

Available online at www.sciencedirect.com



Food Chemistry

Food Chemistry 104 (2007) 376-382

www.elsevier.com/locate/foodchem

Changes in functional characteristics of starch during water caltrop (*Trapa Quadrispinosa* Roxb.) growth

Po-Yuan Chiang^a, Po-Hsien Li^a, Chien-Chun Huang^b, Chiun-C.R. Wang^{c,*}

^a Department of Food Science and Biotechnology, National Chung-Hsing University, Taichung 402, Taiwan, ROC

^b Department of Applied Life Science, Asia University, Wufeng 413, Taiwan, ROC

^c Department of Food and Nutrition, Providence University, Shalu 433, Taiwan, ROC

Received 28 June 2006; received in revised form 8 October 2006; accepted 22 November 2006

Abstract

This study was carried out to establish the changes of physicochemical properties of Taiwan's water caltrop (*Trapa Quadrispinosa* Roxb.) starch at various stages of maturity during growth. Investigations showed that the dry matter and starch contents of water caltrop increased from 9.7% to 25.61% and from 49.4% to 79.4% (d.b.), respectively, as growth progressed (from 14th to 42nd day after fruit development). The shape of the starch granules was smooth, oval and poly-angular during the growth period. The granule size of starch increased with increase of physiological age, ranging from 19.4 μ m to 32.2 μ m. The X-ray diffraction patterns could be classified as a typical A-type crystalline structure. Swelling power and solubility of water caltrop starch increased with increases of growth time. Starches obtained from water caltrop at the early stage exhibited a lower gelatinization temperature (T_o , T_p , T_c) and gelatinization enthalpy (ΔH) than did the late stage of maturity. The rapid viscosity analyzer (RVA) parameters suggested that water caltrop starch paste had a low breakdown, and appeared to be thermo-stable, at the early harvest time. The pasting temperature, peak viscosity, final viscosity and setback value of water caltrop starch increased as growth progressed. Different starch granular size and amylose content could be the major factors influencing starch physicochemical properties during maturity. (© 2006 Elsevier Ltd. All rights reserved.

Keywords: Water caltrop starch; Granule size and shape; X-ray diffraction; Gelatinization temperature; Pasting properties

1. Introduction

Water caltrop (*Trapa Quadrispinosa* Roxb.) belongs to the family *Trapaceae*, one of the free-floating plants, grown in shallow water fields, ponds or swampy lands in tropical and sub-tropical countries (Takano & Kadono, 2005). The interesting features of water caltrop are the colour and shape of its outer cover in which the kernel is encased. The matured *Trapa* is 3–5 cm wide and 5–6 cm long, with one pair of spines in the shoulder and one pair of short spines in the abdomen. The water caltrop meat is covered with a thick jet-black outer pericarp shaped like a horn protruding from the head of a buffalo. The outer pericarp is hard, making it quite difficult to peel off to obtain the internal white fruit (Tulyathan, Boondee, & Mahawanich, 2005). Water caltrop has reasonably high contents of starch, which ranges 65–80% of dry matter (Yang, Chang, Sung, & Lii, 1978). Due to the sweet, tender and delicious taste, cooked water caltrop is one of the popular starchy desserts in Taiwan and southern Asian countries. Water caltrop starch contributes to the textural properties of many foods, such as thickening of soups and sauces locally. Because of easy implementation and management, water caltrop is a potential source of commercial starch in Asian countries (Tsuchiya, Nohara, & Iwaki, 1987; Tulyathan et al., 2005).

Starch has been extensively studied and discussed in the literature. Starch properties depend on physicochemical characteristics, such as cultivars, growth period, environmental factors, granule size, amylose/amylopectin ratio

^{*} Corresponding author. Address: Department of Food and Nutrition, Providence University, 200, Chung-Chi Road, Taichung 43301, Taiwan, ROC. Tel.: +886 4 2665 1166; fax: +886 4 2653 0027.

E-mail address: jcwang@pu.edu.tw (Chiun-C.R. Wang).

 $^{0308\}text{-}8146/\$$ - see front matter \circledast 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.foodchem.2006.11.067

and mineral content (Lisinska & Leszczynski, 1989; Madsen & Christensen, 1996; Noda et al., 2004a; Singh, Singh, Kaur, Sodhi, & Gill, 2003). Several reports have indicated that the X-ray diffraction patterns of starches at different physiological ages show similar characteristics in peak intensity in taro (Wang, Wu, Lai, & Huang, 2001), sweet potato (Noda, Takahata, Sato, Hisamatsu, & Yamada, 1995), potato (Liu, Weber, Currie, & Yada, 2003), and yam (Huang, Lin, & Wang, 2006) starches. The starch granule size and phosphorus content of root and tuber starches increase but amylose remained unchanged during growth (Huang et al., 2006; Liu et al., 2003; Madsen & Christensen, 1996; Noda et al., 1995). Root and tuber starches, with a shorter growth time, exhibited higher gelatinization temperature and pasting temperature but lower peak viscosity (Huang et al., 2006; Liu et al., 2003). The objective of this study was to establish the functional characteristics of the isolated starches from water caltrop during growth. Water caltrop starches were isolated and the physicochemical properties of the starches measured in terms of morphology, semi-crystalline structure, thermal and pasting properties.

2. Materials and methods

2.1. Materials

Water caltrops (T. *Quadrispinosa* Roxb.) were cultivated on June 3rd, 2005, at the local farm (Tainan, Taiwan). Water caltrops were planted in the water field in rows, 75 cm apart with 50 cm between plants under 45 cm depth of water. After three months cultivation, the water caltrop started to flower. According to the previous study (Li, 2006), the maturity of water caltrop is approximately 40 days after fruit development. After 45 days of fruit development, most water caltrops will be over-maturity and will be dropped into the pond automatically. Therefore, the water caltrop was harvested at five dates, days 7, 14, 21, 28, 35 and 42 after fruiting, in this experiment. According to the preliminary test, the meat of water caltrop was filled with moisture, ranging from 94% to 97% at day 7 after fruiting. There was too little sample to analyze the physicochemical properties at day 7. Therefore, the data of physicochemical characteristics of water caltrop starch were collected after day 14 of this study. After harvest, the water caltrops were stored at 4 °C and shipped to the laboratory for starch isolation immediately.

2.2. Water caltrop starch isolation

Water caltrop starches were isolated and purified by the procedure of Xu and Shoemaker (1986). Water caltrops were washed, unshelled, diced and then blended by a domestic blender in distilled water (fruit:water = 1:3). After blending, the mixtures were passed through a 200 mesh sieve. The residues were centrifuged at 13,000g for 15 min, and the supernatant was discarded. The yellow

gummy material was scraped off to discard from the top of the precipitate. The residuals of precipitate were collected and washed with distilled water. The mixtures were centrifuged again. All precipitates were collected and dried in a conventional oven at 40 °C overnight. The starch was ground gently with a mortar and pestle to pass through a 125 μ m sieve, then packed in double plastic bags and stored in a freezer prior to further use.

2.3. Starch and amylose contents

The starch content of the water caltrop was determined by AACC methods (1995), using the Megazyme total starch content assay kit (Meagzyme International Ireland Ltd., Wicklow, Ireland). Amylose content of water caltrop starches was determined by the method given by Willams, Kuzina, and Hlynka (1970).

2.4. Scanning electron microscopy

Scanning electron micrographs (SEM) of water caltrop starch were obtained using a scanning electron microscope (Model ABT-150S, Topon Corp., Japan). Isolated starches were sprinkled on double-sided adhesive tape fixed on an aluminium stub. The sample was coated with a gold–palladium (Model JBS-ES 150, Ion sputter coater, Topon Corp., Japan). An accelerating potential of 15 kV was used during electron microscopy in this study.

2.5. Granule size

The granule size of starches was measured by the method of Tecante and Doublier (1999), using a Laser Particle Sizer (Analysette 22 compact Laser Particle Sizer, Fritsch, Germany). The isolated starches were dispersed in distilled water at 4%. The instrument output had a volume distribution of starch granules as the fundamental measurement. The output data D[4,3] meant that the granule diameter was derived from the volume distribution.

2.6. X-ray diffraction

X-ray diffraction of the starches were measured using a Siemens X-ray diffractometer (Model D5000, Siemens Co., Madison, USA) with the operating conditions set as follows: target voltage 40 kV, current 30 mA, scanning range (2θ) 4–30°, scan speed 0.02°/s, receiving slit width 0.2 nm.

2.7. Swelling power and solubility

Swelling power and solubility of starches from water caltrop were determined by the method of Waliszewski, Aparicio, Bello, and Monroy (2003). Starch suspensions (1% w/ w) were prepared in flasks and were heated to 60, 70, 80 or 90 °C for 30 min. All flasks were shaken every 5 min during heat treatment. After heating, all flasks were left for cooling to room temperature, then centrifuged at 4000g for 15 min. The precipitates was weighed and results calculated for swelling power. The supernatant was collected into a beaker and dried in an oven for 4 h at 105 °C. The dried solid was weighed and was solubility calculated.

2.8. Differential scanning calorimetry

The thermal properties of the isolated starches were measured using a differential scanning calorimeter (Model DSC822, Mettler-Toledo Co., Switzerland). Starch (3 mg) and distilled water were loaded into an aluminium pan and hermetically sealed. The pan was allowed to stand for 2 h at room temperature in order to attain an even distribution of water before heating the calorimeter. An empty aluminium pan was used as reference. The scanning temperature range was 30–120 °C at a heating rate of 5 °C/min. The onset (T_o) , peak (T_p) , conclusion (T_c) temperature, gelatinization enthalpy (ΔH) and gelatinization temperature range (R) of starches were calculated automatically.

2.9. Rapid viscosity analysis

The pasting properties of isolated starches were investigated with a rapid visco analyzer (RVA 3D, Newport Scientific, Australia) (Ross, Walker, Booth, Orth, & Wrigley, 1987). An 8% starch-water suspension (28 g total weight) was prepared and treated with a heating-cooling cycle. The starch suspensions were equilibrated at 50 °C for 1 min, heated to 95 °C at 6 °C/min, then held at 95 °C for 5 min. Afterwards, the paste was cooled to 50 °C at 6 °C/ min and kept at 50 °C for 2 min. The paddle speed was set at 960 rpm in the first 10 s, then kept at 160 rpm throughout the measurement. The peak temperature, peak viscosity (PV), hot paste viscosity (HPV), and cool paste viscosity (CPV), breakdown (BD), and setback (SB) were obtained from pasting curves, where HPV = minimum viscosity at 95 °C, CPV = final viscosity at 50 °C, BD = PV -HPV, and SB = CPV - HPV. The unit of pasting properties of water caltrops starch is expressed as RVU, where RVU is the unit of viscosity from the rapid visco analyzer. Three replicates of each sample were carried out.

2.10. Statistical analysis

Table 1

The mean values and standard deviations of each analysis are reported. All data were analyzed by using single

factor ANOVA. When *F*-value was significant (p < 0.05) in ANOVA, then Duncan's new multiple range test was calculated to compare treatment means.

3. Results and discussion

3.1. Dry matter and starch contents

A summary of the proximate compositions of water caltrop available for this study is presented in Table 1. Moisture represented the largest single constituent of water caltrop, and on average, ranged from 80.4% to 90.3% during the 42 day growth period over which the study was conducted. It is guite obvious that the moisture content of water caltrops decreased quite remarkably during the growth period encompassing days 35-42 after fruiting. The protein and ash contents of water caltrops appeared to increase significantly as growth progressed although the lipid content remained unchanged during the growth period (Table 1). Dry matter and starch contents of plants act as important indicators for quality evaluation of starchy food products (Lisinska & Leszczynski, 1989; Treche & Agbor-Egbe, 1996). Investigations showed that the dry matter and starch contents of water caltrop significantly increased during the growth period (14–42 days) ($p \le 0.05$) (Table 2). Over the 42 day growth period, dry matter content of water caltrop increased slightly at the earlier stages (14-28 days) and then increased significantly at the stages of maturity (35-42) days). The highest dry matter and starch contents of water caltrop were observed at the final harvest time (42 days), this time being judged to be the optimum harvesting time based on starch content. Research on the maturity of potatoes by Mitch (1984) found that potatoes had high contents of dry matter and starch, indicating the optimum time for harvesting. Amylose and phosphorus contents of water caltrop starches, at different development times, are presented in Table 2. Amylose content of water caltrop starches significantly increased with growth time (p < 0.05). Investigations showed that the phosphorus content of water caltrop starches, ranging from 0.56×10^{-20} , to 0.61×10^{-20} , slightly increased during the growth period (Table 2). This finding is consistent with previous reports in potato starch from Christensen and Madsen (1996); Liu et al. (2003). Compared to other starches, potato starch had significantly more organic phosphate than had other tuber starches in the previous reports (Hoover, 2001; Hoover & Hadizeyv, 1981;

roximate compositions of water cattrop during growth							
Growth time (day)	Moisture (%)	Protein (%)	Lipid (%)	Ash (%)	CHO (%) ^g	Dry matter (%)	
14	90.3 ^a	3.51°	0.49 ^a	0.58°	5.12	9.7 ^d	
21	88.3 ^b	4.14 ^b	$0.47^{\rm a}$	0.68 ^{bc}	6.41	11.7 ^c	
28	86.8 ^c	4.28 ^b	$0.48^{\rm a}$	0.79 ^b	7.65	13.2 ^b	
35	85.7 ^c	5.45 ^a	0.52^{a}	0.72 ^b	7.61	14.3 ^b	
42	80.4^{d}	5.67 ^a	0.55 ^a	0.88^{a}	12.5	19.6 ^a	

^{a-e} Means with different letters within the same column differ significantly (p < 0.05) (n = 3).

^f Each of the proximate compositions of water caltrop is expressed on wet basis.

^g Carbohydrate (CHO) content of water caltrop was calculated by the substration as follows: CHO = 100 - (moisture + protein + lipid + ash).

Starch composition	Growth time (da	uys)			
	14	21	28	35	42
Starch content Amylose (%) Phosphorus (×10 ⁻² %, w/w)	49.4 ^e 26.3 ^e 0.56 ^b	61.8 ^d 28.7 ^d 0.56 ^b	72.6° 35.2° 0.62ª	77.0 ^b 37.5 ^b 0.60 ^a	79.4^{a} 40.2^{a} 0.61^{a}
Starch granule size Range (μm) Mean (μm)	5.8–29.4 19.4°	6.8–33.4 21.2°	8.3–37.3 26.9 ^b	8.2–37.2 26.7 ^b	11.4–42.4 32.2 ^a

Table 2 Amylose and phosphorus contents of starch and starch granule size distribution during growth^f

^{a-e} Means with different letters within the same column differ significantly (p < 0.05) (n = 3).

^f Starch, amylose and phosphorus contents of water caltrop starches are expressed on a dry basis.

Lim, Kasemsuwan, & Jane, 1994; Liu et al., 2003) and water caltrop starches (Table 2). The high phosphate monoester content of potato starch confers enhanced paste clarity, high peak viscosity consistency, significant shear-thinning and slow rate of retrogradation (Jane, Kasemsuwan, Chen, & Juliano, 1996).

3.2. Scanning electron microscopy and granule size

Fig. 1 shows that the different physiological ages of water caltrop starch granules were morphologically similar.

The shapes of granules appeared to be smooth, oval and poly-angular during the growth period when viewed by SEM. The granule size of water caltrop starches significantly increased as growth progressed (14–42 days). At final harvest time, the average granule size of starch appeared to be greatest. The granule size distribution of the water caltrop starches was determined by using a laser diffraction analyzer. The results of granule size of water caltrop starch from the laser diffraction (Table 2), with characteristic dimensions in the range 5.8–42.4 μ m, agreed with the results from the scanning electron micrographs.



Fig. 1. Scanning electron microscopy of water caltrop starch during growth (A, B, C, D and E are representative of the 14th, 21st, 28th, 35th and 42nd day, respectively) (bar in each picture is 10 μ m).

The particle size of water caltrop starches, expressed by even particle distribution D (4.3), increased with the increase of growth time from 19.4 µm at the earliest harvest time (14 days) to 32.2 µm at the final harvest time (42 days). Our data are comparable with previous studies in potato starch (Liu et al., 2003) and yam starch (Huang et al., 2006) where the size of starch granules becomes larger with increasing physiological plant age.

3.3. X-ray pattern

The X-ray diffraction patterns of water caltrop starches at different physiological ages show a few minor differences in peak intensity, but similar characteristics with four main reflection intensities (Fig. 2). The four distinctive peaks appeared at the Bragg reflection angle 2θ : 15.2°, 17.1°, 18.2° and 23.5°, supporting a typical A-type X-ray pattern. Compared to the five dates of harvest time, the similar Xray diffraction patterns indicated that the semi-crystalline structure of water caltrop starch was not affected by the growth time, although there were some minor differences in reflection intensity. More detailed investigation, such as by crystallinity measurement, is necessary for the next step. Previous studies have indicated that the semi-crystalline structure of most root and tuber starches is not strongly affected by different growth periods (Huang et al., 2006; Liu et al., 2003; Noda et al., 1995) and this agrees with our study.

3.4. Swelling power and solubility

Swelling power of starch indicated the degree of water absorption of starch granules and solubility reflected the degree of dissolution during the starch swelling procedure (Carcea & Acquistucci, 1997). The swelling power of water caltrop starches, as a function of growth time and temperature, is summarized in Table 3. The swelling power of water caltrop starch was greatly influenced by growth time and heating temperature. The swelling power of water cal-



Fig. 2. A typical X-ray diffraction pattern of water caltrop starch during growth.

Table 3							
Swelling	power	of	water	caltrop	starch	during	growth ^e

Growth time	Swelling power (g/g starch)					
(days)	60 °C	70 °C	80 °C	90 °C		
14	$2.8^{\mathrm{aC}}\pm0.3$	$3.2^{\mathrm{bC}}\pm1.0$	$11.1^{\mathrm{dB}}\pm0.2$	$16.8^{cA} \pm 1.5$		
21	$2.8^{aC}\pm0.3$	$3.3^{bC}\pm0.3$	$13.6^{\mathrm{cB}}\pm0.5$	$17.3^{cA} \pm 0.9$		
28	$3.0^{\mathrm{aC}}\pm0.1$	$3.9^{\mathrm{bC}}\pm1.0$	$17.8^{\mathrm{bB}} \pm 1.1$	$20.3^{\mathrm{bA}}\pm1.7$		
35	$3.1^{\mathrm{aC}}\pm0.4$	$4.1^{\mathrm{bB}}\pm0.1$	$20.7^{\mathrm{aA}}\pm0.7$	$22.7^{bA} \pm 1.9$		
42	$3.4^{aC}\pm0.2$	$4.7^{aB}\pm0.2$	$22.5^{aA}\pm1.3$	$24.3^{\mathrm{aA}}\pm1.3$		

^{a-d} Means with different letters within a column differ significantly (p < 0.05).

^e Means \pm standard deviation (n = 3).

^{A–C} Means with different letters within a row differ significantly (p < 0.05).

trop starch increased with the growth period, from 14 to 42 days, at all heating temperatures (60-90 °C). The highest swelling power of water caltrop starch was 24.3 g/g, which was obtained at 42 days growth time and heating to 90 °C (Table 3). The largest change in swelling power of water caltrop starch was observed between 80 °C and 90 °C, as shown in Table 3. Isolated starch, from all physiological ages, showed a higher swelling power at temperatures above 80 °C, possibly due to starch gelatinization. When starch is gelatinized, the starch-water interaction increases, which results in a substantial increase in the swelling power. Several studies have indicated that the swelling power of starch is strongly affected by heating temperature and this agrees with our study (Wang et al., 2001; Yaday, Guha, Tharanathan, & Ramteke, 2006). However, there was no significant difference in swelling power between the growth periods of 14-21 days and 35-42 days. The solubility of water caltrop starches during the growth period is shown in Table 4. As with the swelling power, the solubility of water caltrop starch increased as growth progressed (p < 0.05). The solubility of water caltrop starch was significantly affected by the growth period and heating from 80 °C to 90 °C. An important factor influencing starch solubility at higher temperature (80-90 °C) could be the leaching of amylose from starch granules. As temperature increased, the solubility of the water caltrop starch increased which agrees with the increase of amylose content at greater physiological ages during the growth period.

Table 4 Solubility of water caltrop starch during growth^e

Growth time	Solubility (%)						
(days)	60 °C	70 °C	80 °C	90 °C			
14	$0.4^{\mathrm{cD}}\pm0.1$	$1.0^{ m cC}\pm0.2$	$10.5^{\text{eB}}\pm0.5$	$20.1^{\text{cA}} \pm 0.3$			
21	$0.5^{\mathrm{bD}}\pm0.1$	$1.1^{\mathrm{bC}}\pm0.7$	$14.9^{\mathrm{dB}}\pm0.3$	$21.6^{\mathrm{bA}}\pm0.5$			
28	$0.5^{abD}\pm0.1$	$1.3^{\mathrm{bC}}\pm0.1$	$15.8^{\mathrm{cB}}\pm0.4$	$22.8^{\mathrm{aA}}\pm0.9$			
35	$0.6^{\mathrm{aD}}\pm0.5$	$1.7^{\mathrm{bC}}\pm0.3$	$17.0^{\mathrm{bB}}\pm0.7$	$24.0^{\mathrm{aA}}\pm0.8$			
42	$0.7^{aD}\pm0.3$	$2.1^{\mathrm{aC}}\pm0.2$	$19.3^{aB}\pm1.4$	$24.1^{\mathrm{aA}}\pm0.3$			

^{a-e} Means with different letters within a column differ significantly (p < 0.05).

^e Means \pm standard deviation (n = 3).

^{A–D} Means with different letters within a row differ significantly (p < 0.05).

3.5. Differential scanning calorimetry

Thermal properties of water caltrop starches at different growth times are summarized in Table 4. All starches showed a single symmetrical endothermic transition during gelatinization. All the parameters of gelatinization temperature (T_o, T_p, T_c) and enthalpy (ΔH) increased with increases of the growth time (p < 0.05) (Table 5). Over the 42 day development period, the gelatinization enthalpy (ΔH) of water caltrop starch tended to increase with growth time and reached maximum levels at 42 days. As gelatinization temperature reflects the degree of orderly arrangement of the molecules in the starch granules, the highest T_0 and ΔH of gelatinization at the final harvest time (42 days) indicates that water caltrop starches at final harvest stages are more ordered than those at earlier stages. A previous study by Wang et al. (2001) showed increases of thermal properties of taro starch during the growth period that agree with this study.

3.6. Rapid viscosity analysis

Table 6

Pasting behaviour of starch is usually studied by observing the changes in the viscosity of a starch system based on

Table 5 Gelatinization properties of water caltrop starch during growth measured by differential scanning calorimetry (DSC)^d

Growth	Parameters of endothermic properties					
time (days)	<i>T</i> _o (°C)	$T_{\rm p}$ (°C)	$T_{\rm c}$ (°C)	Gelatinization range (°C)	$\Delta H (J/g)$	
14	70.7 ^b	75.1 ^d	81.4 ^b	10.7 ^b	10.2 ^c	
21	71.6 ^b	77.0 ^c	83.7 ^a	12.1 ^a	12.2 ^b	
28	72.3 ^b	78.4 ^b	83.4 ^a	11.1 ^b	13.5 ^b	
35	75.8 ^a	78.3 ^b	83.6 ^a	7.8 ^c	13.8 ^b	
42	77.8 ^a	79.4 ^a	84.4 ^a	6.6 ^c	16.0 ^a	

^{a-c} Means with different letters within the same column differ significantly (p < 0.05) (n = 3).

^d $T_{\rm o}$ = onset temperature; $T_{\rm p}$ = peak temperature; $T_{\rm c}$ = closed temperature; ΔH = enthalpy (J/g starch); gelatinization range (°C) = ($T_{\rm c} - T_{\rm o}$).

14010 0			
Pasting properties of v	water caltrop starch d	luring growth measured	by rapid visco analyzer

rheological principles. The pasting properties of water caltrop starches are greatly affected by growth times (Table 6). As the growth times progressed, there was an increasing trend in pasting temperature of water caltrop starch. The results of pasting properties also indicated that the peak viscosity and breakdown of water caltrop starch significantly increased with increases of growth time (p < 0.05). The highest peak viscosity and breakdown were exhibited at the latest harvest time (42 days). A similar tendency was observed in that potato starch, at late harvest time, exhibited higher peak viscosity and breakdown than that at early harvest time (Table 6) (Mishra & Rai, 2006; Noda et al., 2004b).

Several reports have indicated that phosphorus is relatively high in potato starches compared to other starches, i.e. $0.37-0.75 \,\mu\text{g/mg}$ of starch (Jane et al., 1996; Lim et al., 1994; Yusuph, Tester, Ansell, & Snape, 2003). Potato starches contain ten times more phosphorus than do water caltrop starches at all five stages of growth (Table 2). It has been reported that phosphate linkages in potato starches are responsible for paste clarity, high peak viscosity, significant shear-thinning and slow rate and extent of retrogradation (Galliard & Bowler, 1987; Jane et al., 1996). As observed for the early stage of maturity (14 days) of water caltrop starches, there was no noticeable breakdown in viscosity on heating and stirring, in spite of the high peak viscosity level. Like yam starch, water caltrop starch showed a very low breakdown compared to other starches with thermo-stable starch paste at an early stage of maturity. As growth time progressed, water caltrop starches began to show significant changes in breakdown (Table 6). When the temperature dropped to 50 °C, a sharp rise in final viscosity of starch paste was observed at all harvest times. During the cooling cycle, the water caltrop starch, at 42 days after fruiting, showed the highest viscosity of starch paste because a large number of intermolecular hydrogen bonds was formed, which resulted in gel formation and caused a higher viscosity at lower temperature. The latest harvest time (42 days) gave a higher setback of starch paste, indicating a higher retrogradation tendency. This

Growth time (day)	Parameters of pasting l	Parameters of pasting behaviour ^g (RVU)						
	Pasting temperature (°C)	Peak viscosity (P)	Holding viscosity (<i>H</i>)	Final viscosity (<i>F</i>)	Breakdown $(P - H)$	Setback $(F - H)$		
14	76.9 ^d	270.6 ^e	268.9 ^a	445.8 ^e	1.7 ^e	176.9		
21	78.1 ^c	298.2 ^d	256.5 ^b	467.4 ^c	11.7 ^d	210.9		
28	79.0 ^c	310.3 ^c	243.3 ^c	457.2 ^d	67.0 ^c	213.9		
35	79.9 ^b	326.5 ^b	231.4 ^d	472.4 ^b	95.1 ^b	241.0		
42	82.4 ^a	347.9 ^a	207.6 ^e	527.1 ^a	140.3 ^a	319.5		
Potato starch ^h	67.2	410.6	151.3	185.6	259.3	34.3		

^{a-f} Means with different letters within the same column differ significantly (p < 0.05).

^g The unit of pasting properties of water caltrop starch is expressed as RVU, where RVU is the unit of viscosity from the rapid visco analyzer.

^h The parameters of pasting behaviour of potato starch, where the original units of potato paste are expressed as centipose (cp), obtained from Noda et al. (2004b), and Mishra and Rai (2006). The units of pasting parameters (cp) of potato starch are converted to RVU as follows: $1 \text{ cp} = 8.33 \times 10^{-2} \text{ RVU}.$

was most likely due to the greater amounts of amylose and phosphorus present, which resulted in a higher retrogradation tendency.

4. Conclusions

Dry matter and starch contents increases with the increases of growth time. The granule size of the water caltrop starches increased as growth progressed, which agreed with the results for the swelling power. The X-ray diffraction pattern of water caltrop starches showed a typical A-type crystalline structure, not affected by growth time. The RVA results showed that the pasting temperature, peak viscosity and breakdown all increased during maturity of the water caltrops. The results suggested that water caltrop starch pastes had a high setback after cooling, which resulted in a high retrogradation tendency. This study provides useful information in terms of changes of the starch content, granule size and thermograms as well as pasting behaviour of water caltrops that will affect the choice of harvest time and help in the evaluation of the potential use of water caltrop starch in value-added products.

Acknowledgement

The authors express sincere thanks to the National Science Council of Taiwan, ROC, for the financial support (NSC 94-2214-E-005-006).

References

- AACC (1995). Approved methods of the AACC (9th ed.). St Paul, MN: American Association of Cereal Chemists.
- Carcea, M., & Acquistucci, R. (1997). Isolation and physicochemical characterization of Fonio (*Digitaria exillis Stapf*) starch. *Starch*, 49, 131–135.
- Christensen, D. H., & Madsen, M. H. (1996). Changes in potato starch quality during growth. *Potato Research*, 39, 43–50.
- Galliard, T., & Bowler, P. (1987). Morphology and composition of starch. In T. Galliard (Ed.), *Starch: properties and potential* (pp. 55–78). Chichester: John Wiley and Sons.
- Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches, a review. *Carbohydrate Polymers*, 45, 253–267.
- Hoover, R., & Hadizeyv, D. (1981). Characterization of potato starch and it monoglyceride complexes. *Starch*, *33*, 290–300.
- Huang, C. C., Lin, M. C., & Wang, C. R. (2006). Changes in morphological, thermal and pasting properties of yam (*Dioscorea alata*) starch during growth. *Carbohydrate Polymers*, 64, 524–531.
- Jane, J., Kasemsuwan, T., Chen, J. F., & Juliano, B. O. (1996). Phosphorus in rice and other starches. *Cereal Food World*, 41, 827–832.
- Li, P. H. (2006). Physicochemical properties of water caltrop from different varieties and development stages. M.S. Thesis, National Chung-Hsing University, Taichung, Taiwan.
- Lim, S. T., Kasemsuwan, T., & Jane, J. L. (1994). Characterization of phosphorus in starch by 31p nuclear magnetic spectroscopy. *Cereal Chemistry*, 71, 468–472.
- Lisinska, G., & Leszczynski, W. (1989). Potato science and technology. London, UK: Elsevier Applied Science.

- Liu, Q., Weber, E., Currie, V., & Yada, R. (2003). Physicochemical properties of starches during growth. *Carbohydrate Polymers*, 51, 213–221.
- Madsen, M. H., & Christensen, D. H. (1996). Changes in viscosity properties of potato starch during growth. Starch, 48, 245–249.
- Mishra, S., & Rai, T. (2006). Morphology and functional properties of corn, potato and tapioca starches. *Food Hydrocolloids*, 20, 557–566.
- Mitch, E. L. (1984). Potato starch: production and uses. In R. L. Whistler, J. N. BeMiller, & E. F. Paschall (Eds.). *Starch: chemistry and technology* (pp. 479–490). New York: Academic Press.
- Noda, T., Takahata, Y., Sato, T., Hisamatsu, M., & Yamada, T. (1995). Physicochemical properties of starches extracted from sweet potato roots differing in physiological age. *Journal of Agricultural and Food Chemistry*, 43, 3016–3020.
- Noda, T., Tsuda, S., Mori, M., Takigawa, S., Matsuura-Endo, C., Saito, K., et al. (2004a). The effect of harvest dates on the starch properties of various potato cultivars. *Food Chemistry*, 86, 119–125.
- Noda, T., Tsuda, S., Mori, M., Takigawa, S., Endo, C. M., & Hashimoto, N. (2004b). Properties of starches from potato varieties grown in Hokkaido. *Journal of Applied Glycoscience*, 51, 241–246.
- Ross, A. S., Walker, C. E., Booth, R. I., Orth, R. A., & Wrigley, C. W. (1987). The rapid visco-analyzer: a new technique for the estimation of sprout damage. *Cereal Foods World*, 32, 827–829.
- Singh, N., Singh, J., Kaur, L., Sodhi, N. S., & Gill, B. S. (2003). Morphological, thermal and rheological properties of starches from different botanical source – a review. *Food Chemistry*, 81, 219–231.
- Takano, A., & Kadono, Y. (2005). Allozyme variations and classification of Trapa (Trapaceae) in Japan. Aquatic Botany, 83, 108–118.
- Tecante, A., & Doublier, J. L. (1999). Steady flow and viscoelastic behavior of crosslinked waxy corn starch-κ-carrageenan pastes and gels. *Carbohydrate Polymers*, 40, 221–231.
- Treche, S., & Agbor-Egbe, T. (1996). Biochemical changes occurring during growth and storage of two yam species. *International Journal of Food Science and Nutrition*, 47, 93–102.
- Tsuchiya, T., Nohara, S., & Iwaki, H. (1987). Annual and seasonal variations in biomass of a floating-leaved plant, *Trapa Natans* L. in Takahamairi Bay of Lake Kasumigaura, Japan. *Japan Journal of Limnology*, 48, 39–44.
- Tulyathan, V., Boondee, K., & Mahawanich, T. (2005). Characteristics of starch from water chestnut (*Trapa Bispinosa* Roxb.). *Journal of Food Biochemistry*, 29, 337–348.
- Waliszewski, K. N., Aparicio, M. A., Bello, L. A., & Monroy, J. A. (2003). Changes of banana starch by chemical and physical modification. *Carbohydrate Polymers*, 52, 237–242.
- Wang, C. R., Wu, S. P., Lai, L. S., & Huang, S. S. (2001). The changes of composition and physicochemical properties of taro tuber during growth. *Taiwanese Journal of Agricultural Chemistry and Food Science*, 39, 173–184.
- Willams, P. C., Kuzina, F. D., & Hlynka, I. (1970). A rapid colorimetric procedure for estimating the amylose content of starches and flours. *Cereal Chemistry*, 47, 411–420.
- Xu, S. Y., & Shoemaker, C. F. (1986). Gelatinization properties of Chinese water chestnut starch and lotus root starch. *Journal of Food Science*, 51, 445–449.
- Yadav, A. R., Guha, M., Tharanathan, R. N., & Ramteke, R. S. (2006). Changes in characteristics of sweet potato flour prepared by different drying techniques. *LWT Food Science and Technology*, 39, 20–26.
- Yang, C. C., Chang, S. M., Sung, S. C., & Lii, C. Y. (1978). Studies on the starches in Taiwan 2. Taro, water chestnut (*Trapa*) and job's tears. *Food Science (Taiwan)*, 5, 73–87.
- Yusuph, M., Tester, R. F., Ansell, R., & Snape, C. E. (2003). Composition and properties of starches extracted from tubers of different potato varieties grown under the same environmental conditions. *Food Chemistry*, 82, 283–289.