In the present study, the relationship between the blue value and swelling power was positive. Even though this correlation is statistically significant, it was the least significant correlation shown by the blue value among other tested characteristics.

The enzyme digestibility showed negative correlations to all characteristics, except the peak viscosity and breakdown at RVA and the gelatinization enthalpy at DSC. The enzyme digestibility showed the highest correlation to the blue value (0.87), indicating that the amylose content of rice starch is of great importance in predicting the enzyme digestibility of starch. Our results showed that starch containing low amylose started gelatinization at lower temperatures. While heating and cooling, such starch slurry showed higher peak and breakdown viscosities but resulted in a softer gel. Such starch is also easily digestible by enzymes. These properties are probably associated with the reduced compactness in the amorphous area of starch granules and that may facilitate the easy absorption of water to the granule and speed up the disorganization of starch with heating.

Excepting the blue value, no other properties have a significant impact on enthalpy for starch gelatinization. Interestingly, none of the pasting properties measured by RVA correlated to the enthalpy for starch gelatinization as estimated by DSC. Lai *et al.* (2001) proved that the gelatinization properties varied due to the molecular structure of amylopectin and amylose by using two rice cultivars with apparently similar amylose content. From the amylose in the granule, absolute amylose and free amylose could facilitate gelatinization, whereas lipid complex amylose delayed it (Vandeputte *et al.*, 2003a). Furthermore, the same authors expressed that short amylopectin chains with DP 6–9 and long amylopectin chains with DP 12–22 decreased and increased the gelatinization temperatures of rice starch, respectively. Since the amylose content in our samples correlated significantly (0.69) to the peak gelatinization temperature, the amylopectin structure and relative crystallinity of the granule would be the other factors governing gelatinization temperature.

Conclusion

According to the correlation analysis, the amylose content proved to be the most important factor in determining the physico-chemical properties of rice starch. As all properties varied significantly among the varieties tested, the information derived from this study will be useful in future research applications.

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