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Effect and mechanism of ultrahigh hydrostatic pressure on the structure and properties of starches☆

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Abstract

Normal maize, waxy maize, high-amylose maize VII, tapioca, potato, and rice starches were ultrahigh hydrostatic pressurized at 690 MPa. Structures and properties of the pressurized starches were investigated. Each starch was pressurized in powder form, in 1/1 (v/w) ethanol/starch suspension, and in 1/1 and 2/1 (v/w) water/starch suspensions for 5 min and 1 h dwelling times. The crystalline structure, thermal and pasting properties, molecular weight distributions, and morphology of starch granules were analyzed. X-ray diffraction studies showed that the ultrahigh pressure converted starches that displayed the A-type X-ray patterns to the B-type-like pattern. Differential scanning calorimeter thermograms of starches taken right after the pressure treatments showed a newly developed peak that resembled that of the retrograded (B-type) starch. Crystalline structures of starches that displayed the B-type pattern, however, were not changed by the pressure treatments in a water suspension. The ultrahigh hydrostatic pressure did not change the molecular weight distribution of the starch. The pressurization of starches in powder form and in the presence of alcohol resulted in a reduction in peak intensity of the X-ray pattern but no conversion from the A-type to the B-type. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Starch; Amylose; crystallinity; ultrahigh pressure; pasting property

1. Introduction

Starch is the second most abundant biomass found in nature, next to cellulose. It is produced by photosynthesis in the amyloplast of higher plants. Starch can be found in leaves, stems, seeds, fruits, and roots. Starch consists of two major components, amylose and amylopectin. Starch granules are semicrystalline, composed of alternating crystalline and amorphous lamella. The crystalline structure consists of a radial arrangement of amylopectin clusters that are aligned perpendicularly to the growth rings from the hilum to the surface of the granule (Buleon, Pontoire, Riekel, Chanzy, Helbert & Vuong, 1997; French, 1984). Using cross-linking reactions, it is shown that amylose molecules intersperse among amylopectin (Jane, Xu, Radosavljevic & Seib, 1992; Kasemsuwan & Jane, 1994). It is also found that amylose is more concentrated at the periphery of the granule (Jane & Shen, 1993; Pan & Jane, 2000).

The applications of high hydrostatic pressure (HHP) on food products can be traced back to the work of Hite in 1899, who reported a significant reduction in bacteria count in milk after 680 MPa pressure was applied for 10 min (Hoover, 1993). Bridgman, in 1914, discovered that high pressure coagulated egg albumin (Hoover, 1993). The HHP enhances a reaction that results in a volume decrease and retards a reaction with a volume increase (Hoover, Metrick, Papineau, Farkas & Knorr, 1989). HHP is known to break the secondary and tertiary structures and leave the covalent bonds intact (Cheftel, 1992). Pressure in HHP treatment acts instantly and is independent from the size and shape of the substrate (Stute, Heilbronn, Klinger, Boguslawski, Eshtiaghi & Knorr, 1996).

The investigations performed thus far on the effect of HHP on starch can be divided into three categories. First are those in which the application of pressure was not high enough to gelatinize starch (Vainionpa, Forsell & Virtanen, 1993). Second are those in which the pressure application was performed on almost dry starch (Kudla & Tomasik, 1992). And third are those that used ultrahigh pressure (UHP) treatment, which is defined as when the investigation

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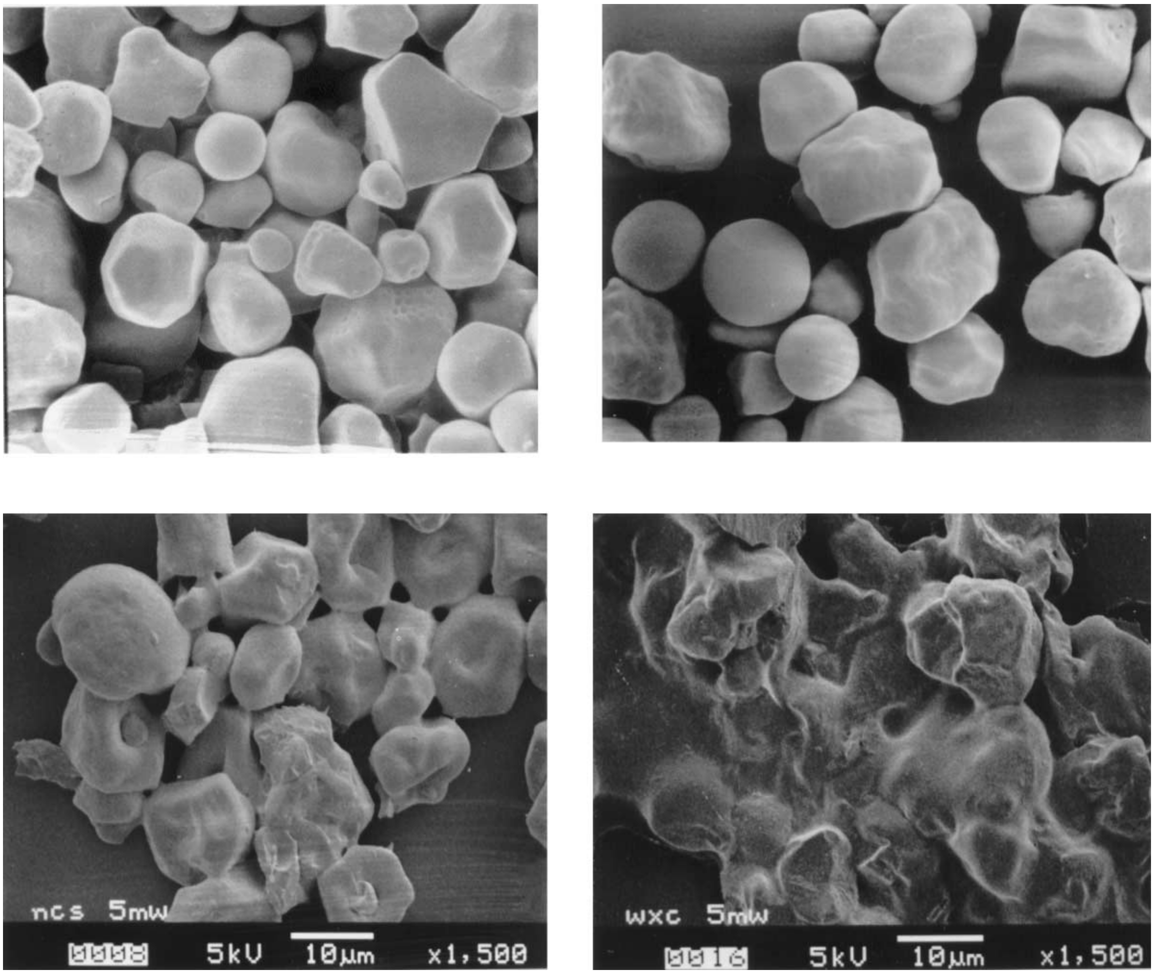

Fig. 1. The SEM of normal maize starch (left) and waxy maize starch (right): control (top), pressurized at 690 MPa in 1/1 water/starch (v/w) ratio for 5 min (bottom).

is carried out with excess water and pressure above 400 MPa. The X-ray studies showed that UHP treated A-type starches were changed to the B-type (Hibi, Matsumoto & Hagiwara, 1993; Stute et al., 1996). The objective of this study was to provide mechanisms for the effects of UHP on the crystalline structure conversion and on the physical properties of starches.

2. Materials and methods

2.1. Materials

Normal, waxy, and high amylose (70%) maize starches were gifts of Cerestar USA (Hammond, IN). Tapioca starch was a gift of National Starch and Chemical Company (Bridgewater, NJ). Potato and rice starches were purchased from Sigma Chemical Co. (St. Louis, MO).

2.2. High hydrostatic pressure treatments

The starch samples were pressurized to 690 MPa (100,000 psi) at room temperature for 5 min and 1 h dwelling times with a warm isostatic HHP unit (Engineered Pressure System Inc., Andover, MA). The unit was an indirect-compression system using a high-pressure intensifier (Critter P60-03, Hydro-Pac Inc., Fairview, PA) to pump the pressure medium, 5% hydraulic oil in distilled water, from the reservoir into the closed vessel, until the desired pressure was reached. The internal measurements of the pressure vessel were 101.6 mm for the diameter and 279.4 mm for the height.

Each sample was pressurized under four different conditions: powder form (original moisture content, 10–16%, dry starch basis [dsb]; suspended in ethanol at 1/1 (v/w) ratio; suspended in water at 1/1 and 2/1 (v/w) water/starch. 100 g of starch were used for each treatment. The sample was double bagged into nylon polyethylene plastic bags (thickness = 3 mm) (Curwood Inc., Chicago, IL) and double sealed using Fresh Vac (CVP System Inc., Downers Grove, IL).

The samples that were pressurized in powder form turned into solid rock; therefore, they were hammered into smaller pieces and then ground with a cyclone mill (UDY Corp., Fort Collins, CO). The samples pressurized in the presence

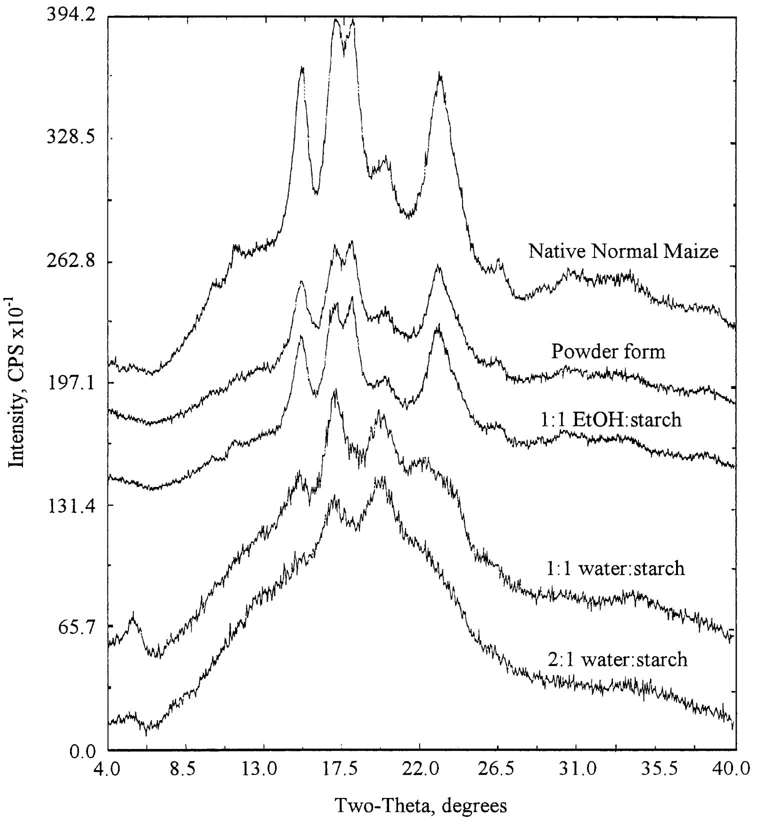

Fig. 2. The X-ray diffraction pattern of normal maize starch pressurized at 690 MPa.

of ethanol remained as suspension that was vacuum filtered and dried in an oven at 40°C for 24 h. Starches that were pressurized in the presence of water formed a cake or gel. The treated sample was broken into smaller pieces, suspended in excess ethanol, and then vacuum filtered, dried, and ground with a cyclone mill. The moisture content was determined by drying at 110°C in an oven for 24 h.

2.3. Morphology of treated starches

2.3.1. Light microscopy

Starch was suspended in a glycerol solution (glycerol/ $H_2O = 2/1$, v/v) and was observed using a microscope equipped with a polarized filter (Labophot, Nikon Tokyo, Japan). The micrograms were taken using a Nikon camera (FX-35WA, Tokyo, Japan).

2.3.2. Scanning electron microscopy

A 1% starch suspension in absolute ethanol was prepared for each sample. One drop of the suspension was applied on the nonsticky side of aluminum tape that was attached to a brass disc. The specimens were coated in a sputter coater (E5100, Polaron) with gold/palladium = 60/40. The prepared samples were observed using a scanning electron microscope at 10 kV (JSM-35, JEOL, Tokyo, Japan).

2.4. X-ray diffraction

The X-ray patterns of starches were obtained with copper (nickel foil-filtered) Kα radiation using a diffractometer (D-500, Siemens, Madison, WI). The samples were first equilibrated in a 100% relative humidity chamber for 24 h at room temperature. The operation setting for the diffractometer was 27 mA and 50 kV. The angle of diffraction (2θ) scanned was from 4 to 40°, with 0.05° step and 2 s count time.

2.5. Differential scanning calorimetry

The gelatinization properties of starch were analyzed using a differential scanning calorimeter (DSC) equipped with an Intra-cooling II system (DSC-7, Perkin-Elmer, Norwalk, CT) following the method of Chen and Jane (1994). The amount of sample used for normal and waxy maize, tapioca, rice, and potato starch was ~2 mg (dsb) each with the addition of deionized water (6 mg). Those samples were sealed in aluminum pans (Perkin-Elmer), equilibrated for 1 h and scanned. The heating rate was 10°C/min over the temperature of 25–110°C. Stainless steel pans were used for high amylose maize starch with ~10 mg (dsb) starch and deionized water (30 mg) and heated to 140°C. The data were averaged from a minimum of three replicates of each starch sample. Direct measurements

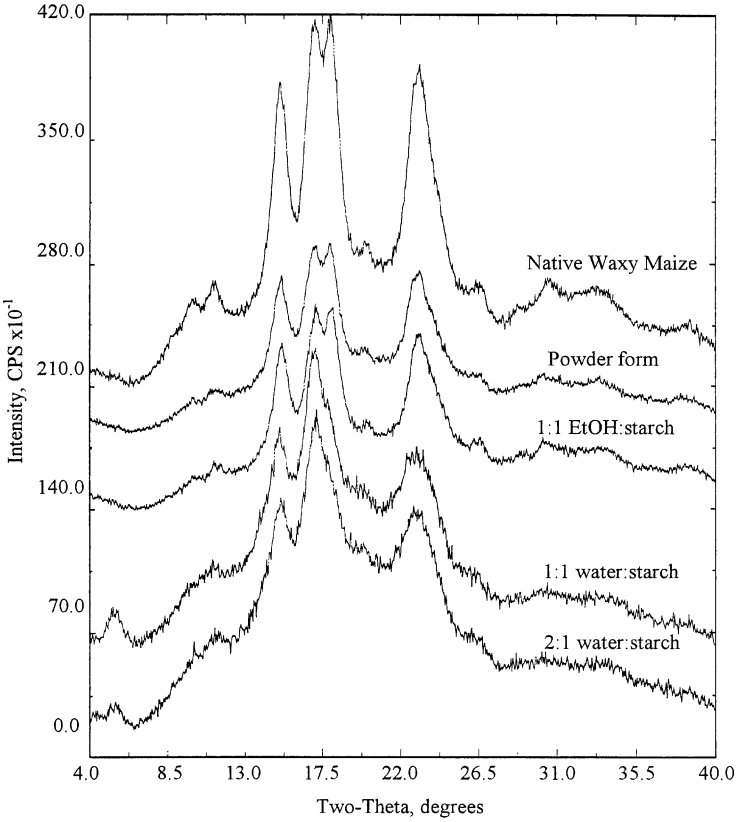

Fig. 3. The X-ray diffraction pattern of waxy maize starch pressurized at 690 MPa.

of pressurized starch samples were conducted by using a total weight of the pressurized starch cake or gel for the DSC test right after pressure treatments. To test if the B-type crystallinity was a result of retrogradation of pressurized starch, control samples of normal maize, waxy maize, tapioca, and rice starches were prepared following the same procedure as for the pressurized starch sample in water suspension. The samples in sealed plastic bags were gelatinized, by heating in a boiling water bath, instead of by pressure. The samples were then suspended in alcohol, filtered, and oven dried. The DSC analysis of the control sample was conducted following the same conditions as that for pressurized samples.

2.6. Rapid ViscoAnalyzer

Pasting profiles were obtained using a Rapid Visco-Analyzer (RVA, Newport Scientific, Sydney, Australia). All the samples were tested at 8% w/w solid concentration (28 g total weight). High amylose maize starch could not be tested because it required a much higher temperature to gelatinize and disperse. The samples were equilibrated at 50°C for 1 min and then heated at a rate of 6°C/min to 95°C and maintained at that temperature for 5 min before cooling to 50°C at a rate of 6°C/min. A constant 160 rpm spindle speed was used. Two replications with two repetitions were done for each sample.

Samples of heat-gelatinized waxy maize starch with and without retrogradation were prepared by heating starch samples with 1/1 and 2/1 (v/w) water/starch, sealed in Mason jars, in an oven at 100°C for 24 h. After the heat treatment, starch samples were either suspended in excess ethanol, filtered, and quickly dried or allowed to dry at 25°C for up to 60 h. The samples were ground and analyzed by RVA under the same conditions as that used for pressurized starch.

2.7. Gel permeation chromatography

The analysis was done following the methods reported by Jane and Chen (1992). A 2.6 (ID) × 80 cm column (Pharmacia Inc., Piscataway, NJ) packed with Sepharose CL-2B gel was used for the analysis. The eluent used was an aqueous solution with 2.5 mM NaCl and 1 mM NaOH at a flow rate of 0.5 ml/min in an ascending direction. Fractions of 4.8 ml were collected and analyzed with a dual channel Autoanalyzer II (Technicon Instrument Corp., Elmsford, NY). The total carbohydrate (determined by anthrone–sulfuric acid method) and the amylose–iodine blue value were measured at 630 and 640 nm, respectively.

3. Results and discussions

Results obtained from samples of 1 h-pressurization were

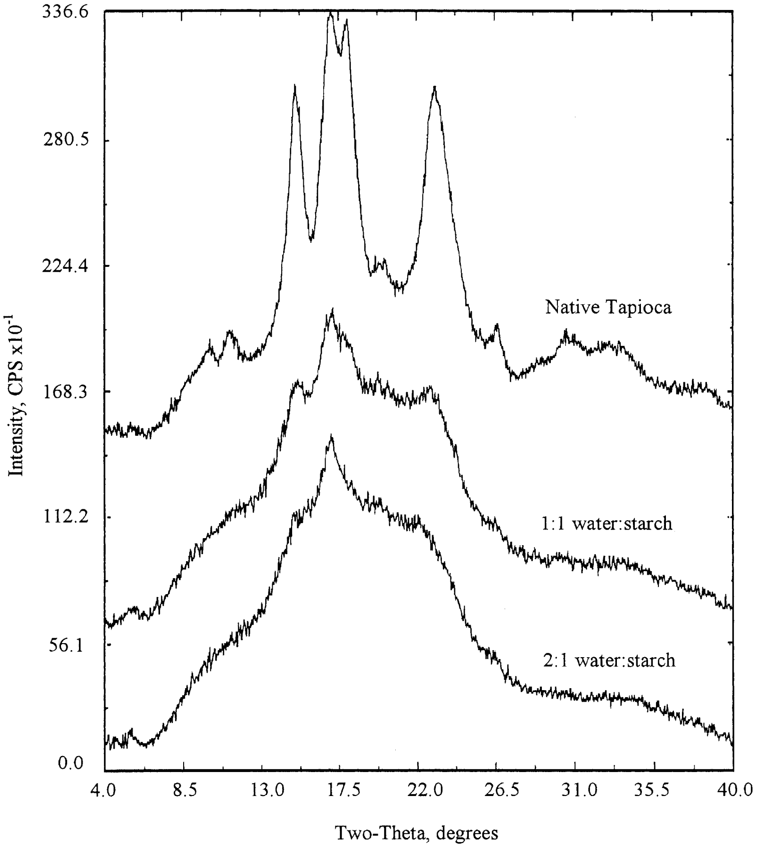

Fig. 4. The X-ray diffraction pattern of tapioca starch pressurized at 690 MPa.

not significantly different from those obtained with 5 min-pressurization. Therefore, we only report results of the 5 min-pressurized samples in this study.

3.1. Morphology of high-pressure treated starches

All the starches that were pressurized in powder form became solid hard rock. The ones pressurized in ethanol suspension did not show any apparent change. The starches that were pressurized in the presence of water became a cake or gel, except for high amylose maize that did not show morphological changes.

The pressurization of 1/1 (v/w) water/starch suspension turned the normal corn and rice starch into brittle gels and into softer gels when the water ratio was doubled. Waxy maize starch turned into a hard gel upon pressurization in 1/1 (v/w) water/starch suspension, and the gel became very sticky when the water ratio was doubled. Tapioca starch resembled waxy maize, but the gel was not as sticky. Potato starch in 1/1 (v/w) water/starch suspension turned into a brittle cake with a lot of free water. In 2/1 (v/w) water/potato starch suspension, the cake became softer with a lot of free water and a thin layer of gel on the surface of the cake.

Light micrographs showed that starches pressurized in powder form displayed more surface cracking than those pressurized in an ethanol suspension (data not shown). The starches that were pressurized in 2/1 (v/w) water/starch suspension showed a higher degree of gelatinization compared with those pressurized in 1/1 (v/w) water/starch suspension. Waxy maize starch pressurized in a 1/1 water/starch suspension partially lost its granular integrity (Fig. 1), whereas normal maize starch retained integrity after pressurization in 1/1 ratio with water (Fig.1). Pressurized potato starch showed less gelatinization than other normal and waxy starches. High-amylose maize (VII) starch did not show any morphological changes. The results agreed with those reported by Hibi et al. (1993).

3.2. X-ray diffraction

X-ray diffraction patterns of normal and waxy maize starch pressurized in powder form and in ethanol suspensions are shown in Figs. 2 and 3, respectively. There was no change in the type of X-ray diffraction pattern, but the intensity of the peaks decreased as a result of loss of crystallinity during pressurization. The same results were observed for all the A- and B-type starch samples. Therefore, the results of other starches pressurized in powder form and in ethanol suspension are not shown. The intensities of X-ray diffraction peaks of starches pressurized in powder form were consistently lower (10–18%) than that of starches treated

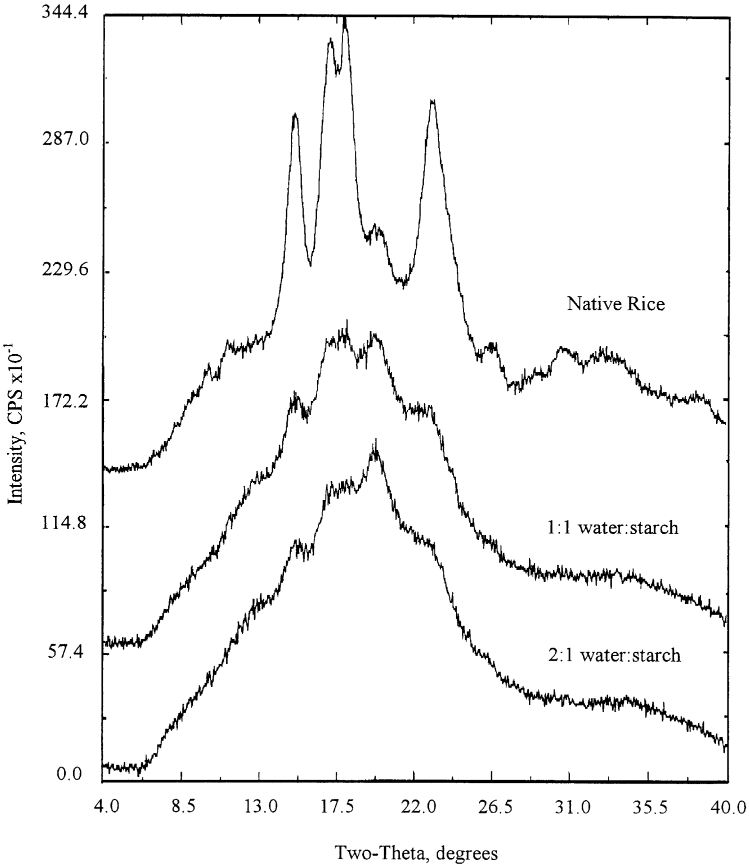

Fig. 5. The X-ray diffraction pattern of rice starch pressurized at 690 MPa.

in ethanol suspension; this suggested that starches in ethanol suspension were more stable to the pressure treatments. This can be attributed to the fact that ethanol is not a plasticizer for starch and may have a space filling effect, which stabilizes the crystallinity of starch.

X-ray diffraction patterns of starches pressurized in the presence of water showed that starches of the A-type X-ray pattern went through a transformation from the A- toward the B-like pattern (Figs. 2–5). The pattern of waxy maize starch pressurized in a 1/1, water/starch suspension (Fig. 3) became a mixture of the A- and B-type pattern (C-pattern). The appearance of a peak at around 6° 2θ and the transformation from a double peak to a single peak at around 17.5° are characteristics of the B-type X-ray diffraction pattern. Nevertheless, the single peak around 22° that is a characteristic of the A-type X-ray diffraction pattern remained unchanged. The X-ray diffraction pattern of pressurized normal maize (Fig. 2) and rice starch (Fig. 5) in water media showed a weak B-pattern with a strong peak at 20° and weak signals at 13° and 8°, indicating the presence of an amylose–lipid complex (V-pattern).

The pressure effect on the X-ray pattern of tapioca starch (Fig. 4) was not as pronounced as for normal and waxy maize. There was a small peak that appeared at 6°, and the double peak around 17.5° became a single peak; those indicated the transformation toward the B-type X-ray pattern. The X-ray diffraction pattern for rice starch (Fig. 5) also displayed a conversion toward a combination of a V- and a weak B-type, but the peaks diminished as a result of starch gelatinization with an increase in water content. Potato and high-amylose maize starches pressurized in aqueous media (Figs. 6 and 7) kept their original X-ray pattern (B-type). These results agreed with those reported by Hibi et al. (1993).

3.3. *Differential scanning calorimetry*

The DSC results of native and pressurized starches are presented in Table 1. Peak 1 was the peak that resembled the thermal transition peak of retrograded starch (B-type crystallinity), and peak 2 was the gelatinization peak of native starch. Starch pressurized in powder displayed a lower gelatinization temperature and enthalpy change than did the native starch. This indicated damaging and loss of molecular order and crystallinity resulting from pressurization. Starch pressurized in an ethanol suspension displayed only slight decreases in both gelatinization temperature and enthalpy change, which were less severe than were the powder samples. The differences between starches treated in powder and in ethanol suspension were consistent with that of the X-ray diffraction results and further suggested the space-filling effect of ethanol. The degree of gelatinization was higher for starch pressurized with a 2/1 than with a 1/1 water/starch ratio with the exception of high-amylose maize starch. There were no gelatinization peaks detected in A-type starches pressurized in a 2/1, water/starch suspension, indicating a total loss of the native crystalline structure and molecular order.

To determine if Peak 1 in the thermogram was due to retrograded starch that developed after the starch had been gelatinized by pressure treatments, we measured the thermal properties of pressurized starch directly, immediately after pressurization. We observed that Peak 1 (dissociation of B-type crystallites) appeared immediately after a 5 min-pressure treatment. The result indicated that the B-type crystallinity was produced by the pressurization of starch. The control samples of various starches gelatinized by heat, followed by the same process, i.e. suspended in ethanol and dried, showed no detectable Peak 1. This further confirmed that at the same starch concentration, the pressure-gelatinized starch could not retrograde under the experimental condition with an exception of waxy maize starch. Waxy maize starch pressurized at 2/1 water/starch ratio displayed the largest enthalpy change of Peak 1, which could be attributed to the fact that the pressurized waxy starch gel was sticky and difficult to disperse in ethanol. Thus, it took longer time to dry. The slow drying process allowed the starch to retrograde to a higher level.

Potato and high-amylose maize starch, with the B-type crystalline structure, were more stable toward pressure treatments in a water suspension. Pressurized in a 2/1 water/starch suspension, potato starch displayed slight gelatinization on the surface of the cake. Because of its lack of homogeneity of the mixture during pressurization in the water/starch suspension, potato starch displayed a large deviation in the enthalpy change by using the direct measurement. Pressurized high-amylose maize starch did not show a significant morphological change. Nevertheless, the decrease in the enthalpy change and increase in the gelatinization temperature indicated its loss of the less stable crystalline structure during pressurization in water suspensions.

The difference between the A- and the B-type starches resulting from the pressure treatment in water suspensions can be attributed to their amylopectin structures. For the B-type crystallite, water fills up the channel in the cell unit of the crystallite and stabilizes the crystalline structure. In the A-type crystalline starch, however, the amylopectin has more scattered branching structures (Jane, Wong & McPherson, 1997). It is feasible that the scattered branch structure is more flexible that allows rearrangements of double helices to generate a channel to include water molecules. Consequently, the crystalline structure went through a transformation from the A- to the B-type crystallite. Water played essential roles in this conversion of

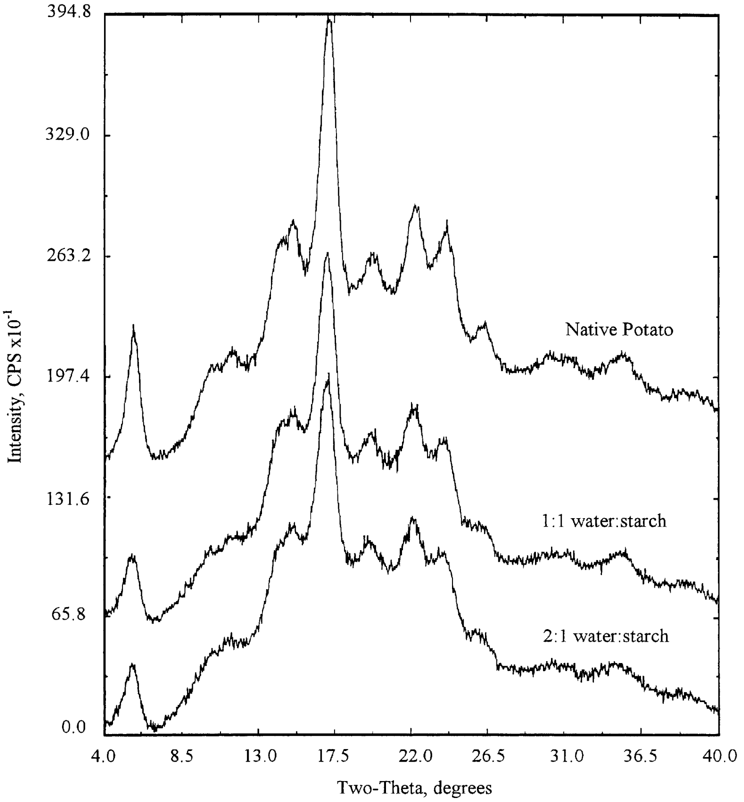

Fig. 6. The X-ray diffraction pattern of potato starch pressurized at 690 MPa.

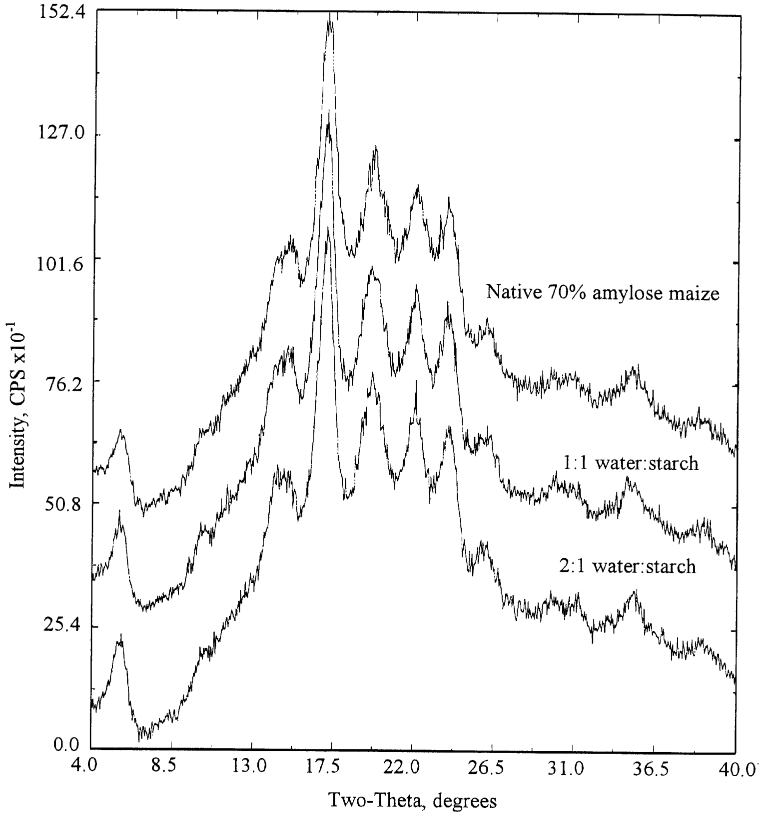

Fig. 7. The X-ray diffraction pattern of high-amylose maize starch pressurized at 690 MPa.

crystalline structures, both as a plasticizer and as an integral part of the B-type crystallites: 36 molecules of water were calculated in each unit cell (Sarko & Wu, 1978).

3.4. Rapid ViscoAnalyzer

Rapid ViscoAnalyzer (RVA) amylograms of native and pressurized starches are shown in Figs. 8–12. The RVA amylogram of native normal maize starch (Fig. 8) displayed the highest peak and final viscosity among all the normal maize starch samples. Normal maize starch pressurized in powder form and in an ethanol suspension displayed slightly less viscosity than the native starch. Pressure treatments of normal maize starch in aqueous media resulted in increased pasting temperatures and decreased paste viscosity. The differences were more severe for those treated with 2X water than with 1X water. These increases in pasting temperature and decreases in viscosity can be attributed to the changes of granular structures during the transformation of crystalline structure. Under the pressure treatment, the native A-type crystalline structure was partially converted to the B-type. During the transition, amylose interacted with lipids to develop a helical complex that displayed the V-type X-ray pattern. Because the amylose–lipid complex intertwined with amylopectin molecules, resulting from the pressure treatment and loss of native molecular order, swelling and dispersion of starch granules were restricted (Jane, Craig, Seib & Hoseney, 1986). Thus, normal maize starch pressurized in water displayed a higher pasting temperature and lower viscosity. Pasting profiles of native and pressurized rice starch (Fig. 11) were similar to those of normal maize starch (Fig. 8) with some minor differences.

In contrast to normal maize and rice starches, waxy maize starch pressurized in water media displayed lower pasting temperatures and higher peak viscosity (Fig. 9). This can be attributed in part to the lack of amylose and lipids in waxy maize starch to form complex that holds amylopectin molecules together and restricts the swelling of granules. Pressurized starch lost substantial amount of crystallinity, and amorphous starch was prompt to swell. In addition, after the conversion from an A-type to a B-type crystallinity, the B-type crystalline starch displayed a lower gelatinization temperature, $T_0 = \sim 40°C$ (Table 1), which agreed with that reported by Whittam, Noel and Ring (1990). Thus, the B-type crystalline starch would gelatinize and swell at a lower temperature. Swelling of the pressurized waxy maize starch granules that had a few pressure-induced inter-molecular associations could expand to a larger volume to reach a higher peak viscosity before granules burst.

RVA amylograms of native and pressurized tapioca starch are shown in Fig. 10. The starch pressurized in ethanol suspension displayed an identical profile to that of the native starch. Tapioca starch pressurized in the dry powder

Table 1
The thermal properties of 5 min HHP-treated starches determined by differential scanning calorimetry (SD is standard deviation; ND is not detected; Di is directly after pressure treatment).

	Peak 1				Peak 2			
Starch type	T_o[a](°C)	T_p[b](°C)	T_o[c](°C)	ΔH[d](J/g)	T_o(°C)	T_p(°C)	T_c(°C)	ΔH(J/g)
Normal maize								
Untreated	ND	ND	ND	ND	66.0 ± 0.1(SD)	70.1 ± 0.2	80.2 ± 0.0	14.0 ± 0.7
In powder form	ND	ND	ND	ND	61.1 ± 0.1	67.2 ± 0.0	78.7 ± 0.3	11.2 ± 0.7
in EtOH (1:1)	ND	ND	ND	ND	65.8 ± 0.4	69.7 ± 0.4	81.5 ± 1.3	13.1 ± 0.4
In H_2O (1:1)	41.3 ± 0.6	49.4 ± 2.5	57.7 ± 1.1	0.5 ± 0.2	63.3 ± 0.4	69.5 ± 0.5	78.1 ± 0.9	1.9 ± 0.1
In H_2O (1:1), Di	44.8 ± 1.1	51.4 ± 0.1	61.9 ± 0.1	0.9 ± 0.1	65.3 ± 0.7	72.5 ± 0.5	79.9 ± 1.1	1.7 ± 0.3
In H_2O (2:1)	40.8 ± 1.5	50.3 ± 1.8	61.9 ± 0.5	0.6 ± 0.1	ND	ND	ND	ND
In H_2O (2:1), Di	46.2 ± 0.4	51.7 ± 0.7	62.8 ± 0.5	0.3 ± 0.0	ND	ND	ND	ND
Waxy maize								
Untreated	ND	ND	ND	ND	64.6 ± 0.2(SD)	70.4 ± 0.3	81.2 ± 0.4	16.1 ± 0.2
In powder form	ND	ND	ND	ND	62.2 ± 0.2	68.4 ± 0.2	80.3 ± 0.8	14.1 ± 0.4
in EtOH (1:1)	ND	ND	ND	ND	64.3 ± 0.2	70.2 ± 0.2	81.9 ± 0.4	15.3 ± 0.1
In H_2O (1:1)	41.8 ± 0.8	47.1 ± 0.6	58.4 ± 1.2	0.7 ± 0.2	64.9 ± 0.1	71.3 ± 0.3	81.3 ± 1.1	3.1 ± 0.4
In H_2O (1:1), Di	43.5 ± 1.7	53.1 ± 1.0	62.9 ± 0.3	1.5 ± 0.3	67.0 ± 0.4	74.1 ± 0.4	84.1 ± 0.7	3.5 ± 0.2
In H_2O (2:1)	40.8 ± 0.5	50.6 ± 0.1	72.3 ± 0.5	4.3 ± 0.5	ND	ND	ND	ND
In H_2O (2:1), Di	40.3 ± 1.6	58.7 ± 2.4	67.6 ± 3.2	0.4 ± 0.1	ND	ND	ND	ND
Tapioca								
Untreated	ND	ND	ND	ND	64.9 ± 0.1(SD)	69.1 ± 0.1	82.2 ± 0.5	14.8 ± 0.3
In powder form	ND	ND	ND	ND	59.8 ± 0.1	66.2 ± 0.1	78.8 ± 0.2	12.2 ± 0.1
in EtOH (1:1)	ND	ND	ND	ND	64.5 ± 0.1	68.7 ± 0.1	82.0 ± 1.0	14.1 ± 0.2
In H_2O (1:1)	ND	ND	ND	ND	61.5 ± 2.4	68.3 ± 2.4	77.2 ± 2.8	2.2 ± 0.1
In H_2O (1:1), Di	42.5 ± 0.9	48.6 ± 1.9	57.4 ± 0.1	0.2 ± 0.0	63.0 ± 0.3	70.7 ± 0.3	81.6 ± 1.4	2.6 ± 0.1
In H_2O (2:1)	45.6 ± 1.3	47.2 ± 1.4	55.7 ± 1.9	0.2 ± 0.1	ND	ND	ND	ND
In H_2O (2:1), Di	ND	ND	ND	ND	ND	ND	ND	ND
Rice								
Untreated	ND	ND	ND	ND	60.6 ± 0.6(SD)	68.3 ± 0.1	84.7 ± 2.3	16.8 ± 4.1
In powder form	ND	ND	ND	ND	55.7 ± 0.3	65.9 ± 0.3	82.9 ± 0.4	14.1 ± 0.5
in EtOH (1:1)	ND	ND	ND	ND	60.1 ± 0.3	68.1 ± 0.1	84.8 ± 3.2	16.6 ± 2.3
In H_2O (1:1)	ND	ND	ND	ND	64.3 ± 0.4	70.3 ± 0.4	80.4 ± 0.5	0.5 ± 0.1
In H_2O (1:1), Di	46.6 ± 0.2	51.8 ± 0.4	58.2 ± 0.7	0.1 ± 0.0	65.6 ± 0.7	75.2 ± 1.5	84.1 ± 1.7	2.3 ± 0.1
In H_2O (2:1)	44.3 ± 0.0	50.5 ± 0.0	56.6 ± 0.0	0.1 ± 0.0	ND	ND	ND	ND
In H_2O (2:1), Di	44.2 ± 0.0	50.8 ± 0.0	57.0 ± 0.0	0.4 ± 0.0	ND	ND	ND	ND
Potato								
Untreated	ND	ND	ND	ND	58.1 ± 0.1(SD)	62.4 ± 0.1	72.5 ± 0.1	18.9 ± 0.3
In powder form	ND	ND	ND	ND	54.4 ± 0.8	60.8 ± 0.3	71.4 ± 0.4	17.3 ± 0.4
in EtOH (1:1)	ND	ND	ND	ND	57.1 ± 0.3	61.5 ± 0.3	71.3 ± 0.6	18.4 ± 0.2
In H_2O (1:1)	ND	ND	ND	ND	57.7 ± 0.2	62.3 ± 0.3	71.6 ± 0.5	14.5 ± 0.5
In H_2O (1:1), Di	ND	ND	ND	ND	58.0 ± 0.1	63.3 ± 0.1	76.0 ± 1.7	13.3 ± 0.2
In H_2O (2:1)	ND	ND	ND	ND	56.0 ± 0.2	62.5 ± 0.2	71.9 ± 0.5	9.9 ± 0.3
In H_2O (2:1), Di	ND	ND	ND	ND	58.3 ± 0.5	64.1 ± 0.9	74.5 ± 0.7	12.5 ± 9.5
70% amylose maize								
Untreated	ND	ND	ND	ND	70.6 ± 0.3(SD)	85.7 ± 0.7	113.1 ± 0.9	13.0 ± 1.0
In powder form	ND	ND	ND	ND	70.4 ± 1.1	96.7 ± 6.8	116.3 ± 3.5	10.6 ± 1.0
in EtOH (1:1)	ND	ND	ND	ND	69.7 ± 0.5	92.1 ± 7.0	112.8 ± 0.7	12.8 ± 0.5
In H_2O (1:1)	ND	ND	ND	ND	72.6 ± 0.5	90.0 ± 7.2	112.7 ± 1.3	8.7 ± 0.7
In H_2O (2:1)	ND	ND	ND	ND	76.5 ± 1.7	100.1 ± 1.4	113.6 ± 1.2	9.5 ± 0.4

[a] Onset.

[b] Peak.

[c] Completion temperature.

[d] Enthalpy change.

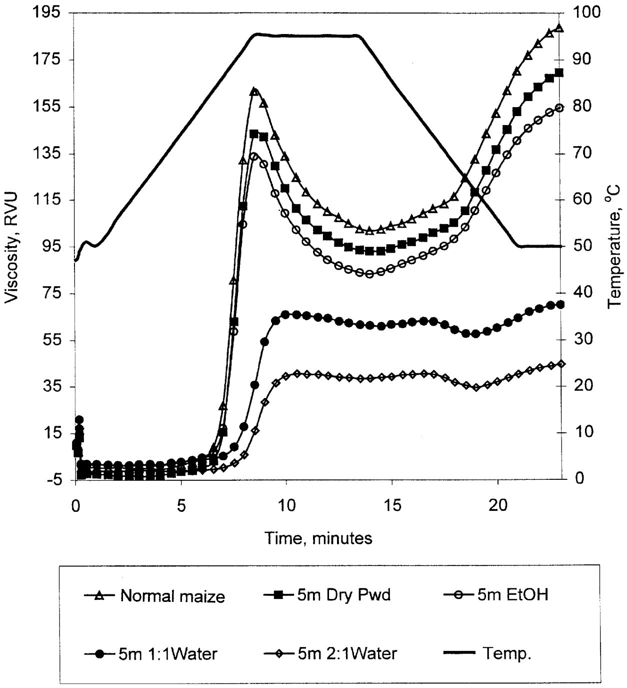

Fig. 8. The RVA amylograms of native and pressurized normal maize starch with 8% solid concentration and 160 rpm spindle speed. The abbreviation for legends in Figs. 8–12 are 'm' for minutes, 'Dry Pwd' for powder form, 'EtOH' for suspension in ethanol, '1.1 and 2.1' for the ratio of water to starch suspension, and 'Temp' for temperature.

form displayed a slightly lower pasting temperature and higher peak viscosity. Tapioca starch that was pressurized in the presence of water showed a substantially higher peak temperature and final viscosity. This indicated association between amylose and amylopectin induced by pressurization, which produced a cross-linking-like network that displayed resistance to sheer force and increased viscosity. Without an amylose–lipid complex, swelling of starch granules was not restricted. The starch pressurized with 2X water displayed a very low pasting temperature indicating the presence of amorphous (pregelatinized) starch.

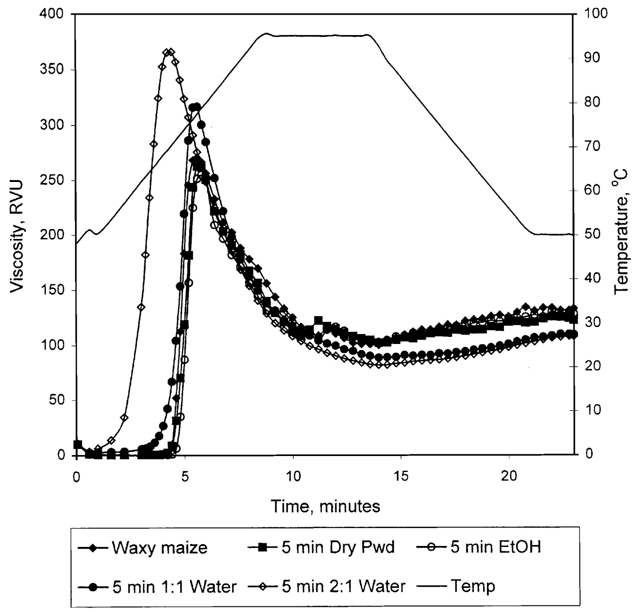

Fig. 9. The RVA amylograms of native and pressurized waxy maize starch with 8% solid concentration and 160 rpm spindle speed.

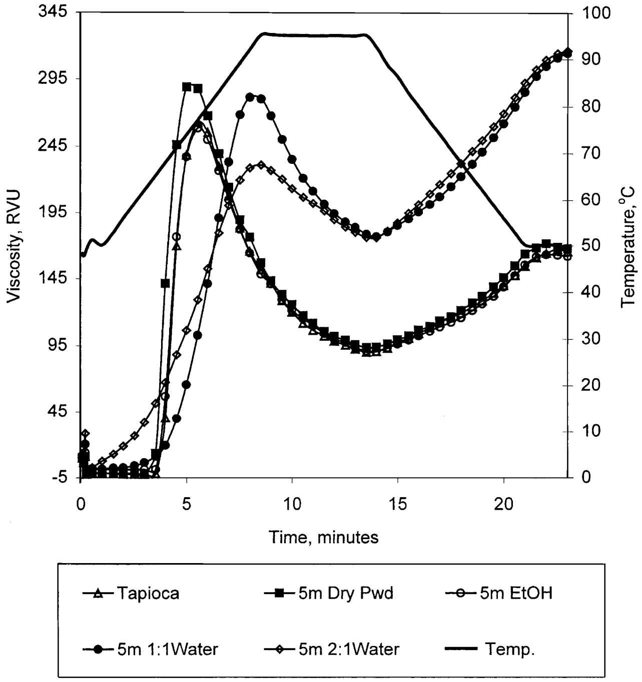

Fig. 10. The RVA amylograms of native and pressurized tapioca starch with 8% solid concentration and 160 rpm spindle speed.

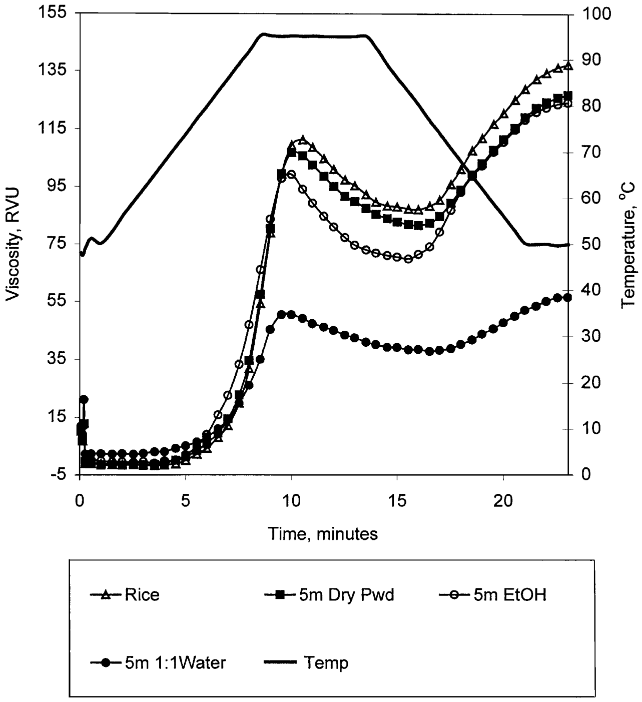

Fig. 11. The RVA amylograms of native and pressurized rice starch with 8% solid concentration and 160 rpm spindle speed.

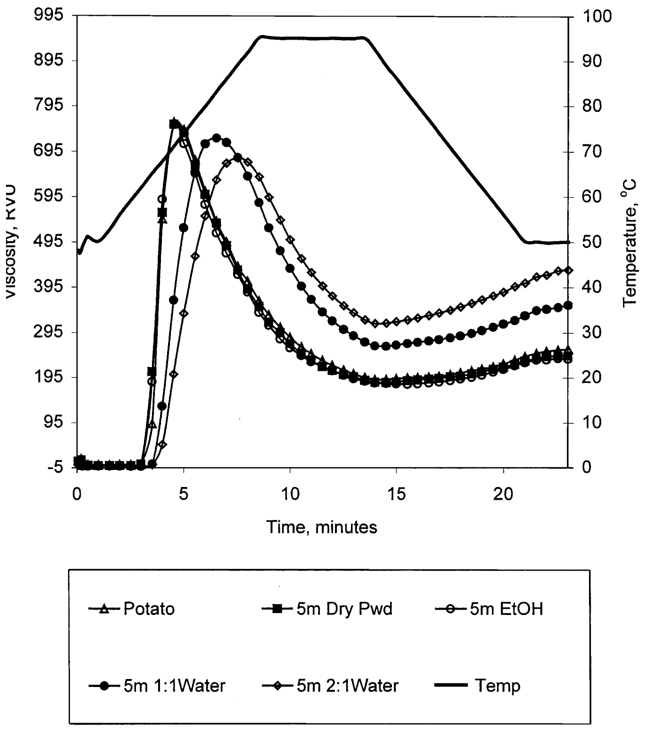

Fig. 12. The RVA amylograms of native and pressurized potato starch with 8% solid concentration and 160 rpm spindle speed.

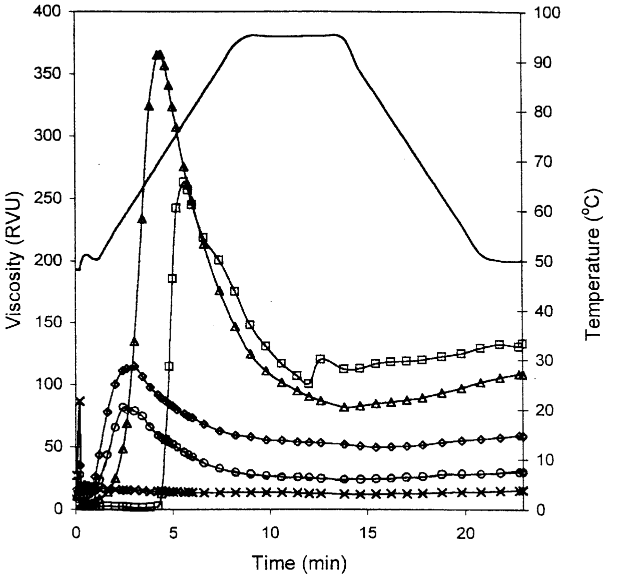

Fig. 13. The RVA amylograms of heat-gelatinized waxy maize starch with and without retrogradation (8% solid concentration and 160 rpm spindle speed). The amylograms are compared with that of native and pressurized waxy maize starch. -□-, Native waxy maize starch; - X -, water/starch (v/w) 2/1, heated in an oven at 100°C for 24 h, washed with ethanol, and dried; -◇-, water/starch (v/w) 1/1, heated in an oven at 100°C for 24 h, and dried at 25°C for 60 h; -O-, water/starch (v/w) 2/1, heated in an oven at 100°C for 24 h, and dried at 25°C for 60 h; -△-, water/starch (v/w) 2/1, pressure (690 MPa) treated for 5 min; — temperature (°C).

RVA amylograms of pressurized potato starch in dry powder and in ethanol suspension forms are similar to that of native potato starch (Fig. 12). Potato starch that was pressurized in the presence of water increased the pasting temperature and the final viscosity but slightly decreased the peak viscosity. The change of the pasting pattern was similar to that of the tapioca starch but without a decrease in pasting temperature. This was consistent with the fact that more crystallinity was retained in pressurized potato starch.

For comparison purpose, RVA amylograms of waxy maize starch gelatinized by heat and with and without retrogradation are shown in Fig. 13. Heat-gelatinized waxy maize starch that was immediately suspended in ethanol and dried was amorphous and showed no X-ray diffraction peaks (data not shown). The starch displayed a low instant viscosity (~15 RVU) without any peak (Fig. 13). Heat gelatinized waxy maize starch that was allowed to retrograde at 25°C displayed a weak B-type X-ray diffraction pattern (data not shown). RVA of the starch displayed a much lower peak viscosity and lower pasting temperature than pressurized waxy maize starch (Fig. 13). This difference further confirmed the conversion of polymorphism by pressurization is independent from retrogradation.

3.5. Gel permeation chromatography

Gel permeation chromatograms (GPC) of native starches and their pressurized counterparts showed no difference in molecular weight distribution. This is in agreement with that reported by Cheftel (1992) and by Hibi et al. (1993). The results confirmed that with 690 MPa pressure, covalent bonds in starch remained intact (results are not shown).

4. Conclusions

High-pressure treatments of A-type starches in the presence of water resulted in partial conversion to the B-type crystallinity. Starches of the B-type X-ray pattern were more resistant to the high-pressure treatment in a water suspension. DSC thermogram of the A-type crystalline starch displayed an additional peak (T_0 between 41–46°C) right after the pressure treatment. This indicated that the crystallinity transformation was a result of pressure-induced rearrangements of double helices in the A-type starch. Pasting properties of pressurized starches changed, depending on the structure of the starch. There were no significant differences between the treatments with 5 min and 1 h dwelling times. GPC results showed that no molecular degradation resulted from the high-pressure treatments.

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