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Structures and rheological properties of corn starch as affected by acid hydrolysis

Ya-Jane Wang[a,*], Van-Den Truong[b], Linfeng Wang[a]

[a]*Department of Food Science, University of Arkansas, 2650 N. Young Avenue, Fayetteville, AR 72704, USA*
[b]*Department of Food Science, North Carolina State University, Raleigh, NC 27695, USA*

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Abstract

Common corn starch was treated with different concentrations of hydrochloric acid, 0.06, 0.14, and 1.0N, for different lengths of time, 18, 6, and 1 h, respectively, to reach a similar peak viscosity as measured by Brabender Viscoamylograph. The fine structures, crystallinity and thermal properties were characterized and the rheological properties were evaluated using both compression and dynamic oscillatory tests. Acid hydrolysis had little effect on amylopectin branch chain-length distribution, gelatinization and retrogradation properties. However, the higher acid concentration (1.0N) degraded both amylopectin and amylose to a greater extent compared with the other two lower acid concentrations (0.06 and 0.14N). The acid treated starches had slightly higher degrees of crystallinity and lower amylose content than did the unmodified starch. Degradation of amylose and amylopectin by a high acid concentration resulted in a decrease in storage modulus (G'), loss modulus (G''), gelling temperature, and gel strength of the acid-thinned starches.

Keywords: Acid-thinned corn starch; Gel strength; Rheological properties

1. Introduction

Acid modification is widely used in the starch industry to prepare thin boiling starches for use in food, paper, textile and other industries (Rohwer & Klem, 1984). The typical procedure to manufacture acid-thinned starch involves treating a concentrated starch slurry (36–40% solids) at a temperature below the gelatinization temperature of the starch (40–60 °C) with mineral acid for a period of time (Wurzburg, 1986). When the desired viscosity or degree of conversion is reached, acid is neutralized and starch is recovered. Hydrolysis can be controlled by the acid concentration, the reaction time, and the temperature. The current knowledge on the mechanism and effects of acid hydrolysis on structures and physicochemical properties of various starches was recently reviewed by Hoover (2000).

The amorphous regions of starch are more rapidly hydrolyzed than are the crystalline regions during acid hydrolysis at temperatures below the gelatinization temperature (BeMiller, 1965). Kerr (1952) demonstrated that in early stages of acid modification the amount of amylose or linear fraction in starch increased and amylopectin was preferentially hydrolyzed, inferring amylose was protected by forming a resistant complex with particles of amylopectin. Results from Cowie and Greenwood (1957) agreed with Kerr's conclusions (1952) and they further suggested that initial acid attack occurred preferentially on the surface layer of the granule before hydrogen ions diffused into the inner regions and the surface layer was predominantly amylopectin.

Acid modification changes the physicochemical properties of starch without destroying its granule structure. The gelatinization temperature and the breadth of the gelatinization endotherm have been shown to increase on hydrolysis (Shi & Seib, 1992). The retrogradation rate of acid-thinned starch gels increased as hydrolysis proceeded (Kang, Kim, Lee, & Kim, 1997). Acid modification also increased solubility and gel strength and decreased viscosity of starches (Kim & Ahn, 1996; Osunsam, Akingbala, & Oguntimein, 1989;). The viscoelastic properties of starches are also affected by acid hydrolysis. Virtanen, Autio, Suortti, and Poutanen, (1993) reported that the gel of acid-modified oat starch, although less rigid, was more elastic

* Corresponding author. Tel.: +1-479-575-3871; fax: +1-479-575-6936.
E-mail address: yjwang@uark.edu (Y.-J. Wang).

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than the corresponding native starch gel. Dynamic rheological tests showed that the dispersions of acid-modified waxy corn starch behaved as Newtonian liquid-like solution, while the unmodified counterpart behaved like weak gels (Chamberlain & Rao, 1999).

Our earlier study reported the differences in physicochemical properties of acid-thinned corn, potato, and rice starches in relation to their structures under the same hydrolysis conditions (Wang & Wang, 2001). The inherent structures of starch before acid modification played an important role in determining its functionality and starch gelation was strongly affected by its amylose content, molecular size of amylose and amylopectin, and short and long branch chains in amylopectin. Although the extent of acid hydrolysis of starch is commercially controlled based on a target viscosity, little work has been done to study the impact of different acid concentrations on the physicochemical properties of acid-thinned starches having a similar viscosity. This study was undertaken to investigate if different acid concentrations would result in different fine structures and consequently the physicochemical properties, particularly rheological properties, of acid-thinned corn starch when they were hydrolyzed to a similar peak viscosity as determined by Brabender Viscoamylograph.

2. Materials and methods

2.1. Materials

Common corn starch (CnGel 03420) was obtained from Cerestar USA, Inc. (Hammond, IN). Isoamylase (1,250,000 units/mg protein, I-2758) was purchased from Sigma (St Louis, MO). All chemicals were ACS grade.

2.2. Preparation of acid-thinned starch

A 40% starch slurry was prepared by adding 400 g starch (dry basis, db) with 0.06N hydrochloric acid (HCl) solution at 50 °C to a final weight of 1000 g in a 50 °C water bath. The reaction was terminated when the peak viscosity of the resulting acid-thinned starch (10%, db) fell between 200 and 300 BU as measured by a Brabender Viskograph-E (C.W. Brabender Instruments, Inc., S. Hackensack, NJ). Thereafter, the slurry was neutralized to pH 5.5 with 1N NaOH and washed three times with twofold volume of deionized water prior to filtration. The starch was dried in a convection oven at 45 °C overnight. The same procedure was repeated with 0.14 and 1.0N HCl.

2.3. Structural characterization of acid-thinned starch

The structures of native and acid thinned starch before and after isoamylase debranching were characterized with high-performance size-exclusion chromatography (HPSEC) and high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) according to the method of Kasemsuwan, Jane, Schnable, Stinard, and Robertson (1995) with modifications (Wang & Wang, 2001). A Waters HPSEC system consisted of a 515 HPLC pump with an injector of 100 μl sample loop, an in-line degasser, a 2410 refractive index detector maintained at 40 °C, and a series of Shodex OHpak columns, including a guard column, KB-802 and KB-804 columns maintained at 55 °C with a column heater. The mobile phase was 0.1 M $NaNO_3$ and 0.2% NaN_3 at a rate of 0.7 ml/min. Dextran standards, ranging from 5200 to 872,300 of weight average molecular-weight (Mw) (PSS Polymer standards service-USA, Inc.) and sugars with degree of polymerization (DP) 1 to 7 (Sigma Chemical Co.) were used to construct the regression line for MW determination. The HPAEC-PAD (Dionex DX500) system consisted of the following components: GP50 gradient pump, LC20-1 chromatography organizer, ED40 electrochemical detector, 4 × 50 mm CarboPac PA1 guard column, 4 × 250 mm CarboPac PA1 analytical column, and AS40 automated sampler. Amylose content was calculated from the peak area under the amylose fraction of the isoamylase-debranched starch chromatogram.

2.4. Iodine affinity and X-ray diffraction

The iodine affinity (IA) of defatted starch was determined in duplicate with amperometric titration (Schoch 1964). The IA of purified corn amylose was assumed as 20.0%. The X-ray patterns of starches were obtained with a copper anode X-ray tube using a Philips Analytical diffractometer of Almelo (The Netherlands). The diffractometer was operated at 27 mA and 50 kV. The scanning region of the diffraction angle (2θ) was from 5 to 45° at 0.1° step size with a count time of 2 s. The starch samples were equilibrated in a 100% relative humidity chamber for 24 h at room temperature. The starch crystallinity was calculated using the upper area (crystalline area) divided by the total area (crystalline and amorphous area). The areas were obtained by using a mechanical polar planimeter (Model L-30, Los Angeles Scientific Instrument Co., Inc., Los Angeles, CA) (Komiya & Nara, 1986).

2.5. Pasting properties and gel strength

Pasting characteristics of acid-thinned starches were determined using a Brabender Viskograph-E equipped with a 700 cmg cartridge operated at a speed of 75 rpm. Acid-thinned starch (10%, db) was mixed with water to a final weight of 450 g and the slurry was heated from 35 to 95 °C at a rate of 1.5 °C/min, held at 95 °C for 20 min and cooled down to 25 °C at a rate of 1.5 °/min. Unmodified corn starch was cooled down to 50 °C because of excessive high viscosity.

The starch paste prepared with the Brabender Viskograph-E was used to measure the gel strength. The paste was

stored at 5 °C for 24 h and measured with a TA-XT2 Texture Analyzer (Texture Technologies Corp., Scardale, NY). The paste was poured into three aluminum dishes (75 mm dia. × 20 mm height). The rims of the dishes were extended with aluminum foil to increase the height of the gel 1 cm above the rim (Takahashi, Maningat, & Seib, 1989). The gel was compressed at a speed of pre-test 2.0 mm/sec, test 0.2 mm/sec, and post-test 0.2 mm/sec, to a distance of 5.0 mm with a cylindrical probe (2.54 mm dia. × 2.54 mm height) under the texture profile analysis (TPA) test mode. The peak force of the first penetration was termed gel strength. Triplicate measurements were performed on each starch sample.

2.6. Thermal properties

Thermal properties of native and acid-thinned starches were measured by using a Perkin–Elmer Pyris-1 Differential Scanning Calorimeter (DSC, Perkin–Elmer Co., Norwalk, CT) equipped with a cooling system according to the method of Wang, White, and Pollak (1992). Gelatinized samples were stored at 5 °C and the samples were re-scanned after 1, 3, and 7 days of storage to determine the enthalpy changes of retrograded starch. The degree of retrogradation was determined as the ratio of enthalpy change of retrograded starch to enthalpy change of gelatinized starch.

2.7. Dynamic rheological measurements

Dispersions of the acid-thinned starch (10% w/w, dry basis) were prepared in deionized water using a magnetic stirring hot plate (Barnstead/Thermolyne, Dubuque, IA). The surface temperature of the hot plate was maintained at 250 °C and stirring speed was set at 750 rpm. Twenty-five ml of starch dispersion in a 50 ml beaker covered with aluminum foil to minimize water evaporation was heated with continuous stirring to reach 75 °C. The sample was immediately transferred into a Couette cup of a stress-controlled rheometer, StressTech (Reologica Instrument AB, Lund, Sweden/ATS Rheosystems, Bordentown, NJ) set at 95 °C and the C25 bob attachment was lowered to measurement position. Dynamic oscillatory tests were performed: (a) during holding the sample at 95 °C for 30 min, followed by a frequency sweep from 0.01 to 20 Hz at this temperature, and (b) ramp cooling at a rate of 1.5 °C/min from 95 to 5 °C, at which the frequency sweep was repeated. During holding and cooling, storage modulus (G') and loss modulus (G'') were monitored at 0.05 Hz. All the tests were conducted in duplicates at a constant stress of 0.7 Pa, which was within the linear viscoelastic region of the formed gels.

3. Results and discussion

3.1. Structural characterization of acid-thinned starch

Corn starch treated with different HCl concentrations reached the target Brabender peak viscosity of 200–300 BU after different lengths of reaction time. Starch treated with 0.06, 0.14 and 1.0N HCl reached the target viscosity in 18, 6 and 1 h, respectively. As the acid concentration increased, the starch hydrolysis rate increased accordingly. Agra, Warnijati, and Rijadi (1969) measured the hydrolysis kinetic of sweet potato at atmospheric pressure and 100 °C and reported that the rate constant was influenced by the catalyst concentration.

The carbohydrate distributions of unmodified and acid-thinned starches analyzed with HPSEC are presented in Fig. 1. Fraction I (Fr. I) consisted of high MW carbohydrates, mainly amylopectin; fraction II (Fr. II) was composed of low MW carbohydrates, mainly amylose. The peak of Fr. Is of acid-thinned starches shifted to a longer retention time after acid treatment with the 1.0N HCl treated starch showing the longest retention time, indicating that the molecular size of amylopectin was decreased by acid with the most degradation from the highest acid concentration, 1.0N HCl. The average MW of each peak is listed in Fig. 1. The peak retention time of Fr. IIs remained relatively unchanged after acid treatment but their proportions increased as a result of amylopectin degradation.

The carbohydrate distribution of isoamylase-debranched starches were resolved by HPSEC and the normalized profiles and the average MW of each peak are shown in Fig. 2. Fr. I consisted of amylose; Fr. II and Fraction III (Fr. III) consisted of long and short branch chains of amylopectin, respectively. The amount of higher MW molecules in amylose fraction (Fr. I) decreased after acid hydrolysis with starch treated with 1.0N HCl showing the most decrease. No significant difference was noted in Fr. II and III among the acid-treated starches. As the HCl concentration increased, more amylose were degraded into lower MW molecules, although most of these lower MW

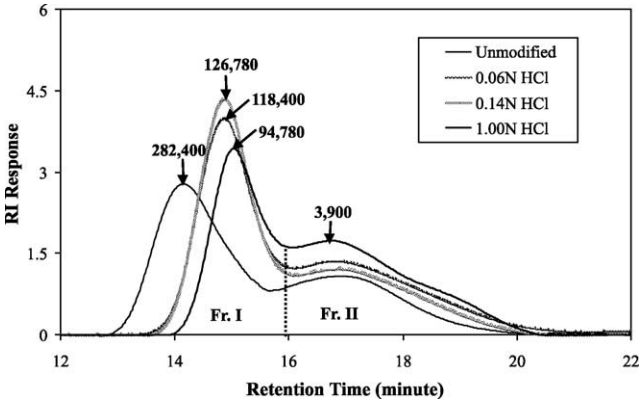

Fig. 1. High-performance size-exclusion chromatograms of unmodified and acid-thinned corn starches. Fr. I-amylopectin, Fr. II-amylose.

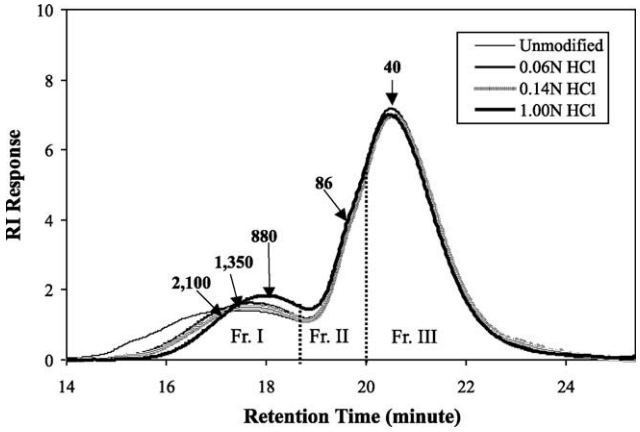

Fig. 2. High-performance size-exclusion chromatograms of isoamylase-debranched unmodified and acid-thinned corn starches. Fr. I-amylose, Fr. II-long branch chains of amylopectin, Fr. III-short branch chains of amylopectin.

molecules still remained within Fr. I. These results together with results from HPSEC of whole starches (Fig. 1) demonstrated that hydrolysis of starch with a higher concentration of HCl hydrolyzed a greater amount of higher MW molecules in both amylose and amylopectin fractions.

There were no differences among the amylopectin branch chain distributions with degree of polymerization (DP) $\leq$ 63 of unmodified and acid-thinned starches (data not shown), confirming the previous HPSEC results of no difference in Fr. IIs and IIIs of isoamylase-debranched starches. The results suggested that only amorphous regions were hydrolyzed in the present study because no change in amylopectin chain length distribution was noted, supporting the conclusion of Robyt, Choe, Fox, Hahn, and Fuchs (1996) that acid first attacked the amorphous regions in starch granule. The present findings also implied that amylose and amylopectin were not likely to be present in separate locations but rather adjacent to each other within starch granule, particularly in the amorphous regions, because both amylose and amylopectin were degraded to a greater extent as the acid concentration increased. Acid apparently did not preferentially attack amylopectin over amylose that is a minor component in common corn starch. When HCl concentration increased, it was possible that more hydrogen ions would be available to penetrate into a greater proportion of amorphous regions, therefore more degradation of amylose and amylopectin molecules took place in starches treated with a higher concentration HCl.

3.2. Iodine affinity and X-ray diffraction

The amylose content by Fr. I of HPSEC of isoamylase-debranched starch and by IA are listed in Table 1. The amylose content of corn starch decreased after acid treatment but no difference was found among the three acid-treated samples, indicating that although high MW amylose molecules were hydrolyzed to different extents

Table 1
Amylose content, gel strength and crystallinity of unmodified and acid-thinned corn starches

Corn starch	Amylose content (%)		Gel strength (g)	Crystallinity (%)
	HPSEC[a]	Iodine affinity		
Unmodified	27.3[a]	27.5[a]	472[d]	25.4
0.06N HCl	25.7[b]	25.4[b]	1089[a]	26.8
0.14N HCl	25.9[b]	25.2[b]	869[b]	27.2
1.00N HCl	25.6[b]	24.8[b]	776[c]	27.9

Average of duplicate measurements. Mean values in the same column with different letters are significantly different ($p < 0.05$).

[a] The amylose content calculated from fraction I of high-performance size-exclusion chromatogram (HPSEC) of isoamylase-debranched starch.

according to the HPSEC results, the hydrolyzed amylose molecules still possessed a sufficient molecular weight to form complex with iodine. The crystalline regions of starch are formed by clusters of short chains of amylopectin and the amorphous regions of amylopectin surround the clusters. Amylose is proposed to be present in the same direction of amylopectin growth and transversely across many amorphous regions within one growth ring (Lineback 1984). Thus, both amylose and amylopectin were degraded by acid but not completely hydrolyzed, and the extent of hydrolysis was affected by the acid concentration as suggested by the present results.

The X-ray diffraction patterns of three acid-thinned starches and their native counterparts are shown in Fig. 3 and the calculated crystallinity values are listed in Table 1. The degree of crystallinity of acid-thinned starches increased slightly with increasing acid concentration with sharper peaks at $2\theta = 17$ and 20°. It has been suggested that cleavage of starch chains in the amorphous regions allowed extensive reordering of the chain segments to give a more crystalline structure with a sharper X-ray pattern (Kainuma & French, 1971). Starch treated with a higher acid concentration showed a slight increase in crystallinity, possibly because of more extensive hydrolysis and subsequently more reordering.

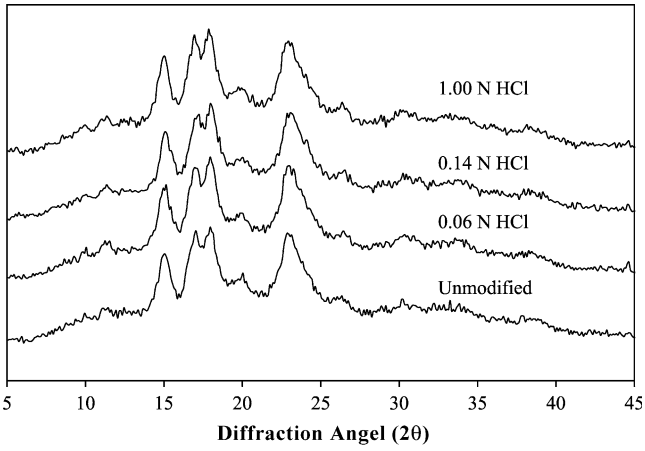

Fig. 3. X-ray diffraction of unmodified and acid-thinned corn starches.

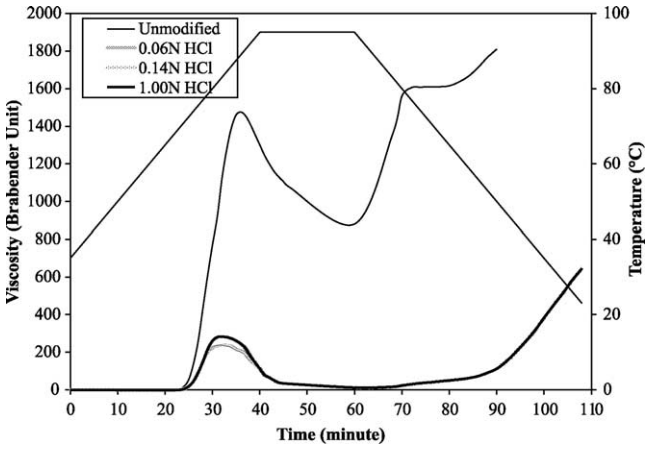

Fig. 4. Pasting profiles of unmodified and acid-thinned corn starches.

3.3. Pasting properties and gel strength

The pasting profiles of unmodified and acid-thinned starches are shown in Fig. 4. The unmodified corn starch had the highest peak and final viscosities and the three acid-treated samples shared a similar pasting temperature and final viscosity. Although more amylose and amylopectin were degraded in 1.0N HCl-treated sample, there were no differences in the peak and final viscosities. It was hypothesized that starch swelling was predominantly controlled by the amylose and/or amylopectin in the amorphous regions close to granule surface. If those amorphous regions were degraded, starch would swell to a similar degree regardless of the extent of further hydrolysis.

The gel strength (10%, d.b.), defined as the maximum force of first compression by total profile analysis, varied significantly among the four samples (Table 1). Unmodified corn starch had the lowest gel strength, suggesting the negative effect of amylopectin branching structure on gel formation since the amorphous regions hydrolyzed by acid is composed of mainly amylopectin branches. The gel strength of acid-thinned corn starches inversely correlated with the acid concentration with the highest acid concentration (1.0N) showing the lowest gel strength (776 g). The decreased gel strength could be attributed to a lower amount of large MW amylose molecules as shown in Fig. 2.

3.4. Thermal properties

Thermal properties of native and acid-thinned starches are summarized in Table 2. A slightly lower onset and peak temperatures were observed for the 1.0N HCl-treated starch but no differences in enthalpy and degree of retrogradation after storage were observed. The slight decrease in gelatinization temperature might reflect the importance of amorphous regions in controlling gelatinization and the structural differences between 1.0HCl-treated starch versus others.

Table 2
Thermal properties of unmodified and acid-thinned corn starches

Starch sample	Gelatinization			Degree of retrogradation (%)[a]		
	Onset temp. (°C)	Peak temp. (°C)	Enthalpy (J/g)	1-day	3-day	7-day
Unmodified	69.7[a]	73.5[a]	13.37[a]	22.8[b]	35.3[a]	36.8[a]
0.06N HCl	69.7[a]	73.4[a]	13.37[a]	24.2[b]	34.1[a]	36.3[a]
0.14N HCl	69.3[a]	73.0[a]	13.10[a]	26.1[a]	34.3[a]	38.7[a]
1.00N HCl	68.4[b]	72.4[b]	12.87[a]	27.1[a]	35.5[a]	39.3[a]

Average of triplicate measurements. Mean values in the same column with different letters are significantly different ($p < 0.05$).
[a] Ratio of retrogradation enthalpy to gelatinization enthalpy.

3.5. Dynamic viscoelasticity

The magnitudes of the elastic component, storage modulus (G') and viscous component, loss modulus (G'') of all acid-treated starches decreased during holding at 95 °C (Fig. 5). The greater values of G'' compared to G' indicated that the acid-thinned starches behaved as liquid-like dispersions at high temperatures. The results were in contrast with the gel-like behavior ($G' > G''$) of heated starch dispersions of native starches from different botanical origins including maize (Biliaderis, 1992; Eliasson, 1986). The liquid-like behavior ($G'' > G'$) of the acid-thinned starches also exhibited in their mechanical spectra as a function of frequency (Fig. 6). Similar behavior of acid converted waxy maize starches in dynamic rheological tests was reported by Chamberlain and Rao (1999).

The G' and G'' values of the acid-treated starches at 95 °C were inversely related to the acid concentrations (Fig. 5). The decreases in G' and G'' associated with increasing acid concentrations are in accordance with the extent of acid hydrolysis on amylose in the amorphous region of starch granules as shown in the previous section. It has been known that during heating of cereal starches, with an exception of oat starch (Virtanen et al., 1993),

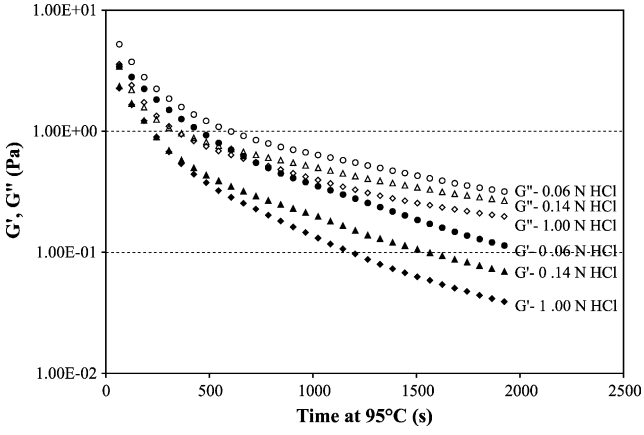

Fig. 5. Changes in G' and G'' of acid-thinned starch dispersions hold at 95 °C.

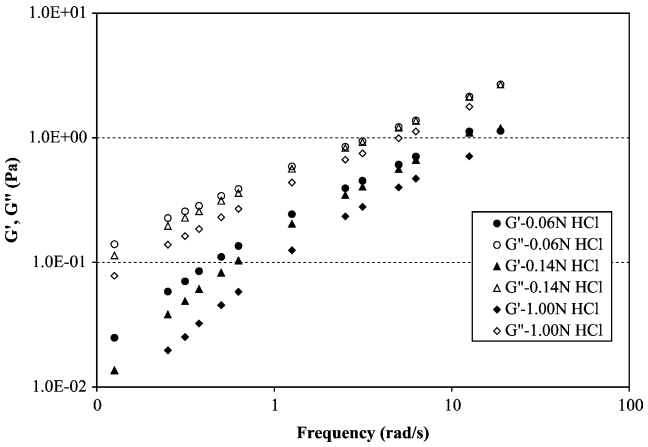

Fig. 6. Frequency sweeps of acid-thinned starch dispersions at 95 °C.

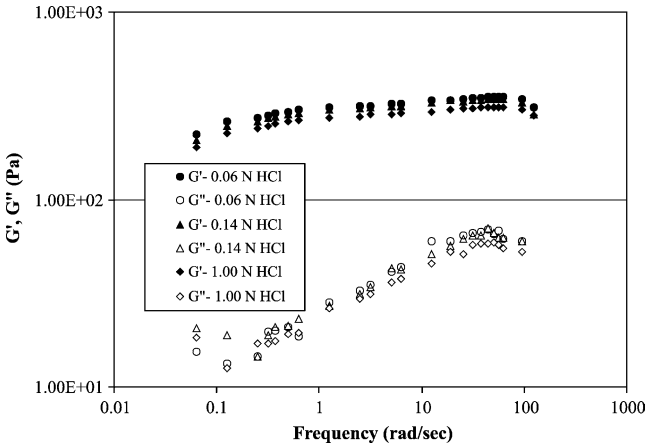

Fig. 8. Frequency sweeps of acid-thinned starch gels at 5 °C.

amylose leaching out of starch granules forms continuous gel matrix embedded with swollen gelatinized granules containing primarily amylopectin (Biliaderis, 1992). Shorter chains of amylose molecules of acid-hydrolyzed starches accounted for low viscous and elastic properties of the heated dispersions. Upon cooling, the sol to gel transformation occurred in all three samples (Fig. 7). Both G' and G'' increased as temperature decreased and the crossover of the cooling curves indicates the gelling point (Rao, 1999). Starch treated with 0.06 and 0.14N HCl had a gelling point at about 57 °C while the 1.00 N HCl treated starch gelled at 50 °C. At 10% concentration as in this study, dispersions of native corn starch gels at about 60–70 °C (Eliasson, 1986; Hansen, Hoseney and Faubion, 1991). This decrease in gelling point of the acid converted starches can be attributed to less entanglement of smaller sizes of amylose molecules in the dispersions and more bonding such as hydrogen bonds needed to be formed during cooling before gelation can occur. The mechanical spectra of the acid-thinned starches exhibited frequency dependency with G' higher than G'' (Fig. 8), indicating that these samples can be classified as weak gels. The differences in G' and G'' magnitudes were not distinct as in the large strain test, gel strength (Table 1), but the trend of the acid concentration effect on the gel strength was similar, i.e. the 1.00N HCl treated sample had the lowest G' followed by the 0.14N and 0.06N samples.

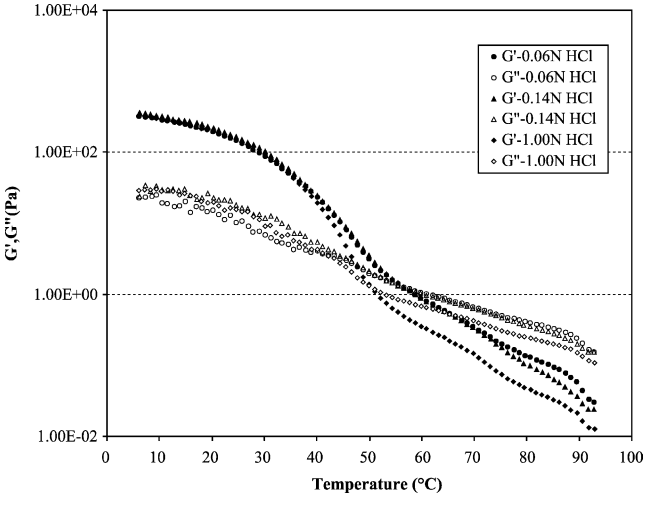

Fig. 7. Changes of G' and G'' of acid-thinned starch dispersions during cooling.

4. Conclusions

Corn starches treated with different concentrations of HCl exhibited different structural profiles and rheological properties even though they were hydrolyzed to a similar viscosity and showed similar amylose content, thermal properties, X-ray diffraction pattern, and amylopectin chain length distribution. Both amylose and amylopectin were hydrolyzed to a greater extent when acid concentration was increased. Even though the acid-thinned starches were tailored to have the same Brabender viscosity profiles, dynamic rheological tests revealed differences in their viscoelastic behaviors and gelling properties upon heating and cooling.

References

Agra, I. B., Warnijati, S., & Rijadi, R. S. (1969). Hydrolysis of sweet potato starch at atmospheric pressure. *Journal of the Directorate General Higher Education of Indonesia*, *2*(3), 34–44.

BeMiller, J. N. (1965). Acid hydrolysis and other lytic reactions of starch. In R. L. Whistler, & E. F. Paschall (Eds.), (*Vol. 1*) (pp. 495, *Starch: Chemistry and Technology*, New York: Academic Press.

Biliaderis, C. G. (1992). Characterization of starch networks by small strain dynamic rheometry. In R. J. Alexander, & H. F. Zobel (Eds.), *Developments in carbohydrate chemistry* (pp. 87–135). St. Paul, Minnesota: American Association of Cereal Chemists, Inc.

Chamberlain, E. K., & Rao, M. A. (1999). Rheological properties of acid

converted waxy maize starches in water and 90% DMSO/10% water. *Carbohydrate Polymers*, *40*, 251–260.

Cowie, J. M. C., & Greenwood, C. T. (1957). Physicochemical studies on starches. Part V. The effect of acid on potato starch granules. *Journal of Chemical Society*, 2658-2665.

Eliasson, A.-C. (1986). Viscoelastic behavior during the gelatinization of starch. *Journal of Texture Studies*, *17*, 253–265.

Hansen, L.M., Hoseney, R.C. & Faubion, J.M., (1991). Oscillatory rheometry of starch-water systems: effect of starch concentration and temperature.. *Cereal Chemistry*, *68*, 347–351.

Hoover, R. (2000). Acid-treated starches. *Food Review International*, *16*, 369–392.

Kainuma, K., & French, D. (1971). Naegeli amylodextrin and its relationship to starch granule structure. I. Preparation and properties of amylodextrins from various starch types. *Biopolymers*, *10*, 1673–1680.

Kang, K. J., Kim, S., Lee, S. K., & Kim, S. K. (1997). Relationship between molecular structure of acid-hydrolyzed rice starch and retrogradation. *Korean Journal of Food Science and Technology*, *29*, 876–881.

Kasemsuwan, T., Jane, J., Schnable, P., Stinard, P., & Robertson, D. (1995). Characterization of the dominant mutant amylose-extender (Ael-5180) maize starch. *Cereal Chemistry*, *72*, 457–464.

Kerr, R. W. (1952). Degradation of corn starch in the granule state by acid. *Starch/Staerke*, *4*, 39–41.

Kim, R. E., & Ahn, S. Y. (1996). Gelling properties of acid-modified red bean starch gels. *Agricultural Chemistry and Biotechnology*, *39*, 49–53.

Komiya, T., & Nara, S. (1986). Changes in crystallinity and gelatinization phenomena of potato starch by acid treatment. *Starch/Staerke*, *38*(1), 9–13.

Lineback, D. R. (1984). The starch granule-organization and properties. *Baker's Digest*, *58*(2), 16 See also pp. 18–21.

Osunsam, A. T., Akingbala, J. O., & Oguntimein, G. B. (1989). Effect of storage on starch content and modification of cassava starch. *Starch/Staerke*, *41*, 54–57.

Rao, M. A. (1999). *Rheology of fluid and semisolid foods: Principles and applications*. Gaithersburg, Maryland: Aspen Publishers, Inc, pp. 332.

Robyt, J. F., Choe, J. Y., Fox, J. D., Hahn, R. S., & Fuchs, E. B. (1996). Acid modification of starch granules in alcohols: Reactions in mixtures of two alcohols combined in different ratios. *Carbohydrate Research*, *283*, 141–150.

Rohwer, R. G., & Klem, R. E. (1984). Acid-modified starch: Production and uses. In J. N. BeMiller, & E. F. Paschall (Eds.), *Starch: Chemistry and technology* (pp. 529–541). Orlando, FL: Academic Press.

Schoch, T. J. (1964). Iodimetric determination of amylose. Potentiometric titration: Standard method. In R. L. Whistler, R. J. Smith, J. N. BeMiller, & M. L. Wolfrom (Eds.), *Methods in carbohydrate chemistry: Starch IV* (pp. 157–160). London: Academic Press.

Shi, Y.-C., & Seib, P. A. (1992). The structure of four waxy starches related to gelatinization and retrogradation. *Carbohydrate Research*, *227*, 131–145.

Takahashi, S., Maningat, C. C., & Seib, P. A. (1989). Acetylated and hydroxypropylated wheat starch: Paste and gel properties compared with modified maize and tapioca starches. *Cereal Chemistry*, *66*, 499–506.

Virtanen, T., Autio, K., Suortti, T., & Poutanen, K. (1993). Heat-induced changes in native and acid-modified oat starch pastes. *Journal of Cereal Science*, *17*, 137–145.

Wang, L., & Wang, Y.-J. (2001). Structures and physicochemical properties of acid-thinned corn, potato and rice starches. *Starch/Staerke*, *53*, 570–576.

Wang, Y.-J., White, P. J., & Pollak, L. (1992). Thermal and gelling properties of maize mutants from the Oh43 inbred line. *Cereal Chemistry*, *69*, 328–334.

Wurzburg, O. B. (1986). Converted starches. In O. B. Wurzburg (Ed.), (pp. 17–40). *Modified starches: Properties and uses*, Boca Raton, FL: CRC Press.