Gel-Chromatography Fractionation and Thermal Characterization of Rice Starch Affected by Hydrothermal Treatment[1]

SHIN LU,[2,3] CHING-YUNG CHEN,[2] and CHENG-YI LII[4]

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ABSTRACT

Two rice cultivars, high amylose TNS 19 and waxy TCW 70, were selected for a study of thermal behavior and molecular redistribution of rice starch after hydrothermal treatments. The treatment conditions included soaking for 2 hr at 40°C and steaming for 10 or 20 min at 0 and 18 psi steam pressure, respectively. Lower temperature endotherms, measured by differential scanning calorimetry, were observed at 65 and 72°C for the untreated TNS 19 and TCW 70, respectively. The hydrothermal treatments caused a shift to higher gelatinization temperatures and lower transition enthalpy changes. Simultaneously, a higher temperature endotherm was observed at ≈115°C for TNS 19 only. The thermal degradation of amylopectin apparently resulted in a decreased amount of large molecules and an increased amount of smaller molecules. The heat-moisture-treated rice flour was mixed with water and heated to gelatinization and then stored at 4 or 25°C. The transition enthalpies increased with concomitant decreases of transition peak temperatures during storage. These results indicate that the extent of retrogradation increases with storage time for both rice cultivars. At 4°C storage, a higher transition enthalpy was observed in waxy TCW 70 from day 7, although at 25°C storage, no similar changes were observed throughout 21 days.

Heating starch with limited moisture content (heat-moisture treatment) dramatically changes its physicochemical properties (Kulp and Lorenz 1981, Lorenz and Kulp 1983). The water-holding capacities and enzyme susceptibility of treated rice flours increase and swelling powers decrease (Fang 1991, Lu et al 1994). Heating a waxy rice cultivar increases the stability of viscograph paste (Chen 1992). These findings indicate that physical changes occur within the starch granules due to the heat plus moisture treatment (Damir 1985).

Differential scanning calorimetry (DSC) has commonly been used for investigating thermal behavior of starches. Gelatinization as well as retrogradation are two important thermal behaviors. DSC data can provide a quantitative measure of gelatinization (Stevens and Elton 1971, Biliaderis et al 1980, Nakazawa et al 1984, Krueger et al 1987), retrogradation (Atwell et al 1988, Yuan et al 1993), and the phase transitions on maize (White et al 1990, 1991; Li et al 1994) and wheat starches (Donovan 1979, Donovan et al 1983), as well as on rice (Biliaderis et al 1986; Tester and Morrison 1990a,b; Marshall 1992; Huang et al 1993). Therefore, an endothermic transition could be observed by DSC. Mahanta and Bhattacharya (1989) indicated that rice starch was thermally degraded and starch structural changes were caused by high-pressure steaming (Chen 1992). The fine structure of maize and rice starch has also been estimated using gel-permeation chromatography (GPC). GPC can quantitatively separate starch using molecular weight distribution and mean degree of polymerization (Juliano 1984; Chinnaswamy and Bhattacharya 1986; Takeda and Hizukuri 1987, 1989; Takeda et al 1987, 1993; Enevoldsen and Juliano 1988; Tester and Morrison 1990b). To further elucidate the effect of hydrothermal treatment on rice starches, studies of their thermal properties and structure redistribution were initiated with DSC and GPC techniques.

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[2]Department of Food Science, National Chung-Hsing University, Taichung, Taiwan 40227, R. O. C.
[3]Corresponding author. E-mail: 215slu@vax9k.nchu.edu.tw
[4]Institute of Chemistry, Academia Sinica Nankang, Taipei, Taiwan, R.O.C.

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MATERIALS AND METHODS

Materials

Two rice cultivars, TNS 19 (nonwaxy) and TCW 70 (waxy) were obtained from Taichung District Experimental Station, Chang-Hwa county, Taiwan in 1990.

The rice samples and an equal amount of water were soaked at 40°C for 2 hr in closed bottles and then steamed in an autoclave under different pressures (0 and 18 psi) for 10 or 20 min. All samples were then freeze-dried (Labconco stopping tray dryer, Lyph-Lock 18, Labconco Co., KS) to ≈10% moisture and then milled with a cyclone sample grinder (Udy Co.) and passed through a 60-mesh screen.

Amylose

Amylose content in the rice flour was determined using a colorimetric method (Williams et al 1970).

DSC

DSC experiments were performed with a Setaram DSC 121 (Setaram Co., France). Heating rate was 5°C/min from 20–150°C. Samples (110–120 mg) were mixed with water (2:3, w/w) and kept at 4°C overnight to allow a uniform distribution of water in the flours. Samples were sealed in stainless crucibles and reweighed before the DSC analysis. For each endotherm, onset (T_o) and peak (T_p) transition temperatures were determined using a computerized system developed by the Setaram Co. The transition enthalpies (ΔH) were determined from the peak area of the endotherm and expressed as joules per gram of dry matter.

GPC

Due to the difficulty of isolating starch from pregelatinized rice, flour rather than starch was used for the chromatographic fractionation for molecular weight distribution of gel permeation of rice as described by Mahanta and Bhattacharya (1989) with some minor modifications.

About 80 mg of defatted flour was dispersed in 5 ml of 0.25N KOH under nitrogen atmosphere in a boiling water bath for 3–4 min. After cooling in the nitrogen atmosphere, the dispersion was neutralized first with 0.5N HCl and then with 0.05N HCl, using phenolphthalein as an indicator added directly into the tube. The volume was made up to 15 ml. The dispersion was filtered through a prefilter sample clarification kit (Water Associates) and

G4 sintered glass disc in a syringe. An aliquot of the filtrate (≈3 ml) containing exactly 10.0 mg (dry weight) of carbohydrate was fractionated by ascending chromatography on a Sepharose CL-2B (Pharmacia Fine Chemicals, Sweden) column (1.6 × 70 cm) operating with a peristaltic pump at a flow rate of 8 ml/hr. Distilled water containing 0.02% sodium azide was used as an eluent. Fractions (4 ml) were collected and aliquots (0.5 ml) of the fractions were used for determination of carbohydrate using a phenol-sulfuric acid method and measured at 490 nm against a glucose standard.

Chain Length Distribution

The chain length distribution (DP) was determined using the gel-filtration method with minor modification (Chinnaswamy and Bhattacharya 1986).

Fraction I (void volume) was freeze-dried in a Virtis freeze dryer and dispersed (4.0 mg) in acetate buffer (5 ml, 0.1*M*, pH 5.3). Crystalline pullulanase (32 IU) (Sigma Chemical Co.) was added and the mixture was incubated at 37°C for 30 hr. The enzyme action was stopped by heating the solution in a boiling water bath for 10 min. The solution was then chromatographed. An aliquot of the filtrate (≈4 ml) was fractionated by ascending chromatography on a Sephadex G-50 (Pharmacia) column (1.6 × 70 cm) operating with a peristaltic pump at a flow rate of 25 ml/hr, using distilled water containing 0.02% sodium azide as an eluent.

Total carbohydrate was analyzed using the phenol-sulfuric acid method (Dubois et al 1956). The reducing value was measured using a modified Park-Johnson procedure (Hizukuri et al 1981): Chain length (DP) = total carbohydrate/reducing value.

RESULTS AND DISCUSSION

Effect of Heat-Moisture Treatment

DSC. Figures 1 and 2 show the gelatinization temperature range for untreated rice flour at ≈60–90°C. The enthalpies of the phase transition of TNS 19 and TCW 70 were 8.66 and 12.21 J/g, respectively. After heat-moisture treatment at 100°C, the gelatinization temperature range tended to increase to 80–95°C, but the transition enthalpy decreased for TNS 19. The endothermal peak of TCW 70 disappeared after heating at 100°C for 20 min, which means that the crystallinity of TCW 70 was easily ruptured. The endothermic peak of the rice flour disappeared during heat-moisture treatment at 121°C, indicating that the crystallinity of the starch kernel was ruptured by heat.

For untreated or 100°C heat-moisture-treated rice flour, there were two endothermic peaks at ≈100°C for TNS 19 but only one peak for TCW 70. After treatment at 121°C, there was only one endothermal peak for TNS 19 and none for TCW 70. Generally speaking, amylose reacts with lipids to form the amylose-lipid complex which gives a thermally reversible endothermic peak at ≈100°C (Kugimiya et al 1980, Biliaderis et al 1986, Mahanta and Bhattacharya 1989). Researchers (Gudmundson and Eliasson 1990, Gudmundson 1992) have reported that the exterior starch chains form complexes with lipids, and the endothermic peak occurs at 100–121°C. Thus, the endothermic peak of TCW 70 was probably from amylopectin-lipid complex. Whether TNS 19 could produce amylose-lipid or amylopectin-lipid complexes is uncertain and requires further study.

GPC. Starch consists of amylose and amylopectin. Amylose is primarily made of linear molecules, and amylopectin from highly

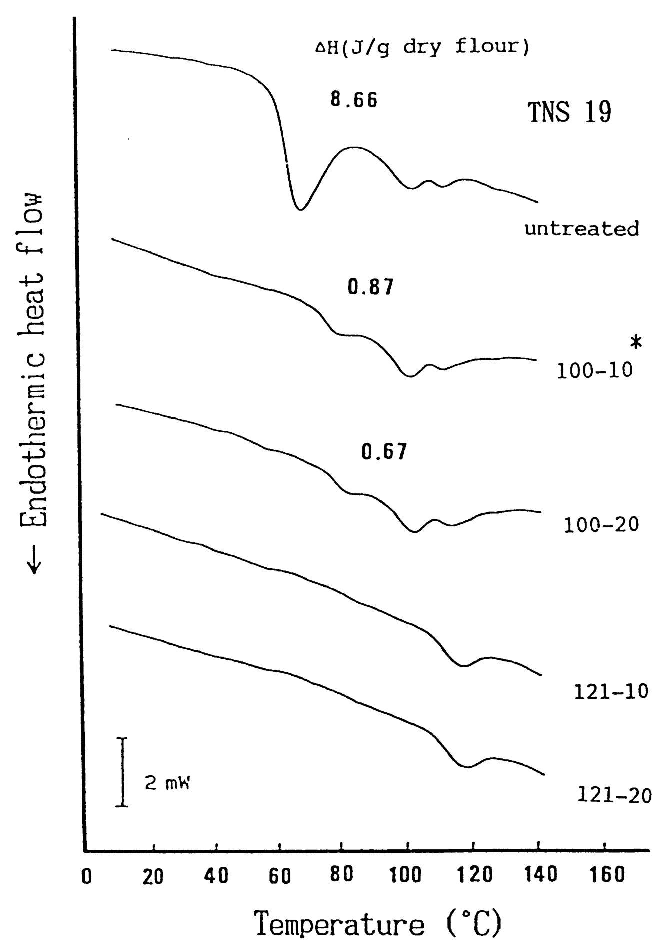

Fig. 1. Differential scanning calorimetry thermal curves of untreated and heat-moisture-treated TNS 19 (nonwaxy) rice flour. * = Steaming temperature (°C) and steaming time (min) of milled rice.

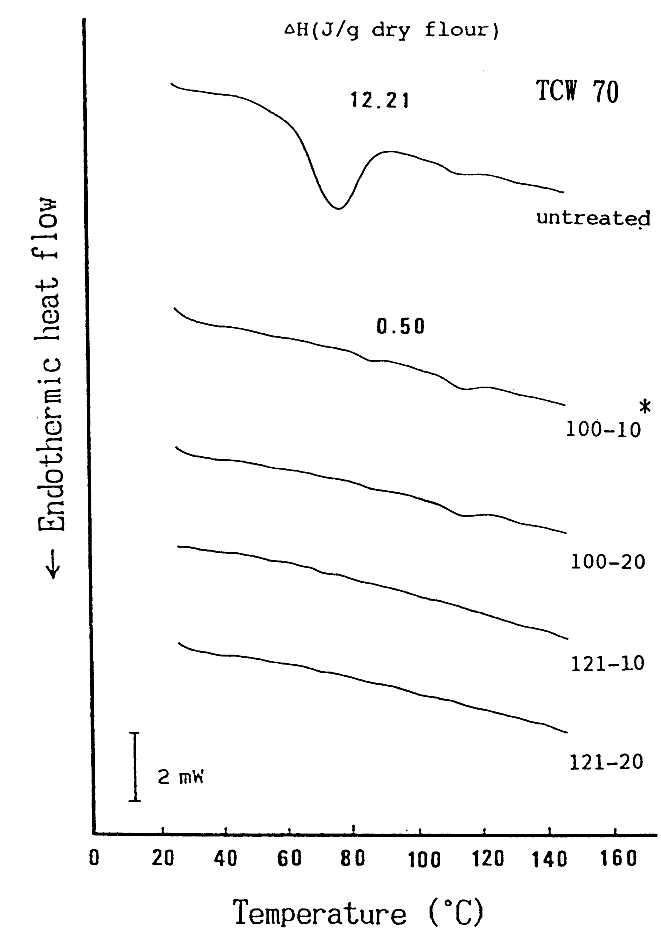

Fig. 2. Differential scanning calorimetry thermal curves of untreated and heat-moisture-treated TCW 70 (waxy) rice flour. * = Steaming temperature (°C) and steaming time (min) of milled rice.

branched macromolecules. The molecular distribution of rice starch after heat-moisture treatment can be studied using GPC to separate molecules by size (Cooper 1983).

The results indicated that there were two main distribution areas for untreated TNS 19. The first fraction appeared around tube 15, and the second distribution area appeared around tube 39 (Fig. 3). However, there was only one distribution area that appeared around tube 15 for TCW 70 (Fig. 4). The first distribution area is presumed to consist of amylopectin that eluted first because the time lag for starch to be eluted is related to molecular size (Mahanta and Bhattacharya 1989, Oates 1990).

After heat-moisture treatment, the total carbohydrate content at the first distribution area decreased for each rice flour. After tube 20, total carbohydrate content tended to increase, especially during heat-moisture treatment at 121°C. Thus, the thermal degradation of amylopectin by heat-moisture contributes to a decrease in the number of large molecules and an increase in the number of

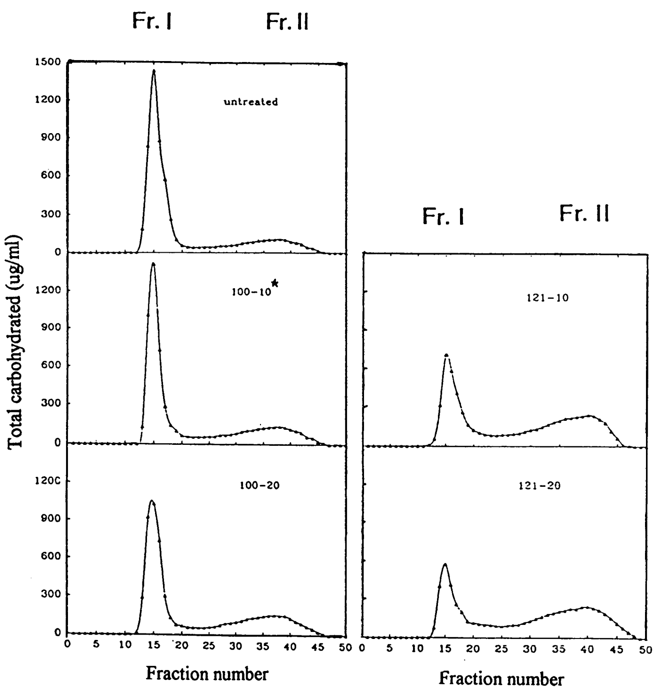

Fig. 3. Effect of heat-moisture treatment on the Sepharose CL-2B gel filtration profiles of TNS 19 rice flour. Column was eluted with 0.02% sodium azide aqueous solution. Flow rate was 8 ml/hr. Fractions (0.5 ml) collected every 30 min and analyzed for total carbohydrate using phenol-sulfuric method. Glucose was used for standard. * = Steaming temperature (°C) and steaming time (min) of milled rice.

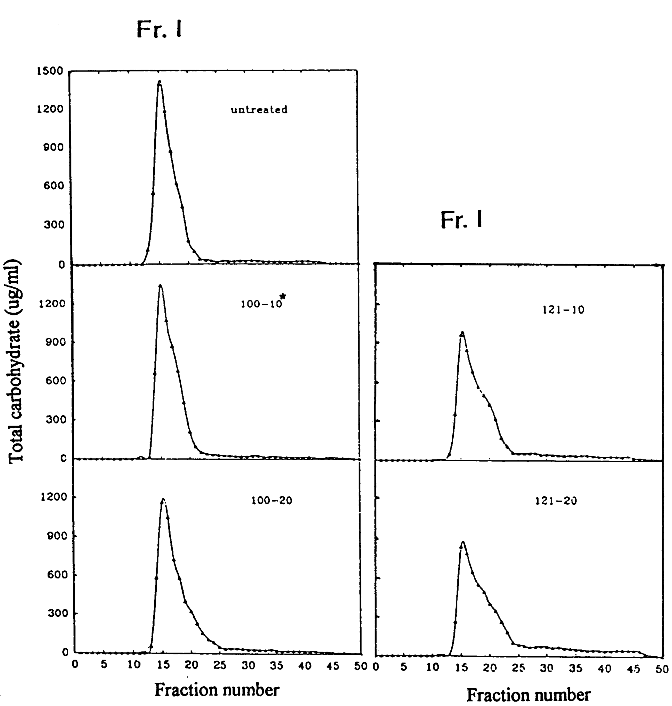

Fig. 4. Effect of heat-moisture treatment on the Sepharose CL-2B gel-filtration profiles of TCW 70 rice flour. Column was eluted with 0.02% sodium azide aqueous solution. Flow rate was 8 ml/hr. Fractions (0.5 ml) collected every 30 min and analyzed for total carbohydrate using phenol-sulfuric method. Glucose was used for standard. * = Steaming temperature (°C) and steaming time (min) of milled rice.

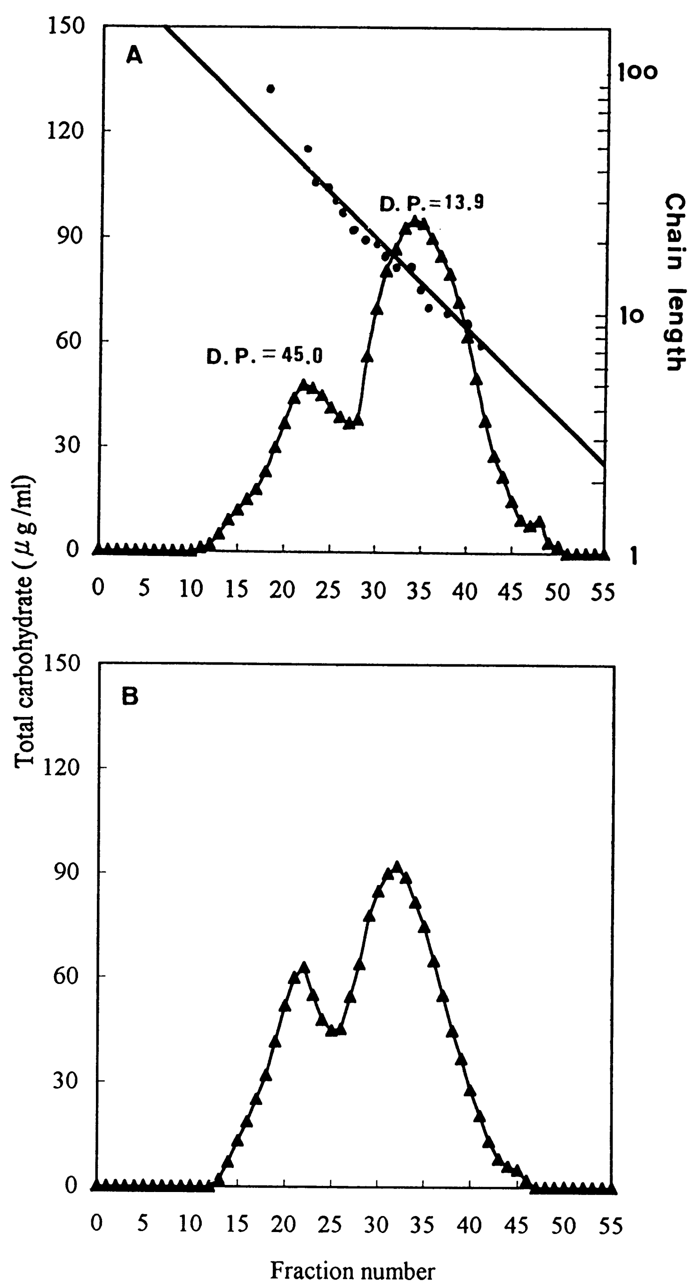

Fig. 5. Effect of heat-moisture treatment on chain length distribution (DP) profiles of TNS 19 amylopectin using debranched pullulanase: untreated **(A)** and **(B)** treated at 121°C for 20 min. Column was eluted with 0.02% sodium azide aqueous solution on Sephadex G-50. Flow rate was 25 ml/hr. Fractions (0.5 ml) collected every 10 min and analyzed for total carbohydrate using phenol-sulfuric method. Solutions (1.0 ml) were analyzed for reducing sugar using Park-Johnson method. Glucose used as standard.

smaller molecules (Mahanta and Bhattacharya 1989, Murugesan and Bhattacharya 1989). The degree of thermal degradation was: 121°C, 20 min > 121°C, 10 min > 100°C, 20 min > 100°C, 10 min.

Heat-moisture treatment leads to the thermal degradation of amylopectin for the rice flour. However, understanding the thermal degradation process requires additional investigation. We used pullulanase to debranch the eluents of the first area from the Sepharose CL-2B and then analyzed the resulting molecular chain length using Sephadex G-50.

The untreated and treated (121°C, 20 min) samples were analyzed. As shown in Figures 5 and 6, the amylopectin consisted of two main chain length distribution areas: the first distribution area contains B chains, and the second distribution area contains A chains (Atwell et al 1980, Takeda et al 1987, Enevoldsen and Juliano 1988). After heat-moisture treatment, the total carbohydrate content of amylopectin in the second distribution area decreased slightly for TNS 19 and TCW 70, which indicated that the exterior linear chain of amylopectin was thermally degraded. Heat-moisture treatment leads to the rupture of molecular structure for starch (Kulp and Lorenz 1981). This may be the main reason that the physicochemical properties of rice flour changes.

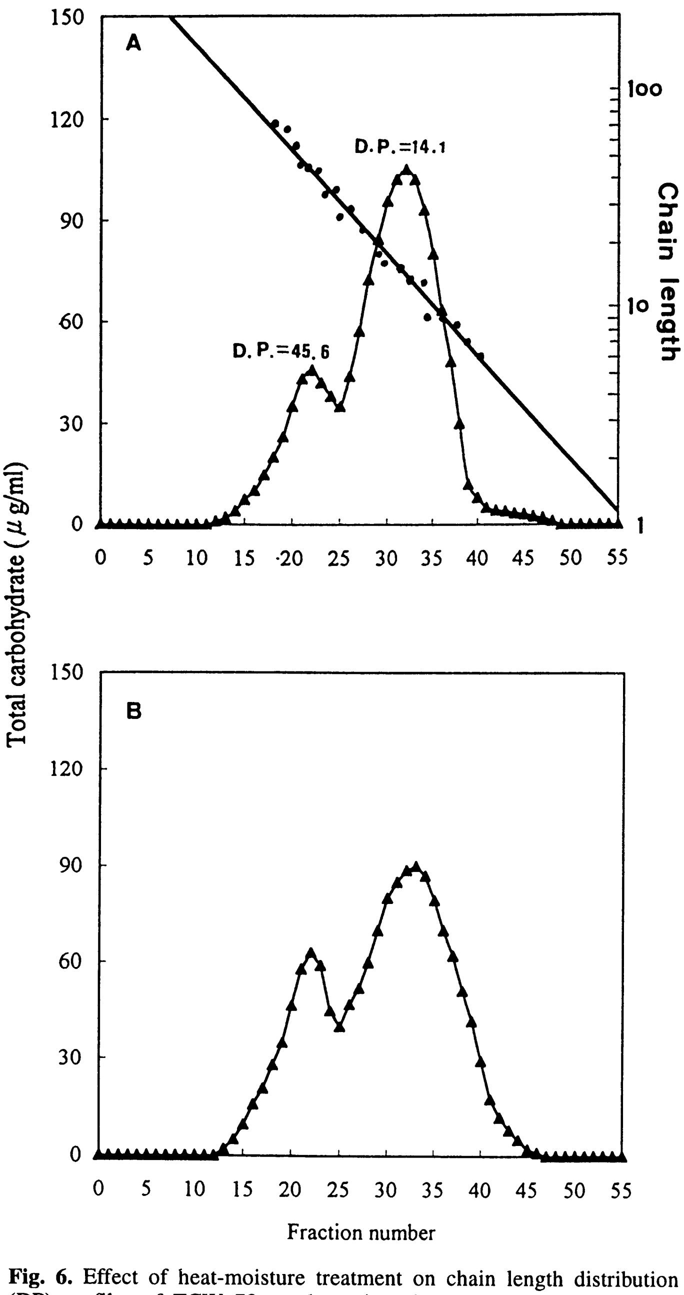

Fig. 6. Effect of heat-moisture treatment on chain length distribution (DP) profiles of TCW 70 amylopectin using debranched pullulanase: untreated **(A)** and **(B)** treated at 121°C for 20 min. Column was eluted with 0.02% sodium azide aqueous solution on Sephadex G-50. Flow rate was 25 ml/hr. Fractions (0.5 ml) collected every 30 min and analyzed for total carbohydrate using phenol-sulfuric method. Solutions (1.0 ml) were analyzed for reducing sugar using Park-Johnson method. Glucose used as standard.

Effect of Retrogradation of Rice Flour During Storage

DSC. The onset temperature (T_o), peak temperature (T_p) and transition enthalpies of each untreated and heat-moisture treated

TABLE I
Differential Scanning Calorimetry Retrogradation Behaviors of Untreated and Heat-Moisture Treated TNS 19 Rice Flour Gels Stored at 4°C for Different Time Intervals

	Transition Temperature (T, °C) and Enthalpy (ΔH, J/g of flour)		
Sample	T_o	T_p	ΔH
8 Hr			
Untreated	30.9 ± 0.3[a]	55.7 ± 0.3	−1.08 ± 0.02
100–10[b]	30.2 ± 0.4	54.9 ± 0.2	−1.52 ± 0.04
100–20	32.3 ± 0.1	54.9 ± 0.4	−1.57 ± 0.08
121–10	32.6 ± 0.7	53.4 ± 0.3	−1.60 ± 0.01
121–20	32.3 ± 0.6	54.3 ± 0.2	−1.59 ± 0.02
16 Hr			
Untreated	33.4 ± 0.3	51.8 ± 0.7	−1.80 ± 0.02
100–10	32.8 ± 0.4	51.6 ± 0.1	−2.11 ± 0.09
100–20	32.4 ± 0.1	51.0 ± 0.5	−2.82 ± 0.10
121–10	32.1 ± 0.2	51.3 ± 0.4	−3.22 ± 0.21
121–20	32.2 ± 0.5	52.9 ± 0.5	−3.26 ± 0.09
1 Day			
Untreated	32.5 ± 0.0	51.9 ± 0.2	−2.56 ± 0.07
100–10	31.9 ± 0.8	50.8 ± 0.4	−3.07 ± 0.13
100–20	32.4 ± 0.5	49.6 ± 0.3	−2.98 ± 0.10
121–10	33.0 ± 0.2	51.4 ± 0.1	−3.47 ± 0.10
121–20	32.6 ± 0.2	50.5 ± 0.1	−3.94 ± 0.07
2 Days			
Untreated	32.1 ± 0.2	45.4 ± 0.1	−4.41 ± 0.13
100–10	32.2 ± 0.6	44.8 ± 0.2	−4.66 ± 0.07
100–20	33.4 ± 0.7	44.4 ± 0.2	−4.79 ± 0.16
121–10	32.0 ± 0.4	43.4 ± 0.3	−4.86 ± 0.01
121–20	31.8 ± 0.0	43.6 ± 0.2	−5.08 ± 0.06
3 Days			
Untreated	31.1 ± 0.2	45.3 ± 0.5	−5.16 ± 0.07
100–10	30.2 ± 0.4	45.8 ± 0.2	−5.39 ± 0.03
100–20	30.3 ± 0.1	45.1 ± 0.4	−5.57 ± 0.13
121–10	31.6 ± 0.6	45.0 ± 0.7	−5.52 ± 0.07
121–20	30.8 ± 0.5	45.1 ± 0.3	−5.61 ± 0.05
7 Days			
Untreated	31.4 ± 0.2	45.9 ± 0.5	−6.26 ± 0.11
100–10	31.5 ± 0.1	46.0 ± 0.1	−6.53 ± 0.10
100–20	31.4 ± 0.4	45.2 ± 0.5	−6.56 ± 0.16
121–10	32.1 ± 0.2	47.0 ± 0.2	−6.71 ± 0.09
121–20	31.8 ± 0.7	47.0 ± 0.7	−6.94 ± 0.07
14 Days			
Untreated	33.3 ± 0.5	46.3 ± 0.4	−7.01 ± 0.06
100–10	32.6 ± 0.4	46.2 ± 0.2	−7.15 ± 0.05
100–20	32.5 ± 0.8	45.1 ± 0.3	−7.29 ± 0.02
121–10	33.4 ± 0.1	46.5 ± 0.2	−7.38 ± 0.03
121–20	33.8 ± 0.1	46.9 ± 0.8	−7.45 ± 0.02
21 Days			
Untreated	33.9 ± 0.5	47.2 ± 0.2	−7.28 ± 0.10
100–10	33.0 ± 0.0	46.7 ± 0.2	−7.50 ± 0.11
100–20	33.7 ± 0.1	47.0 ± 0.1	−7.42 ± 0.14
121–10	34.2 ± 0.2	47.7 ± 0.6	−7.73 ± 0.06
121–20	32.7 ± 0.4	46.7 ± 0.5	−7.95 ± 0.07

[a] Mean ± standard deviation; $n = 3$.

[b] Two coded numbers for each heat-moisture treated rice flour indicate the steaming temperatures (°C) and steaming times (min) of milled rice.

rice flour for TNS 19 and TCW 70 at different storage temperatures after heat-moisture treatments are shown in Tables I–IV. The transition enthalpy of each rice flour increased as the storage lags increased.

As for storage at different temperatures, the enthalpies of the phase transition of the samples at 4°C was higher than for those stored at 25°C. In addition, under the same storage conditions (4 or 25°C), the enthalpy changes and lag time were higher for heat-moisture-treated rice flour at 121°C than for the others. The order was: 121°C, 20 min > 100°C, 20 min > 100°C, 10 min > untreated sample.

As for T_o and T_p, under the same storage temperature, T_o is almost the same, but when the rice was stored at 4°C, T_p had a higher value on the first day and then kept steady for the rest of the experimental period. However, for the samples stored at different temperatures, both T_o and T_p were higher when stored at 25°C than when stored at 4°C. As for different cultivars of rice, the endothermic peak of untreated TNS 19 shows up when stored at 25°C for 16 hr, but the endothermic peak for TCW 70 does not show up until stored for more than 21 days, which indicates that

TABLE II
Differential Scanning Calorimetry Retrogradation Behaviors of Untreated and Heat-Moisture Treated TNS 19 Rice Flour Gels Stored at 25°C for Different Time Intervals

Sample	Transition Temperature (T, °C) and Enthalpy (ΔH, J/g of flour)		
	T_o	T_p	ΔH
8 Hr			
Untreated	ND[a]	ND	ND
100–10[b]	ND	ND	ND
100–20	ND	ND	ND
121–10	49.0 ± 0.2[c]	57.4 ± 0.7	–36 ± 0.07
121–20	48.4 ± 0.4	56.9 ± 0.3	–38 ± 0.02
16 Hr			
Untreated	50.7 ± 0.1	58.5 ± 0.4	–40 ± 0.01
100–10	50.2 ± 0.3	57.9 ± 0.4	–46 ± 0.01
100–20	50.5 ± 0.4	57.2 ± 0.4	–50 ± 0.02
121–10	50.2 ± 0.3	56.7 ± 0.7	–54 ± 0.01
121–20	49.8 ± 0.6	57.5 ± 0.2	–54 ± 0.01
1 Day			
Untreated	50.5 ± 0.2	58.1 ± 0.4	–49 ± 0.02
100–10	48.2 ± 0.2	57.7 ± 0.3	–59 ± 0.02
100–20	50.8 ± 0.4	58.1 ± 0.2	–60 ± 0.01
121–10	51.0 ± 0.5	58.0 ± 0.7	–61 ± 0.01
121–20	51.8 ± 0.7	58.5 ± 0.2	–63 ± 0.01
2 Days			
Untreated	48.5 ± 0.2	58.1 ± 0.2	–76 ± 0.01
100–10	48.8 ± 0.7	57.7 ± 0.6	–87 ± 0.07
100–20	49.4 ± 0.2	58.2 ± 0.0	–96 ± 0.03
121–10	51.1 ± 0.6	58.7 ± 0.4	–100 ± 0.03
121–20	51.8 ± 0.8	58.5 ± 0.6	–1.01 ± 0.02
3 Days			
Untreated	49.7 ± 0.5	59.2 ± 0.2	–1.54 ± 0.03
100–10	48.6 ± 0.7	58.1 ± 0.1	–1.74 ± 0.07
100–20	49.6 ± 0.1	58.9 ± 0.5	–1.76 ± 0.01
121–10	49.0 ± 0.2	58.6 ± 0.3	–1.84 ± 0.01
121–20	48.5 ± 0.4	58.1 ± 0.4	–1.89 ± 0.01
7 Days			
Untreated	48.6 ± 0.4	58.9 ± 0.1	–2.90 ± 0.04
100–10	48.6 ± 0.3	59.1 ± 0.2	–3.21 ± 0.04
100–20	50.5 ± 0.4	57.9 ± 0.2	–3.24 ± 0.01
121–10	49.0 ± 0.3	59.3 ± 0.7	–3.27 ± 0.02
121–20	49.6 ± 0.6	59.0 ± 0.3	–3.41 ± 0.01
14 Days			
Untreated	51.2 ± 0.6	60.6 ± 0.1	–3.92 ± 0.02
100–10	48.2 ± 0.3	59.8 ± 0.1	–4.10 ± 0.01
100–20	49.6 ± 0.6	61.2 ± 0.2	–4.22 ± 0.01
121–10	48.9 ± 0.2	60.6 ± 0.3	–4.51 ± 0.02
121–20	48.3 ± 0.7	59.5 ± 0.7	–4.53 ± 0.02
21 Days			
Untreated	51.7 ± 0.7	61.7 ± 0.7	–4.02 ± 0.02
100–10	51.6 ± 0.3	61.3 ± 0.6	–4.20 ± 0.02
100–20	51.8 ± 0.1	61.8 ± 0.2	–4.52 ± 0.00
121–10	50.2 ± 0.0	61.3 ± 0.2	–4.57 ± 0.03
121–20	50.0 ± 0.5	61.0 ± 0.1	–4.59 ± 0.04

[a] Not detectable.
[b] Two coded numbers for each heat-moisture treated rice flour indicate the steaming temperatures (°C) and steaming times (min) of milled rice.
[c] Mean ± standard deviation; $n = 3$.

TABLE III
Differential Scanning Calorimetry Retrogradation Behaviors of Untreated and Heat-Moisture Treated TCW 70 Rice Flour Gels Stored at 4°C for Different Time Intervals

Sample	Transition Temperature (T, °C) and Enthalpy (ΔH, J/g of flour)		
	T_o	T_p	ΔH
3 Days			
Untreated	32.9 ± 0.2[a]	56.1 ± 0.1	–3.27 ± 0.05
100–10[b]	30.8 ± 0.6	55.5 ± 0.1	–4.20 ± 0.08
100–20	31.0 ± 0.1	55.3 ± 0.1	–4.43 ± 0.03
121–10	30.8 ± 0.3	55.4 ± 0.4	–4.65 ± 0.33
121–20	29.7 ± 0.1	55.1 ± 0.1	–5.21 ± 0.01
7 Days			
Untreated	31.7 ± 0.1	47.0 ± 0.4	–7.63 ± 0.11
100–10	31.7 ± 0.9	46.7 ± 0.2	–8.66 ± 0.23
100–20	32.8 ± 0.7	46.6 ± 0.5	–8.70 ± 0.21
121–10	32.9 ± 0.0	46.7 ± 0.1	–9.04 ± 0.25
121–20	32.9 ± 0.1	46.7 ± 0.5	–9.10 ± 0.10
14 Days			
Untreated	33.7 ± 0.6	47.4 ± 0.2	–8.99 ± 0.11
100–10	33.7 ± 0.1	48.2 ± 0.0	–9.40 ± 0.07
100–20	34.1 ± 0.3	48.2 ± 0.1	–9.64 ± 0.02
121–10	33.9 ± 0.2	48.5 ± 0.2	–10.43 ± 0.24
121–20	33.2 ± 0.5	48.1 ± 0.2	–10.85 ± 0.33
21 Days			
Untreated	34.6 ± 0.2	49.1 ± 0.3	–10.37 ± 0.06
100–10	34.8 ± 0.1	48.5 ± 0.5	–10.52 ± 0.45
100–20	34.5 ± 0.1	47.9 ± 0.3	–10.68 ± 0.13
121–10	34.2 ± 0.3	47.8 ± 0.6	–10.83 ± 0.06
121–20	34.5 ± 0.3	47.9 ± 0.3	–11.26 ± 0.04

[a] Mean ± standard deviation; $n = 3$.
[b] Two coded numbers for each heat-moisture treated rice flour indicate the steaming temperatures (°C) and steaming times (min) of milled rice.

TABLE IV
Differential Scanning Calorimetry Retrogradation Behaviors of Untreated and Heat-Moisture Treated TCW 70 Rice Flour Gels Stored at 25°C for Different Time Intervals

Sample	Transition Temperature (T, °C) and Enthalpy (ΔH, J/g of flour)		
	T_o	T_p	ΔH
7 Days			
Untreated	ND[a]	ND	ND
100–10[b]	ND	ND	ND
100–20	ND	ND	ND
121–10	ND	ND	ND
121–20	ND	ND	ND
14 Days			
Untreated	ND	ND	ND
100–10	ND	ND	ND
100–20	50.7 ± 0.6[c]	58.1 ± 0.2	–0.40 ± 0.02
121–10	50.8 ± 0.6	59.1 ± 0.2	–0.59 ± 0.03
121–20	51.7 ± 0.4	61.0 ± 0.5	–0.62 ± 0.05
21 Days			
Untreated	56.1 ± 0.2	60.2 ± 0.2	–0.21 ± 0.02
100–10	51.8 ± 0.6	61.3 ± 0.4	–0.29 ± 0.01
100–20	52.9 ± 0.5	61.1 ± 0.4	–0.75 ± 0.04
121–10	52.3 ± 0.1	61.2 ± 0.5	–0.81 ± 0.03
121–20	53.0 ± 0.6	61.5 ± 0.3	–0.86 ± 0.03

[a] Not detectable.
[b] Two coded numbers for each heat-moisture treated rice flour indicate the steaming temperatures (°C) and steaming times (min) of milled rice.
[c] Mean ± standard deviation; $n = 3$.

the retrogradation for waxy rice is more stable than that for nonwaxy rice.

Effect of gelatinization-retrogradation. After gelatinization, the amylose helix structure uncoiled, and when the temperature cooled down to favorable conditions, the amylose tended to link together with hydrogen bonding, which allowed the retrogradation to occur faster (Miles et al 1985, Jankowski and Rha 1986). However, retrogradation is affected strongly by amylopectin after longer storage periods (Miles et al 1985, White et al 1989, Roulet et al 1990). Therefore, starch retrogradation is related to the stability of a starch paste during storage conditions. The longer it is stored, the more retrogradation (Longton and Legrys 1981). When stored above 0°C, the lower the temperature, the greater the extent of retrogradation. Eliasson and Ljunger (1988) report that a slow migration of starch can develop more ordered structure crystalline forms at certain temperature ranges.

CONCLUSIONS

Hydrothermal treatment of high-amylose nonwaxy (TNS 19) and waxy (TCW 70) rice cultivars caused a shift to higher gelatinization temperatures and lower transition enthalpy changes. An endothermic peak was observed at ≈115°C for TNS 19 but not for TCW 70, suggesting that the amylose reacted with associated lipids to form an amylose-lipid complex during the heating process. Thermal degradation of the amylopectin by a heat-moisture treatment decreased the amount of large molecules and increased the amount of smaller molecules; the higher the temperature treatment, the greater the degree of thermal degradation. During storage for 21 days at 4 and 25°C, enthalpy of the retrograded starches was measured using DSC. TNS 19 showed slightly increasing enthalpy changes for all treatments at the same storage time. However, for TCW 70, the enthalpy values increased only after hydrothermal treatment. Higher temperatures gave higher enthalpy values after longer storage period (7 days) at 4°C for the waxy TCW 70 rice. These findings could serve as useful indicators for manufacturers wishing to produce better quality rice flours, by selecting appropriate time-temperature hydrothermal conditions for their specific end products.

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