

Carbohydrate Polymers 38 (1999) 161-170

### Carbohydrate Polymers

# Cassava starch granule structure—function properties: influence of time and conditions at harvest on four cultivars of cassava starch

K. Sriroth<sup>a,\*</sup>, V. Santisopasri<sup>b</sup>, C. Petchalanuwat<sup>c</sup>, K. Kurotjanawong<sup>a</sup>, K. Piyachomkwan<sup>d</sup>, C.G. Oates<sup>e</sup>

<sup>a</sup>Department of Biotechnology, Kasetsart University, Bangkok, Thailand.

<sup>b</sup>Department of Biochemistry, Kasetsart University, Bangkok, Thailand.

<sup>c</sup>Department of Agriculture, Ministry of Agriculture, Thailand.

<sup>d</sup>Cassava Starch Technology Research Unit/National Center for Genetic Engineering and Biotechnology, Thailand.

<sup>c</sup>Department of Biochemistry, National University of Singapore, Singapore.

Received 12 January 1998; received in revised form 11 May 1998; accepted 18 June 1998

#### **Abstract**

Impact of environmental conditions on cassava starch variability was examined by studying four commercially important cultivars, Rayong 1, Rayong 60, Rayong 90, and Kasetsart 50 (KU 50). Age of the root and environmental conditions at harvest influenced granule structure and hydration properties. All cultivars were grown under identical field conditions, and harvested at different times. Starches extracted from cassava roots harvested at different times were characterised by unique starch granule structure and function. Apparent amylose size of starches from all cultivars did not change significantly during the trial period. However, apparent amylose content of starches changed, decreasing in the older roots. Granule size distribution was affected by age of the root, gradually changing from normal to bimodal distribution when harvested very late during the trial. The integrity and crystalline structure of starch granules also depended on the environmental conditions, evidenced as a change in peak profile obtained by thermal analysis. This can result in the difference in water uptake of starches, and their consequent swelling power and gelatinization. Pasting temperature of all starches increased during the dry period, and was lowered during the wet period. Peak and final viscosity of starch decreased from early to mid-harvest time when environmental conditions became drier, and increased close to or greater than the original value when conditions became wet again. Breakdown and setback also followed a similar trend to viscosity. This study suggests an impact of time and conditions of harvest on the structural and functional properties of all cassava cultivars, and based on this study, it is recommended that starch should be extracted from either early or very late harvested roots. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Cassava starch; Rayong 1; New cassava cultivars

#### 1. Introduction

Ensuring consistent quality of cassava starch remains a problem despite advances and upgrading of technology used for the extraction of this material. Variation derived from different cultivars accounts for some of the deviation between processing operations in Thailand. However, within a geographic area single cultivars tend to dominate and therefore it is unlikely that this is a source of variation for starch produced in the same factory at different times of the year. Variation reportedly can significantly alter the

functional properties of the starch making application of the native material difficult in some circumstances.

In Thailand a number of cultivars of cassava are grown for commercial purposes. One of the first cultivars to be developed for improved economic return was Rayong 1, which is a selection from a local land race. Due, in part, to its excellent agronomic traits (Rodjanaridpiched et al., 1993) more than 1 million hectares are planted annually to this cultivar. Since 1984, and in parallel with the growth of the cassava industry, several new cultivars suitable for industrial purposes have been developed, including Rayong 3, Rayong 60, Rayong 90 and Kasetsart 50 (Table 1).

Agronomic characteristics of the four cultivars summarized in Table 1 have been examined in extensive trials, designed to determine the most suitable time for harvest, either early (9 months) or late (12 months). The largest trial,

<sup>\*</sup> Corresponding author. Klanarong Sriroth, Cassava and Starch Technology Research Unit, Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI), Kasetsart University, Bangkok 10900, Thailand. Tel.: 662 9405634; Fax: 662 9405634; e-mail: aapkrs@ku.ac.th

Table 1 Recommended cassava cultivars in Thailand

Cultivar	Year released	Parents	Main features
Rayong 1 Rayong 60 Rayong 90 Kasetsart 50	1957 1987 1991 1992	From local cultivars Mcol 1684 * Rayong 1 CMC 76 * V43 Rayong 1 * Rayong 90	High yield, good adaptability Early harvest, high yield High root DM, high yield High root Dm, high yield, good adaptability

conducted at 9 locations in 1994, evaluated the influence of time of harvest on fresh root yield, dry root yield and root dry matter (Rodjanaridpiched et al., 1993). For all cultivars wet root yield was higher at 12 months but dry root yield and root dry material was lower at this time. However, these studies did not evaluate quality of starch produced at the different harvest times, or consider the intervening months. The rate of decrease of dry root yield was greatest for Rayong 60 and Rayong 1.

Plants harvested at 12 months were found to be responding to climatic change, associated with transition from dry to wet season. The authors concluded that post dry season the plants renew their top growth at the expense of root growth, resulting in a reduction of root dry matter content. This response to re-growth was variable between the cultivars.

Cassava roots are harvested manually with a little help from small tools. The harvest can be through the year except in the rainy season (June/July/August). From age of 12 months, the roots are considered as ripe and are often left in the ground until 14–16 months, depending on the economic situation. The young roots contain more water and less starch ( < 20%) as compared with older roots (more than 12 months), but extractability of starch from the older roots is more difficult due to a higher fiber content.

In general, starch structure-function properties alter according to the stage of development of the plant and the botanical source. Demonstrated by most cereals, amylose content is lower at early stages of grain development (Inouchi et al., 1984; Asaoka et al., 1985). A similar trend

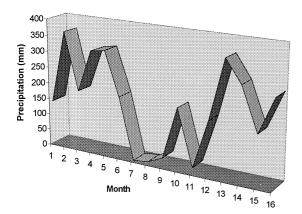


Figure 1. Rainfall during the growing period. Monthly values represent the accumulative rainfall in the previous four weeks.

between amylose content ad developmental age is also seen in potato, where increasing root size is associated with a greater amylose content (Geddes et al., 1965). This is, however, not the case during development of tuberous roots such as cassava (Asaoka et al., 1992) or sweet potato (Noda et al., 1992).

Previous work has demonstrated that both genetic constitution and environmental conditions influence functional properties of the starch, including gelatinization properties (Asaoka et al., 1992). However, this work did not fully describe the influence of rainfall, which will promote canopy growth, on starch functional properties. These factors will be investigated in this article which forms part of a larger study mapping the influence of environmental conditions on starch structure-function properties.

The present study attempts to provide a more detailed understanding of environmental influences and age of the root on quality and functional properties of the extracted starch. This information is important for a number of reasons, primarily it could form the basis of a model to probe structure-function relationships of cassava starch. Understanding the reasons responsible for variability of this starch is required both by the processor and user, hopefully a better appreciation of the mechanisms responsible for variation will lead to the production of higher quality starch.

#### 2. Materials and methods

#### 2.1. Materials

Cassava plants were planted in May 1995 at Rayong Field Crops Research center, Department of Agriculture, Thailand using Split-plot in Randomized Complete Block (RCB) design. During growth, fertilizer (15-15-15) was applied at the rate of 312.5 kg/ha. No extra irrigation was applied. Precipitation was as indicated in Fig. 1.

Soil conditions for the experiment area were; pH 5.4, organic matter content 0.5%, phosphorus and potassium content 24 and 20 ppm, respectively.

Roots were manually harvested each month and samples representing all experimental cultivars collected and analyzed for starch content by a specific gravity method as described by Brautlecht (1953). Starch extraction was conducted within 12 h of harvesting using water as extraction solvent and a laboratory blender for breaking the plant

Table 2 Effect of cultivars and harvesting date on average starch content (%) and yield (ton/ha) of cassava roots.

Cultivars	Age (month)									
	6 10 Starch content (%) Yield (ton/ha) Starch content	Yield (ton/ha)	10 Starch content (%)	Yield (ton/ha)	12 Starch content (%) Yield (ton/ha)	Yield (ton/ha)	14 16 Starch content (%) Yield (ton/ha) Starch content (%) Yield (ton/ha)	Yield (ton/ha)	16 Starch content (%)	Yield (ton/ha)
Rayong 1	18.1	11.3	13.8	17.1	18.6	25.8	23.0	27.7	21.9	22.2
Rayong 60	17.2	7.5	15.4	13.6	19.0	21.8	22.6	28.3	19.7	30.4
Rayong 90	23.3	10.9	20.8	23.1	27.1	34.0	29.1	43.7	26.1	44.5
Kasersart 50		8.0	19.3	16.8	24.7	21.8	27.4	28.5	24.4	31.9

Table 3 Proximate analysis of cassava starches.

Cultivars	Protein (% w/w)	Lipid (% w/w)	Ash (% w/w)	Phosphorus (mg/kg)	
Rayong 1	$0.17 \pm 0.04$	nil	$0.10 \pm 0.02$	$2.45 \pm 0.08$	
Rayong 60	$0.15 \pm 0.02$	0.01	$0.15 \pm 0.04$	$2.20 \pm 0.14$	
Rayong 90	$0.28 \pm 0.06$	nil	$0.08 \pm 0.01$	$2.04 \pm 0.05$	
KU 50	$0.30 \pm 0.04$	0.01	$0.15 \pm 0.02$	$2.04 \pm 0.05$	

tissue to liberate the starch granules. Fiber was separated by sieving through a 170-mesh screen (90  $\mu$ m). After washing several times, starch was oven dried at 50–55°C. Starch properties were analyzed immediately on production with suitable controls to ensure reproducibility of the methods between analysis periods.

#### 2.2. Proximate analysis

The content of protein, fat and ash were determined according to AOAC methods (AOAC, 1990). The amount of phosphorous was quantified by the method described by FAO (Food and Agricultural Organization of the United Nations, 1988).

#### 2.3. Scanning electron microscopy

Dried starch samples were prepared for observation by scanning electron microscopy by sprinkling the starch on double-sided adhesive tape attached to a circular specimen stub and coating with gold using a Baltzers SCD 004 sputter coater. The samples were viewed and photographed using a JEOL JSM-5300LV scanning electron microscope on AGAFAPAN-APX 100 film.

#### 2.4. Sonication for HPSEC

An aqueous starch slurry (20 mg in 15 ml) was gelatinized at 100°C for 10 min, cooled to 50°C and sonicated. Samples, 15 ml, were sonicated in tubes (internal diameter, 20 mm) using a Sonicator<sup>TM</sup> Cell Disrupter, model XL-2020 (Heat systems – Ultrasonic, Inc.) and Misonix probe (external diameter, 4 mm) (Model 419A). Power was set at 45% of the maximum 550 W (output frequency 20 kHz).

#### 2.5. Amylose Size

The proportion of the major starch fractions and apparent molecular size of amylose after sonication were determined by high performance size exclusion chromatography (HPSEC) according to the method of Govindasamy et al. (1992).

#### 2.6. Swelling and Solubility

Swelling and solubility determinations were carried out at 95°C by the procedure of Schoch (1964).

#### 2.7. Differential scanning calorimetry

Gelatinization properties of the starches were analyzed using a Perkin Elmer Differential Scanning Calorimeter (DSC7; Norwalk, CT) equipped with an intercooler. Aluminum pans (Perkin Elmer) were used for the analysis. Starch samples were slurried with water to give a volume fraction between 0.68-0.69. The starch slurry was dispensed, after mixing, into empty aluminum pans and hermetically sealed. Following equilibration at room temperature for 1 h the samples were heated from 20 to 110°C at a heating rate of 10°C/min. An empty pan was used as reference. Enthalpy changes, integrated using DSC software, were calibrated on the basis of the melting of indium metal. All pans were reweighed after cooling. To calculate enthalpy values accurately on a dry basis, each pan was carefully punctured, dried at 110°C for 2 h and reweighed to determine moisture content of the scanned and rescanned samples.

#### 2.8. Granule size distribution

Granule size distribution was determined by image analysis (Carl Zeiss, KS400 v2) recorded directly from a Carl Zeiss Axiophol 2 microscope. Starch samples were suspended in 80% sucrose solution to minimize the effects of refractive index and provide a sharper image of the granules (Baldwin, 1994).

#### 2.9. Pasting profiles

Pasting profiles were recorded on a RVA 4 (Newport Scientific, Australia) using standard program Number 1. The starch sample was 3.00 g (on 14% moisture basis). The starch suspension was held at 50°C for 1 min and subsequently heated to 95°C at 12.2°C/min. Holding time at 95°C was 2.5 min. Subsequently, the sample was cooled to 50°C at 12.2°C/min, where it was kept for 2.1 min. A rotation speed of the paddle of 160 rpm was used and cooling was performed with water circulated through cooler.

#### 3. Results and discussion

During the study two rainy seasons were recorded, the first coinciding with planting and the second in the later months of the trial. Months 7, 8, 9 and 11 were comparatively dry months interspersed with one wet month (month

Table 4 Apparent size and content of amylose in cassava starch at different harvest time<sup>a</sup>.

	Time of l	harvest / months						
	6		10		14		16	
	Dp	Content <sup>b</sup> (%)	DP	Content <sup>b</sup> (%)	DP	Content <sup>b</sup> (%)	DP	Content <sup>b</sup> (%)
Rayong 1	1175	24.1	1188	23.5	1148	20.6	1161	20.6
Rayong 60	1122	22.5	1096	20.5	1035	20.7	1148	20.8
Rayong 90	1202	23.1	1216	21.3	1122	22.3	1135	22.5
KU 50	1175	21.4	1161	21.5	1135	19.5	1121	19.6

 $<sup>^{\</sup>rm a}$  Values are the mean of five determinations, the range of each values was  $<~\pm~0.2\%$ 

## 10). The roots were harvested at 6, 10, 12, 14 and 16 months.

Previous work (unreported) suggested that rainfall had a strong influence if high in the month immediately prior to harvest. However, time of harvest was not a major determinant during the growing period up to 16 months. For this reason and in order to investigate the influence of cumulative conditions, samples were harvested during only "wet" months, and harvesting pre and post dry period was during months that had experienced a similar level of rainfall.

For all cultivars, starch content was lowest at 10th month (Table 2). Plants harvested in the 10th month were subjected to heavy rainfall in the previous four weeks. Prior to which, drought conditions had prevailed for about 2 months. Starch content increased again and reached the maximum at 14th month. In general, root yield increased with a greater age of the cassava plant.

The proximate composition of the starches is presented in Table 3. Starches from different cultivars were low in lipid

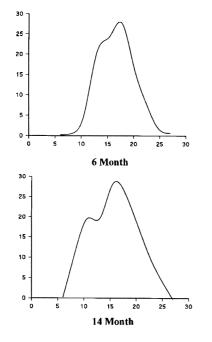
(<0.01%), protein (0.15%-0.30%), ash (0.08%-0.15%) and phosphorous (2.04-2.45 mg/kg). Values were in the range expected for cassava starches (Rickard et al., 1991).

#### 3.1. Starch structure

#### 3.1.1. Macromolecule components

Starch structure was different if extracted from cassava harvested prior to the onset of the rainy season. Apparent amylose size did not appear to be influenced by either age of the root or growing conditions immediately prior to harvest (Table 4).

The proportion of amylose changed within a narrow band during the period of the trial. Starch extracted from roots harvested late in the trial, (14th and 16th month), was generally lower in amylose content (Table 4). Previous studies (Inouchi et al., 1984; Asaoka et al., 1985) have reported a variability of amylose content as influenced by time of harvest. In cereals and potato amylose increases in later



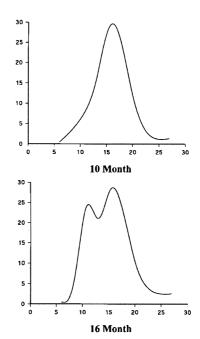


Figure 2. Rayong 1 size distribution profile. A representative example for cassava starch granules obtained from Rayong cultivars as influenced by time of harvest. X axis represents the size of starch granule in micron whereas Y axis represents the percentage of distribution.

<sup>&</sup>lt;sup>b</sup> Amylose content, expressed as a percentage of the total granule carbohydrate

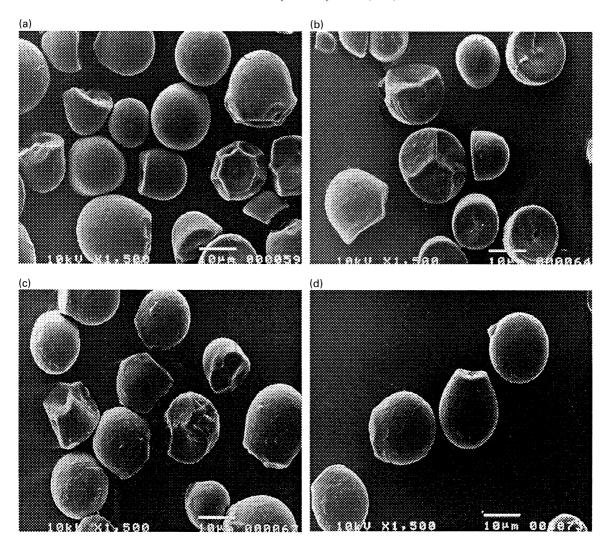


Figure 3. Scanning electron photomicrographs of cassava starch from Rayong 60 at different harvest times (a) 6th, (b) 10th, (c) 14th and (d) 16th month.

stages of development (Inouchi et al., 1984; Asaoka et al., 1985; Gedds et al., 1965). In comparison for cassava and sweet potato there was little difference in amylose content (Asaoka et al., 1992; Noda et al., 1992). Results of the present study are not in agreement with those of Asaoka et al. (1992), amylose content was highest (for all cultivars) at the early harvest time, but dropped to a constant level during the dry period. In two samples, Rayong 60 & 90, amylose content decreased during the extended dry period. For the other two samples amylose decreased during the dry period and continued the trend into the wet period. This suggests that influences on amylose content are more complicated than length of time in the ground.

#### 3.2. Starch granule

The size and morphological appearance of the starch was as expected for cassava starch (Rickard et al., 1991).

Size distribution of the granules followed a trend similar to swelling with respect to harvest time. Slight differences

are evident between cultivars (Fig. 2), though with the exception of KU 50, all were similarly effected by condition at harvest.

The range of granule sizes approached a normal distribution in samples harvested up to 14th month. For all cultivars the mean size was centered at about 15  $\mu$ m and the distribution was from about 8–22  $\mu$ m. There was no significant shift in the mean granule size with harvest time, but for all Rayong cultivars there was a slight shoulder at about 12  $\mu$ m, which developed to such an extent that by the 16th month granule size was bimodally distributed. The two distinct populations of granule were centered at about 15 and 12  $\mu$ m. In contrast, size distribution for granules of Ku 50 appeared to be similar for all times of harvest and normally distributed.

Electron micrographs suggest that granules are considerably irregular in shape with oval, round and truncated granules present within the same sample. There were no apparent differences, between species with respect to granule morphology (Fig. 3 and data not shown).

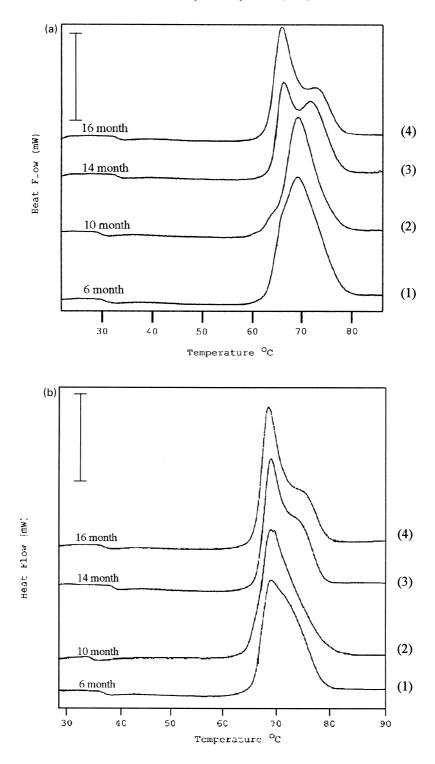


Figure 4. Representative thermoanalysis profiles for cassava starch harvested at different times. (a) Rayong 90; (b) KU 50. Dry sample weight: (a) Rayong 90 (1) 4.54, (2) 4.22, (3) 4.34 and (4) 4.50 mg for 6, 10, 14 and 16 months respectively; (b) KU 50 (1) 4.56, (2) 4.48, (3) 4.45 and (4) 4.51 mg for 6, 10, 14 and 16 months respectively. The bar corresponds to 1 mW.

Comparative information on the integrity and crystal structure of starches can be obtained by thermal analysis. For starches in this study, intercultivar comparisons are only possible for starches collected in the early months. There were only slight difference between the cultivars in respect

to gelatinization temperature and enthalpy. Peak temperatures ( $T_p$ ) were similar for all cultivars and in the range 69–71°C (Kasetsart 50 and Rayong 90/Rayong 1 respectively) (Fig. 4). Starches extracted from roots harvested in later months of the trial exhibited unusual thermal properties

Table 5 Swelling power of cassava starch at 95°C as influenced by time of harvest.

	Time of ha	arvest (months	s)		
	6	10	12	14	16
Rayong 1	55 ± 1	58 ± 7	59 ± 7	53 ± 1	51 ± 2
Rayong 60	$58 \pm 7$	$61 \pm 4$	$54 \pm 7$	$48 \pm 1$	$45 \pm 6$
Rayong 90	$60 \pm 6$	$59 \pm 2$	$55 \pm 2$	$59 \pm 7$	$66 \pm 1$
KU 50	$54 \pm 4$	$77 \pm 12$	$64 \pm 3$	$51 \pm 1$	$51 \pm 2$

that made comparison between the starches difficult. The single endothermic peak evident in samples harvested early in the study developed into a biphasic peak with concomitant increase in temperature of the original peak (Fig. 4). In this study starch samples were hydrated to a point close to that known to influence the gelatinization mechanism. For starch water mixtures containing more than 60% water (WSB) a single symmetrical endothermic peak is usually observed. At moisture contents lower than the critical point, size of the transition progressively decreases with concomitant development of a second transition. The later peak moves to higher temperature as the amount of water is further reduced.

Differences in thermal behavior as influenced by moisture content are assumed indicative of non-equilibrium melting and support the notion that structure reorganization during heating is water dependent. At lower moisture, melting temperature and transition can not be accurately determined because of the resulting broad fusion range.

Temperature of gelatinization (T<sub>P</sub>, T<sub>o</sub>, T<sub>f</sub>) for cassava

starch is variably reported in the literature, values  $(T_p)$  range from as low as 58°C (Asaoka et al., 1992) to as high as 65°C (Yamada et al., 1987) for cassava starch from Thailand. Such differences suggest that genetic variation and environmental conditions impact on structure-function of the starch. Comparisons with the current study would be difficult, as the moisture content is lower than that customarily used for starch thermoanalysis. Though the range recorded in this study for  $T_P$  (69–71°C) is comparable, considering the lower moisture content. Studies at high moisture confirm that the gelatinization temperature  $(T_P)$  is as expected at 66°C (data not presented).

Root and cereal starches are assumed to have similar melting mechanisms. The melting of starch granules is governed by the speed in which water can enter the starch granule. The event is thought to comprise of two stages, involving plasticizing of the amorphous amylose followed by hydration and melting of the crystallites. In excess water rapid plasticizing can occur and the two endotherms merge as one, in the range of the single endotherm, as the rate of water penetration will be the same as the rate of crystallite disruption. At intermediate water conditions the endothermic peak splits forming a biphasic endotherm, as the amorphous regions are slowly plasticized causing a delay in hydration which forces gelatinization temperatures towards higher regions.

This study suggests that starch granules may differ in their response to water uptake and consequent gelatinization, depending on environmental conditions. This phenomenon is not apparent when samples are examined at higher

Table 6
Pasting properties of cassava starch as influenced by time of harvest.

	Pasting temperature (°C)	Peak viscosity (RVU)	Trough (RVU)	Final viscosity (RVU)	Breakdown*	Setback*
Rayong 1						
6	$71.35 \pm 0.35$	$419 \pm 21^{b}$	$169 \pm 17$	$284 \pm 10^{a}$	$250 \pm 6^{b}$	$115 \pm 12^a$
10	$71.38 \pm 0.04$	$363 \pm 10^{\circ}$	$154 \pm 17$	$221 \pm 10^{c}$	$209 \pm 7^{c}$	$67 \pm 8^{c}$
12	$72.60 \pm 0.76$	$357 \pm 2^{c}$	$158 \pm 8$	$205 \pm 10^{\circ}$	$200 \pm 10^{c}$	$47 \pm 4^{d}$
14	$72.00 \pm 0.64$	$436 \pm 33^{b}$	$160 \pm 20$	$245 \pm 16^{b}$	$265 \pm 29^{b}$	$74 \pm 12^{bc}$
16	$71.08 \pm 0.35$	$502 \pm 4^{a}$	$182 \pm 15$	$268 \pm 10^{ab}$	$324 \pm 14^{a}$	$85 \pm 5^{\mathrm{b}}$
Rayong 60						
6	$70.98 \pm 0.16$	$402 \pm 12^{ab}$	$156 \pm 3^{ab}$	$266 \pm 10^{a}$	$246 \pm 15^{ab}$	$111 \pm 11^{a}$
10	$71.30 \pm 0.99$	$382 \pm 25^{bc}$	$156 \pm 18^{ab}$	$238 \pm 13^{b}$	$226 \pm 24^{b}$	$82 \pm 6^{b}$
12	$70.80 \pm 0.57$	$336 \pm 11^{c}$	$133 \pm 8^{c}$	$183 \pm 8^{c}$	$203 \pm 12^{b}$	$50 \pm 4^{c}$
14	$70.30 \pm 0.64$	$351 \pm 37^{c}$	$147 \pm 7^{bc}$	$196 \pm 3^{c}$	$205 \pm 47^{b}$	$50 \pm 7^{c}$
16	$69.50 \pm 0.78$	$459 \pm 45^{a}$	$169 \pm 4^{a}$	$265 \pm 14^{a}$	$288 \pm 41^{a}$	$96 \pm 13^{ab}$
Rayong 90						
6	$71.10 \pm 0.82$	$396 \pm 3^{b}$	$145 \pm 21$	$271 \pm 10^{a}$	$251 \pm 20^{b}$	$125 \pm 13^{a}$
10	$72.90 \pm 0.79$	$395 \pm 27^{b}$	$157 \pm 31$	$243 \pm 19^{a}$	$239 \pm 15^{b}$	$71 \pm 4^{b}$
12	$72.10 \pm 0.49$	$304 \pm 2^{c}$	$158 \pm 14$	$177 \pm 4^{b}$	$150 \pm 18^{d}$	$23 \pm 20^{\circ}$
14	$72.07 \pm 0.40$	$351 \pm 53^{bc}$	$163 \pm 23$	$244 \pm 31^{a}$	$198 \pm 30^{c}$	$69 \pm 22^{b}$
16	$70.68 \pm 0.66$	$480 \pm 12^{a}$	$177 \pm 6$	$262 \pm 6^{a}$	$302 \pm 15^{a}$	$84 \pm 8^{b}$
KU 50						
6	$72.57 \pm 0.70^{bc}$	$439 \pm 4^{b}$	$174 \pm 13$	$278 \pm 17$	$265 \pm 9^{b}$	$98 \pm 6^{a}$
10	$74.32 \pm 0.60^{a}$	$369 \pm 4^{c}$	$145 \pm 19$	$213 \pm 23$	$214 \pm 7^{c}$	$69 \pm 4^{ab}$
12	$73.22 \pm 0.$	$435 \pm 1^{b}$	$170 \pm 27$	$224 \pm 26$	$254 \pm 27^{ab}$	$54 \pm 8^{b}$
14	$71.25 \pm 0.42^{cd}$	$404 \pm 26^{c}$	$160 \pm 4$	$253 \pm 29$	$243 \pm 28^{ab}$	$92 \pm 31^a$
16	$70.38 \pm 0.53^{d}$	$531 \pm 8^a$	$164 \pm 4$	$261 \pm 13$	$369 \pm 6^{a}$	$92 \pm 17^a$

or lower moisture contents. The precise mechanism is not known, but would appear to be subtle and assumed to represent structural differences that cause an apparent variation in the rate of hydration for late harvested samples. For starches extracted from other botanical sources physical properties of starch granules, such as gelatinization temperature, are affected by environmental temperature during growth. This is probably not a key issue in tropical crops where temperature varies very little during the year. However, variation in rainfall could lead to differences in soil temperature in the immediate environment of the growing roots. Tempering, mechanical damage and thermal history of the starch during extraction and drying may also influence thermal properties. This is unlikely to be the case in this study, granules look to be morphologically similar and care was exercised during the extraction, ensuring experimental uniformity throughout.

#### 3.3. Hydration properties

Swelling power of starches followed less of a general trend in some samples, for example Rayong 60 and KU 50 (Table 5). For Rayong 60 starch, swelling power was higher when extracted from root harvested at 6, 10 and 12 months. Swelling power of KU 50 peaked in the 10th month, and then decreased through the extended growing period. For Rayong 1 and Rayong 90, swelling power did not decrease with a similar trend, suggesting that their swelling power might be affected by other factors such as granule size, structure and composition.

#### 3.4. Pasting properties

To detect pasting differences, Rapid Visco Analyser (RVA) was used (Table 6). Pasting temperatures were little effected by harvest time irrespective of the cassava cultivar. Viscosity was high in samples harvested at 6th month, however at the 10th month peak viscosity dropped, reaching a low value by the 12th month for all Rayong cultivars and the 10th month for KU 50. The level of decrease ranged from 15%-23% for Rayong cultivars and 16% for KU 50. With further growing time in the wet season, roots produced starch with a peak viscosity higher than that of the 6th month harvested sample; the percentage increased ranged from 14%-21%, when comparing the increase in peak viscosity between 6th and 16th month samples. Final viscosity followed a similar trend to that of peak viscosity; being low at 10th-12th month, and becoming high again in the wet season at 14th-16th month. At age of 6th month, all cultivars showed the most susceptibility to breakdown and setback, then the viscosity became more stable until the age of 14th-16thmonth. The change in breakdown and setback was compatible with the change in peak and final viscosity of starch solutions, and also the amylose content, implying a relation between pasting properties and amylose content. The root at 6th month contained high amylose content (21%-24%), and produced starch with high final

viscosity and setback. Amylose content of starch decreased later during the dry period, and was also lower in final viscosity and setback. Starch content of the roots was also lowest at 10 months, suggesting utilization of starch by the plant with the onset of rain, immediately post dry period (Table 2). It is reasonable to assume that the internal architecture of the granules will be different, as they will contain a lower proportion of amorphous material. These structural changes are assumed to impact on the functional properties of the starch and are presently being studied.

#### 4. Conclusions

Previous work has shown differences between starch harvested at two extreme times, but the current work suggests that starch properties can change in mid-cycle.

Results of this study also show that starch granules differ in their response to water uptake and consequent gelatinization depending on the environmental conditions at the time of harvest, expressed as a change in peak profile obtained by thermal analysis for samples harvested at 14th and 16th month. This change is similar to that seen when moisture content is reduced. The precise mechanism is not known, and is not evident at higher or lower moisture content. This effect is therefore subtle, but real, and can be assumed to arise from structural differences, which give rise to apparent variation in the rate of hydration for late harvest samples. All the cultivars examined show this phenomenon. In a similar manner the size distribution profile of the granules changed from a normal distribution, gradually developing into a bimodal distribution. Again the mechanism is not known, and we are unable to speculate whether the two phenomena are related.

This study also suggests that starch extracted from roots harvested late will have good pasting and swelling properties. This may be related to the large amylose size in these starches or greater proportion of amylopectin. The dry season has an impact on starch properties, as does the immediate onset of the rainy season. We would therefore recommend based on these findings that starch be extracted from either early or very late harvested roots.

The work reported in this article forms part of a more detailed project to probe the structure-function relationships of cassava starch, future efforts will involve the production of cassava under controlled environmental conditions with subsequent isolation and characterization of structural or functional features of the starch unique to a particular set of environmental conditions.

#### Acknowledgements

This work was kindly supported by Thai Tapioca Development Institute (TTDI) and National Center for Genetic Engineering and Biotechnology (BIOTEC), Ministry of Science, Technology and Environment, Thailand. Technical

assistance of Miss Lee Woan Ping, National University of Singapore is gratefully acknowledged.

#### References

- Asaoka, M., Blanshard, J. M. V., & Rickard, J. E. (1992). Effects of cultivar and growth season on the gelatinization properties of casava starch. Journal Science Food & Agriculture, 59, 53–58.
- Asaoka, M., Okumo, K., Sugimoto, Y., & Fuwa, H. (1985). Developmental changes in the structure of endosperm starch of rice (Oryza sativa L.). Agric. Biol. Chem., 49, 1973–1978.
- Association of Official Analytical Chemists (AOAC) (1990). *Official method of analysis* (15th ed.). Virginia: The Association of Official Agricultural Chemists.
- Baldwin, P. M. (1994). Holes in starch granules: confocal. SEM and light microscopy studies of starch granule structure. Starch/Starke, 46, 341–346.
- Brautlecht, C.A. (1953). Starch: its sources, production and uses. New York: Reinhold.
- Food and Agricultural Organization of the United Nations. 1988 Specifications for Identity and Purity. FAO Food and Nutrition Paper.
- Geddes, R., Greenwood, C. T., & Mackenzie, S. (1965). Studies on the biosynthesis of starch granules. Carbohydrate Research, 1, 71–82.

- Govindasamy, S., Oates, C. G., & Wong, H. W. (1992). Characterisation of changes of sago starch components during hydrolysis by thermostable alpha-amylase. Carbohydrate Polymers, 18, 89–100.
- Inouchi, N., Glover, D. V., Sugimoto, Y., & Fuwa, H. (1984). Developmental changes in starch properties of several endosperm mutants of maize. Starch/Starke, 36, 8–12.
- Noda, T., Takahatana, Y., & Nagata, T. (1992). Developmental changes in properties of sweet potato starches. Starch/Starke, 44, 405–409.
- Rickard, J. R., Asoaka, M. A., & Blanashard, J. M. V. (1991). The physicochemical properties of cassava starch. Tropical Science, 31, 189–207.
- Rodjanaridpiched, C., Limsila, A., Suprahan, D., Boonsenf, O., Poolsanguan, P., Tiraporn, C., & Kawano, K. (1993). Recent progress in cassava varietal improvement in Thailand. In R.H. Howelr (Ed.), Cassava breeding, agronomy research and technology transfer in Asia, Proc. 4th Regional workshop held in Trivandrum, India (pp. 125–134).
- Schoch, T.J. (1964) Swelling power and solubility of granular starches. In R.L. Whistler, R.J. Smith, & J.N. Be Miller (Eds.) *Methods in Carbohydrate Chemistry*, Vol. 4. (pp. 106–108). New York: Academic Press.
- Yamada, S., Nagashima, N., & Kawabata, A. (1987). Thermal properties of some tropical starches by differential scanning calorimetry. Journal Home Econ. Japan., 38, 647.