

Comparison of the Gelatinization Behavior of Organic and Conventional Spelt Starches Assessed by Thermal and Rheological Analyses

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ABSTRACT: The objective of this study was to compare gelatinization properties and molecular composition of starches extracted from locally grown organic and conventional spelt using thermal, rheological, and SEC analyses, along with Concanavalin A method. Organic and conventional spelt was planted in six replicated plots, and the extracted starch was analyzed for their gelatinization properties. DSC showed that the gelatinization temperature ranged from 56.7 to 68.8 °C with an average peak of 62.4 °C, with no evidence for statistical difference in gelatinization properties between treatments. Rheological behavior variation among samples was more pronounced than that between the two growing conditions. The amylose content ranged from 23.0% to 29.8%. There was no significant difference in the molecular weight of amylose and amylopectin irrespective of the plot locations, although a significant difference was found between the amylopectin molecular weight of organic and conventional spelt starches when analyzed collectively. The organic spelt starch studied may substitute the conventional starch when gelatinization behavior is considered.

KEYWORDS: *gelatinization, DSC, rheology, HPSEC, functional properties, spelt starch*

INTRODUCTION

Organic food is produced in compliance with the principles and practices of organic agriculture, which is aimed at a food production system that maintains the sustainability of the social, ecological, and economic systems.¹ The organic food industry has grown rapidly (\$22.9 billion sales in 2008) since the launch of the National Organic Program (NOP) in 2002.² Despite this dramatic growth, research comparing the functionality of organic and conventional ingredients is scarce.

Spelt (*Triticum aestivum* subsp. *spelta*) is a type of ancient wheat widely cultivated and used in bread making during the fifth century in Europe.³ It has been increasing in popularity in recent years due to the continuous effort of spelt millers to market spelt as a high-protein alternative grain for use in products such as bread, breakfast cereal, and pasta,^{4–7} particularly in organically marketed foods.³ Consumers often perceive a sense of well-being from the consumption of organic spelt products, which they claim to provide some health benefits.³

The use of spelt in organic agriculture, which involves no use of synthetic fertilizers, genetically modified materials, or pesticides, is propelled by several factors, such as its ability to thrive in harsh weather, low precipitation, and low nutrient conditions.⁸ These valuable characteristics arise from the presence of a tough hull that provides protection against soil-borne pathogens^{9,10} and thus allows for germination under

stress conditions,¹¹ and the ability to better utilize nutrients in harsh growing conditions.¹²

Starch is the main component in cereal grains including spelt and widely used as a key ingredient in foods dictating the physicochemical properties of finished products. A study of spelt starch properties by Wilson et al.⁸ found that amylose contents of all spelt starches examined were consistently higher than that of a hard red winter wheat standard. The researchers also observed that the onset of gelatinization temperature for several of the cultivars studied was significantly elevated as compared to that of the wheat control, although the peak and conclusion temperatures as well as enthalpy change of gelatinization were not significantly different. The gelatinization temperature range for the spelt starch studied using the rapid visco-analyzer was approximately between 53.6 and 75.7 °C, with significantly higher pasting peaks and final viscosities as compared to wheat starches.⁸

Abed-Aal and Rabalski³ compared the nutritional properties of baked products made from organic spelt to ones from common wheat and found that organic spelt flour and dough contained a higher amount of resistant starch and lower rate and extent of starch digestion, but no difference was observed

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after baking as compared to the common wheat products. Bodroža-Solarov et al.¹³ studied the functional properties of organic spelt flours in comparison to wheat flour and found that the organic spelt contained significantly higher protein and gluten content than wheat. However, these studies did not specifically compare the organic spelt to its conventional counterpart, nor did it focus on the functionality of the starch component.

There is limited study comparing the effect of conventional and organic farming on the properties of starch. However, a study by Fredriksson et al.¹⁴ showed that, although there were quantitative effects of different levels of meat bone meal, liquid manure (representing organic management), and urea fertilizers (representing conventional management) on protein levels in wheat, no significant effect was found on starch. The difference found was mostly attributed to the wheat variety (spring vs winter).

Gelatinization is one of the most important processes that starch must undergo before it can impart its functionality, such as thickening, gelling, and ingredient-binding. Differential scanning calorimetry (DSC) has been utilized to evaluate thermal properties of starch, particularly its gelatinization properties.^{15–19} DSC measurements generally provide information regarding the transition temperatures and enthalpy changes of starch gelatinization.²⁰

Dynamic rheological measurements have also been conducted to characterize the property changes of model starch systems during gelatinization.^{17,21–25} Tattiyakul and Rao²⁴ and Yang and Rao²⁵ analyzed the change in complex viscosity (η^*) versus temperature of cross-linked waxy maize and native corn starch dispersions, respectively, using a rheometer with a parallel plate geometry. The modified Cox–Merz rule (eq 1) was applied to describe the relationship between η^* and apparent viscosity (η_a) at different shear rates:

$$\eta^*(\omega) = C[\eta_a(\dot{\gamma})]^a |_{\omega=\dot{\gamma}} \quad (1)$$

In general, they found that, based on this equation, η^* may be used to estimate values of η_a .

The understanding of starch functionality in starch-containing foods is often supplemented by measuring the amylose to amylopectin ratio and the molecular weight (MW) of amylose.^{8,26–30} In this study, complexation with Concanavalin A (Con A) method along with size exclusion chromatography (SEC) technique were used to determine the amount (%) and the MW of the two components of starch, amylose and amylopectin. The use of multiangle light scattering (MALS) detector attached to the SEC allows for MW determination without the use of standards. The Con A and chromatography methods have been used elsewhere in previous research to study the molecular properties of starch.^{8,29–35}

Therefore, the objective of this study was to compare gelatinization properties and molecular composition of starches extracted from locally grown organic and conventional spelt using thermal, rheological, and chromatographic analyses, along with Con A method.

MATERIALS AND METHODS

Spelt Growing Methods. Spelt (Oberkulmer, var.) was planted in fall 2009 in organic and conventional plots of the Ohio State University's Ohio Agriculture Research and Development Center's long-term Organic Farming Systems Experiment (OFSE) located in Wooster, OH. This experiment specifically compared conventional and certified organic management of agronomic crops in a randomized

block design with six replicates. Soil type was Wooster Silt Loam. The organic plots have been certified organic under USDA's National Organic Program regulations since 2002. All plots were plowed, disked, and prepared for planting in a similar fashion. In the conventional plots, fungicide-treated seed was planted on October 22, 2009 into six-replicate plots (Figure 1). Chemical fertilizer was applied

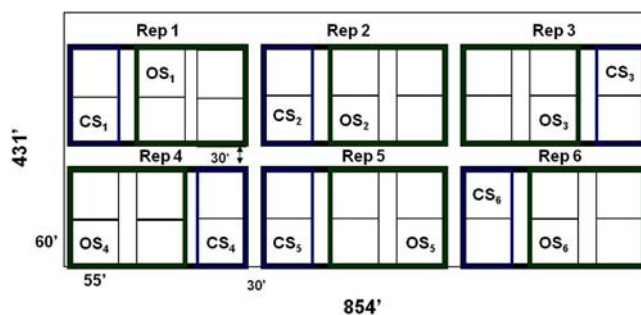


Figure 1. Diagram showing six-replicate plots of conventional (CS) and organic spelt (OS) on the field.

during planting at the rate of 20 kg/ha. Spelt in conventional plots was top-dressed with 90 kg/ha of urea on April 6, 2010, and broad-leaved weeds were controlled with Express (tribenuron methyl) at 24 mL/ha on April 4, 2010. In organic plots, untreated seed was planted on October 22, 2009 and fertilized with an organically approved partially composted poultry manure at 2240 kg/ha (with 4% N, thus delivering about 90 kg of N per ha) at planting and top-dressed with an additional 2000 kg/ha on April 18, 2010. Whole grain samples were collected on August 20, 2010 and stored at room temperature prior to starch analyses. The six field replicates were labeled as such: CS1, CS2, CS3, CS4, CS5, CS6, OS1, OS2, OS3, OS4, OS5, and OS6 (CS signifies conventional spelt; OS signifies organic spelt; the plot numbers 1–6 represent replicates at six field locations), totaling 12 samples.

Starch Isolation. Whole spelt grain was cracked using the Allis-Chalmers wheat mill (Allis-Chalmers Co., Milwaukee, WI) with a roller of 0.5 mm gap size. The starch was extracted from the grain following the protease method described by Reddy and Seib³⁶ and Wilson et al.⁸ with slight modifications as follows. The cracked spelt grain (20 g) was added to 0.02 M HCl (200 mL) at 4 °C and held for 8–10 min. Sodium metabisulphite (100 mg) and thiomersal (2 mg) were added to the mixture, and its pH was adjusted to 7.6 by the addition of tris(dyoxymethyl)aminomethane (2.5 g) and 1 M HCl. Protease (Type XIV, Sigma Chemical Co., St. Louis, MO, 100 mg) was dissolved in 0.02 M HCl (12 mL) and held for 5 min at room temperature to denature α -amylase. The protease solution was added to the slurry, and the mixture was digested for 30 h at 4 °C with continuous stirring. The digest was then filtered through 425, 150, and 74 μ m wire mesh sieves connected in series, and the softened mass was rubbed against the sieve and washed with water (2 \times 20 mL). The filtrate was collected, while the overs were blended in a household blender with water for 30 s and refiltered through the 150 and 74 μ m sieves. The overs were then placed in a test tube and ground with a homogenizer for 30 s. The grinding procedures were repeated once more, and the mixture was filtered through the 74 μ m sieve. All filtrates were combined and centrifuged at 2500g for 10 min. The supernatant was decanted, and the suspended starch was washed with water (3 \times 20 mL), centrifuged, and the dark tailings were removed using a spatula. The starch was washed with 1% NaCl solution (20 mL) and water (3 \times 10 mL). It was subsequently air-dried for about 48 h. Starch recovery from the whole spelt grain was 45%, on average, which is relatively close to that from wheat grain using a similar method with 54% on average.³⁶

Gelatinization Study. Thermal Analysis. Differential scanning calorimetry (DSC) Q100 (TA Instruments, New Castle, DE), previously calibrated using indium, was used to determine the gelatinization temperature range of the starch. Starch samples of 2–

3 mg were weighed into a stainless steel pressure pan, and water was added to the starch in a 1:4 starch-to-water ratio. The sample pan was hermetically sealed (Perkin-Elmer Instruments LLC, Shelton, CT), let stand for 1 h at room temperature to hydrate the starch, and placed against an empty reference pan inside the DSC cell, previously flushed with nitrogen gas. Samples were equilibrated at 25 °C and heated to 100 °C at a 5 °C/min rate. Analysis was performed in triplicate for all samples, measuring the onset (T_o), peak (T_p), and conclusion temperatures (T_c), and change of enthalpy of gelatinization (ΔH).

Rheological Analysis. Each sample was mixed in distilled water to prepare 5% starch dispersions (w/w). The slurry was continuously stirred for approximately 30 min at room temperature to hydrate and homogenize the sample. Gelatinization using the rheometer was performed following the procedure described by Tattiyakul and Rao²⁴ with a few modifications. A starch dispersion of 0.64 mL was applied to the bottom plate of an AR 2000ex rheometer (TA Instruments, New Castle, DE) with parallel plate geometry (40 mm diam) and a 500 μm gap. A solvent trap was used to minimize water evaporation, and standard conditions of 1 Hz and 0.5% strain (previously determined to be in the linear viscoelastic region) were applied. A temperature ramp from 25 to 95 °C at a ramp rate of 2.1 °C/min was conducted, followed by a time sweep for 5 min at 95 °C. The effect of temperature change on complex viscosity (η^*) was investigated. Analysis was performed in triplicate.

Molecular Composition Analysis. Amylose Content Determination. The amylose content of isolated spelt starch was measured using the Con A method involving the precipitation of amylopectin–Con A complex, according to the procedure described by the manufacturer for the Megazyme amylose/amylopectin assay kit (Megazyme International Ltd., Wicklow, Ireland).^{8,30,34}

Dispersion of Starch Component. A starch sample (125 mg) was added into a 50 mL tube, followed by 5 mL of 90% dimethyl sulfoxide (DMSO), and boiled for 1 h with continuous stirring. It was then removed from heating and stirred overnight at room temperature. Ethanol (100%, 25 mL) was added to precipitate the starch. The sample was centrifuged at 3444g for 10 min, and the supernatant was decanted. Ethanol precipitation and centrifugation were repeated three more times to remove residual DMSO, and the pellet was vacuum-dried to remove traces of ethanol prior to SEC analysis.³⁷

Chromatographic Analysis. The high performance size exclusion chromatography (HPSEC) analysis was performed as described in previous studies.^{37,38} Dried starch was resuspended in water at 2 mg/mL concentration. The suspension was vortexed and boiled in a household pressure cooker (Cuisinart Electric Pressure Cooker) for 30 min. After rigorous vortexing, the sample was processed through a syringe fitted with a nylon filter of 5 μm pore size and injected into the HPSEC system previously washed with double-distilled water. The system consisted of an SEC column (Sephacryl 500 HR by GE Healthcare, Piscataway, NJ) attached to the MALS (Dawn Heleos-II at 685 nm GaAs laser diode, Wyatt Technology Corp., Santa Barbara, CA) and RI detectors (Optilab rEX, Wyatt Technology Corp., Santa Barbara, CA). The eluent was 0.02% NaN_3 in water with a flow rate of 1.3 mL/min. The collection time was set at 120 min. Fraction peaks were analyzed by ASTRA software (v.3.4.14 Wyatt Technology Corp., Santa Barbara, CA) for MW. The second-order Berry model was used for curve fitting. MW calculation was based on a dn/dc value of 0.146. The analysis was performed in duplicate.

Statistical Analysis. Means and standard deviations were calculated, and differences among the plot locations and growing methods were analyzed using two-way ANOVA and *t* test on SPSS Statistics 19 (IBM Corp., Armonk, NY). Scheffé method was applied as a posthoc test. Significant differences were determined when $p \leq 0.05$. Correlation of starch molecular composition and physicochemical properties were calculated on the basis of the Pearson product-moment correlation coefficient (*r*) using Sigma Plot 11.0 (Systat, San Jose, CA).

RESULTS AND DISCUSSION

Thermal Analysis. DSC thermograms of organic and conventional spelt starches (Figure 2) indicate that there was

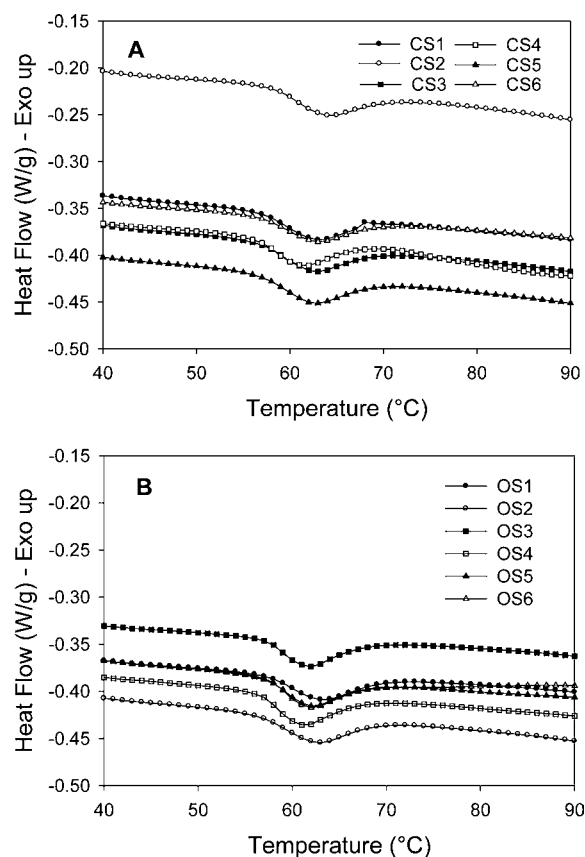


Figure 2. Gelatinization profiles of (A) conventional and (B) organic spelt starches using DSC.

slight variation in the gelatinization temperature of the starches (Table 1). In general, gelatinization ranged from 56.7 to 68.8 °C with an average peak temperature of 62.4 °C. This temperature range is slightly higher than that of wheat starch (approximately 50–66 °C)²⁶ and is consistent with the measurements of Wilson et al.⁸

Cooke and Gidley³⁹ suggested that the change in enthalpy during gelatinization represents the degree of crystallinity and amylopectin double-helical order. Tester and Morrison²⁷ further suggested that the level of crystallite perfection is reflected in the gelatinization temperature. A higher temperature of gelatinization can be attributed to the higher amount of longer-chain amylopectin, which requires greater thermal energy to dissociate.^{17,18} Sasaki and Matsuki²⁶ determined that gelatinization temperature of various wheat starches positively correlated with proportion of longer-chain amylopectin (DP > 35), suggesting that longer-chain amylopectin is able to form more extensive double helical structures and perhaps more stable and larger crystallites.

There was no clear trend suggesting significant difference in gelatinization properties between organic and conventional starches analyzed by DSC. Variation was also evident among the different plot locations (indicated by numbers 1–6). Gelatinization temperature is influenced by many factors. Although the starches studied originate from the same cultivar and are both in the native form, other factors that may have

Table 1. Gelatinization Properties of Starches of Spelt Grown under Conventional or Organic Management (Mean \pm Standard Deviation)

sample ^a	T_o ($^{\circ}$ C) ^b	T_p ($^{\circ}$ C)	T_c ($^{\circ}$ C)	ΔH (J/g)
CS1	57.2(\pm 0.3) abc	62.7(\pm 0.2) bcd	67.2(\pm 0.3) abcd	2.05(\pm 0.23) a
CS2	58.0(\pm 0.4) c	63.4(\pm 0.6) d	68.4(\pm 0.8) d	2.15(\pm 0.11) a
CS3	57.8(\pm 0.3) bc	62.1(\pm 0.6) abcd	67.5(\pm 0.6) abcd	2.60(\pm 0.26) a
CS4	56.8(\pm 0.2) a	61.5(\pm 0.3) ab	66.6(\pm 0.2) abc	2.49(\pm 0.51) a
CS5	57.2(\pm 0.1) abc	62.8(\pm 0.3) cd	68.2(\pm 0.6) bcd	2.25(\pm 0.08) a
CS6	57.0(\pm 0.3) ab	62.7(\pm 0.4) bcd	68.4(\pm 0.2) d	2.25(\pm 0.09) a
OS1	57.7(\pm 0.2) bc	63.1(\pm 0.4) cd	68.8(\pm 0.8) d	2.23(\pm 0.11) a
OS2	56.7(\pm 0.1) a	62.8(\pm 0.0) bcd	68.3(\pm 0.3) cd	2.46(\pm 0.08) a
OS3	57.5(\pm 0.2) abc	62.1(\pm 0.2) abc	66.1(\pm 0.1) a	2.44(\pm 0.28) a
OS4	57.0(\pm 0.3) ab	61.3(\pm 0.1) a	66.5(\pm 0.0) ab	2.51(\pm 0.17) a
OS5	57.3(\pm 0.1) abc	62.1(\pm 0.1) abcd	67.1(\pm 0.1) abcd	2.26(\pm 0.07) a
OS6	57.6(\pm 0.1) abc	61.7(\pm 0.2) abc	66.4(\pm 0.3) ab	2.53(\pm 0.21) a

^aCS = conventional spelt, OS = organic spelt, and 1–6 indicate plot locations. ^bMeans followed by different letters are significantly different at $p \leq 0.05$ by two-way ANOVA, $n = 3$.

been affected by growing method, such as amylose and amylopectin content, granular morphology, degree of polymerization, and chain-length distribution, as well as the presence of minor components such as lipids and phospholipids, may influence gelatinization behavior.^{17,18,27,40,41} However, no such trend was observed in this study.

Rheological Analysis. The change in complex viscosity (η^*) of spelt starches during heating (Figure 3) indicates that there was variation in the rheological properties of the starch

from spelt crops planted within the same growing conditions at different plot locations. In general, the variation among samples was more pronounced than that between the two growing conditions. This difference may be attributed to the reaction rate of starch components with water as well as the physical-transformation rate (such as the melting of crystalline regions),⁴² which may then suggest varying structural properties, such as molecular composition and chain-length distribution within the starch granules.

There was hardly any significant difference in the onset temperature (T_o) of increase in η^* (average value of 64.4 $^{\circ}$ C) as well as in the peak complex viscosity (η^*_p , average value of 17.2 Pa s) among all samples (Table 2). Similarly, no significant

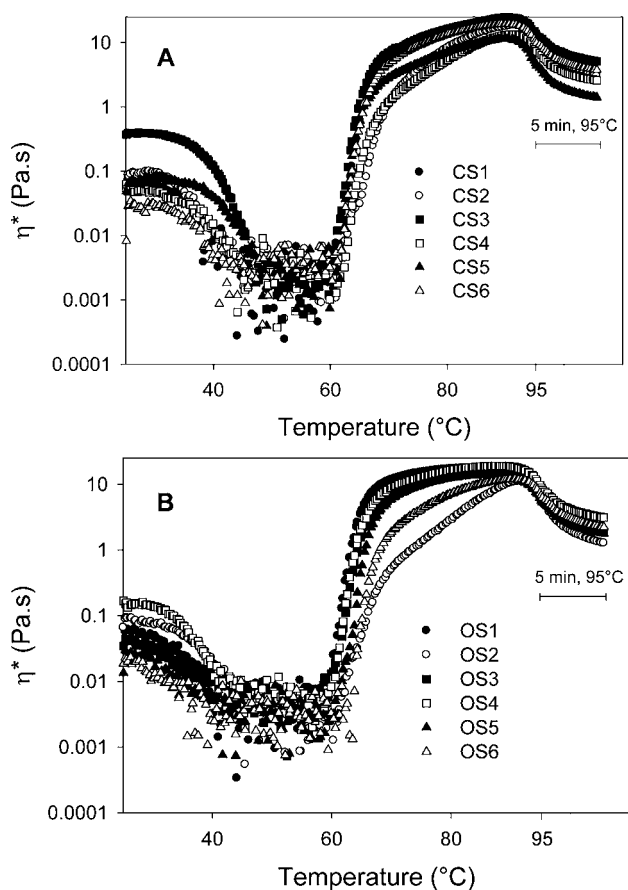


Figure 3. Complex viscosity (η^*) of (A) conventional and (B) organic spelt starches as a function of temperature (25–95 $^{\circ}$ C) and holding at 95 $^{\circ}$ C for 5 min (1 Hz, 0.5% strain).

Table 2. Onset Temperature (T_o), Peak Temperature (T_p), and Peak Complex Viscosity (η^*_p) of Conventional and Organic Spelt Starches during Gelatinization (Mean \pm Standard Deviation)

sample ^a	T_o ($^{\circ}$ C) ^b	T_p ($^{\circ}$ C)	η^*_p (Pa s)
CS1	63.4(\pm 0.5) abc	89.9(\pm 1.6) a	22.5(\pm 4.9) ab
CS2	67.5(\pm 1.4) bc	91.9(\pm 0.1) a	16.9(\pm 1.8) ab
CS3	64.2(\pm 0.8) abc	88.8(\pm 1.3) a	25.5(\pm 4.7) b
CS4	65.2(\pm 3.2) abc	86.1(\pm 5.4) a	14.9(\pm 5.7) ab
CS5	63.6(\pm 0.2) abc	90.3(\pm 0.3) a	10.8(\pm 1.4) a
CS6	64.1(\pm 0.6) abc	90.3(\pm 0.9) a	19.1(\pm 0.5) ab
OS1	62.1(\pm 0.6) a	84.8(\pm 3.2) a	18.6(\pm 1.9) ab
OS2	68.0(\pm 2.3) c	91.8(\pm 0.6) a	12.06(\pm 1.2) a
OS3	62.6(\pm 0.4) ab	89.0(\pm 1.8) a	17.8(\pm 1.4) ab
OS4	62.7(\pm 0.3) ab	87.9(\pm 1.2) a	19.2(\pm 0.9) ab
OS5	64.3(\pm 0.1) abc	86.4(\pm 1.2) a	14.2(\pm 2.0) ab
OS6	64.7(\pm 1.4) abc	90.8(\pm 0.5) a	14.9(\pm 5.6) ab

^aCS = conventional spelt, OS = organic spelt, and 1–6 indicate plot locations. ^bMeans followed by different letters are significantly different at $p \leq 0.05$ by two-way ANOVA, $n = 3$.

difference was found in the peak temperature (average of 89.0 \pm 2.8 $^{\circ}$ C) among the six plot locations or between the two growing methods. Minor significant differences observed were potentially due to the variation in molecular composition (see below).

Rheological behavior of starch dispersion during gelatinization is mostly ascribed to the granular structure and intergranular interaction, that is, entanglement among starch

molecules in neighboring granules as they become more tightly packed.²³ Amylose is also thought to contribute to the rigidity of the gelatinized starch dispersion. According to Eliasson,²¹ a starch gel can be regarded as a suspension with starch granules as rigid fillers (dispersed phase) in a polysaccharide matrix of amylose leaching to the surrounding water (continuous phase). The increase in elastic and viscous moduli (G' and G'') can be divided into two stages. The initial increase (around 60–75 °C) is due to the progressive swelling of starch granules until they are fully and tightly packed. The later increase leading to the final peak (around 75–95 °C) can be attributed to an increased gel volume after amylose and some of the amylopectin leach out. Complex viscosity is recognized as a direct function of G' and G'' .⁴³ There were noticeably two distinctive stages that can be observed in most of the complex viscosity curves (Figure 3), and thus it can be accepted that these processes occurred during gelatinization.

Yang and Rao²⁵ analyzed the change in η^* of corn starch dispersion during heating and found a two-stage increase in η^* over increasing temperature. Agreeing with Eliasson,²¹ they explained that the initial rise in η^* can be attributed to swelling of starch granules resulting in increased interaction among the granules. There is also sometimes a noticeable slight decrease in η^* following the first rise, which coincides with the conclusion temperature of DSC crystalline melting peak.²¹ Increase in η^* occurs further upon heating due to continued swelling, causing the formation of gel network, amylose leaching, and granule disruption, after which further heating results in granule rupture and decrease in η^* , indicating the weakening of starch network,²⁵ as was also observed in Figure 3.

Molecular Composition Analysis. The amylose content was determined by the Con A method using the Megazyme amylose/amylopectin assay kit. HPSEC was applied to analyze the molecular composition of the starches. The MALS detector elucidates the MW of amylose and amylopectin in the starches. Figure 4 displays representative chromatographs of the

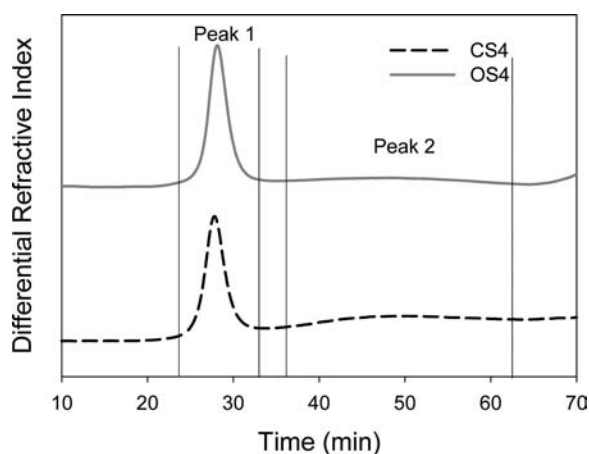


Figure 4. Chromatographic profile of representative conventional and organic spelt starches (CS4 and OS4). Peak 1 represents amylopectin, and peak 2 represents amylose.

conventional and organic spelt starches (CS4 and OS4). It was previously suggested that peak 1 corresponds to the amylopectin fraction of the starch, while peak 2 represents amylose.^{44,45} The amylose content and calculated molecular weights of amylose and amylopectin are summarized in Table 3.

Table 3. Amylose Content and Molecular Weights (MW) of Starch Components Analyzed by Megazyme Amylose/Amylopectin Kit and HPSEC, Respectively^a

sample	amylose content (%)	MW (g/mol) ^b	
		peak 1	peak 2
CS1	26.2	1.36×10^8	2.08×10^7
CS2	25.5	2.84×10^8	1.58×10^7
CS3	27.3	2.72×10^8	1.87×10^7
CS4	25.7	4.15×10^8	1.56×10^7
CS5	27.0	2.45×10^8	1.90×10^7
CS6	29.8	1.89×10^8	2.24×10^7
OS1	26.1	3.22×10^8	2.36×10^7
OS2	24.6	3.88×10^8	1.61×10^7
OS3	27.7	3.63×10^8	2.10×10^7
OS4	23.0	3.86×10^8	2.39×10^7
OS5	29.4	2.44×10^8	1.68×10^7
OS6	28.0	3.74×10^8	1.18×10^7

^aPeak 1 represents amylopectin, and peak 2 represents amylose. ^bNo significant difference was found in amylose content and MW of peak 1 and peak 2 among the 12 samples ($p > 0.05$). However, significant difference was found in MW of peak 1 when t -test was performed to compare the overall organic versus conventional spelt starches ($p \leq 0.05$).

The amylose content ranged from 23.0% to 29.8%. These values are slightly lower than those found in a previous study using the same determination method, with amylose content of 30–33% among starches from different spelt cultivars, and 30–31% amylose from the same cultivar (Oberkulmer var.).⁸ The average amylose content of conventional and organic spelt starches from the six replicates was 26.9% and 26.5%, respectively, which were comparable to that of the hard red winter wheat control in the previous study (26.1%).⁸

Two-way ANOVA did not determine any significant difference among the MW of amylose and amylopectin in the 12 spelt starches, possibly due to the relatively high variability among the results. This large variability may be ascribed to the existence of interaction among starch components, that is, amylopectin–amylopectin or amylose–amylopectin²⁹ that may produce aggregates and thus yield higher MW values. However, the MW of amylopectin was found to be significantly higher in the organic spelt starch (3.46×10^8) than the conventional starch (2.57×10^8) when analyzed collectively ($p = 0.035$, two-tailed independent t test).

The variation in amylose/amylopectin content and molecular weights between the two starches may explain the significant differences observed in thermal and rheological properties of the starches. Although a significantly higher amylopectin MW was found in the organic spelt, there is no literature-supported evidence that this would affect gelatinization properties. Many studies have instead focused on exploring the impact of variation in branch chain length on gelatinization properties. As an instance, Sasaki and Matsuki²⁶ studying the effect of wheat starch structure on its gelatinization property found that gelatinization temperature and enthalpy had positive correlations with the proportion of long-chain amylopectin ($DP > 35$). However, it is worth noting that the MW of amylopectin correlated positively with the enthalpy of endothermic peak ($r = 0.732$, $p = 0.00675$), indicating a possibly higher level of crystallinity in the organic starch.

The significantly higher MW of amylopectin in the organic starch, which is due to greater degree of polymerization and

may possibly be due to increased chain length, may be expected to contribute to further swelling of the starch and thus higher peak viscosity, as well as more extensive retrogradation, as seen in previous studies.^{26,31} However, this effect was not observed in the peak complex viscosity between conventional and organic starches (Table 2), which may suggest that an even greater difference in the MW of amylopectin may be necessary to yield a significant difference in complex viscosity. Earlier findings showed that high MW fractions of amylopectin promote further swelling (thus, increase in viscosity) at earlier time than the lower MW counterparts.^{26,46}

Previous studies reported that pasting peak viscosity of wheat and rice starches negatively correlated with their amylose content, especially for low-amylose starch.^{28,47} However, this relationship was not observed in our study, as the correlation between peak complex viscosity and percent amylose was weak ($r = 0.0115$). The pasting viscosity of starch can be influenced by many other factors pertaining to the molecular structure, such as the chain average degree of polymerization and branching, MW, and percent crystallinity.⁴⁶ Specifically, Mua and Jackson⁴⁶ found that amylopectin with low MW (approximately 7×10^7 – 8×10^7), high branching ratios (>1.5), and short branch chains (DP of 15–18) exhibited low peak viscosity and high peak temperatures during pasting of corn starch.

In conclusion, on the basis of the thermal and rheological analyses of the spelt starches, no significant difference in gelatinization properties could be attributed to the growing methods (conventional versus organic). There was no significant difference in the molecular composition of amylose and amylopectin when plot locations and two growing conditions were both considered as influencing factors. Nonetheless, when each of the six conventional and organic starches was analyzed collectively regardless of the plot locations, the amylopectin MW of the organic spelt starch was observed to be significantly higher than that of the conventional counterpart. This significant difference, however, did not contribute to the differing rheological behavior between the conventional and organic starches. The amylopectin MW was also found to correlate positively with the enthalpy of endothermic peak.

Therefore, the organic spelt starch studied may be used to substitute for the conventional starch when gelatinization behavior is considered. A future study is needed to evaluate the effect of organic versus conventional growing method, in a controlled manner, on the complete profile of the starch molecular composition including the degree of polymerization of amylose and amylopectin. It will also be worthwhile to explore the relationship between amylopectin branch chain lengths and the functional properties of the organically and conventionally grown starches.

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Notes

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ABBREVIATIONS USED

NOP, National Organic Program; DSC, differential scanning calorimetry; η^* , complex viscosity; $\eta^*_{p, peak}$, peak complex viscosity;

η_{app} , apparent viscosity; MW, molecular weight; SEC, size exclusion chromatography; MALS, multiangle light scattering; RI, refractive index; OFSE, organic farming systems experiment; CS, conventional spelt; OS, organic spelt; T_o , onset temperature; T_p , peak temperature; T_c , conclusion temperature; DMSO, dimethyl sulfoxide; HPSEC, high performance size exclusion chromatography; DP, degree of polymerization; G' , elastic modulus; G'' , viscous modulus

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