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Effects of molecular size and chain profile of waxy cereal amylopectins on paste rheology during retrogradation

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Abstract

Amylopectins were purified from five waxy cereal starches (corn, sorghum, barley, wheat, and rice) in amorphous state by ethanol precipitation from dimethyl-sulfoxide (DMSO) solution followed by removing any amylose complexes with butanol in water. Their molecular weights (M_w) were determined by size-exclusion chromatography in tandem with multi-angle laser light scattering and refractive index detectors. Chain length distributions were determined by debranching followed by size-exclusion chromatography coupled with a refractive index detector. Amylopectin pastes (15% dry solids) were also analyzed using a dynamic rheometer while cooling to 4 °C and storing for 20 days, and the relations between the structural and rheological characteristics were investigated. The weight-average molecular weights (M_w) of the waxy cereal amylopectins ranged from 204.4×10^6 to 344.4×10^6 g/mol, and the average chain length (CL_w) ranged from 26.8 to 30.4. Among the tested starches, waxy rice had the largest amylopectin molecules and the longest $B \geqslant 2$ chains. The order of chain length of $B \geqslant 2$ chains among the samples were waxy rice > waxy corn = waxy sorghum > waxy barley = waxy wheat. But there were no difference in the CL_w of total chains among the amylopectins. Storage (G') and loss (G'') moduli of amylopectin pastes (15% solids) significantly increased during the cooling period from 95 to 4 °C, which was more than the increase during cold storage for 20 days at 4 °C. Among the waxy samples, waxy rice displayed the greatest moduli increases both during the initial cooling and during the cold storage. Among the structural parameters measured, the M_w of amylopectin and CL_w of $B \geqslant 2$ chains correlated positively with complex modulus(G^*) increases.

Keywords: Amylopectin; Molecular weight; Chain profile; Rheology; Retrogradation

1. Introduction

Starch is a major component in a variety of foods, and is often used as a food additive to change or improve texture and stability. During ordinary storage, however, starch pastes or solutions tend to retrograde, which coincides with significant changes in rheological and textural properties of a food. Starch chain association, which is the cause of retrogradation, induces gel formation or precipitation and decreases enzyme susceptibility of starch. Starch retrogradation is normally analyzed by rheological or textural measurements.

Starch retrogradation is affected by various features in molecular structure of starch, including ratio of amylose and amylopectin, and their chain lengths (Gidley & Bulpin, 1989; Hizukuri, 1996). Amylose level greatly affects starch retrogradation because amylose chains associate more readily than amylopectin. The association between amylopectin molecules is retarded mainly because of the frequent α-1,6 branch linkages resulting in outer chain lengths averaging less than ~25 anhydroglucose units. The ratio of amylose and amylopectin and their chain profiles are dependent on the botanical source of starch. Waxy mutants

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of cereals contain exclusively amylopectin in starch granules. Due to the lack of amylose, the rheological properties of waxy starch paste or gel depend on the size of amylopectin molecules and chain profiles.

Numerous studies have shown that the chain structure of amylopectin affects retrogradation properties of waxy starch paste or gels (Gidley, 1985; Jane et al., 1999; Kalichevsky, Orford, & Ring, 1990; Lu, Chen, & Lii, 1997; Shi & Seib, 1992; Suzuki, Takeda, & Hizukuri, 1985). And it is known that the chain profile of amylopectin is different between A-crystal type cereal starches and B-crystal type root starches. The amylopectin in A type starches have higher weight and number percents of short A chains than those in B type starches (Hizukuri, 1985; Kalichevsky et al., 1990; Ring et al., 1987). That difference in A chain content has been cited to explain A type amylopectins retrograde more slowly than does B type. Jane et al. (1999) and Shi and Seib (1992) reported that long chains with DP > 50 accelerate retrogradation of amylopectin, whereas the short chains (DP 6 ∼ 9) retarded it.

In the past, most studies have been carried out with native starches that contained non-starch components, such as proteins and lipids. Although these impurities are minor they do affect the pasting viscosity and rheological properties of starch. Moreover, the effect of molecular size of amylopectin on the pasting properties was not examined. In this study, amylopectins were isolated in pure amorphous state form five waxy cereal starches. The molecular sizes and chain profiles of the waxy cereal amylopectins were determined, and the relations were examined between the molecular and chain structures, and the dynamic rheology of amylopectin pastes, during cooling and cold storage.

2. Materials and methods

2.1. Materials

Waxy barley, waxy rice, and waxy sorghum were purchased from a local grocery, from which the starches isolated using 0.2% aqueous sodium hydroxide (Lim, Lee, Shin, & Lim, 1999). Waxy wheat starch was isolated from waxy wheat grains provided by Kansas State University (Manhattan, KS), following the method of Shi and Seib (1995). Waxy corn starch was provided by Samyang Genex, Inc. (Seoul, Korea). Isoamylase (EC 3.2.1.68), from *Pseudomonas*, was purchased from Hayashibara Biochemical Laboratory (Okayama, Japan), and pullulan standards were purchased from Sigma–Aldrich Corp. (St. Louis, MO).

2.2. Amylopectin preparation

The waxy starches were further purified using dimethyl sulfoxide (DMSO) and ethanol. Each starch sample was dissolved in 90% DMSO (1% starch solids) by heating in a boiling water-bath for 1 h with gentle magnetic stirring. The solution was stirred for 24 h at room temperature, and then starch was precipitated by adding ethanol (3 × volume). The starch was washed with excess ethanol to remove residual DMSO, and then dried in a convection oven (25 °C) overnight. From the purified starches, amylose was removed following the method of Takeda, Hizukuri, and Juliano (1986) by forming complex with butanol. Amylopectin in the supernatant was precipitated by adding ethanol and the precipitate was vacuum-dried (25 °C) overnight.

2.3. Molecular weight analysis

The dried pure amylopectin (10 mg) was dissolved in 90% DMSO (5 ml) by heating in a boiling water-bath. The heating time was different among the amylopectin samples to give the maximum solubility (almost 100%), determined by measuring the total carbohydrate content in the filtrate (5.0 μm pore size) (Han & Lim, 2004); 80 min for waxy rice amylopectin (wr); 50 min for waxy corn (wc) and waxy sorghum amylopectin (ws), and 30 min for waxy barley (wb) and waxy wheat amylopectin (ww). The amylopectin solution (1 ml) was then applied to a medium-pressure size-exclusion column (SEC) chromatography packed with Toyopearl HW 65 F resins (2.6 × 70 cm, Tosoh Corp. Tokyo, Japan). Multi-angle laser light scattering (MALLS) (632.8 nm, DAWN DSP-F, Wyatt Technology, Santa Barbara, CA) and a differential refractive index (RI) detectors (Optilap DSP, Wyatt Technology, Santa Barbara, CA) were connected to the SEC to determine the average molecular weight (M_w). The DMSO (90%) containing 50 mM LiBr, previously filtered through 0.2 μm Nylon 66 membrane filter (Supelco, PAA), was used as mobile phase, and flow rate was 0.8 ml/min.

2.4. Chain length distribution

The dried amylopectin (100 mg) was dissolved in deionized water (40 ml) was autoclaving for 15 min at 121 °C. Then acetate buffer (1 M, pH 3.5, 400 μl) and isoamylase solution (30 unit/mg amylopectin) were sequentially added to the amylopectin solution. Debranching was carried out by incubating the solution in a shaking water-bath at 45 °C for 24 h. The solution was adjusted to pH 6.0–6.5 with 1 M sodium hydroxide, and then was boiled for 10 min to inactivate the enzyme. The solution was filtered through a mixed cellulose ester filter (3.0 μm, Advantec mfs, Inc. Pleasanton, CA), and the filtrate (100 μl) was injected at the top of a medium-pressure SEC packed with Superdex 75 HR (10 × 300 mm, Amersham Pharmachia, Uppsala, Sweden). Flow rate was 0.4 ml/min and the mobile phase was an aqueous sodium azide (0.02%) had been filtered through a 0.1 μm cellulose ester filter (Advantec mfs, Inc. Pleasanton, CA).

Because the light scattering intensity was very low with the debranched starch chains, chain length was determined with a RI detector, using pullulan standards of different molecular weights (70,000, 47,300, 22,800, 11,800, 5,900, and 738).

2.5. Degree of branching

Approximated degree of branching (DB) of the amylopectins was calculated following the equation;

$$\mathrm{DB}(\%) = \frac{\text{DP of total starch/DP of debranched starch} - 1}{\text{DP of total starch} - 1} \times 100$$

2.6. Rheological measurement of amylopectin paste

The dried amylopectin was pasted in distilled water (15% dry solids) containing 0.02% sodium azide by heating the mixture in a boiling water-bath for 1 h with mechanical stirring. The hot paste was immediately transferred to a concentric cylinder adaptor (20 mm diameter, 4.2 mm gap)of a dynamic rheometer (RS-150, Haake Inc, Germany), preheated to 95 °C for the analysis. The paste surface was covered with silicon oil to prevent water evaporation during the measurement. The frequency for dynamic oscillatory measurement was 1 Hz. The storage (G') and loss (G'') moduli were measured while the paste was cooled to 4 °C at a rate of 1 °C/min. The paste was also stored at 4 °C up to 20 days, and the changes in G', G'', and complex moulus, $G^* = (G'^2 + G''^2)^{1/2}$, were measured occasionally. All tests were conducted in triplicates in the linear viscoelastic range.

3. Results and discussion

3.1. Molecular weight distribution

During the dissolution and chromatographic separation of starch, shear forces may induce chain aggregation and degradation, but these changes are minimized by using DMSO as solvent (Bradbury & Bello, 1993; Han & Lim, 2004; Jackson, 1991). In the present study, weight-average molecular weight (M_w) and radius of gyration (R_g) of five waxy starch amylopectins were measured in 90% DMSO solution containing LiBr (50 mM). A low level of water in DMSO enhances the solubilization of starch by preventing the rapid swelling of starch granules creating a viscous barrier that hinders DMSO penetration inside the granule (Jackson, 1991; Peng & Perlin, 1987). The lithium bromide in the DMSO solution reduces electrostatic interactions between the solvent and SEC resins (Yokoyama, Renner-Nantz, & Shoemaker, 1998). The recovery of starch from SEC, based on the RI response, was over 98%.

All amylopectins from five waxy cereal starches eluted in a symmetrical peak at the same elution volume (data not shown). There was no tailing in the elution peak, which confirmed the absence of amylose. But, the M_w and R_g of the five amylopectins, calculated based on the light scattering intensity, were not identical (Table 1). The M_w and R_g values ranged from 204.4 to 344.4 and from 216.4 to 252.0 nm, respectively. Among the amylopectins tested, wr exhibited the highest M_w (344.4×10^6 g/mol), whereas wb had the smallest (204.4×10^6 g/mol). Yoo and Jane (2002) measured the M_w and R_g of various waxy cereal starches in an aqueous solution. The differences they found were similar to those in the present study.

Waxy corn starch has been analyzed by SEC-MALLS-RI system with DMSO as solvent by several researchers (Klavons, Dintzis, & Millard, 1997; Millard, Dintzis, Willett, & Klavons, 1997; Yokoyama et al., 1998). Yokoyama et al. (1998), using pure DMSO containing 50 mM lithium bromide as solvent and mobile phase, reported the M_w and R_g of waxy corn starch to be 215×10^6 g/mol and 252 nm, respectively. More recently, Han and Lim (2004) measured M_w and R_g of waxy corn starch in 90% DMSO, are found 254×10^6 g/mol and 241 nm, respectively. The M_w (277.4×10^6 g/mol) of waxy corn amylopectin obtained in the present was slightly higher, and R_g lower than previously reported. It is suggested that the difference in the data may be related to amylopectin purity, which was higher in the present work because of removal of residual amlyose.

3.2. Chain length distribution

The refractive index chromatograms for the debranched amylopectins, measured by a medium-pressure SEC, exhibited tetra-modal chain distributions (Fig. 1). The chromatographic patterns were similar among the amylopectins tested, indicating that the chain distributions of the A-type waxy cereal amylopectins were not much different. The amylopectin chain fractions separated on the chromatogram were assigned as $B \geqslant 2$, B1, A1, and A2 chains as shown in Fig. 1. It was noticeable that the A chains were separated into two populations on the chromatograms. The SEC resin (Superdex 75), used for the analysis, readily fractionated a mixture of dextrans in a wide range of M_w's (from 30,000 to 500 g/mol). Because of the resolving power of the solid-phase, especially in low M_w range, the column fractionated the A chains into the larger A1 and the smaller A2 chains ($\mathrm{CL_w}$<10). Hizukuri (1986) and Ong et al. (1994) found two chain fractions in a range of $\mathrm{CL_w}$ of less than 20 for starches. Hizukuri

Table 1
Weight-average molecular weight (M_w) and radius of gyration (R_g) of waxy cereal amylopectins isolated from waxy corn (wc), waxy sorghum (ws), waxy barley (wb), waxy wheat (ww), and waxy rice (wr) starches[a]

Amylopectins	M_w ($\times 10^6$ g/mol)	R_g (nm)
wc	277.4b	227.2a
ws	280.3b	242.7a
wb	204.4c	223.6a
ww	259.6b	216.4a
wr	344.4a	252.0a

[a] Values with different alphabets in each column differ in statistical significance ($p < 0.05$).

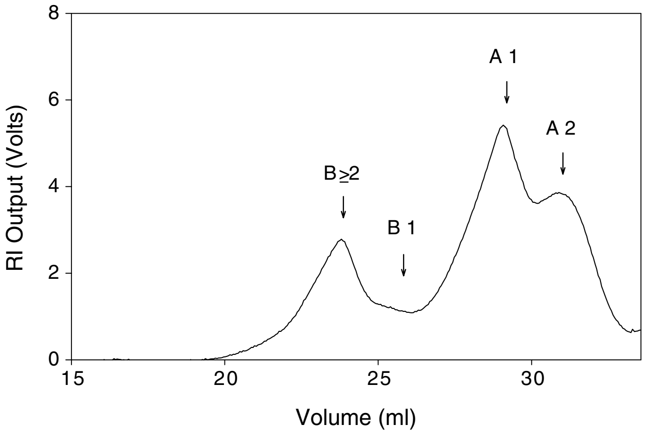

Fig. 1. Chain distribution for waxy corn amylopectin.

(1986) claimed that these two chain fractions were B1 (CL_w18–19) and A (CL_w11–13) chains. On the other hand, Ong, Jumel, Tokarczuk, Blanshard, and Harding (1994) designated the two fractions as A1 (CL_w14–15) and A2 (CL_w10) chains. Likewise, in our experiment, those fractions were assigned as A1 and A2 chains, with CL_w for the five samples ranging between 18.7 and 22.9, and between 8.7 and 10.1, respectively (Table 2).

For the five waxy amylopectins, the chain lengths (CL_w) at the peak of the four fractions separated by SEC, calculated based on the elution volume of pullulan standards, were 71.9–79.4, 41.7–47.7, 18.7–22.9, and 8.7–10.1, respectively (Table 2). The CL_w for all the chains in the debranched amylopectins ranged from 26.8 (ww) to 30.4 (wr), and there was no significant difference among the waxy cereal amylopectins (Table 2). Jane et al. (1999) reported that the CL_w of A-crystal type starch amylopectin, mainly from cereals, were in a range of 18.8–23.5 and that of B-crystal type amylopectins were about 30. Hizukuri (1985) found that the A-type amylopectin had CL_w 23–29, which was closer to the values reported here. As with prior studies on various starches (Kalichevsky et al., 1990; Lu et al., 1997; Ring et al., 1987; Shi & Seib, 1995; Suzuki et al., 1985) we found that there was no significant difference among cereal starches in their chain lengths.

Table 2
Weight-average chain length (CL_w) and relative percentage of chain fractions (in parenthesis), and degree of branching (DB, %)[b]

	$B \geqslant 2$	B1	A1	A2	Average[a]	DB (%)
wc	76.2b (20.2)	43.4a (5.3)	21.9a (41.6)	10.1a (32.7)	30.2a	3.3a
ws	75.3b (20.7)	47.7a (5.7)	19.6b (45.6)	9.6a (28.1)	30.1a	3.3a
wb	72.7c (19.9)	41.7a (5.3)	18.9b (48.0)	8.7a (26.9)	27.9a	3.6a
ww	71.9c (17.9)	44.0a (6.6)	18.7b (46.7)	9.3a (28.8)	26.8a	3.4a
wr	79.4a (20.6)	43.4a (5.2)	22.9a (35.5)	9.6a (38.9)	30.4a	3.3a

[a] The average chain length (CL_w) for total amylopectin chains.

[b] Values with different alphabets in each column differ in statistical significance ($p < 0.05$).

Although the average CL_w of amylopectin chains was not different among the waxy cereal amylopectins tested, the CL_w of $B \geqslant 2$ and A1 chains showed statistical differences (Table 2). The wr contained longer $B \geqslant 2$ chains than those of other amylopectins. The CL_w values of the $B \geqslant 2$ chains for wc and ws were similar (76.2 and 75.3, respectively), higher than those for wb and ww (72.1 and 71.9, respectively).

The relative mass percentage for A chains (A1 + A2) was over 70% for all amylopectins, based on the RI chromatograms. Several studies (Hizukuri, 1986; Jane et al., 1999; Shi & Seib, 1995) reported that waxy cereal starches consisted of about 70–80% of A chains (DP 6–25). That similarity suggests that we correctly assigned the two chain fractions labeled A1 and A2 chains. Regarding the A chain profile too, waxy rice amylopectin exhibited uniqueness. The A1 chains of wr showed highest CL_w (22.9) but the proportion for A1 chains was least (35.5%) among the samples. But the level of shorter A2 chains (38.9%) was greatest among the amylopectins. The waxy barley (wb) and waxy wheat (ww) amylopectins had slightly smaller percentages for $B \geqslant 2$ chains than for the other waxy starches. There was no statistical difference in the degree of branching (DB), which was in a range of 3.3–3.6%.

3.3. Rheological properties

Fig. 2 shows the changes in dynamic moduli (G', G'', and G^*) of the amylopectin pastes (15%, w/w) as the pastes were gradually cooled from 95 to 4 °C in the rheometer cell. Due to the increased chain stiffness and chain associations induced by the cooling, all the moduli increased as the temperature approached 4 °C. The initial moduli as well as the degree of increase during cooling were similar among the amylopectin samples except waxy rice (wr) (Fig. 2). The wr paste showed the highest moduli at the initial hot stage, and the modulus increases were the most during the cooling among the amylopectin pastes tested. The waxy barley (wb) and waxy wheat amylopectins (ww) displayed almost identical modulus changes, and the similarity agreed with the chain profiles data (Table 2).

The magnitude of loss modulus (G'') was greater than that of storage modulus (G') for wc, ws, wb, and ww samples, whereas wr sample showed the reverse data (Fig. 2). It indicates that wr paste had elastic behavior whereas other pastes have more viscous behavior. Thus not only in the modulus values but in the difference between G' and G'', wr amylopectin produced the paste unique and different from the paste of other amylopectins.

During cooling the wc and ws pastes showed a slightly greater increase in modulus than those of wb and ww. The wb and ww amylopectins contained a low percentage of $B \geqslant 2$ chains. The long B chains are more likely to interact between chains because of many possible contact

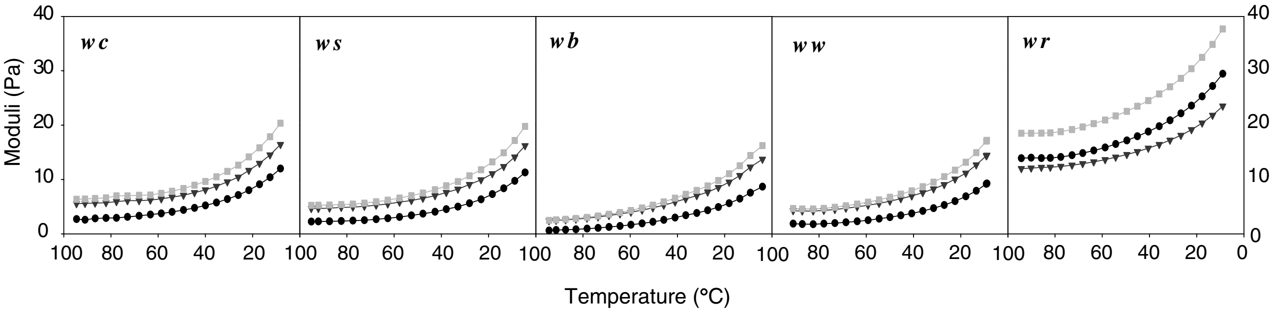

Fig. 2. Modulus changes of waxy cereal amylopectin pastes (15%, w/w) during cooling (95–4 °C) (■ – G^*, ▼– G'', ●– G').

points, which translated to higher moduli. The amylopectins (wb and ww) containing the least proportions of the long B chains resulted in the least chain associations, which gave the lowest paste modulus.

The complex modulus (G^*) of the amylopectin pastes as it changed temperature were replotted against the log of temperature, as shown in Fig. 3 for ws. In the modulus curve, two different stages in modulus increase were observed. The modulus increase in the first stage, while the paste remained above ~50 °C, was minor compared to that in the second stage where the paste became much cooler. In the hot stage, the starch chains in the paste retained a high degree of mobility so that the response to oscillatory strain was insignificant. But as the temperature fell further, the amylopectin mobility was effectively reduced by increased intermolecular association so that the response to the oscillation became significant. Thus, the modulus increase in the second stage may represent the phenomenon of overall chain association in the pastes.

As expected from the Fig. 2, among the amylopectins tested, wr paste had the highest value of the slope (0.472) for the G^* increase in the second stage, followed by wc (0.391), ws (0.382), ww (0.346), and wb (0.280) (Table 3). These data indicate that waxy rice amylopectin had the highest chain association (retrogradation) induced by cooling among the cereal waxy amylopectins, whereas waxy barley amylopectin had the least tendency of chain association. The temperature at the intersection between the first and the second stages of modulus increase ($T_{\text{intercept}}$) might be another important parameter to characterize starch chain associations. It may represent the onset temperature for chain association. It was also significantly greater for wr sample (48.0 °C) than the others (33.7– 43.6 °C).

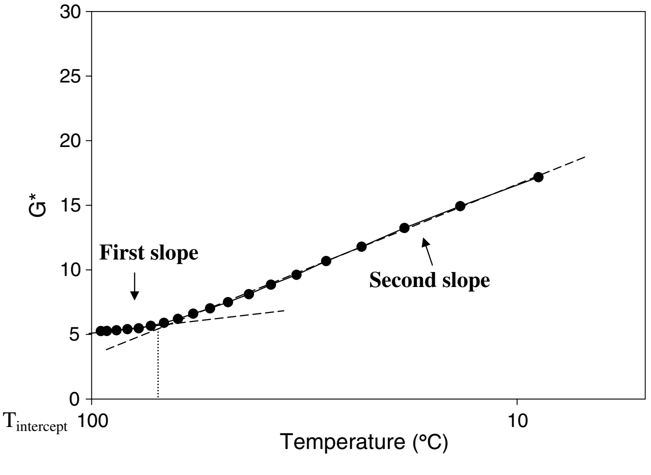

Fig. 3. Complex modulus (G^*) change versus temperature in log scale during the cooling of ws paste (95–4 °C).

The modulus changes were also measured as the pastes were stored at a low temperature for an extended period of 20 days at 4 °C. Whereas the cooling effect was measured with a continuous oscillation, immediately after amylopectins were pasted, the cold storage effect was measured occasionally while the paste was stored. Comparing Figs. 2 and 4, the modulus increases was more substantial during the cooling period from 95 to 4 °C (Fig. 2) than that over the extended storage period at 4 °C (Fig. 4). The modulus increase of amylopectin pastes during the cooling stage of the fresh paste may be more different compared to cold storage, where the 15% amylopectin pastes changed little and remained relatively soft after 20 days (Table 4).

Nevertheless, comparing the different starches, the wr paste showed an exceptional trend in modulus increase during the cold storage (Fig. 4). The stored wr paste displayed similar value of G' and G'', and the increases of both moduli were greater than those of other pastes. This trend revealed that the molecular association during the storage period was greater for the wr amylopectin paste than for the other pastes. The significantly higher G^* for wr paste compared to those for others suggests that wr behaves the paste characteristics different from those of other amylopectins.

Table 3
Kinetic parameters of G^* of waxy cereal amylopectin pastes during cooling (95–4°C)

	First slope ($dG^*/d\log T$)	Second slope ($dG^*/d\log T$)	T_{inter}[*]
wc	0.028a	0.391ab	39.8 b
ws	0.013a	0.382b	36.0b
wb	0.010a	0.280c	33.7b
ww	0.014a	0.346bc	43.6b
wr	0.016a	0.472a	48.0a

Values with different alphabets in each column differ in statistical significance ($p < 0.05$).

[*] Intersection temperature between first and second stage of G^* increase.

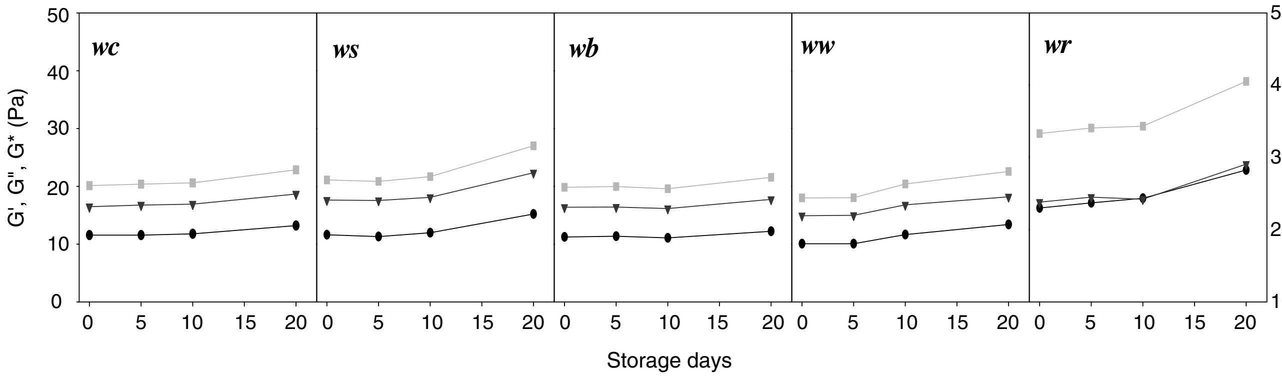

Fig. 4. Modulus changes of waxy cereal amylopectin pastes (15% w/w) during a cold storage (4 °C) up to 20 days (■ – G^*, ▼– $G0''$, ●– G').

Table 4
Correlation coefficient (r) between paste moduli (G^*) and structural factors

	G^* at 95 °C	ΔG^* during cooling (95–4 °C)	Second slope ($dG^*/d\log T$)	G^* of 0 day at 4 °C	ΔG^* during storage (0–20 days)
M_w (g/mol)	0.81	0.98	0.99	0.65	0.85
A chain (%)	−0.11	−0.24	−0.45	−0.15	−0.19
B chain (%)	0.12	0.27	0.47	0.17	0.21
CL_w in $B \geqslant 2$	0.77	0.83	0.90	0.74	0.08
Average CL_w	0.32	0.43	0.73	0.32	0.15
DB (%)	0.30	0.42	0.85	0.30	0.14

The changes in G', G'', and G^* displayed the same trends (Figs. 2 and 4). The G^* value was chosen for correlation with the structural features, because it was influenced largely by the network density in a viscoelastic materials. The M_w of amylopectin correlated positively with the G^* at 95 °C and 4 °C ($r = 0.81$, 0.65, respectively), and with G^* during the cold storage for 20 days ($r = 0.85$). It indicates that the chain association in an amylopectin paste was highly dependent on molecular size. The larger polymer chance for the chains to associate in a given volume of solution. The complex modulus (G^*) had a positive relation also with the percent proportion of B chains ($r = 0.12$, 0.27), but a negative relation with that of A chains ($r = -0.11$, -0.24), although the correlation coefficients (r) were not great. This result agreed with the findings reported by Jane et al. (1999). Because the differences in chain profile were not significant among the amylopectins tested, it was not easy to observe strong correlations. But the CL_w of $B \geqslant 2$ chains, the longest chains in amylopectin, display a strong correlating with the paste modulus ($r = 0.77$ and 0.74 for G^* values at 95 and 4 °C, respectively). Therefore, as discussed with previous data, the shorter CL_w for $B \geqslant 2$ chains for wb and ww, compared to other samples, led to the less changes paste moduli, as shown in Figs. 2 and 4. But waxy rice amylopectin (wr) that had a higher CL_w (79.4) for $B \geqslant 2$ chains could form the paste with large initial moduli and also the significant increases during cooling and cold storage. The slope for modulus at the second stage of cooling (actual retrogradation) for five amylopectins was also correlated strongly with M_w and CL_w in $B \geqslant 2$ chains ($r = 0.99$, 0.90, respectively).

Among the structural features of the amylopectin chains of cereal waxy starches, the G^*, and possibly other moduli (G' and G'') of the amylopectin pastes, depended on the molecular weight and chain length of $B \geqslant 2$ chains of amylopectin. And among the existing waxy cereals, waxy rice formed the strongest network in paste or gel due to its highest tendency of retrogradation, from its largest molecular size and highest CL_w of $B \geqslant 2$ chains. The A chains in waxy rice amylopectin were also somewhat different: more A2 chains than A1 chains. But apparently this difference did not affect the paste rheology. Possibly, it was because that the overall proportion of total A chains (74.4%) was not different among the amylopectins.

4. Conclusions

Among the five amylopectins purified from waxy cereal starches, their molecular weights and chain lengths (CL_w) of long B chains ($B \geqslant 2$) were the most determining factors for the modulus change of 15% amylopectin pastes during time and temperature-indeed retrogradation. The M_w was positively correlated with initial paste moduli and their increases during cooling and storing of the amylopectin paste. Although the waxy cereal amylopectins are not much different in molecular and chain structures, waxy rice amylopectin had significantly higher values for M_w and CL_w of $B \geqslant 2$ chains than other waxy cereal amylopectins. Those differences resulted in the higher initial moduli and greater modulus increases for the paste during cooling and cold storage.

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