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Food Chemistry 105 (2007) 917–925

Food Chemistry

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Influence of prior acid treatment on acetylation of wheat, potato and maize starches

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Received 25 September 2006; received in revised form 18 April 2007; accepted 19 April 2007

Abstract

Functional properties of acid-thinned, acetylated, and acid-thinned acetylated wheat, potato, and maize starches were investigated. Total amylose content and the extent of amylose leaching were increased after acid-thinning in all the starches indicating creation of more linear segments. Acid treatment decreased the swelling factor of potato starch at all tested acid concentrations but slightly increased it in wheat and maize starches in low acid treatment. Acid-thinning increased gelatinization temperatures and enthalpy but greatly decreased peak viscosity of all the starches. Wheat and maize starches showed early viscosity increase after acid-thinning but it was delayed in potato starch. Potato starch produced firmer gels after acid-thinning but wheat starch gave weaker gels. For maize starch, gel hardness was increased with low concentration acid treatment. Unchanged melting enthalpy of amylose–lipid complex in acid-thinned starch reflects its resistance to acid hydrolysis. Amylopectin retrogradation of potato and maize starches was not affected by acid modification but it decreased in wheat starch. Acetylation decreased gelatinization temperature and enthalpy, amylopectin retrogradation and gel hardness, but increased swelling factor, amylose leaching and peak viscosity. Acid-thinning decreased the degree of substitution. Introduction of acetyl groups to acid-thinned starches decreased gelatinization and retrogradation transition parameters and produced very soft gels.

Keywords: Acetylation; Acid-thinning; Acid-thinned acetylated

1. Introduction

Acid-thinning and acetylation are two common techniques for making modified starches. Acid-thinning plays a key role in manufacture of gum and candies. Acetylation alters a wide range of functional characteristics of native starches such as conferring higher peak viscosity and paste clarity and increasing freeze-thawed stability. Acid-modified starch is usually prepared by acidifying aqueous starch slurry with dilute acid (HCl, H_2SO_4, or H_3PO_3) at a temperature below the gelatinization point. Acid treatment can modify the starch granules without substantial changes in the granular form of starch. While acid molecules preferentially attack less compact amorphous regions, acid hydrolysis can take place at branch points as well as in the linear segments. It has been reported that at the early stages, the extent of acid hydrolysis is much greater in amylopectin than in the amylose fraction of maize starch (Rohwer & Klem, 1984). According to Wang and Wang (2001) acid molecules primarily attack the amorphous region and both amylose and amylopectin are simultaneously hydrolyzed. Bertoft (2004) reported that the long chains and shortest chains of amylopectin molecules are sensitive to lintnerisation, probably because they are located outside the crystallites. Acid treatment can markedly alter physicochemical properties of native starches. Increases have been reported for both transition temperatures and the breadth of the transition endotherm, however, the effect of acid treatment on the gelatinization enthalpy varied with the starch source, type and concentration of acid and the hydrolyzing time (Atichokudomchai,

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doi:10.1016/j.foodchem.2007.04.042

Varavinit, & Chinachoti, 2002; Jacobs, Eerlingen, Rouseu, Colonna, & Delcour, 1998; Jayakody & Hoover, 2000; Muhr, Blanshard, & Bates, 1984; Tang, Burn, & Hills, 2001; Thirathumthavorn & Charoenrein, 2005). Low peak viscosity development and accelerated shear-thinning and higher gelling power were common for acid treated starch. The gelling power of maize starch was reported to be inversely correlated with the acid concentration (Wang, Truong, & Wang, 2003). The extent of retrogradation as measured by DSC was reported to increase with progressive acid hydrolysis of tapioca starch (Atichokudomchai et al., 2002), but amylopectin retrogradation of rice starch stored at 4 °C for 7 days was unaffected (Thirathumthavorn & Charoenrein, 2005). By introducing acetyl groups to native starches, useful functional properties such as higher peak viscosity, higher paste clarity and improved cold storage can be achieved (Gonzalez & Perez, 2002; Hoover & Sosulski, 1985; Liu, Ramsden, & Corke, 1997, 1999). The prime action of substituted acetyl groups is the reduction of starch bond strength between molecules preventing the inter-chain association (Liu et al., 1997). Although many investigations have been carried out on the influence of acid-thinning on starch structural and functional properties very little information is available on the use of acid-thinning as a pre- or post-treatment for other modifications. Reordering and self-association of macromolecules resulting after acid-thinning may change the location of reaction site and thus acid treatment before acetylation may increase the utility of starch resulting in novel starch properties. One avenue for the production of novel starch products is the control of the reaction site on the starch macromolecules (BeMiller, 1997).

2. Materials and methods

2.1. Materials

Potato, wheat, and maize starches and fungal α-amylase were from Sigma Chemical Co., (St. Louis, MO, USA). Acetic anhydride was from Merck Co., Darmstadt, Germany.

2.2. Methods

2.2.1. Total amylose content

An amylose/amylopectin assay kit from Megazyme International Ireland Co., Wicklow, Ireland, was used to estimate the total amylose content of all the starches. This assay is based on the principle of specific formation of amylopectin complex with Concanavalin (Con A), after a pretreatment to remove lipids.

2.2.2. Swelling factor

Swelling factor, the ratio of the volume of swollen starch granules to the volume of dry starch was determined by the method of Tester and Morrison (1990), when starch (50 mg, db) was heated at 85 °C.

2.2.3. Amylose leaching

Distilled water or HCl solution (10 ml) was added to starch (20 mg, db) in a screw cap tube. Tubes were then heated at 85 °C for 30 min. After cooling to ambient temperature, samples were centrifuged at 2000*g* for 10 min. Amylose content of supernatant (0.1 ml) was estimated as described by Chrastil (1987).

2.2.4. Differential scanning calorimetry

Gelatinization and dissociation parameters of amylose–lipid complex were measured using a TA 2920 Modulated DSC Thermal Analyzer differential scanning calorimeter equipped with a thermal analysis data station (TA Instruments, Newcastle, DE). Starch (3 mg) was directly measured into the aluminum DSC pan and distilled water (9 μL) was added with a microsyringe. Pans were sealed, and allowed to stand for 1 h at room temperature for even distribution of water. The scanning temperature and the heating rates were 30–120 °C and 10 °C/min respectively. An empty pan was used as reference for all measurements.

2.2.5. Pasting properties

Pasting properties of starches were determined using a Rapid Visco-Analyser (RVA) model 3 D (Newport Scientific, Warriewood, Australia). Distilled water (25.5 g) was added to starch (2.5 g, db) in the RVA canister to obtain a total constant sample weight of 28 g. The slurry was then manually homogenized using the plastic paddle to avoid lump formation before the RVA run. A programmed heating and cooling cycle was set for 22 min, where it was first held at 50 °C for 1.0 min, heated to 95 °C in 7.5 min, further held at 95 °C for 5 min, cooled to 50 °C within 7.5 min and held at 50 °C for 1 min.

2.2.6. Gel textural analysis

Gel hardness was determined on the starch gel made in the RVA testing using a TA-XT2 Texture Analyzer (Stable Micro Systems, Godalming, Surrey, England). After RVA testing, the paddle was removed and the starch paste in the canister was covered by Parafilm and stored at 4 °C for 24 h. The gel was compressed at a speed of 0.5 mm/s to a distance of 10 mm with a 6 mm cylindrical probe. The maximum force peak in the TPA profile represents the gel hardness.

2.2.7. Retrogradation

After gelatinization test the sample was stored at 4 °C for 24 h to initiate nucleation. After that samples were kept at 40 °C for 10 days before rescanning. Temperature range and heating rate were 30–120 °C and 10 °C/min respectively.

2.2.8. Acid modification

A 40% (db) starch slurry was acid-modified as described by Singh and Ali (2000) with slights modifications using 0.1 M, 0.5 M and 1M hydrochloric acid at 50 °C for 1.5 h. The slurry was stirred frequently during the treatment period, neutralized with 1 M NaOH at the end and washed with distilled water repeatedly until the filtrate was free from acid molecules.

2.2.9. Acetylation

Acetylation was carried out as described by Wang and Wang (2002) with some slight modifications. Starch (100 g db) was dissolved in distilled water (185 ml) to make 35% slurry. The pH of the slurry was adjusted with 1 M NaOH to 8.0–8.5 and then mechanically stirred for 30 min. Acetic anhydride (8 g) was slowly (dropwise) added to the slurry while maintaining at pH 8.0–8.5. The reaction was continued for 60 min before acidifying to pH 5.5 with 1 M HCl. The slurry was then washed with three fold distilled water three times and dried at 35 °C.

2.2.10. Determination of degree of substitution

The degree of substitution for the acetylated starches was determined according to Wurzburg (1964). Blanks with unmodified starches were analyzed concurrently.

$$\begin{aligned}\%\ \text{Acetyl} = & [\text{ml.(Blank)} - \text{ml.(Sample)} \times \text{normality of acid} \\ & \times 0.043 \times 100]/\text{Wt. of starch sample(g db)}\end{aligned}$$

$$\begin{aligned}&\text{Degree of substitution(D.S.)} \\ &\quad = 162 \times \%\ \text{acetyl}/4300 - (42 \times \%\ \text{acetyl})\end{aligned}$$

3. Results and discussion

3.1. Swelling factor and amylose leaching

Swelling factor and amylose leaching of native, acid-thinned, and acid-thinned acetylated starches are presented in Table 1. A slight increase of swelling factor was found for acid-thinned wheat and maize starches from 0.1 M HCl treatment but it decreased with increased acid concentration. For potato starch, swelling factor decreased in all acid-thinned samples. Potato starch was the most affected starch by acid treatment. Swelling factor of maize starch was little affected by acid treatment compared with wheat and potato starches. The disruption of hydrogen bonding between adjacent starch polymers by acid could increase the swelling ability of starch granules at low concentration but with greater erosion of the amorphous region at higher concentration of acid it would decrease the swelling power. Jayakody and Hoover (2000) observed increased swelling factor for cereal starches at the first stage of acid hydrolysis. They suggested that interaction between hydrolyzed amylose and water could increase the swelling ability at the early stage of the treatment. Jane, Wong, and McPherson (1997) postulated that the branch points of B-type amylopectin like in potato starch are mainly located in the amorphous region making them susceptible to acid hydrolysis, but branch points of A-type starches amylopectin like those of cereals are scattered in both amorphous and crystalline regions and thus are less susceptible to acid hydrolysis. This might be one reason for the observed greater acid hydrolysis in potato starch. Apparent amylose content and the extent of amylose leaching were increased in all the starches after acid-thinning indicating that acid hydrolysis creates more linear segments that can behave as amylose. The higher the concentration of acid used, the more the apparent amylose content and the degree of amylose leaching. The highest content of total amylose resulting in acid-thinned potato starch is expected because of its greater susceptibility to acid degradation. Perhaps longer average unit chain length of potato starch amylopectin could create more linear segments than those of shorter length. As commonly observed, acetylation increased swelling factor of all the starches. By weakening the bonding forces between starch chains, larger bulky acetyl groups prevent the inter-chain association and thereby increase the hydration and swelling power of starch granules. Increased amylose leaching after acetylation may be attributed to increased starch chain mobility due to the extensive hydration of acetylated starch granules. Inhibition of inter-chain association could also facilitate more amylose chains to come out from the starch granule on heating. Introduction of acetyl groups to acid-thinned starches caused further reduction of swelling factor. Weaker starch granules due to acid degradation could be further weakened by acetylation as a result of decreasing bonding forces between adjacent starch chains and the structurally weaker granules would permit less swelling. After acid modification substitution was decreased in all the starches. Degradation of amylose and amylopectin and realignment and self-association of starch macromolecules during acid treatment could reduce the reaction sites for acetylation.

3.2. Gelatinization

DSC curves for gelatinization of native, acid-thinned and acid-thinned acetylated starches are presented in Fig. 1 and summarized in Table 2. Increases were found for gelatinization temperature and enthalpy of all the starches after acid modification. The effect was more pronounced as the acid concentration was increased. These increases were greater in potato starch while maize starch was less impact. Acid can easily hydrolyze more accessible amorphous regions than highly ordered crystalline regions, consequently eroded amorphous regions would have less impact on destabilizing the crystalline region in the gelatinization process, requiring more energy to pull the crystals apart (Donovan, 1979). Higher transition temperatures of acid hydrolyzed starch could be due to longer amylopectin double helices resulting from acid hydrolysis than in unhydrolyzed amylopectin helices, because branch points in unhydrolyzed amylopectin may reduce the length of helix-forming side chains (Morrison, Tester, Gidley, & Karkalas, 1993). Jayakody and Hoover (2000) suggested that the higher ΔH resulting from acid hydrolysis reflects the formation of more double helical starch due to the interaction between amylose–amylose and amylose–amylo-

Table 1
Swelling factor (SF), amylose leaching (AL), total amylose content (AMC), gel hardness (GH), and degree of modification (DS), of native, acid-thinned, acetylated, and acid-thinned acetylated wheat, potato, and maize starches

Starch	Treatment	SF at 85 °C	AL at 85 °C	AMC (%)	GH (g)	DS
Wheat	Native	14.8 ± 0.2	9.2 ± 0.2	24.3 ± 0.4	80 ± 1.4	
	0.1 M	16.9 ± 0.3	13.3 ± 0.4	26.1 ± 0.1	30 ± 0.3	
	0.5 M	13.8 ± 0.6	22.5 ± 0.6	28.2 ± 0.2	28 ± 0.9	
	1 M	10.3 ± 0.2	25.8 ± 0.3	30.1 ± 0.4	13 ± 1.1	
	AC	20.8 ± 0.2	14.4 ± 0.1		27 ± 0.8	0.143
	0.1 M-AC	20.2 ± 0.1	12.9 ± 0.5		–	0.136
	0.5 M-AC	15.4 ± 0.1	20.1 ± 0.7		–	0.130
	1 M-AC	15.2 ± 0.4	22.9 ± 0.8		–	0.123
Potato	Native	50.5 ± 0.7	15.5 ± 0.3	24.7 ± 0.2	36 ± 0.7	
	0.1 M	42.2 ± 0.9	18.8 ± 0.3	25.8 ± 0.2	38 ± 0.7	
	0.5 M	28.9 ± 0.5	25.1 ± 0.4	28.1 ± 0.2	78 ± 1.2	
	1 M	21.2 ± 0.3	30.1 ± 0.1	34.3 ± 0.5	56 ± 1.3	
	AC	55.3 ± 0.1	16.9 ± 0.4		18 ± 0.9	0.138
	0.1 M-AC	38.0 ± 0.2	17.7 ± 0.4		14 ± 0.8	0.127
	0.5 M-AC	26.6 ± 0.2	23.9 ± 0.6		–	0.120
	1 M-AC	16.8 ± 0.1	28.1 ± 0.4		–	0.114
Maize	Native	20.4 ± 0.4	14.1 ± 0.4	23.4 ± 0.3	58 ± 1.5	
	0.1 M	21.7 ± 0.4	15.9 ± 0.5	25.1 ± 0.4	63 ± 1.4	
	0.5 M	20.2 ± 0.8	23.5 ± 0.3	27.2 ± 0.7	27 ± 0.8	
	1 M	18.5 ± 0.3	25.8 ± 0.7	29.1 ± 0.3	24 ± 0.5	
	AC	22.5 ± 0.5	15.1 ± 0.3		23 ± 1.1	0.132
	0.1 M-AC	20.8 ± 0.1	15.3 ± 0.8		17 ± 0.8	0.128
	0.5 M-AC	20.3 ± 0.3	21.2 ± 0.2		–	0.124
	1 M-AC	17.5 ± 0.5	23.1 ± 0.1		–	0.119

AC = acetylated.
1 M, 0.5 M and 1 M = concentrations of HCl.
M-AC = acid-thinned acetylated.
Values are mean of triplicate determination ± standard deviation. For gel hardness values are at least mean of duplicate determination ± standard deviation.

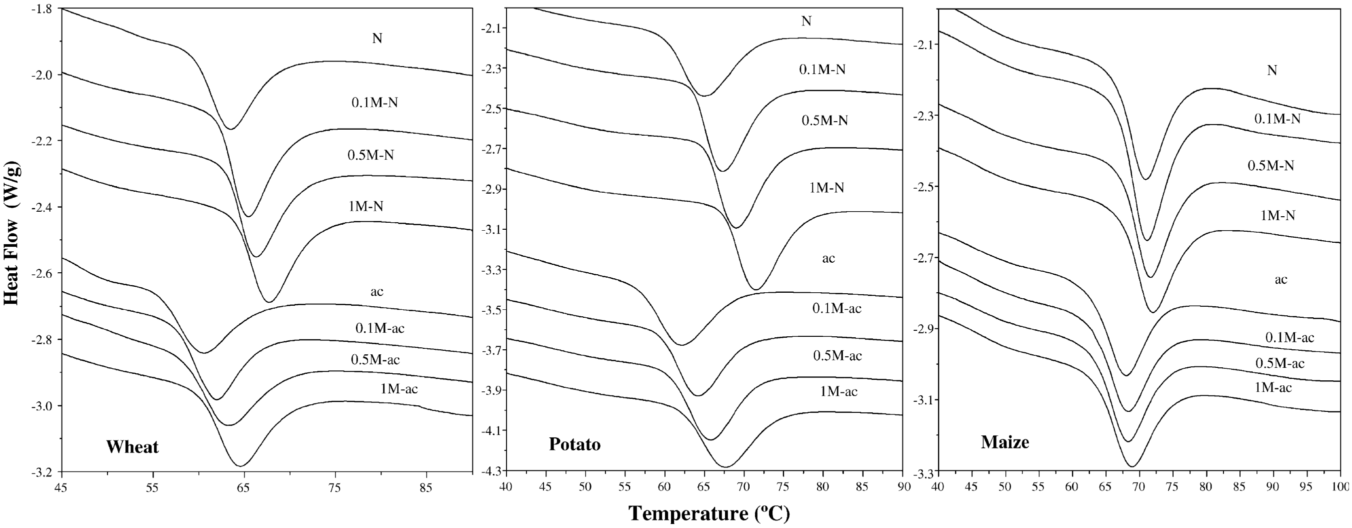

Fig. 1. DSC curves of native, acid-thinned, acetylated, and acid-thinned acetylated wheat, potato and maize starches. N = native; ac = acetylated; M-ac = acid-thinned acetylated.

pectin chains during acid hydrolysis. This is quite possible because cleavage of macromolecules by acid could lead to a greater realignment and self-association of starch macromolecules forming more double helical-like structures. Consistent with previous studies, acetylation decreased gelatinization temperature and enthalpy of all the starches. Substituted acetyl groups inhibit the inter-chain association of starch chains promoting granule hydration. Extensively hydrated granules required less energy to reach gelatinization. Acetylation of acid treated starches reduced the endo-

Table 2
Gelatinization parameters of native, acid-thinned, acetylated, and acid-thinned acetylated wheat, potato, and maize starches

Starch	Treatment	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/g)
Wheat	Native	58.0 ± 0.6	63.0 ± 0.4	74.5 ± 0.1	9.6 ± 0.3
	0.1 M	62.0 ± 0.4	65.3 ± 0.3	75.0 ± 0.2	9.9 ± 0.2
	0.5 M	62.9 ± 0.9	66.2 ± o.2	76.2 ± 0.5	9.9 ± 0.2
	1 M	64.2 ± 0.2	68.0 ± 0.3	78.5 ± 0.2	11.1 ± 0.1
	AC	55.2 ± 0.6	60.1 ± 0.4	70.3 ± 0.2	8.5 ± 0.4
	0.1 M-AC	57.8 ± 0.6	62.0 ± 0.8	70.6 ± 0.5	8.3 ± 0.2
	0.5 M-AC	59.3 ± 0.4	63.5 ± 0.9	73.5 ± 0.2	9.2 ± 0.4
	1 M-AC	60.0 ± 0.3	64.5 ± 1.1	74.6 ± 0.1	9.4 ± 0.1
Potato	Native	60.0 ± 0.2	65.0 ± 0.4	76.1 ± 0.1	15.2 ± 0.2
	0.1 M	63.7 ± 0.8	67.4 ± 0.5	78.0 ± 0.4	15.6 ± 0.3
	0.5 M	65.1 ± 0.7	69.0 ± 0.3	80.0 ± 0.3	15.9 ± 0.3
	1 M	67.0 ± 0.3	71.1 ± 0.4	82.0 ± 0.2	16.9 ± 0.4
	AC	56.2 ± 0.5	61.8 ± 0.2	73.1 ± 0.7	14.5 ± 0.5
	0.1 M-AC	59.2 ± 0.1	64.0 ± 0.3	76.1 ± 0.8	15.2 ± 0.1
	0.5 M-AC	60.5 ± 0.4	65.4 ± 0.7	76.5 ± 0.6	15.3 ± 0.3
	1 M-AC	62.0 ± 0.6	67.1 ± 0.4	80.1 ± 0.2	15.7 ± 0.1
Maize	Native	66.1 ± 0.2	70.7 ± 0.1	80.2 ± 0.3	11.5 ± 0.3
	0.1 M	67.2 ± 0.4	71.0 ± 0.2	80.2 ± 0.2	11.7 ± 0.3
	0.5 M	67.5 ± 0.2	71.4 ± 0.3	82.6 ± 0.5	11.9 ± 0.4
	1 M	67.8 ± 0.2	71.9 ± 0.2	82.8 ± 0.3	12.7 ± 0.5
	AC	62.5 ± 0.4	67.8 ± 0.6	77.1 ± 0.8	10.1 ± 0.3
	0.1 M-AC	62.9 ± 0.2	68.6 ± 0.2	78.8 ± 0.1	10.2 ± 0.4
	0.5 M-AC	63.2 ± 0.4	68.3 ± 0.5	78.5 ± 0.2	10.5 ± 0.1
	1 M-AC	63.4 ± 0.1	68.7 ± 0.1	78.5 ± 0.2	10.6 ± 0.2
Wheat (AMLC)	Native	93.4 ± 0.3	98.5 ± 0.4	104.1 ± 0.4	0.78 ± 0.09
	0.1 M	93.7 ± 0.4	98.7 ± 0.2	104.1 ± 0.5	0.75 ± 0.06
	0.5 M	95.2 ± 0.2	100.3 ± 0.1	105.6 ± 0.3	0.80 ± 0.01
	1 M	95.3 ± 0.3	101.2 ± 0.1	105.9 ± 0.1	0.75 ± 0.07

Gelatinization parameters: T_o = onset, T_p = peak, and T_c = conclusion.
ΔH = gelatinization enthalpy, AC = acetylated, AMLC = amylose–lipid complex.
1 M, 0.5 M, and 1 M = concentrations of HCl.
M-AC = acid-thinned acetylated.
All values are mean of triplicate determination ± standard deviation.

thermic transition temperature and enthalpy compared to corresponding acid treated native starches. But the transition temperature and enthalpy were increased with the increase of acid concentration in acid-thinned acetylated starches (Table 2). This indicates that the action of acetyl groups has been weakened in acid treated starches probably due the eroded amorphous region and greater realignment and self- association of macromolecules resulting from acid degradation. The reduction of substitution ability after acid treatment could also contribute to this development. Wheat starch amylose–lipid complex showed apparently unchanged ΔH for all acid treatments indicating its resistance to acid hydrolysis. The melting temperature of amylose–lipid complex slightly shifted to a higher temperature with increase of acid concentration (Table 2 and Fig. 2).

3.3. Pasting properties

Pasting profiles of native, acid-modified, acetylated, and acid-modified acetylated starches are presented in Fig. 3 and summarized in Table 3. After acid treatment rapid reduction of peak viscosity (PV) resulted in all the starches, while onset of viscosity was earlier in acid-thinned wheat and maize starches but delayed in potato starch (Fig. 3). In dilute starch paste, viscosity is primarily governed by swelling characteristics and leaching of soluble carbohydrates (mainly amylose). Early onset of PV is indicative of early and rapid swelling of starch granules. This is consistent with the observed swelling factor. Thus delayed PV onset of acid-modified potato starch is consistent with the observed decreased swelling factor after acid-thinning. Erosion of amorphous region by acid molecules could result in weaker starch granules. Weaker granules are more deformable at stirring and thus reduce the viscosity. During the cooling phase, regaining viscosity (CPV) is primarily due to realignment of amylose chains into a certain level of order (retrogradation). Acid-thinning reduced the cold paste viscosity. However, by creation of more linear segments as reflected in total amylose content and greater amylose leaching, the cold paste viscosity should be increased in acid-thinned starches. However, the decreased CPV may be due to inadequate time for the cooling phase in RVA programme used. Similar low amylose retrogradation tendency was reported for acid-modified rice starches which were subject to insufficient time in the RVA cooling

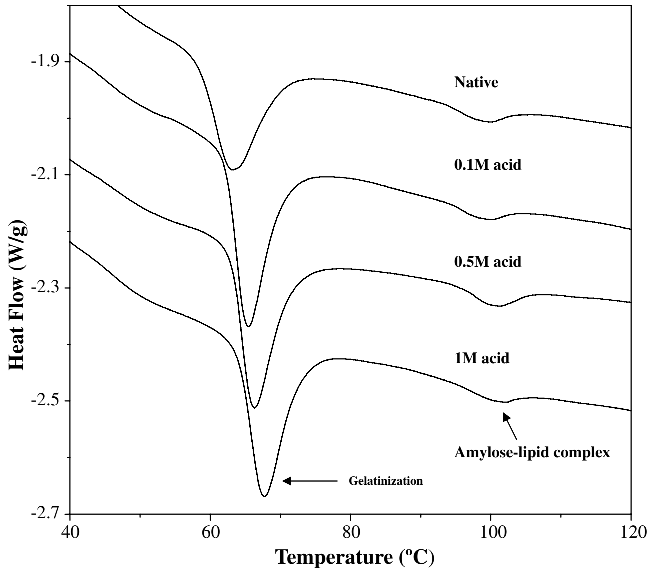

Fig. 2. DSC curves of native and acid-thinned wheat starch. Large and small endotherms represent the gelatinization endotherm and amylose–lipid complex endotherm, respectively.

phase (Thirathumthavorn & Charoenrein, 2005). Acetylation increased PV of all the native starches and caused early onset of viscosity development. This anticipated consequence is in agreement with the increased swelling power after acetylation. Extensively hydrated weaker acetylated starch granules disintegrate more easily at higher temperature resulting a greater shear-thinning. However, slightly increased hot paste viscosity (HPV) in acetylated potato starch may reflect some physical interaction occurring in the collapsed fragile starch particles. Acetylation increased the CPV of maize and wheat starch but decreased it potato starch. Substituted acetyl groups could promote creation of junction zones in amylose molecules facilitating realignment of amylose in the cold starch paste depending on the molecular characteristics of the amylose. Introduction of acetyl groups to acid-thinned starch, particularly in higher concentration acid treated potato and maize starches reduced PV than their corresponding acid-thinned starches. The action of acetyl groups may further weaken bonding forces between starch chains in acid-modified starch that have already been weakened by acid degradation, and thus more weaker granules could undergo rapid breakdown under shear force limiting viscosity development.

3.4. Gel hardness

Gel hardness of native starch followed the order: wheat > maize > potato. Acid treatment increased the gel hardness of potato starch in all cases. The hardest potato gel was produced at 1 M HCl treatment (Table 1). Gel hardness of wheat starch greatly decreased after acid-thinning. For maize starch, the hardest gel was produced at 0.1 M HCl but hardness was greatly reduced when acid concentration was increased. Acetylation greatly reduced the gel hardness of all native starches and the introduction of acetyl groups to acid-thinned starches produced very soft gels. Gel hardness of all acid-thinned acetylated wheat starches was not measurable under the test conditions. A similar trend was observed for acetylated 0.5 M, and 1 M acid-thinned maize and potato starches. A starch gel can readily form when gelatinized starch or starch paste undergoes coiling as a result of amylose aggregation. According to Ring (1985) a starch gel is a composite in which swollen gelatinized starch granules reinforce an interpenetrating amylose gel matrix. Doublier, Llamas, and Le Meur

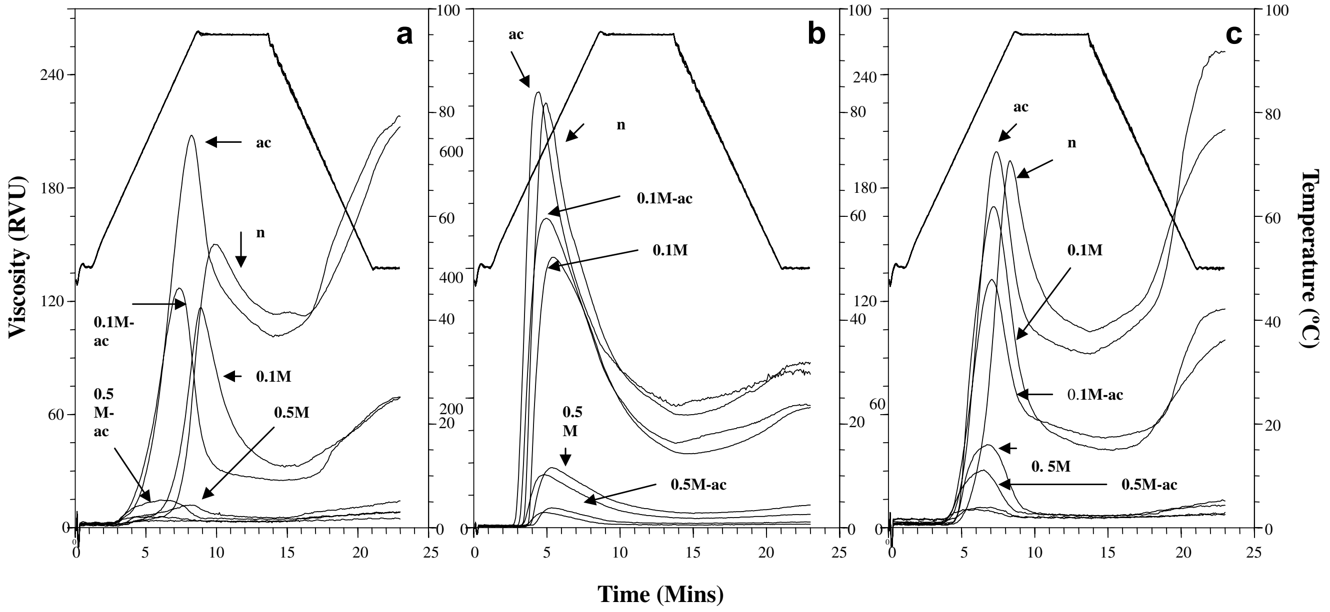

Fig. 3. RVA curves of native, acid-thinned, acetylated, and acid-thinned acetylated wheat (a), potato (b), and maize (c) starches. n = native, ac = acetylated, 0.1 M, 0.5 M, and 1 M = acid concentration used for the modification, 0.1 M-ac and 0.5 M-ac = acid-thinned acetylated.

Table 3
Pasting properties of native, acid-thinned, acetylated, and acid-thinned acetylated wheat, potato, and maize starches

Starch	Treatment	PV	HPV	BD	CPV	SB
Wheat	Native	153 ± 1.2	114 ± 1.4	39 ± 0.8	216 ± 1.6	101 ± 1.4
	0.1 M	116 ± 1.5	32 ± 0.8	84 ± 1.1	69 ± 1.7	36 ± 0.7
	0.5 M	12 ± 0.8	5.0 ± 0.7	7.0 ± 0.8	14 ± 1.2	9 ± 0.4
	1 M	6 ± 0.6	3 ± 0.6	3 ± 0.4	8 ± 0.8	5 ± 0.4
	AC	207 ± 0.9	102 ± 1.5	107 ± 1.3	218 ± 1.1	117 ± 1.3
	0.1 M-AC	127 ± 1.2	25 ± 0.8	101 ± 1.6	70 ± 1.4	44 ± 1.4
	0.5 M-AC	15 ± 0.6	4 ± 0.4	10 ± 1.7	8 ± 0.3	4 ± 0.8
	1 M-AC	5 ± 0.4	2 ± 0.7	3 ± 0.6	5 ± 0.2	2 ± 0.4
Potato	Native	655 ± 1.4	174 ± 1.7	481 ± 1.9	254 ± 1.8	81 ± 1.1
	0.1 M	416 ± 1.3	114 ± 1.3	302 ± 1.7	185 ± 1.7	71 ± 0.7
	0.5 M	92 ± 0.9	22 ± 0.7	70 ± 1.8	35 ± 1.2	13 ± 1.2
	1 M	30 ± 0.7	6 ± 0.5	24 ± 0.7	8 ± 0.8	2 ± 0.6
	AC	724 ± 1.6	63 ± 0.8	661 ± 0.4	245 ± 1.2	182 ± 1.5
	0.1 M-AC	476 ± 1.9	130 ± 0.4	346 ± 0.7	188 ± 1.4	58 ± 1.1
	0.5 M-AC	81 ± 1.4	14 ± 0.9	67 ± 1.1	20 ± 1.6	6 ± 0.4
	1 M-AC	24 ± 0.9	4 ± 0.5	20 ± 0.3	5 ± 0.8	2 ± 0.2
Maize	Native	194 ± 1.1	163 ± 1.4	90 ± 0.8	210 ± 1.8	107 ± 1.6
	0.1 M	170 ± 0.7	40 ± 1.1	129 ± 1.5	10 ± 0.6	58 ± 1.1
	0.5 M	44 ± 0.6	6 ± 0.8	37 ± 1.1	14 ± 0.7	8 ± 0.5
	1 M	11 ± 0.8	5 ± 0.7	6 ± 0.7	8 ± 0.2	3 ± 0.2
	AC	199 ± 0.9	92 ± 0.6	107 ± 0.8	252 ± 1.8	160 ± 1.4
	0.1 M-AC	131 ± 0.5	47 ± 0.4	84 ± 0.5	115 ± 2.2	68 ± 0.9
	0.5 M-AC	30 ± 0.8	60 ± 0.7	24 ± 06	12 ± .7	5 ± 0.4
	1 M-AC	10 ± 0.6	5 ± 0.7	5 ± 0.5	7 ± 0.4	2 ± 0.5

PV = peak viscosity; HPV = hot paste viscosity; BD = breakdown; SB = setback; AC = acetylated.
0.1 M, 0.5 M and 1 M = concentrations of HCl.
M-AC = acid-thinned acetylated.
Values are at least mean of duplicate determination ± standard deviation.

(1987) suggested that the main structural parameters involved in starch gelation are the deformability of swollen starch particle and the amylose concentration of the continuous network. Morris (1990) explained that starch gel properties relate to the characteristics of the gel matrix, the amylose, the deformable fillers (swollen granules) that are embedded in the continuous amylose matrix, the volume fraction of the filler, and the filler-matrix interaction. Mechanical properties of a starch gel would depend on the rheological characteristics of the amylose matrix, the volume fraction and the rigidity (deformability) of the gelatinized granules, and the interactions between the dispersed and the continuous phases (Eliasson, 1986). Amylose retrogradation depends on the molecular characteristics and the chain length of the amylose (Gidley, 1990). The harder acid-modified starch gel therefore could be due to its optimum chain length with higher concentration of linear segments in the continuous network as evidenced by greater amylose leaching (Table 1). Softer gel resulting from acid-thinned starches may be due to the greater loss of granular rigidity (deformability) of swollen starch particles in the discontinuous media. Perhaps the chain length of amylose segments after acid degradation may also negatively affect the effectiveness of the aggregation, although amylose concentration increased after acid-thinning of those starches. Acetylation decreased the gel hardness of all the starches and caused further weakening of the gel in acid-modified starches. By inhibiting the intermolecular association of starch chains acetyl groups prevent the close proximity of amylose chains and thereby hinder amylose aggregation via hydrogen bonding. Softer granules resulting in acid-thinned acetylated starch could cause a greater reduction of granular rigidity (deformability) of swollen particles in the discontinuous phase leading to formation of a very soft starch gel.

3.5. Retrogradation

The extent of amylopectin retrogradation in native starches followed the order: potato > maize > wheat. Reordering of amylopectin in potato and maize starch gel was not apparently affected after acid modification but it decreased in wheat starch (Table 4). It has been shown that chain length of amylopectin with DP 12–22 are more prone to reassociate during the retrogradation, whereas greater relative proportion of amylopectin with DP 6–9 and DP > 25 decreased amylopectin retrogradation enthalpy (Vandeputte, Vermeylen, Geeroms, & Delcour, 2003). Acid can hydrolyze branch points of amylopectin and thereby affect the average chain length distribution of amylopectin whereas the cleavage of macromolecules by acid molecules could facilitate realignment and self-association of macromolecules forming more double helical-like structures in starch gel. Thus the melting enthalpy of retrograded acid-modified starch could be attributed to the interplay of the above two factors. Acetylation decreased amylopectin

Table 4
Melting enthalpy (ΔH_R) of retrograded amylopectin starch crystals of native, acid- thinned, acetylated, and acid-thinned acetylated starches

Starch	Treatment	ΔH_R (J/g)
Wheat	Native	0.6 ± 0.1
	0.1 M	0.3 ± 0.05
	0.5 M	0.2 ± 0.03
	1 M	–
	AC	–
	0.1 M-AC	–
	0.5 M-AC	–
	1 M-AC	–
Potato	Native	4.6 ± 0.1
	0.1 M	4.4 ± 0.2
	0.5 M	4.5 ± 0.3
	1 M	4.6 ± 0.01
	AC	1.8 ± 0.02
	0.1 M-AC	2.2 ± 0.04
	0.5 M-AC	2.4 ± 0.07
	1 M-AC	3.0 ± 0.02
Maize	Native	1.2 ± 0.02
	0.1 M	1.3 ± 0.01
	0.5 M	1.2 ± 0.1
	1 M	0.8 ± 0.02
	AC	0.2 ± 0.01
	0.1 M-AC	0.4 ± 0.05
	0.5 M-AC	0.6 ± 0.02
	1 M-AC	0.7 ± 0.04

AC = acetylated.
0.1 M, 0.5 M, and 1 M = concentrations of HCl.
M-AC = acid-thinned acetylated.

retrogradation to a greater extent in all the native starches. No retrogradation was evident for all the wheat starches after acetylation. This is expected as the bulky acetyl groups attached to amylopectin prevent the reordering of amylopectin chains in the starch paste. Acetylation also decreased retrogradation of acid-modified starches but to a lesser extent compared to corresponding acetylated native starches (Table 4). This tendency was more pronounced when acid concentration is increased for acid-thinning. This is consistent with the decreased degree of modification after acid treatment.

4. Conclusions

Increased total amylose content and degree of amylose leaching reflect creation of more linear segments during acid modification probably due to the cleavage of amylopectin branch points. Such cleavage, including amylose chains, facilitates more realignment and self-association of macromolecules within the starch granules affecting gelatinization, pasting, and retrogradation properties. Gelling power after acid-thinning depends on the botanical source of starch and the acid concentration used for modification. Amylose–lipid complex has greater resistance to acid degradation. As commonly exhibited, acetylation decreased gelatinization parameters and retrogradation and increased swelling power, amylose leaching, and peak viscosity. Decreased substitution in acid-thinned starches shows that acid degradation reduces the number of reaction sites probably due to the realignment and self-association of amylose and amylopectin during acid treatment.

Acknowledgements

This work was supported by grants from the University of Hong Kong Committee on Research and Conference Grants, and the Hong Kong Research Grant Council.

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