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Effect of acid–alcohol treatment on the molecular structure and physicochemical properties of maize and potato starches

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Abstract

The molecular structure and physicochemical properties of acid–alcohol treated maize and potato starches (0.36% HCl in methanol at 25 °C for 1–15 days) were investigated. The yields of the modified starches were ranging from 91 to 100%. The average granule size of modified starches decreased slightly. The solubility of starches increased with the increase of treatment time, and the pasting properties confirmed the high solubility of modified starches. The gelatinization temperatures and range of gelatinization increased with the increase of treatment time except T_o (onset temperature) of maize starch. Molecular structures of modified starches suggested the degradation of starches occurred mostly within the first 5 days of treatment, and degradation rate of potato starch was higher than maize starch both in amylopectin and in amylose. Maize starch was found less susceptible to acid–alcohol degradation than potato starch.

Keywords: Starch; Acid–alcohol treatment; High-performance size exclusion chromatography

1. Introduction

Acid hydrolysis has been used to modify starch granule structure and produce 'soluble starch' for many years. In industry, acid-modified starch is prepared with dilute HCl or H_2SO_4 at 25–55 °C for various time periods. The product, thin boiling starch, is used extensively in food, textile and paper industries (Wurzburg, 1986). Although the viscosity or fluidity properties of acid-hydrolyzed starch varies with the conditions used during modification, the yield of the modified starch consistently decreases with the increases of acid concentration and hydrolysis time.

For obtaining the maximum conversion of raw starch into soluble starch with minimal production of low molecular weight dextrins, Small (1919) proposed a preparation procedure by refluxing starch granules in 95% ethanol containing 0.2–1.6% (w/v) HCl for 6–15 min. Ma and Robyt (1987) showed that treatments of potato and waxy maize starches with different anhydrous alcohols (methanol, ethanol, 2-propanol, and 1-butanol) containing 0.36% HCl at 65 °C for 60 min produced starches with different values of average degree of polymerization (DP), with the highest value being obtained in methanol and the lowest value in 1-butanol. The yields of the modified starches were high (ranging from 100 to 88%), and the size distribution of the starch chains was narrower and more homogeneous than that of native starch. It was proposed that the different alcohols produced different concentrations of acid inside the granules. Hydrolysis of the glycosidic linkage was taking place exclusively inside the granule with the granule-bound water. However, the hydrolysis of potato starch granules in the presence of the above alcohols with 0.36% HCl did not proceed indefinitely, the DP values of the modified products rapidly dropped and became constant after 72 h of reaction (Fox & Robyt, 1992).

Most studies on acid–alcohol modification of starch concerned the effects of acid concentrations, starch concentrations, and alcohol types and concentrations on the DP values (Fox & Robyt, 1992; Robyt, Choe, Fox, Hahn, & Fuchs, 1996; Robyt, Choe, Hahn, & Fuchs, 1996), the particle size and morphology (Jane, Shen, Wang, & Maningat, 1992) of the modified starches, and the viscosity and stability of the emulsion made from the modified starches (Chun, Lim, Takeda, & Shoki, 1997). Few reports

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(Ma & Robyt, 1987) concerned the effect of acid–alcohol modification on the molecular size distribution, and its end results on the physicochemical properties, of the modified starch. In this report, commercial maize and potato starches were hydrolyzed by 0.36% HCl in methanol at 25 °C for 1–15 days. The treatment effects on the granule size, morphology, solubility and swelling power, and gelatinization properties of starch were investigated. The changes of molecular size distribution of modified starches were also determined by high-performance size exclusion chromatography (HPSEC) and discussed with the change of the physicochemical properties for further elucidating the effects of acid–alcohol modification on starch.

2. Materials and methods

2.1. Materials

2.1.1. Starches

Maize starch was obtained from Roquette Company (France) and potato starch was obtained from Parachem company (Denmark). The moisture content of maize starch was 12.6% (w/w), and potato starch was 13.7%.

2.1.2. Enzyme

Isoamylase (EC 3.2.1.68) of *Pseudomonas amyloderamosa* (59,000 UI/mg) was purchased from Hayashibara (1 mg/ml). All reagents were of analytical grade.

2.2. Methods

2.2.1. Acid–alcohol modification

Starch (25 g) was suspended in 100 ml methanol (<0.3% water) in a 250 ml flask. The suspension was stirred and conducted at 25 °C. Reaction was started by adding 1 ml of concentrated (36% by weight) HCl, and allowed to proceed for 1, 3, 5, 7, 9, 11, 13, and 15 days, respectively. The reaction was stopped by adding 14 ml of 1 M $NaHCO_3$, and then cooled in an ice-bath. The starch was centrifuged at $3500 \times g$ for 5 min and washed four times with 50% ethanol. The precipitate was air-oven dried at 40 °C. The yield was calculated by weight of the recovery starch to the initial weight of dry starch.

2.2.2. Size distribution and morphology of starch granule

The size distribution of starch granule was determined by using a laser light scattering based particle size analyzer (Mastersizer Micro, Malvern Instruments, UK.). Granule morphology of starch was studied with a scanning electron microscope (SEM ABT150S, Topcon, Japan). Starch samples were mounted on circular aluminum stubs with double sticky tape, coated with gold, and then examined and photographed at an accelerating potential of 10 kV.

2.2.3. Solubility

Starch (0.1 g, dry basis) was heated in 40 ml of water to the desired temperature (65, 75, 85, and 95 °C) for 30 min. The formation of lump was prevented by continuously stirring. The mixture was centrifuged at $4000 \times g$ for 15 min, then the supernatant was decanted and the swollen starch sediment weighed. An aliquot of supernatant was evaporated overnight at 130 °C and weighed. The solubility was the ratio in weight of the dried supernatant to the initial weight of the dry starch.

2.2.4. Pasting properties

Pasting properties of starch was determined by using a Rapid Visco-Analyzer (RVA 3D+, Newport Scientific, Australia). Each starch suspension (7%, w/w, dry basis for maize and 6% for potato; 28 g total weight) was equilibrated at 50 °C for 1 min, heated to 95 °C at a rate of 12 °C/min, maintained at 95 °C for 2.5 min, and then cooled to 50 °C at a rate of 12 °C/min. Paddle speed was set at 960 rpm for the first 10 s and then 160 rpm for the rest of the analysis.

2.2.5. Thermal properties

Thermal properties of starch during heating were determined by using a differential scanning calorimeter (DSC, Micro DSC VII, Setaram, France). Starch sample (about 150 mg, dry basis) was weighed in the sample pan, mixed with distilled water (about 450 mg), and sealed. The samples were heated from 25 to 120 °C at a heating rate of 1.2 °C/min. Onset (T_o), peak (T_p) and conclusion (T_c) temperatures together with gelatinization enthalpy (ΔH) were quantified.

2.2.6. Molecular weight distribution

The molecular weight distribution of starches were determined by HPSEC (MacPherson & Jane, 2000). The solution of native starch was prepared by solubilizing 75 mg (dry basis) of starch with 15 ml, 90% dimethyl sulfoxide (DMSO) solution in a boiling water bath for 1 h with constant stirring, continuously stirred for 24 h at room temperature. Starch was precipitated from an aliquot of DMSO solution (2.1 ml) with excess absolute ethyl alcohol and centrifuged at $4000 \times g$ for 10 min. The precipitated amorphous starch pellet was resolubilized in deionized water (15 ml, 95 °C) and stirred with a magnetic stirrer in a boiling water bath for 30 min. To the acid–alcohol modified starch, the starch solution was prepared by solubilizing 10 mg (dry basis) of starch with 15 ml deionized water and stirred with a magnetic stirrer in a boiling water bath for 1 h.

Each starch solution was filtered through a 5.0 μm syringe filter, and then the filtrate (100 μl) was injected into an HPSEC system. This system consisted of an HP G1310A isocratic pump (Hewlett Packard, USA), refractive index (RI) detector (HP 1047A), and a multiangle laser light-scattering (MALLS) detector (Dawn DSP, Wyatt Tech., USA) with a helium–neon laser light source ($\lambda = 632$ nm).

The columns used were PWH (guard column), G5000PW and G4000PW (TSK-Gel, Tosoh, Japan) columns connected in series and kept at 70 °C. The mobile phase was 100 mM phosphate buffer (pH 6.2) containing 0.02% NaN_3 at a flow rate of 0.5 ml/min.

The electronic outputs of the RI and MALLS detectors were collected by ASTRA software (ver. 4.50, Wyatt Tech., USA). Peaks were assigned using the RI chromatograms. The MALLS and RI signals were used to determine the molecule weight of amylopectin (first peak). Because of the reduced sensitivity of MALLS for small molecular weight species, the molecular weight of the second peak (amylose and degraded amylopectin fragments) of starches was calculated from the RI signal using a calibration curve constructed from a series of pullulan molecular weight standards (peak molecule weight 5.6, 11.8, 22.9, 46.0, 95.3, 200.0, 359.0, and 769.5×10^3 Da; Polymer Standards Service, USA).

2.2.7. Chain length distribution

Starch solution (2.5 mg starch/2.45 ml H_2O) was prepared according to the procedures described above. The solution was cooled, acetate buffer (0.05 ml, 1.0 M, pH 3.4) and isoamylase solution (10 μl, 5.9 U/μl) was added, and the mixture incubated in a shaker bath at 45 °C for 24 h (Suzuki, Hizukuri, & Takeda, 1981). The solution was neutralized with 0.1 M NaOH, and deionized with Amberlite IR-120-P and Amberlite IR-93 (Sigma, USA) ion exchanger. The solution was diluted to 5 ml, and heated in boiling water bath for 10 min. Debranched starch solutions were then filtered using a 0.45 μm syringe filter. The filtrate was injected (100 μl) into the HPSEC system. The system was the same as that used for the determination of molecular weight distribution, except the columns used were one $G3000PW_{XL}$ and two $G2500PW_{XL}$ (TSK-Gel, Tosoh, Japan) connected in series. A typical HPSEC profile of debranched starch showed trimodel distribution. The molecular weight of first peak (amylose) was determined by using MALLS and RI signals, and the molecular weight of the second and third peaks (long chain and short chain of amylopectin) were calculated from the RI signal using a calibration curve constructed from a series of pullulan molecular weight standards (peak molecule weight 1.0, 5.6, 11.8, 22.9, and 46.0×10^3 Da; Polymer Standards Service, USA).

3. Results and discussion

3.1. Yields, size distribution and morphology of starch granules

The yields of the starches modified by 0.36% HCl in methanol at 25 °C for 1–15 days were high, ranging from 91 to 100% (Table 1). Compared to their counterpart native starches, the average granule size of the modified starches showed a decrease tendency. For the potato starch after 15 days of treatment, the average granule size decreased from 47.2 μm of native starch to 44.8 μm (Table 1). The changes of granule size of maize starch after modification were less obvious. Examined by SEM, the native maize starch (Fig. 1A and B) showed polygonal, irregular shape, while potato starch (Fig. 1E and F) had oval or spherical-like shape. The granule surface of the native starches was smooth without obvious fissures or cavities. After 15 days of modification, no significant configuration changes such as fragmentation or swelling was found. However, the granule surface of maize starch changed rough, and the naturally occurred, randomly distributed surface openings (Fannon, Hauber, & BeMiller, 1992) of some granules became more obvious (Fig. 1C and D). The granule surface of potato starch also changed rough with partial protuberances (Fig. 1G and H).

Table 1
Yields and average granule sizes of native starches and starches treated by 0.36% HCl in methanol at 25 °C for 1–15 days

Time (days)	Yield[a](%)		Average granule size (μm)	
	Maize	Potato	Maize	Potato
Native	–	–	13.7 ± 0.1	47.2 ± 0.2
1	98.5	98.0	13.4 ± 0.0	47.6 ± 0.1
3	98.4	98.4	13.6 ± 0.0	46.1 ± 0.9
5	98.4	99.8	13.6 ± 0.0	47.5 ± 0.4
7	100.0	100.0	13.6 ± 0.0	47.9 ± 0.1
9	97.1	94.6	12.4 ± 0.2	47.6 ± 0.0
11	97.2	96.4	12.5 ± 0.3	45.4 ± 0.1
13	91.7	92.7	12.8 ± 0.0	43.3 ± 0.2
15	97.7	95.2	13.2 ± 0.0	44.8 ± 0.7

[a] (Weight of starch after acid–alcohol treatment)/(weight of starch before treatment) × 100%.

3.2. Solubility and pasting properties of starches

Fig. 2 shows the solubility of maize and potato starches measured at different temperatures (65–95 °C). In spite of the measurement temperature, the solubility of native maize starch was less than 10% and potato starch less than 22%. After acid–alcohol modification, the solubility of starches obviously increased with the increase of hydrolysis time. Maize starch showed slower increasing tendency than that of potato starch, and its solubility value leveled off after 11 days of treatment. While the solubility of potato starch increased rapidly, and reached its maximum value after 3 days of treatment. As the measurement temperature was above 75 °C, the solubility of modified potato starches were higher than 90%. This indicated the starch granules were nearly fully dissolved. Results of pasting properties (Fig. 3) of starches measured by the RVA confirmed the high solubility of modified starches. Native potato starch had higher peak viscosity and lower pasting temperature than the native maize starch. After the acid–alcohol treatment the pasting viscosity of the modified starches decreased

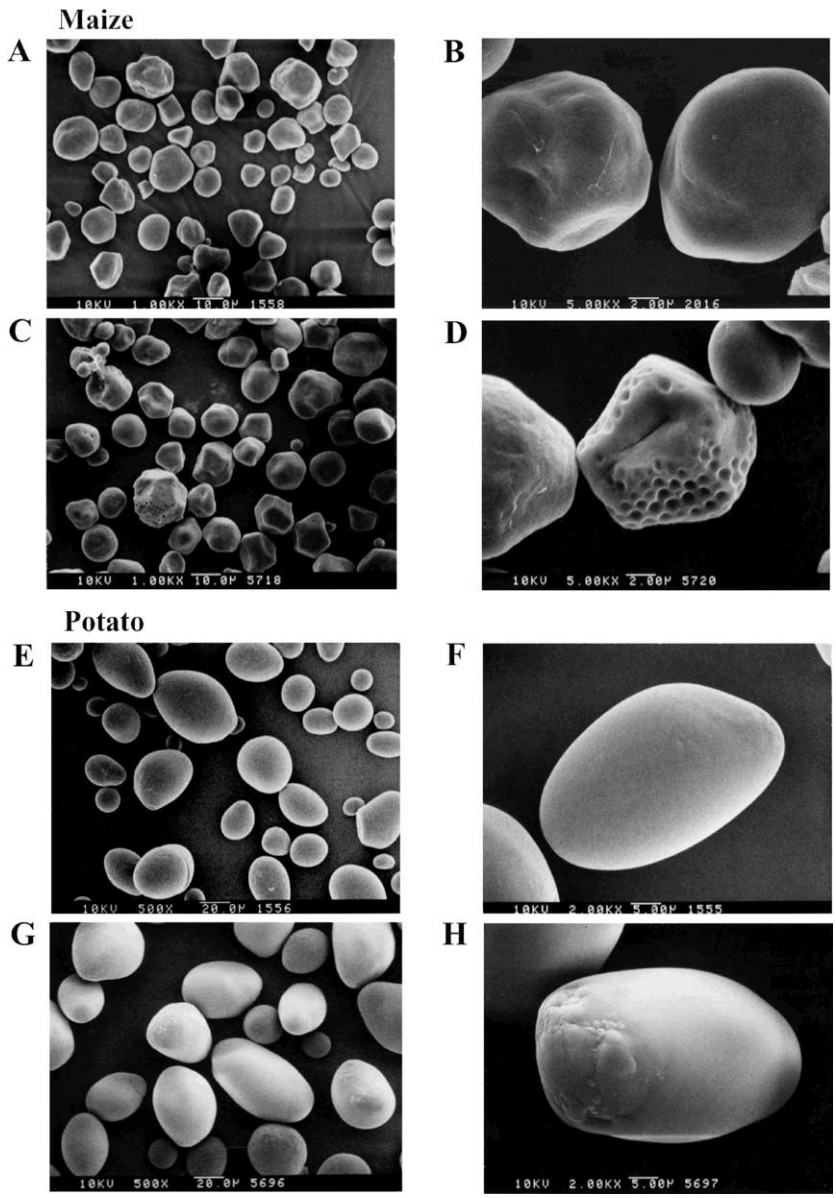

Fig. 1. Scanning electron micrograms of maize and potato starches: native (A, B, E, F), and treated by 0.36% HCl in methanol at 25 °C for 15 days (C, D, G, H).

obviously for both potato and maize starches. Among the modified starches prepared, only the maize starch after acid–alcohol treated for 1 day showed the entire profile of the RVA viscoamylograph similar to that of the native starch. Other modified starches showed either very lower (< 100 cps) or undetectable peak viscosity.

3.3. Thermal properties of starches

Thermal properties of starches during heating determined by the DSC are shown in Table 2. The T_o of maize starches decreased from 61.1 °C for native starch to 58.6 °C for starch treated for 15 days. In contrast, the T_o of potato starches increased from 56.1 °C for native starch to 58.2 °C for starch treated for 15 days. For both maize and potato starches, the T_p and T_c increased with the increase of treatment time. Accordingly, the range of gelatinization increased from 12.2 to 23.9 °C for maize starch, and from 12.8 to 19.8 °C for potato starch. While the ΔH of modified starches were lower than their counterpart native starches, there were no obvious differences among the enthalpies of starches treated by different times. These results indicated the gelatinization temperature and range of gelatinization of starches after treatment were increased except the T_o of maize starch.

3.4. Molecular weight distribution of starches

Molecular weight distributions of starches are shown in Fig. 4. The first fractions (F1) in the profiles corresponded to amylopectin, and the second fractions (F2) to the low molecular weight molecules. For the acid–alcohol treated

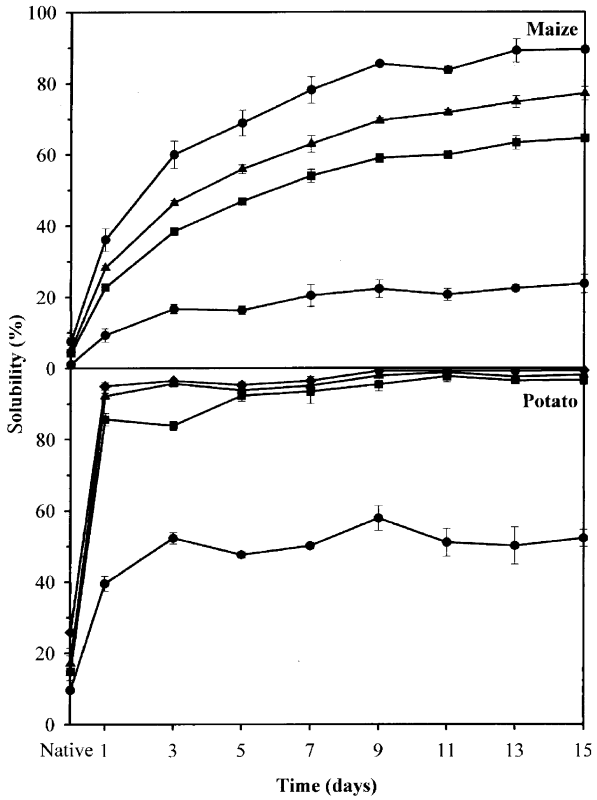

Fig. 2. Solubility of starches measured at 65 (●), 75 (■), 85 (▲), and 95 °C (◆), respectively. Starches were hydrolyzed by 0.36% HCl in methanol at 25 °C for 1–15 days.

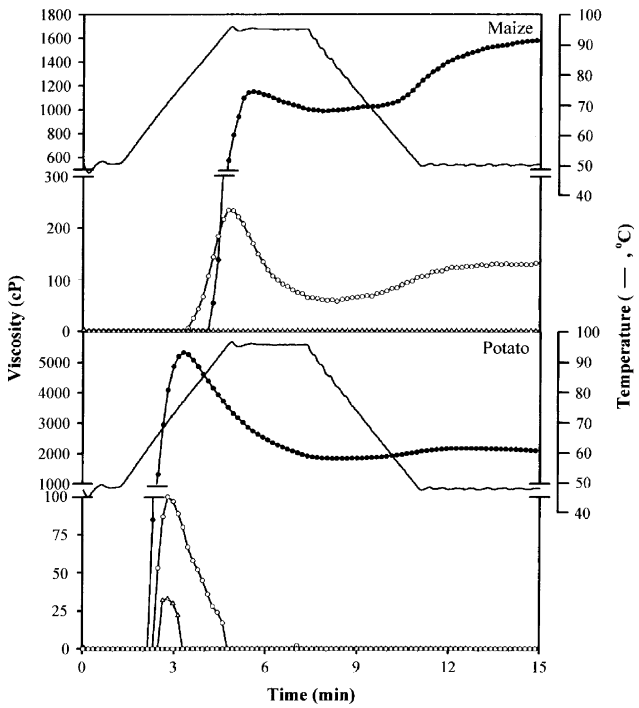

Fig. 3. RVA amylograms of native starches (●) and starches treated by 0.36% HCl in methanol at 25 °C for 1 (○), 3 (△), and 5 days (□), respectively.

Table 2
Gelatinization temperatures and enthalpies of native starches and starches treated by 0.36% HCl in methanol at 25 °C for 1–15 days

Time (days)	Gelatinization temperature[a] (°C)			$T_o - T_c$ (°C)	Enthalpy[b] (J/g)
	T_o	T_p	T_c		
Maize					
Native	61.1	66.6	73.3	12.2	11.9
1	59.4	65.0	72.9	13.5	10.9
3	58.6	66.2	77.6	19.0	9.5
5	58.8	66.8	77.2	18.4	10.6
7	58.4	67.3	79.0	20.6	9.8
9	58.4	68.5	80.9	22.5	9.9
11	59.0	68.6	81.1	22.1	9.6
13	58.8	69.6	82.7	23.9	10.1
15	58.6	69.9	82.5	23.9	10.3
Potato					
Native	56.1	61.5	68.9	12.8	16.9
1	56.8	63.0	73.1	16.3	15.8
3	55.6	61.3	71.6	16.0	14.7
5	56.2	62.5	73.2	17.0	14.6
7	57.0	63.5	74.6	17.6	15.2
9	56.5	62.8	74.6	18.1	15.1
11	57.4	63.5	74.9	17.5	15.8
13	57.5	63.8	76.8	19.3	15.8
15	58.2	64.5	78.0	19.8	15.4

[a] T_o, T_p, and T_c stand for the onset, peak, and conclusion temperature of gelatinization, respectively. Standard deviations ≤ 0.6 °C.
[b] Standard deviations ≤ 0.5 J/g.

starches, the areas of F1 fractions decreased with the increase of treatment time, while the areas of F2 fractions increased. This indicated the degradation of amylopectin to low molecular weight molecules due to the acid–alcohol hydrolysis. The degradation of amylopectin could cause the disruption of granular structure and the increase of leaching when starch was heated with water. Consequently, high extents of starch solubility (Fig. 2) and low pasting viscosity (Fig. 3) were observed.

Compared to the gradual degradation pattern of maize starch, potato starch showed a stepwise pattern (Fig. 4). The molecular weight distribution profiles of potato starches treated by 0.36% HCl in methanol at 25 °C for 5–11 days were overlapped with each others. The same is true for the distribution profiles of potato starches treated for 13 and 15 days. Fig. 5 shows the change of weight average degree of polymerization (DP_w) of maize and potato starches as a function of hydrolysis time. The results indicated the decrease of DP_w mostly occurred within the first 5 days of treatment.

The reduction in DP_w for the first 5 days of treatment could be described by the following equation (Chang, Tai, & Cheng, 2001)

$$1/M_t = 1/M_0 + kt/m = 1/M_0 + k't$$

where k or k' represents the rate constant, t, the reaction time, M_0, the DP_w of native starch, M_t, the DP_w of starch

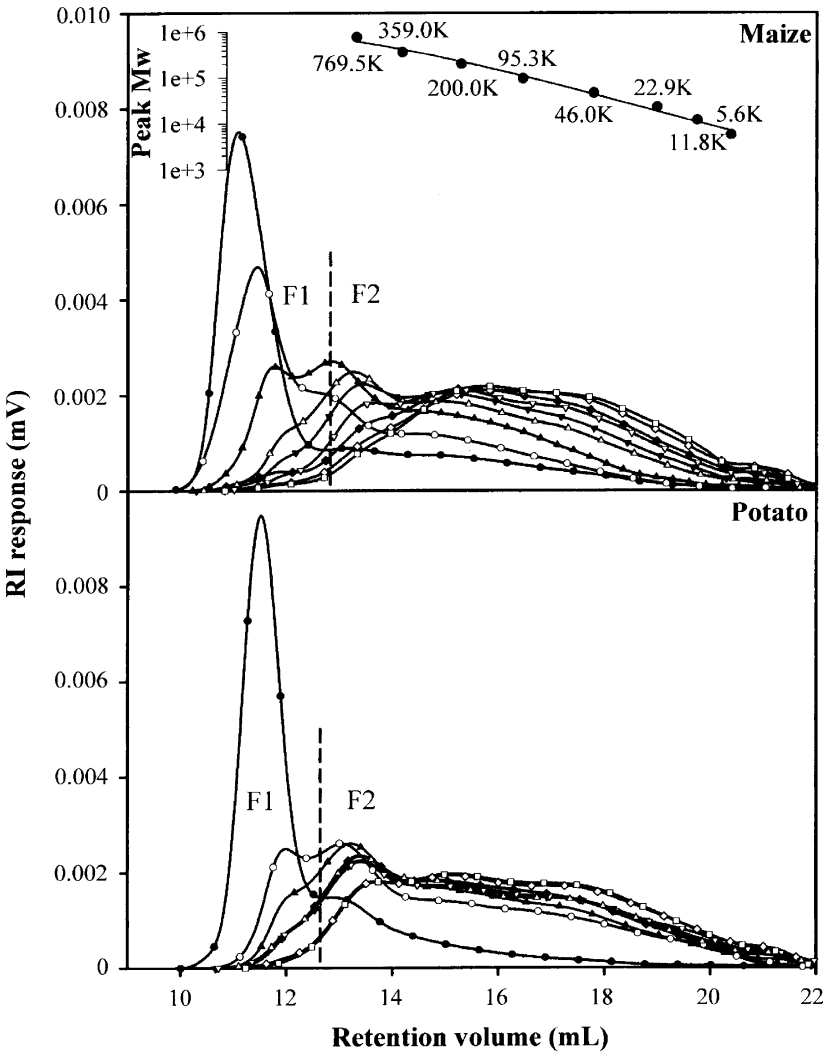

Fig. 4. HPSEC chromatograms of native starches (●) and starches treated by 0.36% HCl in methanol at 25 °C for 1 (○), 3 (▲), 5 (△), 7 (▼), 9 (▽), 11 (◆), 13 (◇), and 15 days (□), respectively.

after treated for time t and m, the monomer molecular weight. Fig. 6 shows a linear relationship of both starches between the inverse of weight average molecular weight and treatment time at the initial stage of degradation (first 5 days). The results showed the value of k' was 1.174×10^{-5} for potato starch and 4.590×10^{-6} for maize starch, which revealed the degradation rate of potato starch was higher than maize starch.

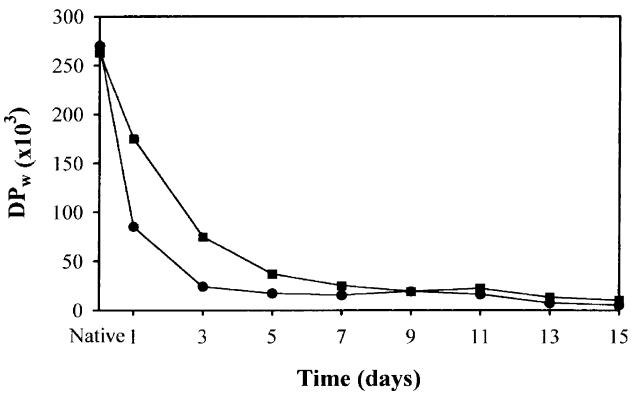

Fig. 5. Changes of weight average degree of polymerization (DP_w) of maize (■) and potato (●) starches as a function of hydrolysis time.

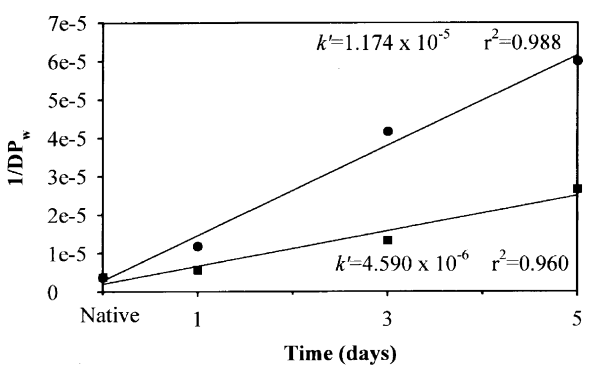

Fig. 6. Kinetics of degradation of maize (■) and potato (●) starches treated by acid–alcohol.

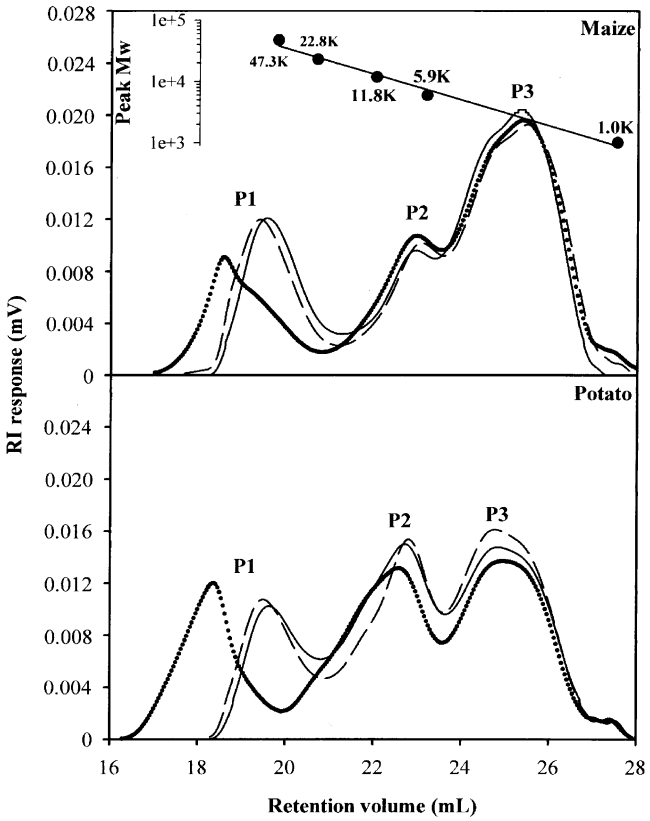

Fig. 7. Chain length distributions of native starches (···) and starches treated by 0.36% HCl in methanol at 25 °C for 7 (- - -) and 15 days (—), respectively.

3.5. Chain length distribution of starches

Both maize and potato starches showed trimodel chain length distributions even after 15 days of treatment (Fig. 7). The fractions in the profiles from low to high retention volume are corresponded to amylose (P1), long chains (P2) and short chains (P3) of amylopectin, respectively. The contents of each fractions indicated no obvious difference between native starches and starches after treatment (Tables 3 and 4). The DP_n of P1 of maize and potato starches decreased after treatment with different degradation rates. The DP_n value of P1 of potato starch decreased rapidly within the first 3 days of treatment, while maize starch showed a slower degradation rate and the DP_n reached a limit after 11 days of treatment. The DP_n value of P2 for both maize and potato starches decreased within the first 9 days of treatment, and then increased after 11–15 days of treatment. The increase of DP_n of P2 after 11–15 days treatments may result from the degradation of P1 fraction. Furthermore, no significant change on the value of P3 was found. These results revealed both amylose and long chain of amylopectin were degraded during acid–alcohol treatment and the degradation rate of amylose of potato starch after treatment was faster than that of maize starch. Results of the molecular weight distribution and chain length distribution of starch after treatment indicated the degradation rate of both amylopectin and amylose for potato starch were faster than those of maize starch.

4. Conclusion

Starches degraded by acid–alcohol treatment showed high yields of starch granules and no significant configuration change of granule. The solubility of the modified starch increased with the increase of hydrolysis time, and corn starch showed slower increasing tendency than that of potato starch. The pasting viscosity of the modified starch decreased significantly. The gelatinization temperature and range of gelatinization of starches after treatment were increased except the T_o of maize. These results indicated although there was no significant configuration change of starch granules after treatment, the high extents of solubility and low pasting viscosity

Table 3
Weight percentage and chain length of debranched maize starch

Time (days)	P1			P2			P3		
	%[a]	DP_n[b]	DP_w[c]	%	DP_n	DP_w	%	DP_n	DP_w
Native	23.1 ± 2.7	1252 ± 56	4955 ± 183	22.6 ± 1.2	58 ± 2	64 ± 2	54.3 ± 3.9	15 ± 0	18 ± 0
1	21.9 ± 1.9	1064 ± 23	2437 ± 175	18.0 ± 0.5	54 ± 1	58 ± 1	58.3 ± 1.2	15 ± 0	18 ± 0
3	23.4 ± 0.7	984 ± 50	2153 ± 89	18.3 ± 0.7	51 ± 1	55 ± 2	58.3 ± 0.8	16 ± 0	18 ± 0
5	23.1 ± 1.1	872 ± 17	1868 ± 52	18.8 ± 0.5	51 ± 0	55 ± 1	58.0 ± 1.7	15 ± 0	18 ± 0
7	24.5 ± 0.7	772 ± 23	1669 ± 25	19.2 ± 1.5	51 ± 0	56 ± 1	56.3 ± 0.8	15 ± 0	18 ± 0
9	23.9 ± 1.6	691 ± 32	1410 ± 79	18.1 ± 0.6	51 ± 2	56 ± 2	57.9 ± 1.6	15 ± 0	18 ± 0
11	22.2 ± 1.1	577 ± 33	1279 ± 74	17.0 ± 0.3	54 ± 1	59 ± 1	60.8 ± 0.8	15 ± 0	18 ± 0
13	21.5 ± 0.1	565 ± 24	1128 ± 30	19.1 ± 0.8	54 ± 2	59 ± 3	59.4 ± 0.9	16 ± 1	18 ± 1
15	22.4 ± 1.2	543 ± 11	1124 ± 22	16.6 ± 0.5	59 ± 0	64 ± 0	61.1 ± 0.9	16 ± 0	20 ± 0

[a] (Area of peak)/(total area) × 100%.
[b] Number average degree of polymerization.
[c] Weight average degree of polymerization.

Table 4
Weight percentage and chain length of debranched potato starch

Time (days)	P1			P2			P3		
	%[a]	DP_n[b]	DP_w[c]	%	DP_n	DP_w	%	DP_n	DP_w
Native	22.7 ± 0.6	4202 ± 271	8868 ± 381	36.8 ± 0.6	69 ± 1	83 ± 2	40.4 ± 0.9	16 ± 0	19 ± 0
1	20.4 ± 0.3	649 ± 24	1488 ± 143	32.7 ± 0.3	61 ± 1	68 ± 1	46.9 ± 0.5	17 ± 1	20 ± 0
3	21.9 ± 0.6	535 ± 55	1315 ± 63	31.8 ± 0.4	62 ± 1	69 ± 1	46.4 ± 0.7	17 ± 0	20 ± 0
5	20.0 ± 0.5	530 ± 53	1019 ± 58	32.6 ± 0.4	61 ± 2	68 ± 2	47.4 ± 0.3	15 ± 1	19 ± 1
7	20.4 ± 1.1	489 ± 41	1064 ± 41	33.0 ± 0.4	60 ± 1	68 ± 1	47.3 ± 1.1	16 ± 0	19 ± 0
9	19.9 ± 0.6	453 ± 29	1047 ± 45	33.8 ± 1.7	59 ± 3	67 ± 2	46.3 ± 1.2	16 ± 1	19 ± 1
11	21.9 ± 0.3	501 ± 46	949 ± 23	37.2 ± 0.4	62 ± 1	71 ± 1	40.9 ± 0.1	15 ± 0	18 ± 0
13	20.2 ± 0.6	495 ± 35	858 ± 22	37.5 ± 0.2	64 ± 2	74 ± 2	42.3 ± 0.4	15 ± 1	19 ± 1
15	18.9 ± 0.3	479 ± 55	862 ± 23	36.0 ± 0.5	63 ± 0	72 ± 0	45.0 ± 0.8	16 ± 0	19 ± 0

[a] (Area of peak)/(total area) × 100%.
[b] Number average degree of polymerization.
[c] Weight average degree of polymerization.

revealed the acid–alcohol treatment caused the disruption of structure inside the starch granules and the increase of leaching when starch was heated with water. Results of HPSEC indicated that potato starch had faster rate of degradation than corn starch, both in amylose and amylopectin.

Acid hydrolysis is considered to yield the crystalline resistant parts of the granule and thus allows an estimation of the easily degradable fraction or amorphous part of starch (Robin, Mercier, Charbonnière, & Guilbot, 1974). B-type starches are usually less susceptible to acid hydrolysis than A-type starches (Gèrard, Colonna, Bulèon, & Planchot, 2002; Robin et al., 1974). However, the results of this study indicated that under acid–alcohol treatment potato starch (a typical B-type starch) showed higher degradation rate than that of maize starch (a typical A-type starch). In other words, the results indicated that the A-type starch was less susceptibility to acid–alcohol degradation. This implied that the susceptibility of starches with different crystalline structures treated by acid treatment in water and alcohol were different. This might resulted from the acid–alcohol treatment hydrolyzed the starch granule in a mechanism different from that of acid hydrolysis in water. The discussion of mechanism on starch treated by acid in water and alcohol is needed for further study.

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