Relationships between Functional Attributes and Molecular Structures of Amylose and Amylopectin Fractions from Corn Starch[†]

J. P. Mua and D. S. Jackson*

256 Food Industry Building, Department of Food Science and Technology, University of Nebraska, Lincoln, Nebraska 68508-0919

Understanding starch structure−function relationships is vital to the continued development for new uses for starch. Fractionated corn amylose and amylopectin, with known molecular weights, chain lengths, and branching and crystalline ratios, were studied for pasting, gel textural, and retrogradation properties by rapid viscoanalysis, textural profile analysis, and differential scanning calorimetry. Amylose fractions with weight-average molecular weights (M_w) of 2.47−1.36E+05 had chain number-average degrees of polymerization (DP_n) of 500−1000, 0−1 branch points per 1000 glucose units, higher setbacks, and high final viscosities and resulted in firmer gels than their lower M_w counterparts. Cohesiveness was inversely proportional to crystallinity, while stringiness increased with increasing DP_n. Amylopectin fractions of low M_w (7.89−7.08E+07) with high branching ratios (>1.5), short branch chains (weight-average degree of polymerization, 15−18), and crystallinity >28% had high peak temperatures and low peak viscosity and shear thinned less. When cooled, these amylopectins formed weak gels, but during storage, the gels firmed and retrograded more than did their high M_w counterparts.

Keywords: *Corn; amylose; amylopectin; pasting; textural profile analysis; differential scanning calorimetry; DSC; molecular weight; retrogradation; crystallinity*

INTRODUCTION

Understanding starch functional properties such as gelatinization, pasting (rheology), and retrogradation is vital for effective use of starch in food systems and other industrial applications. Research evidence suggests that starch functionality depends to a great extent on the molecular structure, size, and weight of starch's amylose and amylopectin components. Nevertheless, starch structure−function relationships have not yet been well established. To begin to understand which molecular characteristics contribute to cooked-starch functionality, pure fractions of amylose and amylopectin with distinct molecular weights and structures are necessary. These distinct fractions would allow researchers to more closely identify the functional contribution of, for example, molecular weight or polymer branching, free from the interaction of the distinctly different amylose and amylopectin polymers. Of course, understanding polymer subfraction molecular structure should only be construed as a necessary first step in truly understanding polymer structures and their interaction in the native granule or a starch polymer mixture.

The rheology of starch, when cooked in excess water, depends in part on the starch's amylose to amylopectin ratio and on the arrangements of these polymers within granules (Morrison and Tester, 1991; Bahnassey and Breene, 1994). Amylose and amylopectin differ in molecular weight distribution and molecular structures (Hizukuri, 1985; Takeda et al., 1992; Ong et al., 1994); hence, they display different rheological and viscoelastic

(Evans and Haiseman, 1980; Dengate and Meredith, 1984; Carcea et al., 1992; Wang and White, 1994), gel (Russell and Oliver, 1989; Leloup et al., 1991; Jane and Chen, 1992), and retrogradation (Kulp and Ponte, 1981; Levine and Slade, 1987; Villareal et al., 1993) properties.

Brabender viscoamylography or rapid viscoanalysis and textural profile analysis have played a crucial role in determining starch rheological changes during pasting (Walker et al., 1988) and when the resultant cooled gels are stored (Sanderson et al., 1988). Differences in granule swelling (onset of viscosity), peak temperature, peak viscosity, and shear thinning among starches have been mostly attributed to amylopectin (Ring and Stainby, 1985; Doublier et al., 1987; Hoseney, 1994; Bahnassey and Breene, 1994). Meanwhile, differences in setback and final viscosity during pasting and in gel firmness during storage have been mostly attributed to amylose and amylopectin, respectively (Ott and Hester, 1965; Leloup et al., 1991; Vasanthan and Hoover, 1992). These conclusions, however, have always been drawn from the study of pasting and gel textural properties of starches containing <1−70% amylose (Bahnassey and Breene, 1994). How each of these polymers would paste and gel if separated, and what effect their molecular structure would have, are yet to be fully understood.

Differential scanning calorimetry (DSC) has been of great value in studying loss of granule crystalline order during gelatinization and the reordering of such systems during aging (Russell and Oliver, 1989). Molecular structure events such as chain ordering and aggregation, collectively called retrogradation, influence the staling of baked goods (Prokopowich and Biliaderis, 1995). Using DSC, Orford et al. (1987) found that retrogradation increases in starch were due to amylopectin recrystallization and were influenced by a starch's botanical origin (greater retrogradation: pea > potato

---

Amylose and Amylopectin Fractions from Corn Starch

J. Agric. Food Chem., Vol. 45, No. 10, 1997 **3849**

Table 1. Sample Preparation Treatments and Polymer Fraction Identification

corn starch type (slurries % w/v)	heat treatments and holding times	centrifugation components (3000g/8 min)	solvent used for precipitation (a) or dispersion (b)	polymer fraction	sample identification
waxy (1.5)	75 °C for 30 min	residue	methanol (b)[a]	amylopectin	AP1
		supernatant	methanol (a)[b]	amylopectin	AP2
regular (4.0)	60 °C for 1 h[c]	final residue	methanol (b)[a]	amylopectin	AP3
	70 °C for 1 h[d]	final residue	methanol (b)[a]	amylopectin	AP4
		supernatants	butanol (a)[e]	amylose	AM1
	80 °C for 1 h[f]	final residue	methanol (b)[a]	amylopectin	AP5
		supernatants	butanol (a)[e]	amylose	AM2
50% amylose (3.0)	90 °C for 1 h[f]	supernatants	ethanol (a)[g]	amylose	AM3
	100 °C for 1 h[f]	supernatants	ethanol (a)[g]	amylose	AM4
70% amylose (3.0)	90 °C for 1 h[f]	supernatants	ethanol (a)[g]	amylose	AM5
	100 °C for 1 h[f]	supernatants	ethanol (a)[g]	amylose	AM6

[a] Methanol (85% v/v) was used to reslurry residue, followed by centrifugation. [b] Methanol (one-third the volume of the supernatant) was used to precipitate amylopectin from supernatant. [c] After first centrifugation, residues were reslurried, reheated, and centrifuged; procedure was repeated four times. [d] After first centrifugation, residues were reslurried, reheated, and centrifuged; procedure was repeated three times. [e] Butanol (one-third the volume of the supernatant) was used to precipitate amylose from supernatant. [f] After first centrifugation, residues were reslurried, reheated, and centrifuged; procedure was repeated two times. [g] Ethanol (half the volume of the supernatant) was used to precipitate amylose from supernatant.

> maize > wheat). Roulet et al. (1990) found pea and potato starches to be more prone to retrogradation than waxy starches, while Russell (1987) reported that differences in retrogradation rates between starches were due to amylopectin, amylose, and amylose−lipid complex domains. Shi and Seib (1991) reported that recrystallization or retrogradation of gelatinized starch was dependent on amylopectin structure in an unknown fashion. Slower retrogradation in cereal amylopectins, when compared to pea, tuber, and canna starches, was attributed to shorter average branched chains in cereal amylopectin (Orford et al., 1987; Kalichevsky et al., 1990).

The objective of this research was to characterize the pasting and other textural properties of corn starch amylose and amylopectin gelled fractions with differing molecular weights and structure characteristics.

MATERIALS AND METHODS

Starch Fractionation and Characterization. Six amylose and five amylopectin fractions were isolated from four corn starch types (<1, 25, 50, 70% amylose) (American Maize Products, Hammond, IN) by a combined aqueous (aq) leaching and alcohol precipitation method, as shown in Table 1 and outlined by Mua and Jackson (1995, 1997a). Samples were freeze-dried and then solublized in aqueous methyl sulfoxide (90% v/v) and characterized for polymer weight-average (M_w) and number-average (M_n) molecular weights, polydispersity (M_w/M_n), and branching ratios using high-performance size exclusion chromatography and multiple-angle laser light scattering (HPSEC/MALLS) as described by Mua and Jackson (1997b). Number-average and weight-average degrees of polymerization (DP$_n$ and DP$_w$, respectively) were also determined by HPSEC/MALLS for amylose and amylopectin, respectively. Percent crystallinity was also determined using X-ray analysis as described in the previous study (Mua and Jackson, 1997b).

Pasting Properties. The procedure outlined by Walker et al. (1988) was employed in this study. All fraction slurries were prepared by combining 3 g [dry basis (db)] of starch and 25 mL of deionized distilled water in an aluminum cup except for waxy corn starch, which was prepared using 2.5 g (db). A plastic stirring paddle was placed in the cup, which was then inserted into a Newport Scientific Rapid Viscoanalyzer (Foss Food Technology, Eden Prairie, MN), connected in series to a Thermocline software equipped computer (Foss Food Technology). The sample was stirred at 960 rpm for 7 s to disperse the starch, after which time the stir drive motor switched to 160 rpm for the remainder of the test. The samples were equilibrated at 50 °C for 2 min and then heated to 95 °C for 5 min and held at 95 °C for another 5 min before being cooled to 50 °C for 8 min. Rapid viscoanalyzer (RVA) parameters

obtained were peak viscosity, peak time, peak temperature, shear thinning, setback, and final viscosity.

Gel Textural Attributes. Aqueous starch fraction suspensions (6% w/v db) were heated (1.5 °C/min) to 95 °C, held for 30 min, cooled to room temperature, and subsequently stored at 4−5 °C for 1, 3, and 14 days. Gel (4.5 cm diameter and 5 cm high) textural characteristics were analyzed as described by Sanderson et al. (1988), using an Instron universal testing machine (Model 4045, Instron Inc., Canton, MA) equipped with a 2.5 cm probe and 100 N load cell. Gel properties measured were fracturability (newtons), adhesive force (newtons), cohesiveness, and stringiness (Mua and Jackson, 1997a). Fracturability represents the initial force required by the probe to break the gel's surface. Adhesive force represents the resistance encountered by the probe as it is retrieved from the gel's interior. Stringiness represents the elasticity of the gel, and cohesiveness is obtained by dividing the area of the second crushing cycle by the area of the first cycle.

Retrogradation Behavior. Dried starch fractions (10−11 mg db), in excess water (20% w/v) were scanned from 30 to 150 °C at 5 °C/min, using a DuPont Model 910 differential scanning calorimeter. The resulting gels were stored at 4−5 °C for 1, 2, 3, 5, 7, and 14 days and then rescanned to melt the retrograded crystallites. Data collected were fitted into the Avrami equation to study fraction gel retrogradation kinetics as previously described (Zhang and Jackson, 1991; Mua and Jackson, 1997a).

Statistical Analysis. Analysis of variance was used to analyze data collected in triplicate for pasting, textural profile analysis, and retrogradation using Statistical Analysis System software (version 6.11, SAS Institute Inc., Cary, NC). All measurements were obtained using a completely randomized block design. Mean values and least significant differences (LSD) at ($P < 0.05$) were calculated for each analysis. Regression analysis was used to determine relationships between structural and functional properties.

RESULTS AND DISCUSSION

Molecular Characterization. Table 2, adapted from our previous study (Mua and Jackson, 1997b), reveals the branching ratio, chain length (degree of polymerization, DP), and percent crystallinity values of the six amylose and five amylopectin fractions with various molecular weight (weight-average, M_w; number-average, M_n; M_w/M_n) distributions.

Pasting Properties. The pasting profiles of amylose (AM1, AM2, AM3, AM4, AM5, AM6) and amylopectin (AP1, AP2, AP3, AP4, AP5) fractions are shown in Figures 1 and 2. High peak viscosity values for amylopectin fractions confirm the increased viscosity role of amylopectin when native starches are heated to 95 °C. High setback values for amylose and low M_w

Table 2. Molecular Weight and Structural Parameters of Corn Amylose (AM) and Amylopectin (AP) Fractions[a] Determined by HPSEC/MALLS

sample	M_w[b]	M_n[c]	M_w/M_n[d]	branching ratio	LCBF[e]	chain length (DP)[f]			crystallinity[l] (%)
						F-1[g]	F-2[h]	F-3[i]	
AM2[j]	4.89E+05	3.27E+05	1.5241	0.3372	956	1014			24
AM4	2.47E+05	1.33E+05	1.9037	0.8456	961	864			13
AM1	1.36E+05	1.18E+05	1.3593	0.3350	1568	500			22
AM5	1.15E+05	6.25E+04	1.8765	0.6848	401	472			18
AM6	1.06E+05	5.44E+04	1.9427	0.7339	313	324			15
AM3	1.03E+05	6.78E+04	1.5147	1.0480	743	363			18
LSD[k]	7.91E+04	7.67E+04	0.6210	0.4554	1779.4	540.7			12.4
AP1	9.88E+07	9.11E+07	1.0843	2.0182		139	86	37	21
AP2	8.94E+07	7.21E+07	1.2754	1.4907		113	41	15	17
AP3	7.98E+07	7.62E+07	1.0466	4.3483		86	59	12	28
AP4	7.63E+07	6.61E+07	1.1670	2.9391		118	37	16	30
AP5	7.08E+07	5.85E+07	1.2031	1.5770		173	56	18	36
LSD	1.70E+07	2.85E+07	0.3384	3.4216		74.3	23.5	8.6	18.3

[a] Values are means of two analyses. [b] Molecular weight weight-average. [c] Molecular weight number-average. [d] Polydispersity. [e] Long chain branch frequency (numbers indicate where branch points occur per 1000 polymerized glucose units). [f] Number-average and weight-average degree of polymerization for amylose and amylopectin, respectively. [g,h,i] Represent long, intermediate, and short branch chains, respectively. [j] See Table 5 for full description. [k] Least significant difference ($P < 0.05$). [l] Percent crystallinity was determined by X-ray analysis.
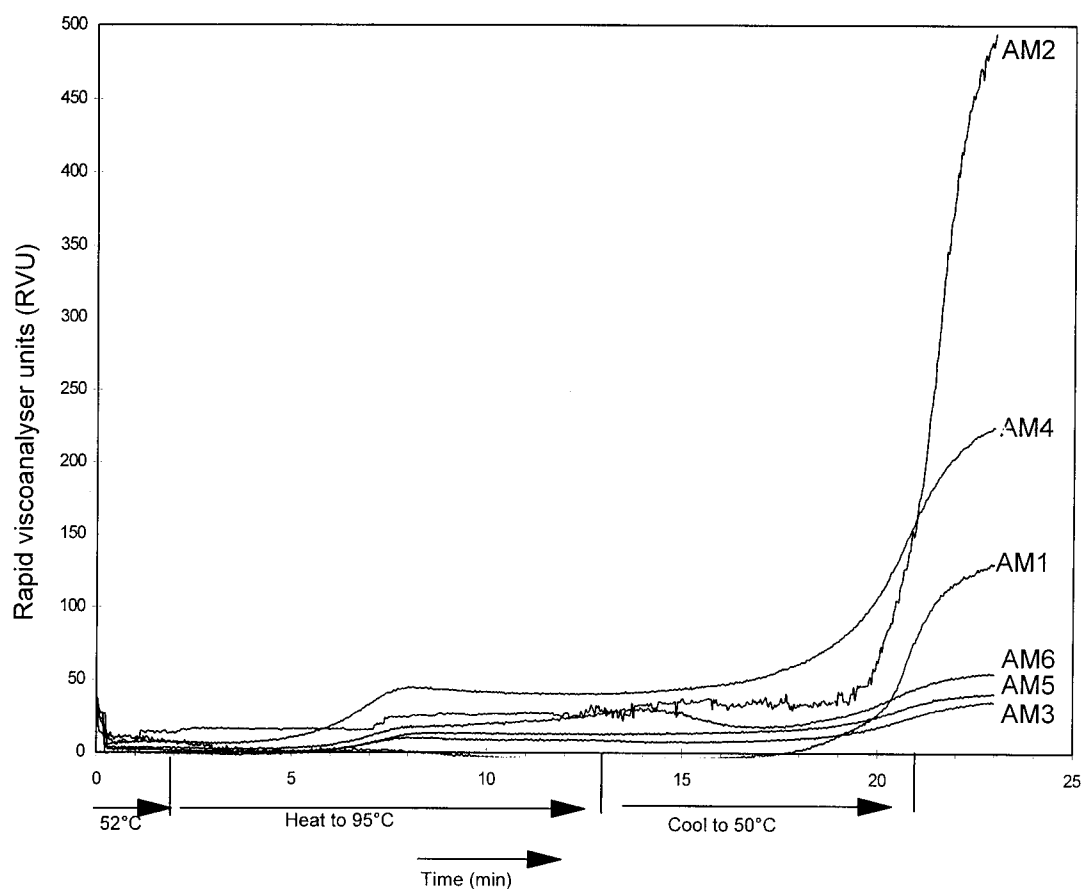
Figure 1. Pasting properties of corn amylopectin fractions measured using the rapid viscoanalyzer.

amylopectin fractions suggest that retrogradation, upon cooling of a starch paste, may be attributed to amylose (to a great extent) and some amylopectins.

No peak viscosity, peak time, peak temperature, or shear thinning was observed for any of the amylose fractions, but significantly ($P < 0.05$) different setback and final viscosity values were found (Table 3). Low–high M_w fractions (AM1, AM4, AM2) with chain DP_n of 500–1000 had higher setback and final viscosity values than their lower (AM3, AM5, AM6) M_w counterparts. Relationships were observed between amylose setback and M_w or DP_n and between final viscosity and M_w or DP_n (Table 4).

Significant ($P < 0.05$) differences were found for all six pasting properties among some of the five amylopectin fractions (Table 3). The high M_w fractions (AP1, AP2) had high peak viscosity values, but their lower M_w counterparts (AP3, AP4, AP5) showed longer peak times and higher peak temperatures. The fractions (AP1, AP2) underwent more shear thinning, had less setback, and showed lower final viscosity units than their counterparts (AP3, AP4, AP5). Evidence of rapid water absorption during heating (Figure 1), lower peak time, and temperature (Table 3; Figure 1), due to less branching (Table 4), may have enabled the fractions (AP1, AP2) to attain high peak viscosity, thereby rendering the
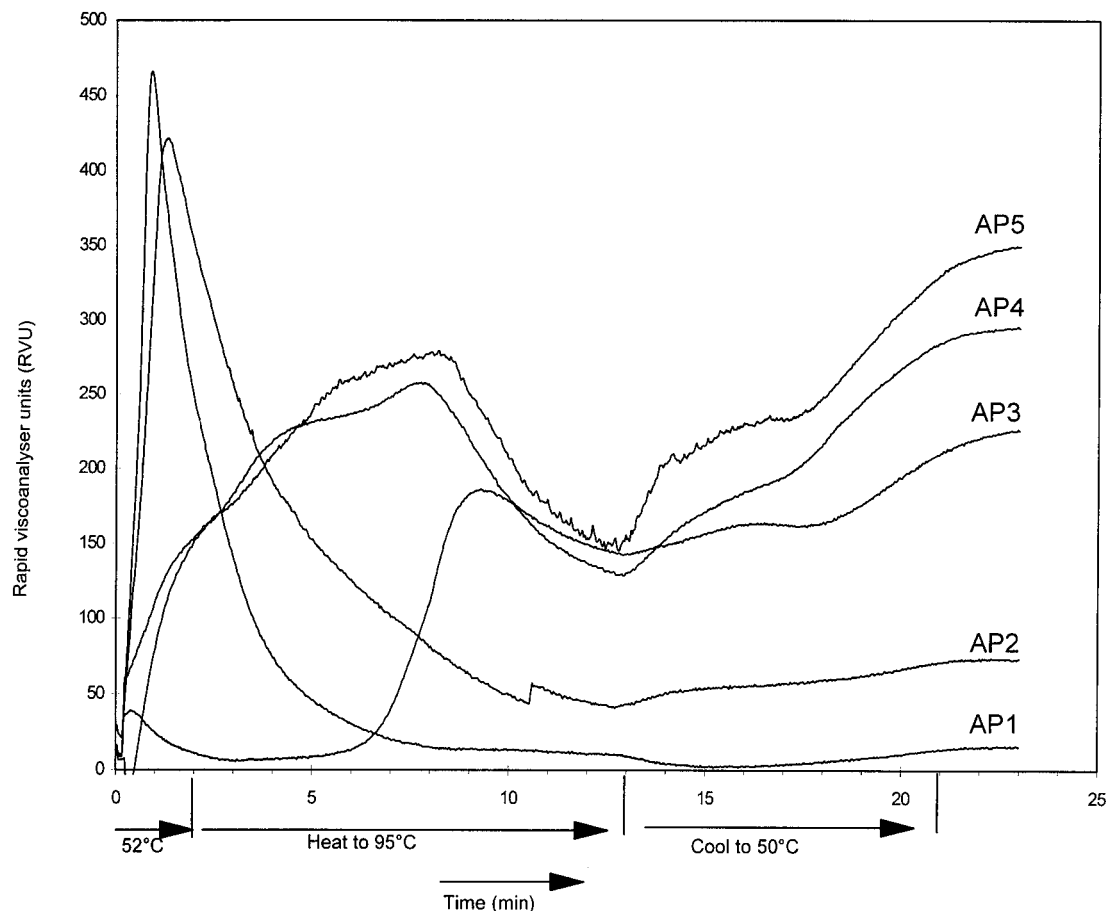
Amylose and Amylopectin Fractions from Corn Starch

J. Agric. Food Chem., Vol. 45, No. 10, 1997 **3851**

Figure 2. Pasting property profiles of corn amylose fractions measured by the rapid viscoanalyzer.

Table 3. Rheological Properties of Amylose and Amylo-pectin Fractions Determined by Rapid Viscoanalysis[a]

sample	peak viscosity (RVU)[b]	peak time (min)	peak temp (°C)	shear thinning (RVU)	setback (RVU)	final viscosity (RVU)
AM1					129.57	129.57
AM2					500.45	500.45
AM3					22.69	31.98
AM4					176.03	211.89
AM5					22.47	41.40
AM6					30.58	47.26
LSD[c]					26.017	23.430
AP1	435.53	1.53	50.17	364.36	23.57	28.69
AP2	444.83	1.74	50.22	430.39	10.75	93.75
AP3	195.87	9.00	95.00	51.43	123.57	268.01
AP4	220.04	7.62	95.21	153.34	138.17	249.83
AP5	274.65	7.33	93.57	108.39	245.70	367.01
LSD	68.139	0.5715	1.169	63.347	76.813	75.295

[a] Values are means of three analyses. [b] Rapid viscoanlysis units (arbitrary). [c] Least significant difference ($P < 0.05$).

polymers more susceptible to shear. As a result, the depolymerized chains may not have undergone reasso-ciation upon cooling of the paste, hence resulting in a low setback and final viscosity.

These results suggest that the molecular weight and structure of amylose and amylopectin contribute greatly to rheological changes during starch pasting. Correlations for amylopectin fractions (Table 4) suggest that increase in M_w and decrease in branching result in high peak viscosity and susceptibility to shear, while decrease in M_w results in increased setback and final viscosity. Peak temperature was correlated with percent crytal-linity. For amylose, setback and final viscosity increased with increases in M_w and DP_n, but marked gelation upon cooling of fraction pastes was observed for high and one low M_w and DP_n fractions.

Textural Profile Analysis. Table 5 shows amylose gel textural properties. All amylose fraction gels increased in firmness (high fracturability values) during the 14 days of storage, but the low−high M_w fractions (AM1, AM4, AM2) showed marked firmness from day 1 of storage (Table 5). The higher the fracturability value, the firmer the gel. Cohesiveness seemed to decrease for all amylose fractions over the storage period, but on the 14th day the high M_w fraction (AM4) was more cohesive than the other samples. Adhesive force increased apparently for the high−low M_w fractions (AM2, AM4 AM1), while each of the lower M_w fractions (AM3, AM5, AM6) had no apparent changes during the 14 days of gel storage (Table 5). The low M_w fraction (AM6) was found to be the most adhesive sample. Except for the low M_w amylose fraction (AM3), stringiness apparently increased with storage time (14 days) for all samples.

Amylose gel textural properties were correlated with M_w, DP_n, and crystallinity (Table 4). Fracturability or firmness increased proportionately with M_w or DP_n, while cohesiveness was inversely associated with crystalline ratio; stringiness was proportional to DP_n. High (AM2, AM4) and low (AM1) M_w fractions with DP_n (>500) produced the firmest gels, while cohesiveness increased with decreasing percent crystallinity and an increase in DP_n increased stringiness.

Amylopectin gel textural properties are shown in Table 5. Gel firmness increased during the 14 days of storage for the low M_w fractions (AP3, AP4, AP5), whereas there was no measured fracturability for the high M_w (AP1, AP2) fractions. Cohesiveness and adhesive force decreased for all fraction gels during storage, whereas stringiness increased for all fractions.

3852 *J. Agric. Food Chem.,* Vol. 45, No. 10, 1997

Mua and Jackson

Table 4. Correlation Coefficients for Regression Models between Functional Properties (Pasting, Gel Textural Profile Analysis, and Retrogradation) and Molecular Weight or Molecular Structure Characteristics for Amylose and Amylopectin Fractions

	amylose				amylopectin			
functional properties	M_w[a]	branch ratio	DP_n[b]	crystallinity (%)	M_w	branch ratio	DP_w[c]	crystallinity (%)
pasting								
peak viscosity					0.8051*	−0.7295*	0.5950	−0.0148
peak temp (°C)					−0.5057	−0.5359	−0.4519	0.8903*
shear thinning					0.8086*	−0.6541	0.4898	−0.0341
setback	0.9855***	−0.6232	0.8937**	0.5911	−0.9127*	0.1170	−0.3847	0.5512
final viscosity	0.9843***	−0.5926	0.9196**	0.5365	−0.9771**	0.2786	−0.6305	0.4600
TPA[d]								
fracturability	0.7681*	−0.6221	0.8567*	0.2433	0.8200*	0.8926*	−0.9578*	−0.9632
cohesiveness	−0.1550	0.3754	0.1910	−0.7164*	−0.6960	−0.2327	−0.0365	0.7712
adhesive force	0.0347	0.4412	−0.0709	0.1893	0.2402	0.1792	0.2448	−0.4768
stringiness	0.4673	−0.5325	0.7105*	0.0028	−0.7877*	0.4998	−0.7378**	−0.1809
retrogradation								
Avrami exponent					−0.9501**	0.2995	−0.8913*	0.4530
enthalpy					−0.8212*	0.7166*	−0.6406	0.0427
recrystallization					−0.8798*	0.6360	−0.6410	0.1412

[a] Weight-average molecular weight. * Represents significance $P < 0.05$, ** represents significance $P < 0.01$, and *** represents significance $P < 0.001$. [b] Number-average degree of polymerization. * Represents significance $P < 0.05$, ** represents significance $P < 0.01$, and *** represents significance $P < 0.001$. [c] Weight-average degree of polymerization. * Represents significance $P < 0.05$, ** represents significance $P < 0.01$, and *** represents significance $P < 0.001$. [d] Gel textural profile analysis (14th day values).

Table 5. Textural Profile Analysis Results for Amylose and Amylopectin Fraction Gels Stored at 4−5 °C for 14 Days[a]

	fracturability			cohesiveness			adhesive force (N)			stringiness		
sample	day 1	day 3	day 14	day 1	day 3	day 14	day 1	day 3	day 14	day 1	day 3	day 14
AM1	21.3574	21.3277	39.8133	0.7795	0.6973	0.5648	−0.0327	−0.0451	−0.0618	0.7873	0.4814	1.1809
AM2	25.9000	35.3330	47.9000	0.6166	0.5798	0.4887	−0.0194	−0.0192	−0.0521	0.8572	0.5472	1.2247
AM3		0.6666	20.4700	0.7199	0.5693	0.5412	−0.0142	−0.0139	−0.0144	0.7436	0.3059	0.6780
AM4	24.2401	23.0777	45.3733	0.9569	0.7736	0.7027	−0.0306	−0.0268	−0.0576	0.9623	0.4596	1.3778
AM5	2.3333	3.7970	23.9934	0.6143	0.4465	0.5319	−0.0497	−0.0389	−0.0469	0.7654	0.4600	1.2028
AM6	3.6372	7.7200	31.0601	0.6758	0.6638	0.5454	−0.0845	−0.0819	−0.0854	0.8312	0.6754	0.9841
LSD[b]	12.0983	11.6801	17.8627	0.2621	0.2085	0.0916	0.0267	0.0142	0.0332	0.0994	0.1099	0.1906
AP1				0.9104	0.8329	0.5898	−0.0256	−0.056	−0.0718	0.3940	0.673	1.7058
AP2				0.8611	0.7694	0.5453	−0.0360	−0.057	−0.0648	0.6964	0.7194	2.2921
AP3	11.4401	19.3871	24.7175	0.8469	0.6214	0.5595	−0.0405	−0.0745	−0.0810	1.0060	0.4833	0.9405
AP4	2.3534	4.7570	14.0777	0.9539	0.8803	0.6843	−0.0055	−0.0270	−0.0763	0.5640	0.1320	0.9184
AP5	2.6173	3.5300	13.5500	0.8571	0.8771	0.7199	−0.0220	−0.0231	−0.0719		0.3291	0.7871
LSD	1.2105	5.0756	1.6395	0.2047	0.2127	0.0958	0.0336	0.0165	0.0541	0.2089	0.4850	0.1111

[a] Values are means of three analyses. [b] Least significant difference ($P < 0.05$).

However, the high M_w fractions (AP1, AP2) with seemingly lower branch ratios were stringier than the other samples.

Amylopectin gel textural attributes were influenced by DP_w for short branch chains, branching, and M_w (Table 4). Relationships were observed between fracturability and M_w, or branch ratio, whereas fracturability was inversely correlated to DP_w. Low M_w fractions (AP3, AP4, AP5) that had branching ratios of 1.6−4.4 produced gels high in firmness. Stringiness was proportional to M_w but inversely proportional to DP_w. This suggests that increase in stringiness for amylopectin results from decreasing M_w and an increase in short branch chain lengths..

Retrogradation. Initial gelatinization (Figure 3a) and initial melting of crystallites (Figure 3b), as measured by DSC, were observed for native corn starches and amylopectins, respectively, but not for amylose fractions (Figure 3c). The percentage of crystals as measured by X-ray analysis (Table 2) for amylose fractions (15−24%) was close to that for two (AP1, AP2) amylopectin fractions (17−21%). These two amylopectin fractions did not retrograde as severely as did their counterparts (Table 6; Figure 4). Low M_w amylopectin fractions (AP3, AP4, AP5) with percent crystallinity >28% as measured by X-ray analysis (Table 2) had recrystallized more than those with <28% crystallinity on the 14th day of storage (Figure 4).

Amylopectin branching ratios did not significantly differ (Table 2), but branching did affect retrogradation (Table 4). In a previous study we observed that retrogradation increased when the Avrami exponent approached unity (Mua and Jackson, 1997a). In this study, high−low M_w amylopectin fractions (AP2−AP5) with short branched chains of DP_w 12−18 increased in degree of retrogradation (Figure 4), but the high M_w fraction (AP1) with DP_w 37 did not. This fraction also showed a different X-ray pattern from the rest of the samples (Mua and Jackson, 1997b). Recrystallization of >89% was observed for fractions with short branch chains with DP_w 12−18. Our results agree with the reports of Shi and Seib (1992), who found that retrogradation of four waxy starches (two rices, corn, and barley) appeared to be proportional to the mole unit of chains with DP 14−24.

Regression analysis revealed relationships between the Avrami exponent and M_w, or DP_w, between enthalpy and M_w or branching, and between recrystallization and M_w. The Avrami exponent was close to unity with a DP_w of 12 but tended to increase with an increasing DP_w for short branched chains. The Avrami exponent also increased with a decrease in M_w. Enthalpy and recrystallization increased with a decrease in M_w, but enthalpy was proportional to branch ratio. These findings suggest that low M_w amylopectin fractions with rela-
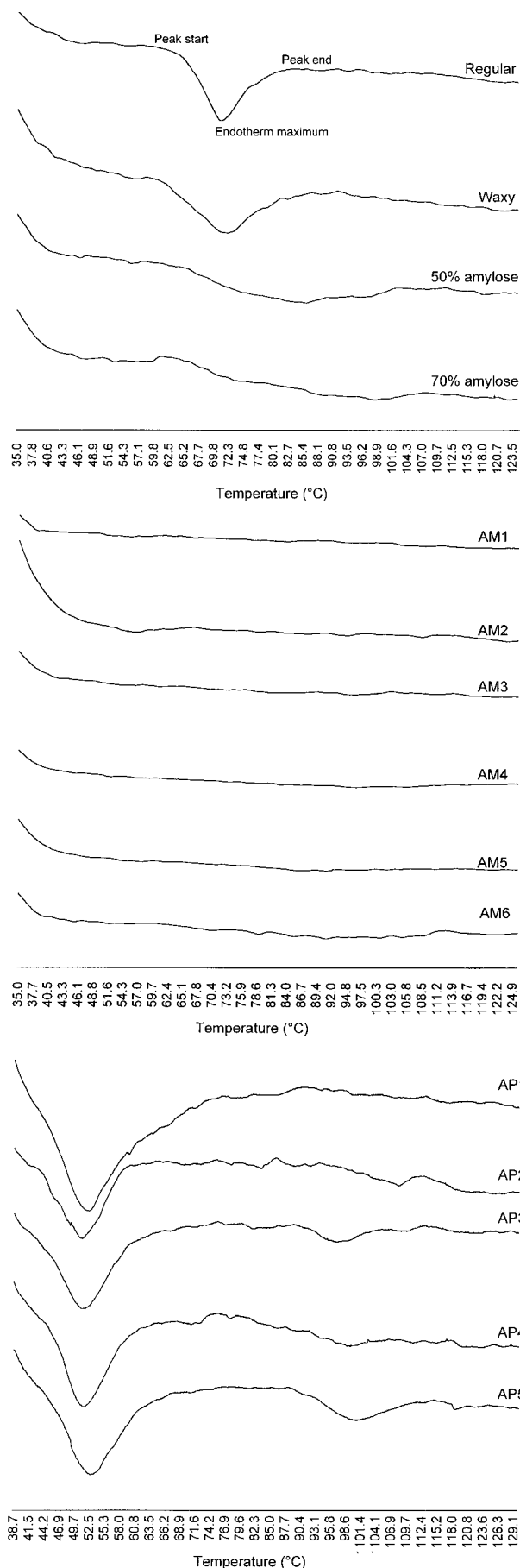
Figure 3. Initial differential scanning calorimetry thermograms of (a, top) native regular, waxy, and 50 and 70% high amylose corn starches, (b, middle) corn amylopectin fractions, and (c, bottom) corn amylose fractions, scanned at 5 °C/min from 30 to 150 °C.

Table 6. DSC[a] Enthalpy, Recrystallization, and Avrami Exponent Parameters of Fractionated Amylopectin Fractions

sample	enthalpy initial day[d]	day 14	recrystallization[b] (%)	Avrami exponent[c]
AP1	6.280[e]	0.630	10	−0.316
AP2	4.268	0.787	16	0.727
AP3	3.819	3.981	105	1.170
AP4	3.785	3.784	100	1.244
AP5	4.228	2.918	89	1.352
LSD[f]	2.439	1.029	20.1	

[a] Values are means of three analyses. [b] Calculated by dividing the enthalpy value of a retrograded fraction by the melting temperature enthalpy value for that fraction. [c] $n = 1$ represents rodlike growth from instantaneous nuclei; $n = 2$ represents rodlike growth from sporadic nuclei. [d] Initial scanning enthalpy for a sample rescanned on a given day. [e] Amount of energy (J) required to melt the crystallites in 1 g of starch. [f] Least significant difference at $P < 0.05$; means in the same column that are greater than the LSD value are significantly different.
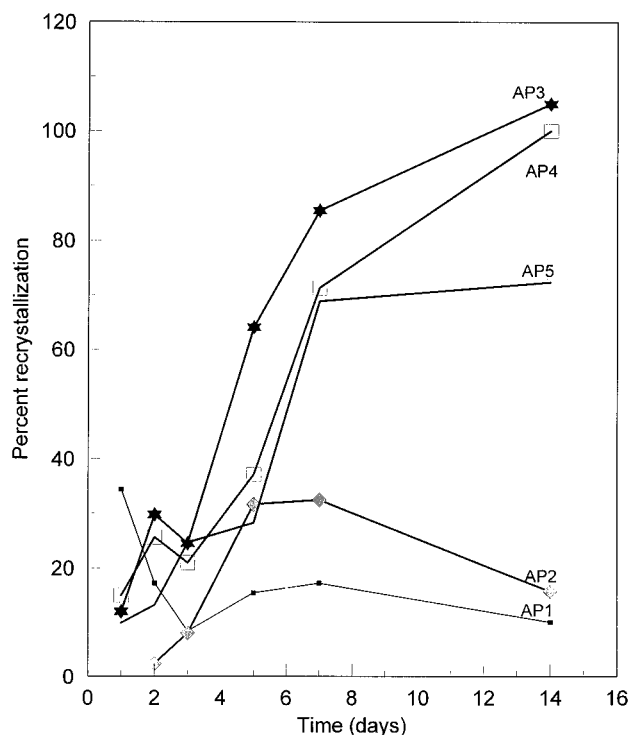

Figure 4. Amylopectin fraction rates of recrystalliztion as measured by DSC (days 1−14). Values were obtained by dividing the enthalpy value of the retrograded fraction by the initial melting temperature enthalpy value for that fraction.

tively high branching and short branched chains (DP_w = 12−18) caused an increase in retrogradation.

Conclusion. This research strongly indicates that characterization of molecular weight and branching attributes possess potential for predicting some functionality aspects for corn starches and may play a vital role in establishing relationships between the structure and function of other starches. Amylose M_w was correlated with chain DP_n, and both parameters had more proportional relationships with pasting and gel textural properties. Amylopectin M_w was correlated with DP_w for short branched chains, which were predominant in regular and waxy corn starches. The DP_w, in turn, was inversely associated with percent crystallinity. However, M_w, DP_w, and branching greatly influenced the pasting, gel textural, and retrogradation functions of starch.

Amylose fractions with M_w of 2.47−1.36E+05 containing chains with $DP_n > 500$ and long chains with 0−1

3854 *J. Agric. Food Chem.,* Vol. 45, No. 10, 1997

Mua and Jackson

branch points per 1000 glucose units (LCBF) produced higher setback and final viscosity pastes and resulted in firmer gels than their lower M_w counterparts. Cohesiveness decreased with increasing percent crystallinity, while stringiness increased with increasing DP_n.

Amylopectin fractions of high−low (8.98−7.08E+07) M_w with branch ratios >1.5, short branched chains (DP_w = 12−18), and crystallinity >28% gave high peak temperature, low peak viscosity, and lower shear thinning values when pasted. Upon cooling, they formed weak gels, but during storage, these gels firmed and retrograded more.

LITERATURE CITED

Bahnassey, Y. A.; Breene, W. M. Rapid viscoanalyzer (RVA) pasting profiles of wheat, corn, waxy, corn, tapiocca and amaranth starches (*A. hypochondriacus* and *A. cruentus*) in the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Staerke* **1994**, *48*, 134−141.

Carcea, M.; Cubadda, R.; Acquistucci, R. Physiochemical and rheological characterization of sorghum starch. *J. Food Sci.* **1992**, *57*, 1024−1028.

Dengate, H. N.; Meredith, P. The pasting characteristics of various sized starch granules from wheat. *Stearke* **1984**, *25*, 305−309.

Doublier, J. L.; Paton, D.; Llamas, G. A rheological investigation of oat starch pastes. *Cereal Chem.* **1987**, *64*, 21−26.

Evans, I. D.; Haiseman, D. R. Rheology of gelatinized starch suspensions. *J. Texture Stud.* **1980**, *10*, 347−370.

Hizukuri, S. Relationship between the distribution of the chain length of amylopectin and the crystalline structure of starch granules. *Carbohydr. Res.* **1985**, *141*, 295−305.

Hoseney, R. C. Cereal starch. In *Principles of Cereal Science and Technology*; Hoseney, R. C., Ed.; American Association of Cereal Chemists: St. Paul, MN, 1994; Vol.4, Chapter 2.

Jane, Y. L.; Chen, J. F. Effect of amylose molecular size and amylose branch chain length on paste properties of starch. *Cereal Chem.* **1992**, *69*, 60−65.

Kalichevsky, M. T.; Orford, P. D.; Ring, S. G. The retrogradation and gelation of amylopectin from different botanical sources. *Carbohydr. Res.* **1990**, *198*, 49−45.

Kulp, K.; Ponte, J. M. Staling of white pan bread: fundamental causes. *Crit. Rev. Food Sci. Nutr.* **1981**, *15*, 1−48.

Leloup, V. M.; Colonna, P.; Buleon, A. Influence of amylose-amylopectin ratio gel properties. *J. Cereal Sci.* **1991**, *13*, 1−13.

Levine, H.; Slade, L. Recent advances in starch retrogradation. In *Recent Developments in Industrial Polysaccharides*; Stilva, S. S., Crescenzi, V., Dea, I. C. M., Eds.; Gordon and Breach Science: New York, 1987; Vol. 2, pp 387−430.

Morrison, W. R.; Tester, R. F. Chemical and physical factors that affect cereal starches. In *Cereals International*; Martin, D. J., Wrigley, C. W., Eds.; Royal Australian Chem. Inst: Melbourne, Australia, 1991; pp 135−138.

Mua, J. P.; Jackson, D. S. Fractionation of regular corn starch: a comparison of aqueous leaching and aqueous dispersion methods. *Cereal Chem.* **1995**, *72*, 508−511.

Mua, J. P.; Jackson, D. S. Retrogradation and gel textural properties of corn amylose and amylopectin fractions. *J. Cereal Sci.* **1997a**, in press.

Mua, J. P.; Jackson, D. S. Fine structure of corn amylose and amylopectin fractions with varying molecular weights. *Food Chem.* **1997b**, *45*, 3840−3847.

Ong, M. H.; Jumel, K.; Tokarczuk, P. F.; Blanshard, J. M. V.; Harding, S. E. Simultaneous determinations of molecular weight distributions of amylose and the fine structures of amylopectins of native starches. *Carbohydr. Res.* **1994**, *260*, 99−117.

Orford, P. D.; Ring, S. G.; Carroll, V.; Miles, M. J.; Morris, V. J. The effect of concentration and botanical source on the on the gelation and retrogradation of starch. *J. Sci. Food Agric.* **1987**, *39*, 169−177.

Ott, M.; Hester, E. E. Gel formation as related to concentration of amylose and degree of starch swelling. *Cereal Chem.* **1965**, *42*, 476−484.

Prokopowich, D. J.; Biliaderis, C. G. A comparative study of the effect of sugars on the thermal and mechanical properties of concentrated waxy maize, wheat, potato and pea starch gels. *Food Chem.* **1994**, *52*, 255−262.

Ring, S. G.; Stainby, G. J. A simple method for determining the shear modulus of food dispersions and gels. *J. Sci. Food Agric.* **1985**, *36*, 607−613.

Roulet, P.; Macinnes, W. M.; Gummy, D.; Wursch, P. P. Retrogradation kinetics of eight starches. *Staerke* **1990**, *42*, 99−101.

Russell, P. L. The ageing of gels from starches of different amylose/amylopectin content studied by differential scanning calorimetry. *J. Cereal Sci.* **1987**, *6*, 147−158.

Russell, P. L.; Oliver, G. The effect of pH and NaCl content on starch gel ageing. A study by differential scanning calorimetry. *J. Cereal Sci.* **1989**, *10*, 123−138.

Sanderson, G. R.; Bell, V. L.; Clarke, R. C.; Ortega, D. The texture of gellan gum gels. In *Gums and Stabilizers for the Food Industry*; Philips, G. O., Williams, P. A., Wedlock, D. J., Eds.; IRL Press: Oxford, U.K., 1988; Vol. 4, Part 2.

Shi, Y. C.; Seib, P. A. The structure of four waxy starches related to gelatinization and retrogradation. *Carbohydr. Res.* **1992**, *227*, 131−145.

Takeda, Y.; Maruta, N.; Hizukuri, S. Structures of amylose subfractions with different molecular sizes. *Carbohydr. Res.* **1992**, *226*, 279−285.

Vasanthan, T.; Hoover, R. Effect of defatting on starch structure and physiochemical properties. *Food Chem.* **1992**, *45*, 337−347.

Villareal, C. P.; Juliano, B. O.; Hizukuri, S. Varietal differences in amylopectin staling of cooked waxy milled rices. *Cereal Chem.* **1993**, *70*, 753−758.

Walker, C. E.; Ross, A. S.; Wrigley, C. W.; McMaster, G. J. Accelerated starch paste characterization with the rapid visco-analyzer. *Cereal Foods World* **1988**, *33*, 491−494.

Wang, L. Z.; White, P. J. Functional properties of oat starches and relationships among functional and structural properties. *Cereal Chem.* **1994**, *71*, 451−458.

Zhang, W.; Jackson, D. S. Retrogradation behavior of wheat starch gels with differing molecular profiles. *J. Food Sci.* **1992**, *57*, 1428−1432.