

Impact of Annealing on Susceptibility to Acid Hydrolysis and Physico-Chemical Properties of Cassava Starch

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ABSTRACT

Native cassava starch was subjected to modifications by annealing and acid hydrolysis. The effects of annealing on the susceptibility to acid hydrolysis, granular morphology and size distribution, molecular structure and the physico-chemical properties of cassava starch were investigated. The acid hydrolyzed starch granule surface became slightly roughened with a preserved birefringence pattern. Smaller granules were obtained after acid hydrolysis with fragments of granules observed after prolonged hydrolysis for 16 and 32 d. The molecular weight distribution of cassava starch remained unchanged after annealing while degradation of starch components occurred to differing extents after acid hydrolysis. No difference in acid hydrolysis extent was observed between native and annealed cassava starches. Acid hydrolyzed starches possessed significantly lower pasting viscosity than native and annealed starches. In general, the swelling power of cassava starch decreased while solubility increased after longer hydrolysis time. Gelatinization temperatures slightly increased during the first phase of hydrolysis and then decreased accompanied with broader endotherms. A significant increase in gelatinization enthalpy was observed in starch hydrolyzed for 16 and 32 d. The extent of retrogradation of cassava starch increased progressively with decreasing molecular weight of the acid hydrolyzed starches. In addition, the glass transition temperatures of amorphous native and annealed cassava starches at limited moisture were depressed successively with increasing hydrolysis time.

Keywords: cassava, starch, annealing, acid hydrolysis, physico-chemical properties

INTRODUCTION

Annealing is an incubation process of starch in excess water at a temperature between glass transition and the onset of gelatinization temperatures of starch for a set period of time (Stute, 1992). The gelatinization temperature is increased, the gelatinization temperature range is narrowed and the gelatinization enthalpy is

increased or unchanged by annealing (Tester and Debon, 2000).

Acid hydrolysis is widely used to prepare soluble starch for the food, paper and textile industries among others (Rohwer and Klem, 1984). Acid hydrolyzed starch is usually prepared by treatment of starch with hydrochloric acid to provide starch with a low molecular weight. The physico-chemical properties of starch are modified

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by acid hydrolysis while its granular structure is retained. After acid hydrolysis, the gelatinization temperature of starch is initially increased and the transition temperature range is broader (Hoover, 2000).

Acid hydrolysis has been also intensively employed to study the arrangement of amylose and amylopectin as well as the structure of crystalline lamellae in starch granules. Two distinct steps are generally observed during the acid hydrolysis of starch. The first phase involves a relatively fast degradation of starch components mainly in amorphous regions, while the second phase is attributed to a slow hydrolysis of crystalline lamellae. The role of the amorphous and crystalline regions in the starch granule can be further elucidated through the annealing process. The annealing mechanism of acid hydrolyzed starch has been examined to understand the role of amorphous and crystalline regions (Jacob *et al.*, 1998), while the susceptibility of annealed starch granules to acid hydrolysis has been investigated to gain more insight on changes to the amorphous and crystalline lamellae (Nakazawa and Wang, 2003). The impact of annealing on acid hydrolysis however, has been reported to be dependent on the annealing method, temperature and starch origin (Hoover and Vasanthan, 1994; Jacobs *et al.*, 1998; Nakazawa and Wang, 2003; Qi *et al.*, 2005; Waduge *et al.*, 2006). Conflicting information has been presented with respect to the susceptibility of annealed starches to acid hydrolysis.

In the present work, the effects of annealing on the susceptibility of cassava starch to acid hydrolysis and the physico-chemical properties of cassava starch were investigated.

MATERIALS AND METHODS

Native cassava starch was obtained commercially from Sangan Wongse Co. Ltd. (Nakorn Ratchasima, Thailand).

Annealing experiment

Cassava starch was suspended in distilled water (1:3 w/w) and incubated at 50 °C for 72 h. Annealed cassava starch was collected by filtration and dried overnight at 50 °C.

Acid hydrolysis

Cassava starch samples were hydrolyzed in 2.2 N HCl aqueous solution (1:1.5 w/v). The suspensions were kept at ambient temperature for up to 32 d with stirring. Hydrolyzed cassava starch was collected by filtration, neutralized with NaOH solution, washed with distilled water and then dried overnight at 50 °C. The yield of acid hydrolyzed starch was expressed by the weight of recovered starch to the initial weight of starch.

Light and polarized light microscopy

Starch granules suspended in 80% sucrose solution were viewed under a normal and polarized light microscope (Meiji Techno., Japan) at 200× magnification.

Granular morphology by scanning electron microscopy

The granular morphology of the starch was observed under a JEOL JSM-5310 scanning electron microscope (SEM; JEOL, Hertfordshire, UK) at 10-KV acceleration and 3,000× magnification.

Molecular weight distribution

The molecular component of starch was evaluated by high performance size exclusion chromatography (HPSEC) according to the method of Govindasamy *et al.* (1992). A starch solution was prepared by dissolving 40 mg of starch (dry basis) in 10 mL of distilled water in a boiling water bath for 20 min with constant stirring. For complete gelatinization, the starch solution was subjected to ultrasonication for 18 s. The sample was filtered through an 8 µm filter and 20 µL of the filtrate was injected into the

HPSEC system. The system consisted of a pump and three columns in series (one ultrahydrogel linear and two ultrahydrogel 120) maintained at 40 °C and connected with a refractive index detector. A series of dextran with molecular weights ranging from 5 to 670 kDa was used as a standard.

Swelling and solubility

Cassava starch (0.1 g) was heated in 15 mL of water to 35, 65 and 85 °C for 30 min and centrifuged at 2,200 rpm for 15 min. The sediment pastes were then weighed. The supernatants were also collected, dried and weighed. The swelling power and solubility were determined according to Schoch (1964).

Pasting properties

The viscosity changes of cassava starch upon heating and cooling were monitored using a rapid viscosity analyzer (RVA) according to the method of Sriroth *et al.* (1999). Cassava starch slurry (9.2% w/w) was heated from 50 to 95 °C at the rate of 12 °C/min, maintained at 95 °C for 2.5 min and then cooled to 50 °C at the same rate.

Thermal analysis

Characterization of gelatinization and retrogradation

The gelatinization properties of the cassava starch samples were determined using a differential scanning calorimeter (DSC; DSC7, Perkin-Elmer, Massachusetts, USA) following the method of Sriroth *et al.* (1999). Cassava starch suspensions (30% w/w) were heated from -40 to 120 °C at 10 °C/min. The onset (T_o), peak (T_p) and conclusion (T_c) temperatures and enthalpy (J/g dry starch) of gelatinization were determined from the melting transition of amylopectin. The gelatinized samples were kept at 4 °C for 7 d before rescanning to detect amylopectin recrystallization. The extent of retrogradation was determined as the retrogradation enthalpy.

Characterization of glass transition

Glass transition of amorphous cassava starches was performed using a differential scanning calorimeter (DSC; DSC7, Perkin-Elmer, Massachusetts, USA) following the method of Tran *et al.* (2007). The glass transition temperature and specific heat (ΔC_p) of amorphous cassava starch at limited moisture content (10~12%) were determined.

Statistical analysis

All tests were performed at least in duplicate. Statistically significant tests were performed using analysis of variance (ANOVA) at the 95% confidence level ($P < 0.05$). Significant differences among mean values were determined by Duncan's multiple range test.

RESULTS AND DISCUSSION

Yield, size and morphology of starch granule

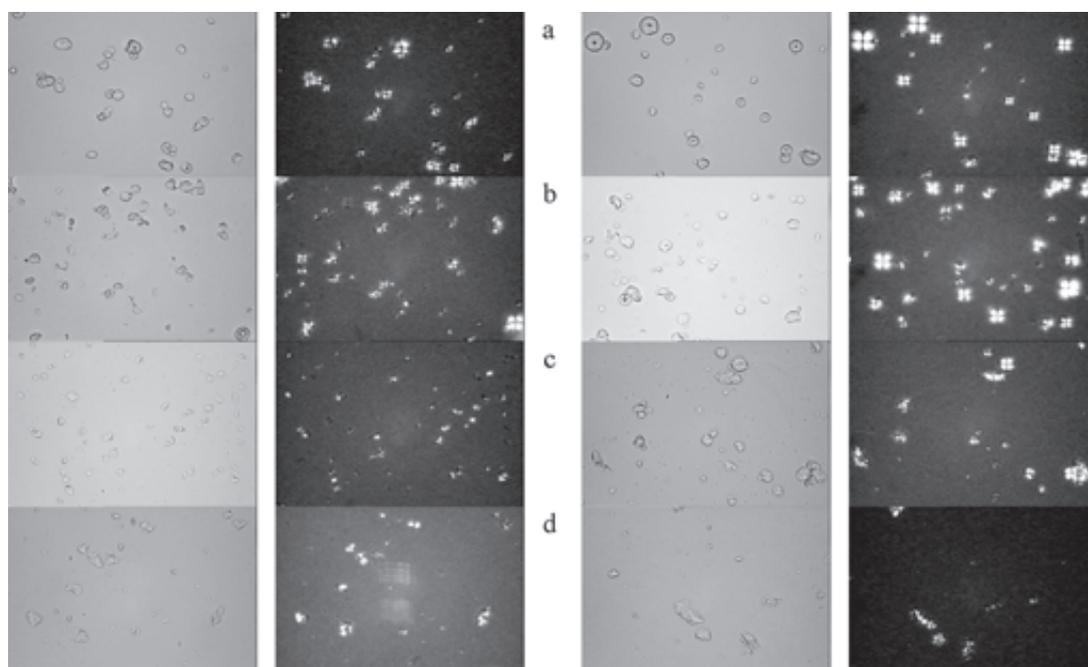
Acid hydrolysis of native and annealed starch for the same period resulted in relative yields ranging from 46 to 87% (Table 1). Less starch yield was obtained with prolonged acid hydrolysis as smaller water soluble molecules were produced.

Native and annealed cassava starch had average granule diameters of 14.4 and 14.1 μm , respectively. Their average diameters were reduced with increased hydrolysis time, reaching 7.5 and 7.3 μm , respectively, with an increased fraction of granules smaller than 10 μm , while preserved birefringence patterns were observed under a polarized light microscope (Table 1 and Figure 1).

The granular structures of native, annealed and acid hydrolyzed cassava starches examined by SEM are shown in Figure 2. The native and annealed cassava starch granules had a smooth surface with no fissures. The granule surfaces of native and annealed cassava starches became rougher with increasing hydrolysis time. Smaller granules were obtained after acid hydrolysis with fragments of granules after prolonged hydrolysis for 16 and 32 d.

Table 1 Yield (mean \pm SD) and granule size of native and annealed cassava starches after acid hydrolysis for various periods.

Hydrolysis time (day)	%Yield	Granule size			
		Average (μm)	Distribution (%)		
			<10 μm	10-20 μm	>20 μm
Native		14.38	13.81	64.10	22.09
1	87.06 \pm 1.18	13.84	14.82	66.80	18.38
2	84.94 \pm 0.03	14.73	14.82	59.68	25.49
4	82.46 \pm 0.18	11.92	26.44	64.21	9.34
8	71.51 \pm 0.07	11.98	30.77	57.79	11.44
16	58.18 \pm 0.20	9.61	51.68	44.55	3.76
32	46.24 \pm 0.59	7.54	73.03	25.98	0.98
Annealed		14.06	14.59	64.01	21.40
1	85.37 \pm 0.73	13.96	18.29	59.84	21.87
2	83.83 \pm 0.48	13.47	19.06	62.67	18.27
4	81.57 \pm 0.01	13.46	18.55	65.23	16.21
8	72.58 \pm 1.60	12.95	24.61	58.59	16.80
16	58.16 \pm 0.42	8.84	66.15	28.02	5.84
32	46.70 \pm 0.54	7.29	75.82	23.98	0.19

**Figure 1** Brightfield and polarized micrographs of native (right) and annealed (left) cassava starches after acid hydrolysis for: (a) 0 d; (b) 8 d; (c) 16 d; and (d) 32 d.

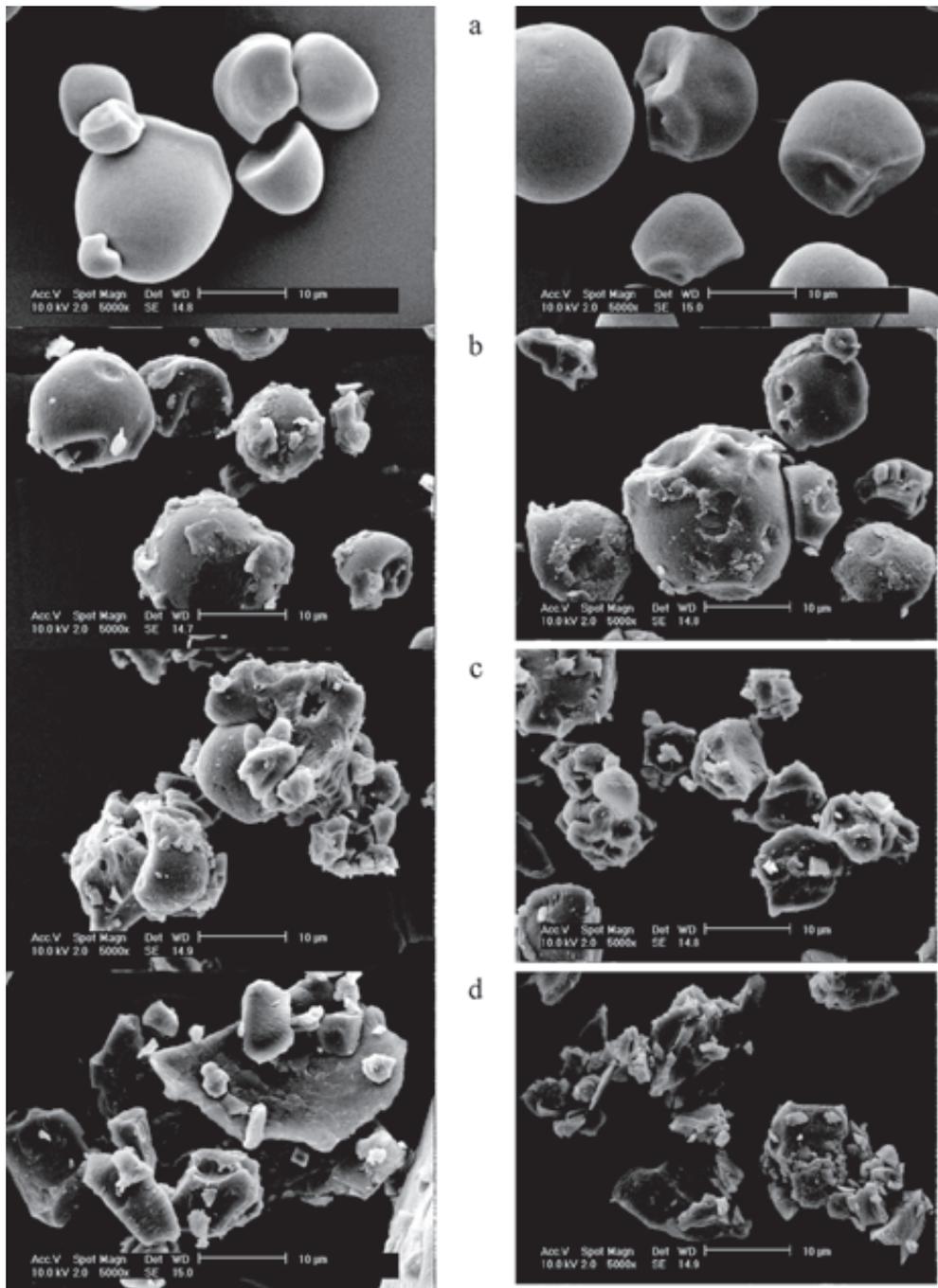


Figure 2 Scanning electron microscope (SEM) micrographs of native (right) and annealed (left) cassava starches after acid hydrolysis for: (a) 0 d; (b) 8 d; (c) 16 d; and (d) 32 d.

Molecular weight distribution

Figure 3 shows the molecular size distribution of cassava starch after annealing and acid hydrolysis as determined by HPSEC. The chromatograms revealed two fractions: fraction I (Fr. I) consisted of high molecular weight molecules (mainly amylopectin) and fraction II (Fr. II) corresponded to low molecular weight molecules. Fr. I of cassava markedly shifted to a longer retention time with an increase in acid hydrolysis time. The weight fraction of Fr. I decreased dramatically from 72.5 to 1.2% for native starch and from 76.5 to 1.7% for annealed cassava starch within 4 d of acid hydrolysis, while there was an increase in the proportion of Fr. II. Only Fr. II was detected for both native and annealed cassava starches after hydrolysis for longer than 4 d. The results indicated that the degradation of amylopectin to lower molecular weight molecules was caused by acid hydrolysis, especially after a longer period of hydrolysis.

Swelling and solubility

The swelling power of native, annealed and acid hydrolyzed cassava starches increased to different extents as the temperature increased

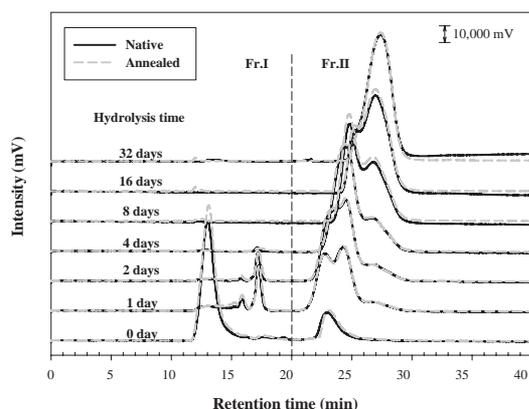


Figure 3 High performance size exclusion chromatography (HPSEC) chromatograms of native and annealed cassava starches after acid hydrolysis for various periods.

(Figure 4a). Acid hydrolysis limited the water absorption and swelling of cassava starch, especially at high temperature due to the loss of amorphous regions responsible for swelling capacity. At 85 °C, native and annealed starches exhibited swelling power of 38.0, while their swelling power was reduced progressively after a longer hydrolysis period reaching 13.4 and 17.2, respectively after 32 d of hydrolysis. The solubility of native and annealed cassava starch at 65 °C evidently increased from 10 to 78% after hydrolysis for longer than 2 d (data not shown). The solubility of native and annealed cassava starches was approximately 25.6 and 21.0%, respectively, at 85 °C, while that of acid hydrolyzed cassava starches was greater than 90% (Figure 4b).

Pasting properties

Both native and annealed cassava starch exhibited comparative pasting profiles (Figure 5). Annealing resulted in a slight increase in the pasting temperature and a decrease in the peak viscosity. After acid hydrolysis, the pasting viscosity of cassava was significantly decreased and not detectable at 9.2% starch concentration (data not shown). The decrease in viscosity of cassava starch after acid hydrolysis was attributed to the greater extent of molecular degradation.

Gelatinization and retrogradation

The DSC endotherm of annealed cassava starch became narrower with a higher onset temperature of gelatinization than that of native starch (Figure 6). The gelatinization onset temperatures (T_o) of both native and annealed samples slightly increased with increasing hydrolysis time up to 2 d and then decreased accompanied with broader endotherms (Table 2). A more pronounced effect was observed in starch hydrolyzed with acid for a longer period indicating greater heterogeneity of the starch crystalline regions. The temperature range of gelatinization ($T_c - T_o$) of the native and annealed starches

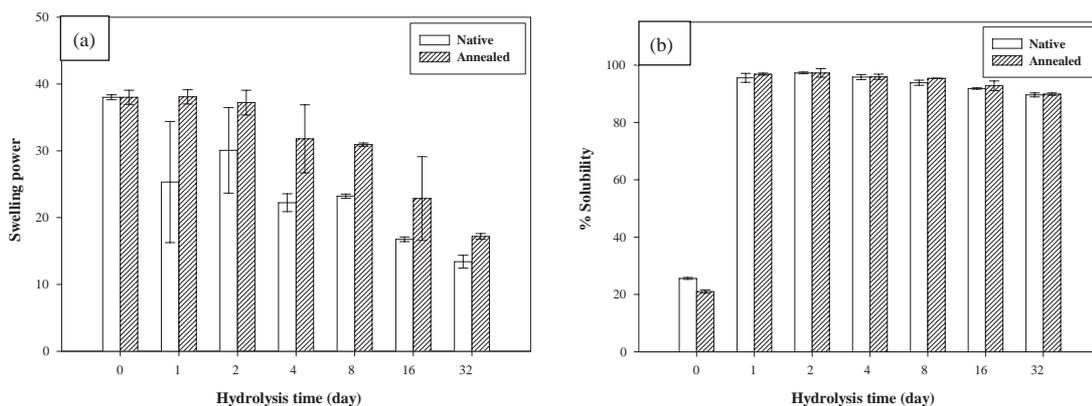


Figure 4 Swelling (a) and solubility (b) of native and annealed cassava starches after acid hydrolysis at 85 °C for various periods. (Vertical bars indicate the SD range).

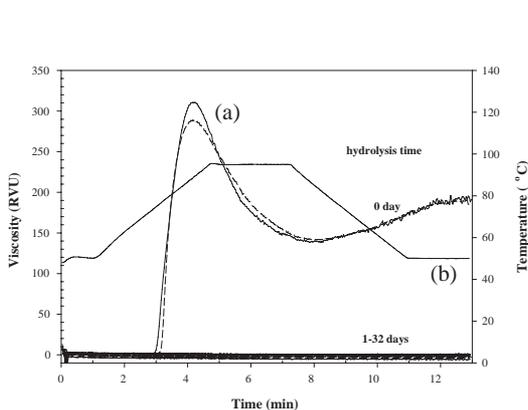


Figure 5 (a) Paste viscosity profiles of native (solid line) and annealed (dotted line) cassava starches (9.2% solid) after acid hydrolysis as determined by rapid visco analyzer; and (b) the temperature profile.

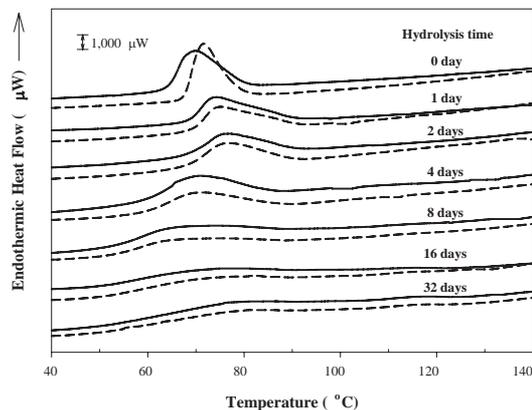


Figure 6 DSC gelatinization endotherms of native (solid line) and annealed (dashed line) cassava starches at 70% moisture content and heating rate of 10 °C/min after acid hydrolysis for various periods.

increased from 17 to 73 °C and from 11 to 73 °C, respectively, after 32 d of hydrolysis. Cassava starches after hydrolysis for 16 and 32 d exhibited endotherms (50~125 °C) with shoulders within the temperature range of 105~125 °C. A wide range in the value of (Tc - To) may be attributed to the presence of the crystalline structure composed of small crystallites possessing slightly different crystal strengths (Vansanathan and Bhatt, 1996). Extensive acid hydrolysis of cassava starches

probably produced several types of crystallites with different thermal stability. Furthermore, partially hydrolyzed amylose remaining in starch granules might retrograde or interact with hydrolyzed amylopectin and increase the gelatinization temperature (Perera *et al.*, 2001). Atichokudomchai *et al.* (2002) previously reported broader gelatinization endotherms in the temperature range 22.5~53 °C for acid hydrolyzed cassava starches compared to their native

counterpart (18.8 °C); they proposed that the shorter amylose chain length retrogrades, resulting in a higher content of double helices in the starch granules which in turn increases the value of T_o and the gelatinization enthalpy of the cassava starch within 4 d of hydrolysis.

The melting transition temperature of amylopectin crystallites is generally lower than that of amylose crystallites, indicating that branch crystallites are less stable than linear crystallites (Shin *et al.*, 2004). Based on the thermal stability of amylose and amylopectin, it was possible that the melting endotherm was attributed to a few

branched crystallites and some linear crystallites. The shoulder accompanying the endotherm at 105~125 °C was possibly derived from linear crystallites representing double helical segments of retrograded amylose. The gelatinization enthalpy of cassava starch tended to decrease slightly after 8 d of hydrolysis and increased with a longer hydrolysis period, indicating that more energy was associated with melting the amylopectin and possibly the retrograded amylose.

Retrograded native and annealed cassava starches exhibited melting endotherms in the temperature range 40~60 °C which became

Table 2 Gelatinization characteristics (mean \pm SD) of native and annealed cassava starches after acid hydrolysis for various periods. (T_o = onset temperature; T_c = conclusion temperature).

Gelatinization Characteristics	Hydrolysis time (day)	Treatment		
		Native	Annealed	Average
T_o (°C)	0	64.10 \pm 0.09	67.57 \pm 0.12	65.83 \pm 2.01 ^a
	1	68.15 \pm 0.41	67.63 \pm 2.40	67.89 \pm 1.44 ^a
	2	68.53 \pm 0.22	68.18 \pm 0.44	68.35 \pm 0.35 ^a
	4	60.97 \pm 2.25	59.53 \pm 0.11	60.25 \pm 1.54 ^b
	8	53.09 \pm 0.38	53.41 \pm 0.22	53.25 \pm 0.31 ^c
	16	51.13 \pm 2.25	51.69 \pm 0.90	51.41 \pm 0.63 ^c
	32	53.92 \pm 5.06	49.93 \pm 6.12	51.92 \pm 5.13 ^c
	Average	59.98 \pm 7.19	59.70 \pm 8.02	
$T_c - T_o$ (°C)	0	16.79 \pm 0.15	11.32 \pm 0.45	14.05 \pm 3.17 ^d
	1	21.57 \pm 0.81	20.93 \pm 1.36	21.25 \pm 0.99 ^{cd}
	2	20.17 \pm 2.41	21.84 \pm 0.93	21.00 \pm 1.78 ^{cd}
	4	25.20 \pm 2.96	27.51 \pm 0.07	26.36 \pm 2.17 ^c
	8	43.03 \pm 2.79	37.98 \pm 1.79	40.50 \pm 3.49 ^b
	16	61.58 \pm 17.20	71.43 \pm 1.23	66.50 \pm 11.47 ^a
	32	72.80 \pm 6.43	73.05 \pm 2.58	72.92 \pm 4.01 ^a
	Average	37.30 \pm 22.09	37.72 \pm 23.95	
Enthalpy (J/g)	0	16.97 \pm 1.73	16.11 \pm 2.14	16.54 \pm 1.66 ^{ab}
	1	14.35 \pm 1.71	12.16 \pm 0.20	13.25 \pm 1.60 ^{bc}
	2	12.30 \pm 0.53	13.05 \pm 1.30	12.67 \pm 0.92 ^c
	4	14.45 \pm 1.10	13.33 \pm 1.97	13.89 \pm 1.45 ^{bc}
	8	13.90 \pm 3.36	11.01 \pm 0.66	12.46 \pm 2.58 ^c
	16	16.40 \pm 1.42	16.52 \pm 3.74	16.46 \pm 2.31 ^{ab}
	32	19.97 \pm 1.23	18.94 \pm 4.78	19.46 \pm 2.91 ^a
	Average	15.48 \pm 2.75	14.45 \pm 3.31	

a, b, c, d Means in the same column with different superscript lower-case letters are significantly different ($P < 0.05$).

slightly broader after acid hydrolysis for longer than 2 d (Table 3). The retrogradation extent of both native and annealed cassava starches was significantly enhanced by acid hydrolysis as short linear chains can be rearranged more readily.

Glass transition

Amorphous native cassava starch at 10~12% moisture content showed a subsequent baseline shift attributed to a glass transition at 76.5 °C detected by DSC (Table 4). The glass transition of cassava starch was slightly shifted to 77.6 °C after annealing. With increasing hydrolysis

time, the glass transition temperatures (T_g) of native and annealed starches were progressively depressed by 3.5 to 30.1 °C and 5.3 to 24.6 °C, respectively, from 1 to 32 d hydrolysis. Amorphous starch samples had a specific heat (ΔC_p) of glass transition in the range 0.0340~0.1641 J g⁻¹K⁻¹. The reduction in specific heat was observed in both native and annealed cassava starch after acid hydrolysis for longer than 8 d.

CONCLUSION

Annealing of starch hardly affected the

Table 3 Retrogradation characteristics (mean \pm SD) of native and annealed cassava starches after acid hydrolysis for various periods. (To = onset temperature; Tc = conclusion temperature).

Retrogradation characteristics	Hydrolysis time (day)	Treatment		
		Native	Annealed	Average
To (°C)	0	35.96 \pm 0.34	42.67 \pm 0.94	39.31 \pm 3.91 ^{cd}
	1	37.81 \pm 0.84	38.43 \pm 4.99	38.12 \pm 2.95 ^d
	2	38.03 \pm 2.33	42.03 \pm 0.02	40.03 \pm 2.67 ^{cd}
	4	38.53 \pm 4.07	43.77 \pm 0.39	41.15 \pm 3.84 ^{bc}
	8	42.35 \pm 0.34	44.49 \pm 0.16	43.42 \pm 1.25 ^{ab}
	16	43.55 \pm 0.29	45.15 \pm 0.43	44.35 \pm 0.97 ^a
	32	45.48 \pm 0.98	44.94 \pm 0.55	45.21 \pm 0.72 ^a
	Average	40.24 \pm 3.66 ^B	43.07 \pm 2.67 ^A	
Tc - To (°C)	0	25.06 \pm 2.40	18.10 \pm 1.99	21.58 \pm 4.41 ^c
	1	25.11 \pm 0.87	27.78 \pm 9.89	26.44 \pm 5.93 ^{bc}
	2	27.96 \pm 2.23	22.01 \pm 0.93	24.98 \pm 3.71 ^{bc}
	4	31.30 \pm 2.63	24.81 \pm 0.76	28.06 \pm 4.07 ^b
	8	42.64 \pm 5.83	26.99 \pm 0.55	34.82 \pm 9.65 ^a
	16	32.62 \pm 4.50	26.65 \pm 0.07	29.63 \pm 4.32 ^{ab}
	32	33.46 \pm 0.17	25.81 \pm 0.08	29.63 \pm 4.42 ^{ab}
	Average	31.16 \pm 6.32 ^A	24.59 \pm 4.34 ^B	
Enthalpy (J/g)	0	5.02 \pm 0.93	3.89 \pm 0.08	4.46 \pm 0.84 ^f
	1	5.91 \pm 0.97	6.02 \pm 1.26	5.97 \pm 0.92 ^{ef}
	2	6.82 \pm 1.62	6.86 \pm 0.51	6.84 \pm 0.98 ^e
	4	9.51 \pm 0.36	10.06 \pm 0.16	9.79 \pm 0.39 ^d
	8	16.23 \pm 1.81	14.99 \pm 0.82	15.61 \pm 1.35 ^c
	16	19.47 \pm 2.37	19.45 \pm 2.74	19.46 \pm 2.09 ^b
	32	21.70 \pm 1.50	22.55 \pm 2.41	22.13 \pm 1.71 ^a
	Average	12.10 \pm 6.73	11.97 \pm 6.97	

a, b, c, d, e, f Means in the same column with different superscript lower-case letters are significantly different ($P < 0.05$).

A, B Means in the same row with different superscript capital letters are significantly different ($P < 0.05$).

Table 4 Glass transition characteristics of amorphous native and annealed cassava starches after acid hydrolysis for various periods. (To = onset temperature; Tg = glass transition temperature).

Glass transition	Hydrolysis time (day)	Treatment			
		Native		Annealed	
		Average		Average	
To (°C)	0	61.75 ± 2.60	64.25 ± 0.69	63.00 ± 2.12 ^a	
	1	61.37 ± 2.60	62.15 ± 4.14	61.76 ± 2.86 ^a	
	2	57.36 ± 1.10	56.36 ± 1.62	56.86 ± 1.27 ^b	
	4	51.54 ± 0.24	52.82 ± 3.15	52.18 ± 1.97 ^c	
	8	48.84 ± 2.38	51.80 ± 1.06	50.32 ± 2.28 ^c	
	16	47.26 ± 3.12	50.37 ± 2.44	48.81 ± 2.91 ^c	
	32	40.19 ± 0.09	49.70 ± 4.05	44.94 ± 5.97 ^d	
	Average	52.61 ± 7.81 ^B	55.35 ± 5.94 ^A		
Tg (°C)	0	76.54 ± 0.37	77.60 ± 0.18	77.07 ± 0.66 ^a	
	1	73.07 ± 0.94	72.34 ± 0.28	72.70 ± 0.70 ^{ab}	
	2	68.60 ± 0.85	68.00 ± 0.00	68.30 ± 0.60 ^{bc}	
	4	68.20 ± 0.10	67.67 ± 0.66	67.93 ± 0.49 ^{bc}	
	8	61.07 ± 7.92	64.80 ± 1.88	62.94 ± 5.17 ^{cd}	
	16	60.00 ± 4.53	63.87 ± 0.00	61.93 ± 3.44 ^d	
	32	46.47 ± 8.95	53.07 ± 3.58	49.77 ± 6.75 ^e	
	Average	64.85 ± 10.28	66.76 ± 7.43		
Specific heat (J/g/K)	0	0.1533 ± 0.0098	0.1641 ± 0.0243	0.1587 ± 0.0164 ^a	
	1	0.1035 ± 0.0237	0.1146 ± 0.0252	0.1090 ± 0.0210 ^{bc}	
	2	0.1146 ± 0.0122	0.1250 ± 0.0041	0.1198 ± 0.0096 ^{abc}	
	4	0.1490 ± 0.0299	0.1496 ± 0.0089	0.1493 ± 0.0180 ^{ab}	
	8	0.1572 ± 0.0126	0.1241 ± 0.0079	0.1406 ± 0.0210 ^{ab}	
	16	0.0963 ± 0.0125	0.0662 ± 0.0359	0.0813 ± 0.0280 ^{cd}	
	32	0.0829 ± 0.0731	0.0340 ± 0.0093	0.0584 ± 0.0511 ^d	
	Average	0.1224 ± 0.0377	0.1111 ± 0.0464		

^{a, b, c, d, e} Means in the same column with different superscript lower-case letters are significantly different ($P < 0.05$).

^{A, B} Means in the same row with different superscript capital letters are significantly different ($P < 0.05$).

molecular weight distribution, while acid hydrolysis resulted in the progressive degradation of the cassava starch components. Compared with native starch samples, annealed cassava starch samples possessed higher pasting and gelatinization temperatures, narrower gelatinization temperature ranges, relatively unchanged enthalpy and a slightly lower retrogradation extent, as well as lower peak viscosity. Annealing conditions used in this study, however, showed no apparent affect on the susceptibility of cassava starch to acid hydrolysis, or to changes in the morphology or physico-

chemical properties (for example, swelling, solubility and the pasting profile) of cassava starch. Cassava starches with lower molecular weight components after acid hydrolysis appeared to have lower swelling power and viscosity, greater solubility and a broader range of gelatinization temperatures with an increasingly enhanced extent of retrogradation. The Tg value of amorphous starches at limited moisture content (10~12%) was progressively reduced with respect to a decrease in the molecular weights of the starch components after prolonged acid hydrolysis.

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