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Combined rheological and optical investigation of maize, barley and wheat starch gelatinisation

Ihwa Tan [a,1], P.J. Torley [a,b], P.J. Halley [a,*]

[a] Centre for High Performance Polymers, School of Engineering, The University of Queensland, St. Lucia, Brisbane, Qld 4072, Australia
[b] Food Science and Technology Group, School of Land, Crop and Food Sciences, The University of Queensland, St. Lucia, Qld 4072, Australia

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Abstract

Microstructural and rheological changes during gelatinisation are important indicators of starch functionality. A combined rheometer and optical microscope system (Rheoscope 1, Thermo Haake) was used to monitor the gelatinisation of different starches (maize starch containing 0%, 24%, 55% and 85% amylose; wheat starch and barley starch) suspended in a 0.1% guar solution (to minimise settling during the initial stages of gelatinisation). The 0.1% guar solution was selected after Rapid Visco Analyser, Modulated DSC and settling studies indicated that it minimised any effect on starch gelatinisation compared to carboxy methyl cellulose and xanthan. The Rheoscope study demonstrated that the viscosity of the starch during gelatinisation is related to changes in starch granules as a result of swelling. There was a two to threefold increase in starch granule size during the gelatinisation for all starches except for high amylose maize starches. Viscosity development during the gelatinisation was affected by the presence of B-type granules, whose presence tended to reduce the overall viscosity increase, indicating the importance of starch granules size and their distribution in determining the rheological responses of starch during gelatinisation.

Keywords: Rheo-optics; Starch gelatinisation; Amylose content; Barley; Maize; Wheat; Guar gum; Guar; Xanthan gum; Xanthan; CMC

1. Introduction

Starch gelatinisation is commonly defined as an irreversible order–disorder transition of starch granules from a structured state to a disordered state (starch pastes) upon heating in the presence of plasticisers. The normal sequence of events during gelatinisation process include granular swelling, loss of birefringence, loss of molecular orders and crystallinity, heat uptake, marked increase in viscosity and the polysaccharides (amylose) solubilisation (Cooke & Gidley, 1992; Derby, Miller, Miller, & Trimbo, 1975; Donovan, 1979). These events underlie the technologically important properties of starch pasting and retrogradation, and are undoubtedly relevant to starch processing, its suitability for particular end uses as well as the final product properties (Cooke & Gidley, 1992).

While these events are the typical changes manifested during starch gelatinisation, variations in the features of these changes are evident between starches from different species and varieties (Bocharnikova, et al., 2003; Fredriksson, Silverio, Andersson, Eliasson, Aman, 1998; Jay-Lin & Chen, 1992; Lii, Tsai, & Tseng, 1996; Matveev, et al., 2001; McPherson & Jane, 1999; Tester & Morrison, 1990; Tsai, Li, & Lii, 1997; Yuryev, Kalistratova, van Soest, & Nieman, 1998; Zeng, Morris, Batey, & Wrigley, 1997). Numerous studies have been dedicated to understanding of the mechanisms underlying starch gelatinisation and to investigate the basis for the observed differences in the gelatinisation behaviour of starches from different plant origins and

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E-mail addresses: ihwa.tan@gmail.com (I. Tan), p.halley@uq.edu.au (P.J. Halley).

[1] Present address: PT Charoen Pokphand Indonesia, Research & Development Centre, J1. Parangtritis Raya Blok A-5E No. 12A, Jakarta 14430, Indonesia. Fax: +62 21 693 0364.

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species (Jay-Lin & Chen, 1992; Lii et al., 1996; Tsai et al., 1997; Zeng et al., 1997). These studies involve the use of a wide range of measurement techniques such as microscopy which monitor the changes in starch granules upon heating in the presence of water, calorimetry which report on the energy uptake during gelatinisation as well as the transition temperatures, NMR spectroscopy and with X-ray diffraction studies which measure the loss of molecular order and crystallinity during gelatinisation, respectively, viscosity measurements which examine the change in viscosity during starch gelatinisation and so on (Biliaderis, Maurice, & Vose, 1980; Cameron & Donald, 1992,1993; Cooke & Gidley, 1992; Derby et al., 1975; Lelievre, 1973; Schuster, Ehmoser, Gapes, & Lendl, 2000; Wootton & Bamunuarachchi, 1979).

These investigations have furthered the understanding of starch gelatinisation process over the past decades, however most of these studies relied on the application of many different techniques [and thus samples] and utilise the different types of information collected from these measurements to fully understand the mechanisms of starch gelatinisation and the structural parameters dictating starch gelatinisation behaviour (Conde-Petit, Nuessli, Handschin, & Escher, 1998; Cooke & Gidley, 1992; Crochet, Beauxis-Lagrave, Noel, Parker, Ring, 2005; Jenkins & Donald, 1998; Liu, Lelievre, & Ayoung-Chee, 1991; Liu, Charlet, Yelle, & Arul, 2002; Waigh, Gidley, Komanshek, & Donald, 2000). Hence, comparison between the different techniques used must consider discrepancies in the experimental conditions and the different physical and thermodynamic constraints that may exist.

Pasting properties of starch have been investigated in various studies using a wide range of rheometers along with some other complementary techniques such as sedimentation studies, swelling and/or solubility studies as well as granule size distribution measurements of raw, partially and fully gelatinised starch granule (Carnali & Zhou, 1996; Ellis, Ring, & Whittam, 1989; Evans & Haisman, 1979; Genovese & Rao, 2003; Paterson, Hardacre, Li, & Rao, 2001; Rao, Okechukwu, & da Silva, 1997; Rao & Tattiyakul, 1999; Svegmark & Hermansson, 1993). The characteristic pasting properties of starch can be considered as the rheological response of a system containing mixtures of swollen and fragmented granules embedded in a continuous phase containing the solubilised macromolecular components that were leached out during gelatinisation (Carnali & Zhou, 1996; Doublier, 1987; Nunez-Santiago, Bello-Perez, & Tecante, 2004).

The unique rheological responses noted during starch gelatinisation can be attributed to the changes in starch granular sizes and their overall distributions, changes in the granules concentration (volume fraction of the granules as they swell), the granules deformability as a result of water penetration and the presence of solubilised starch macromolecules in the continuous phase (Carnali & Zhou, 1996; Ellis et al., 1989; Evans & Haisman, 1979; Genovese & Rao, 2003; Paterson et al., 2001; Rao et al., 1997; Rao & Tattiyakul, 1999; Svegmark & Hermansson, 1993). These hypotheses were deduced by comparing results obtained in separate studies of granule sedimentation, swelling characteristics and size distribution measurements and subsequently relating these results to the rheological properties (Carnali & Zhou, 1996; Ellis et al., 1989; Evans & Haisman, 1979; Genovese & Rao, 2003; Paterson et al., 2001; Rao et al., 1997; Rao & Tattiyakul, 1999; Svegmark & Hermansson, 1993).

The objective of this research is to study starch gelatinisation using rheological and direct observation of the starch granule characteristics under identical conditions (such as starch concentration, suspension medium, heating rate, shear). To achieve this it is necessary to use an instrument that combines rheological and microscopic imaging, such as the Rheoscope. Two Rheoscope experiments were performed to study the process of gelatinisation over a range of different starch types: (i) regular starches from different botanical sources, and (ii) maize starches with different amylose contents.

One of the main limitations during the measurements of starch rheological properties in Rheoscope is the rapid sedimentation of starch granules. Since the geometry of the equipment cannot be modified, it was decided to add hydrocolloids to the water used to suspend the granules to increase its viscosity to the point that settling does not occur. As hydrocolloids can affect starch gelatinisation (Christianson, Hodge, Osborne, & Detroy, 1981; Mandala & Bayas, 2004; Shi & BeMiller, 2002; Tester & Sommerville, 2003) it is necessary to use a type and level of hydrocolloid that has minimal effect on starch gelatinisation. To do this a series of three preliminary experiments were performed to evaluate the effect of hydrocolloids on: (i) starch pasting in the RVA, (ii) starch thermal transitions measured by Modulated Temperature DSC (MTDSC) and (iii) starch granule settling. Based on these preliminary results, the solution used to suspend the starch for the starch for the Rheoscope study was selected.

2. Experimental methods

2.1. Materials

A range of starches from different botanical origins were investigated in this study, namely waxy maize (0% amylose), maize starch (24% amylose), Gelose 50 maize (55% amylose) and Gelose 80 maize (85% amylose) (Penford Australia Ltd.), wheat starch (25% amylose, wheaten cornstarch, Penford Australia Ltd.), barley starch (15% amylose, Division of Plant Industries, CSIRO, Canberra). The amylose content was determined using a iodine binding technique (Morrison & Laignelet, 1983; Tan, 2006). The hydrocolloids used in this study were xanthan (Kingfood Australia Pty Ltd.), guar (Ace Gum Industries PVT Ltd.) and carboxy methyl cellulose (CMC, Hercules). All starches and gums used were food grade materials used without further preparation.

2.2. Rapid Visco Analyser measurements

The pasting properties of all starch samples were analysed in triplicates with a Rapid Visco Analyser RVA 4 controlled by Thermocline for Windows (version 2.2, Newport Scientific Pty Ltd., Warriewood, Australia). The RVA sample preparation procedure and heating profile have been given previously (Torley, Rutgers, D'Arcy, & Bhandari, 2004). The samples contained 3.00 g of starch and 25.00 g of water or the appropriate hydrocolloid solution.

The RVA pasting curve was analysed to determine a series of characteristic parameters of: initial viscosity (viscosity during 50 °C holding period); pasting temperature (temperature at which viscosity starts to increase); peak viscosity (maximum viscosity during heating to or hold at 95 °C); trough viscosity or holding strength (minimum viscosity after peak viscosity has been reached); final viscosity (viscosity at end of run).

2.3. Settling studies

The settling studies were performed according to the method described by Sajeev, Kailappan, Sreenarayanan, and Thangavel (2002). In the present instance, settling studies were performed in 100 ml measuring cylinders (25 mm diameter, 186 mm fill height) filled with 100 ml of a 5% suspension of starch in either water, or a 0.1% hydrocolloid solution. The height of starch accumulated at the bottom ("sediment height") was noted at different times. As the starch settled, a well defined interface between the top layer of almost clear water and increasingly concentrated starch suspension was formed and the position of this interface ("interface height") was noted. These tests were performed in duplicates.

2.4. Modulated Temperature Differential Scanning Calorimetry

Starch-solution concentrations of around 10% (i.e., 0.3 g of starch in 2.5 g of water or hydrocolloid solution) were selected for MTDSC studies to correspond to the concentrations used for RVA studies. The starch was mixed with the required amount of solvents and left to equilibrate overnight at room temperature. Test samples were carefully weighed (<20 mg) into aluminium pans and hermetically sealed.

A TA 2920 Modulated Temperature DSC (MTDSC; TA Instruments Inc, New Castle, Delaware, USA) was used to investigate the gelatinisation process. The scan intervals were 10–160 °C for all starches. A heating rate of 5 °C/min was chosen and the modulation was set at ±1 °C for every 60 s. These conditions were selected to minimize error that may results from incomplete modulation of the sample volume (Lai & Lii, 1999; Wunderlich, Boller, Okazaki, & Ishikiriyama, 1997). At least triplicate analyses were conducted for each starch-solution combination.

The Universal Analysis software was used to analyse the DSC to determine the onset (T_o), peak (T_p) and end temperatures (T_e) and enthalpy of the starch gelatinisation transition. In MTDSC the sample experiences a sinusoidal modulation (oscillation) overlaid on the conventional linear heating or cooling ramp, which provides the benefits of separating the total heat flow signal into its heat capacity (reversible thermal event) and kinetic components (irreversible event, in this case the gelatinisation process).

2.5. Rheoscope measurements

The pasting profiles of starch pastes were also measured using Rheoscope 1 (Thermo Haake, Karlsruhe, Germany), which combines a viscometer with an optical microscope and digital video camera. The microscope and camera are located integrated underneath the temperature controlled glass bottom plate of the viscometer. The Rheoscope was connected to a DC30 water bath, allowing for heating and cooling ramp of the test fluid during the measurements.

A 60 mm diameter parallel plate geometry was used. A gap size of 0.5 mm and a starch concentration of 2% were selected as the best compromise for image clarity and viscosity measurements. The shear rate applied in all measurements was 100 s^{-1}. Silicon oil was added around the sample to minimize water evaporation.

A 20 min temperature ramp profile to mimic the temperature profile used in RVA could not be obtained in the Rheoscope due to limitation of the water bath and allowable maximum temperature for the camera (90 °C). A temperature ramp profile as close as practical to the RVA profile was therefore employed in Rheoscope measurements, where the starch solutions were subjected to equilibration at 50 °C for 2 min, heated to 90 °C over a period of 14 min, held at 90 °C for 8 min, cooled back to 50 °C over 36 min and finally held at 50 °C for 4 min, giving a total of 64 min. All Rheoscope measurements were performed in duplicate.

The granule size (length and width) was measured during Rheoscope gelatinisation studies using a facility available in the Rhesocope software that allows measurement of object size. The size (in μm) was calculated by the software based on the number of pixels and microscope's magnification. The granules in a fixed area of the image were measured. The granules size at a particular time was the average of 20 granules measured per time point, with the sample including both small and large size granules. For one starch type, images from two Rheoscope gelatinisation runs were analysed and averaged.

The changes in B-type starch granule concentrations (small size granule), were observed from comparison of the proportion of small granules to large granules obtained from average granule size measurement (described above).

2.6. Experimental design

2.6.1. Preliminary experiments

Interactions between starch and other hydrocolloids can affect the pasting properties of the starch. Since the objective of this study is measure the relationship between viscosity and changes in the granule, it is necessary to use a type and level of hydrocolloid that has minimal effect on starch gelatinisation, while minimising granule settling during the initial stages of Rheoscope analysis. To do this a series of three preliminary experiments were performed to evaluate the effect of hydrocolloids on: (i) starch pasting in the RVA, (ii) starch thermal transitions measured by MTDSC and (iii) starch granule settling.

In the RVA study, the factors examined were hydrocolloid type (CMC, guar and xanthan), and level of hydrocolloid (0.1%, 0.2%, 0.3%, 0.4% and 0.5%) in the solution used to suspend the starch for RVA analysis. A water only control was performed. RVA analyses were performed in duplicate or triplicate, and the curves were analysed to determine initial, peak, trough, final, breakdown and setback viscosities. One starch type, regular maize starch, was used in this experiment.

The MTDSC study was performed in two parts. In the first part, the factors examined were hydrocolloid type (CMC, guar and xanthan), and level of hydrocolloid (0.1%, 0.3% and 0.5%) in the solution used to hydrate the starch for MTDSC analysis. A water only control was performed. MTDSC analyses were performed in triplicate, and the curves were analysed to determine starch thermal properties. One starch type, regular maize starch, was used in this experiment.

The second part of the MTDSC study was performed to determine the effect of a 0.1% guar solution on the gelatinisation of the starches used in subsequent Rheoscope studies. The initial RVA and MTDSC screening trials had been performed on a single starch type (regular maize starch) and it was possible that starches from different botanical sources or with higher or lower amylose content may respond differently. The factors examined were starch type (waxy maize, regular maize, Gelose 50, Gelose 80, barley and wheat) and the level of guar (0% and 0.1%) in the solution used to hydrate the starch for MTDSC analysis. MTDSC analyses were performed in triplicate, and the curves were analysed to determine starch thermal properties.

In the starch granule settling study, the factor examined was suspension medium (water, 0.1% CMC, 0.1% guar and 0.1% xanthan). Settling studies were performed in triplicate and the sediment height and interface height were recorded. One starch type, regular maize starch, was used in this experiment.

2.6.2. Rheoscope experiments

The objective of the Rheoscope study was to understand the relationship between viscosity changes during pasting and changes in granule characteristics. To do this, the Rheoscope component was divided into studies of the gelatinisation of: (i) regular starches from different botanical sources, and (ii) maize starches with different amylose contents.

The Rheoscope studies were performed in two parts. In the first, regular starches from different botanical sources (barley, 15% amylose; maize, 24% amylose; wheat, 25% amylose) suspended in 0.1% guar solution were analysed by Rheoscope. Rheoscope trials were performed in at least duplicate, and sample viscosity, temperature and digital images were recorded. The digital images were subsequently analysed to determine the dimensions of the starch granules at different times during the trial.

In the second part of the Rheoscope study, starches from a single botanical source (maize) but differing in their amylose content (0%, 24%, 55% and 85%) suspended in 0.1% guar solution were analysed by Rheoscope. Rheoscope trials were performed in triplicate, and sample viscosity, temperature and digital images were recorded.

3. Results and discussion

3.1. RVA – hydrocolloid effect on gelatinisation

The pasting properties of starch suspended in hydrocolloid solutions (xanthan, guar and CMC) at various levels of addition (0–0.5%) were investigated (Fig. 1; curves for 0.2%, 0.3% and 0.4% level of addition are omitted for clarity). The effect of hydrocolloid type and level on the pasting curve parameters were determined (Fig. 2).

The pasting curves parameters for maize starch suspended in a xanthan solutions were similar to maize starch suspended in water, and showed little change with increasing level of xanthan addition (Fig. 2). However, the pasting curves themselves showed differences in shape, particularly between the start of gelatinisation and peak viscosity (Fig. 1). This indicates that the effect of xanthan on the swelling behaviour of starch granules, and consequently the gelatinisation process, are influenced by the level of xanthan present.

The addition of guar and CMC results in more significant changes in the pasting characteristics of maize starch gelatinisation (Figs. 1 and 2). As shown in Fig. 2, increasing the concentration of guar leads to a general shift of the entire pasting curve to higher viscosities and the extent of this shift is proportional to the level of guar. While the time at which maize starch gelatinisation occurs in guar is similar for all concentration, the rate of the viscosity development at 0.4% and 0.5% guar are higher than the other guar concentrations. As anticipated, a general trend is visible in the RVA curve parameters (namely the initial, peak, trough and final viscosity) where the increase in these parameters is evidently proportional to the increase in guar concentration (Fig. 2).

The pasting curves for maize starch gelatinisation in the presence of CMC have a rather different shape from that of gelatinisation in water (Fig. 1). A slower increase in viscos-

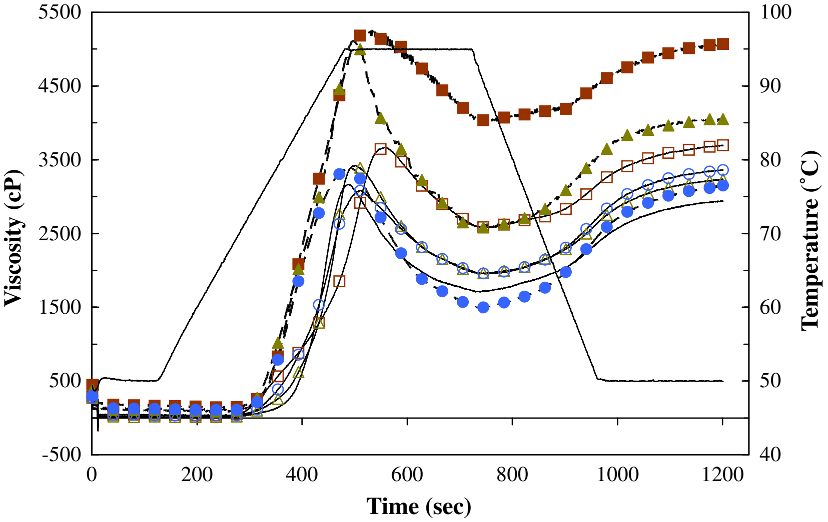

Fig. 1. The RVA pasting curves for normal maize starch suspended in water and suspended in xanthan, guar and CMC solutions at 0.1% and 0.5% level of addition. Legend: □, 0.1% CMC; ■, 0.5% CMC; △, 0.1% guar; ▲, 0.5% guar; ○, 0.1% xanthan; ●, 0.5% xanthan.

ity is noticeable with the addition of as little as 0.1% CMC, which is indicated by the delayed occurrence of the peak viscosity for all CMC concentrations. As with guar, a general shift in the entire pasting curves to higher viscosities is observed with the addition of CMC with an extent that is proportional the amount of CMC added.

The initial viscosity increased with increasing levels of all hydrocolloid, though CMC gave a higher initial viscosity compared to xanthan and guar (Fig. 2). The increase in the initial viscosity for systems containing xanthan and guar are practically comparable. Although this observation may suggest that the addition of hydrocolloid can increase the viscosity of the continuous phase, a further sedimentation study is required to confirm the ability of these hydrocolloids to minimise the sedimentation of starch granules.

An increase in the xanthan concentration from 0% to 0.5% lead to a notable increase in the initial viscosity, however there was no corresponding increase in peak, trough and final viscosities (Fig. 2). By contrast, increasing the concentration of guar and CMC increased the initial viscosity and also increased the peak, trough and final viscosities. This suggests that the variation in the RVA pasting parameters with the addition of guar and CMC is merely a consequence of the increase in the viscosity of the continuous phase with increasing guar or CMC concentration.

The rheological responses of starch during gelatinisation are affected by the presence of hydrocolloid in solution and the degree to which the starch pasting properties is affected varies according to the hydrocolloid type and concentration. Although the RVA pasting parameters are only slightly affected by the variation in the concentration of xanthan (Fig. 2), the shapes of their RVA pasting curves (Fig. 1) are quite different from the RVA curve for maize starch gelatinisation in water. This implies that the starch granules may swell differently in the presence of xanthan. Alternatively, the addition of guar and CMC, which results in a general shift of the entire pasting curves to higher viscosities and thus their RVA pasting parameters, suggests that these hydrocolloids do not exhibit any other substantial effects on the starch gelatinisation process other than increasing the viscosity of the continuous phase. The addition of CMC however, causes the slowing down of the increase in viscosity possibly due to the substantially higher solution viscosity and thus the peak viscosity was noted at later times for all CMC concentrations.

From comparisons of the results from these RVA studies, it was concluded that guar would be the best hydrocolloid to use in Rheoscope since it exerts the least effect on starch gelatinisation compared to xanthan and CMC. It appears that the use of any hydrocolloid type at a concentration of 0.1% is acceptable since their RVA pasting characteristics are not substantially altered compared to maize starch suspended in water only. Thermal analysis using Modulated Temperature DSC (MTDSC) will be used to confirm the magnitude of effect of hydrocolloid addition on starch gelatinisation and to explore the molecular basis for the observed changes in starch gelatinisation as shown in the RVA pasting curves.

3.2. MTDSC – hydrocolloid effect on gelatinisation

MTDSC allows the separation of the (total) heat flow signal into the heat capacity (reversible heat flow) and the kinetics components (non-reversible heat flow) (Lai & Lii, 1999; TA Instruments, 1996). The use of this technique allows determination of both reversible and non-reversible thermal transitions in a single experiment. These transitions are the ambiguously regarded glass transition (as indicated from the heat capacity change, evident from the reversible heat flow) and the gelatinisation endotherm (as discernible from the non-reversible heat flow).

Analysis of the non-reversible heat flow signal of MTDSC endotherm for normal maize starch gelatinisation

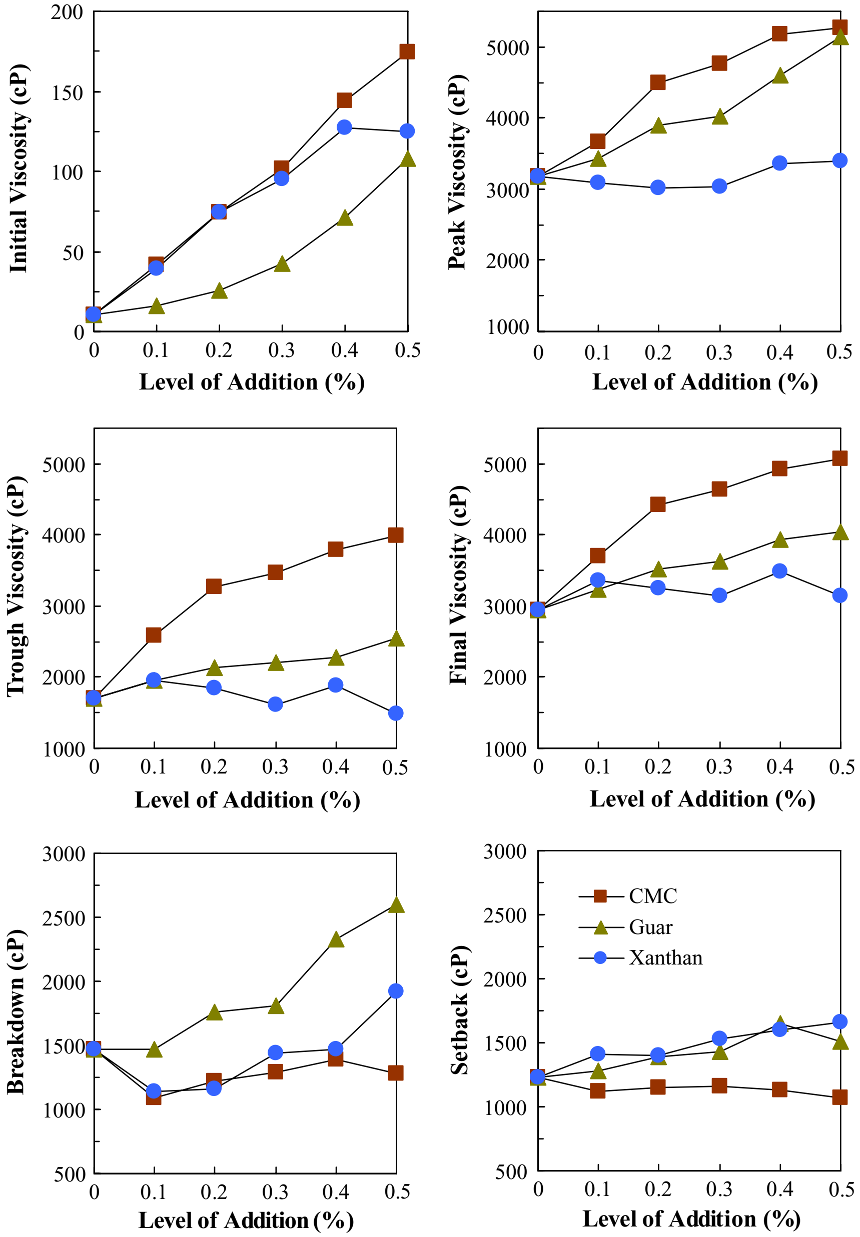

Fig. 2. Hydrocolloid type and level of addition effect on the RVA pasting characteristics of normal maize starch. Legend: ■, CMC; ▲, guar; ●, xanthan. Average standard deviation for each parameter was: 7.8 cP, initial; 62.5 cP, peak; 60.9 cP, trough; 49.1 cP, final; 51.1 cP, breakdown; 45.2 cP, setback.

in the presence of guar, xanthan or CMC did not reveal any significant variation in their gelatinisation transition and the glass transition temperatures (Table 1). The similarity in the gelatinisation onset temperature (T_o) implies that the observed increase in solvent viscosity due to addition of the hydrocolloids is not significant enough to alter the solvent ingress rate into the granules hence gelatinisation still proceed at the same temperature. The glass transition (T_g), is consistently detected within the gelatinisation endotherm in all systems containing the different hydrocolloid type and level of addition. As proposed previously (Tan, Wee, Sopade, & Halley, 2004), this indicates an order–disorder transition, with starch macromolecules going from being highly restrained within the granular packing to entangled macromolecules during the gelatinisation process.

The gelatinisation enthalpy is not significantly affected by the addition of all three hydrocolloids at 0.1% (Table 1), suggesting that the thermal energy involved during gelatinisation to break the structural element in starch granular packing is not substantially altered in the presence of 0.1% hydrocolloid. However, an appreciable increase in the gelatinisation enthalpy value was observed in systems containing 0.3% and 0.5% xanthan. By contrast, an increase in CMC and guar level of addition did not lead to considerable changes in the enthalpy values. The values

Table 1
The gelatinisation and glass transition temperatures, and enthalpy and heat capacity change observed for maize starch gelatinisation in water and in solutions containing different levels of guar, xanthan and CMC measured by MTDSC

Solution	Gum level (%)	Gelatinisation characteristics (non-reversible heat flow)				Step transition (reversible heat flow)	
		T_o (°C)[a]	T_p (°C)[a]	T_e (°C)[a]	ΔH (J/g starch)[b]	T_g (°C)[c]	ΔC_p (J/g °C)[d]
Water	0	58.05	63.89	71.88	11.028	65.02	0.411599
CMC	0.1	57.50	64.10	72.45	11.085	63.04	0.551062
	0.3	58.15	63.83	72.75	12.230	64.59	0.554784
	0.5	58.19	64.21	72.20	11.996	66.26	0.379254
Guar	0.1	57.72	64.08	74.69	11.363	62.60	0.467769
	0.3	57.97	64.11	73.14	11.062	63.51	0.449217
	0.5	57.49	64.09	72.93	11.450	61.84	0.514679
Xanthan	0.1	57.40	64.01	72.74	11.340	62.59	0.565912
	0.3	58.05	63.81	72.23	11.312	64.45	0.464121
	0.5	58.56	64.38	72.17	11.485	66.34	0.383206

[a] The maximum standard error for gelatinisation onset (T_o), peak (T_p) and end (T_e) temperatures analyses was 2.4%.
[b] The maximum standard error for gelatinisation enthalpy (ΔH) analysis was 6.7%.
[c] The maximum standard error for analysis of glass transition (T_g) temperature was 3.2%.
[d] The maximum standard error for specific heat capacity (ΔC_p) analysis was 11.9.

for heat capacity change (ΔC_p) on the other hand, demonstrate rather different trends. While the ΔC_p for the maize starch gelatinisation is not affected by the addition of guar, some slight variation in the ΔC_p values is observed with increasing xanthan and CMC level of addition. The reason for such variation is still unclear at present.

The MTDSC results indicate that guar has the least effect on the starch gelatinisation process, which is similar to the results of previous studies that also showed that low levels of added gums had a limited effect on starch gelatinisation (Biliaderis, Arvanitoyannis, Izydorczyk, & Prokopowich, 1997; Ferrero, Martino, & Zaritzky, 1996; Gonera & Cornillon, 2002). This confirms the RVA results which point towards guar as the best hydrocolloid to use in the Rheoscope study. Since these studies were only performed using only one type of starch (normal maize starch), further MTDSC tests were performed to investigate whether the addition of guar would have the same effect on the gelatinisation of starches from different botanical sources. The thermal characteristics for the different starches are not affected by gelatinisation in a 0.1% guar solution (Table 2). This indicates that the use of 0.1% guar in the Rheoscope study generally has little effect on the gelatinisation of starch from different plant species and plant varieties. The gelatinisation temperature of the starches is similar to an earlier study DSC studies of maize starches at high moisture content, which show a 15–17 °C increase in T_p as the amylose increased from 0% to 70% (Matveev et al., 2001). A further settling study is required to ensure that the addition of guar is sufficient to minimise the rapid

Table 2
The gelatinisation thermal characteristics and the step transition for starches from different botanical origin as measured by MTDSC

Botanical source	Guar content (%)	Gelatinisation characteristics (non-reversible heat flow)				Step transition (reversible heat flow)	
		T_o (°C)[a]	T_p (°C)[a]	T_e (°C)[a]	ΔH (J/g starch)[b]	T_g (°C)[c]	ΔC_p (J/g°C)[d]
Barley	0.0	48.6	54.9	63.6	7.17	53.6	0.44
	0.1	48.2	55.3	64.8	7.49	52.7	0.37
Wheat	0.0	51.5	57.9	67.2	7.99	58.4	0.33
	0.1	49.7	57.2	67.7	7.47	59.5	0.33
Waxy maize	0.0	60.8	67.7	75.9	13.27	66.5	0.49
(0% amylose)	0.1	60.8	67.7	78.4	13.03	66.4	0.48
Regular maize	0.0	57.6	65.3	73.9	11.24	63.8	0.34
(24% amylose)	0.1	58.0	65.4	76.5	11.04	63.0	0.33
Gelose 50 maize	0.0	64.9	81.7	96.1	22.50	70.8	0.38
(55% amylose)	0.1	65.6	83.2	95.4	21.67	74.7	0.38
Gelose 80 maize	0.0	65.4	81.6	89.4	14.22	70.5	0.24
(85% amylose)	0.1	65.3	79.1	92.4	13.99	83.9	0.25

[a] The maximum standard error for gelatinisation onset (T_o), peak (T_p) and end (T_e) temperatures analyses was 3.6%.
[b] The maximum standard error for gelatinisation enthalpy (ΔH) analysis was 9.9%.
[c] The maximum standard error for analysis of glass transition (T_g) temperature was 3.9%.
[d] The maximum standard error for ΔC_p analysis was 7.7%.

sedimentation of starch granules during the entire gelatinisation process.

3.3. Hydrocolloid effect on starch settling

Fig. 3 shows that a 0.1% solution of the three hydrocolloids reduced the rate of starch settling compared to starch in water. Xanthan and CMC hinder starch settling to the greatest extent. In xanthan and CMC sediment accumulation was only noted after 90 min, compared to 5 min for water and 10 min for guar. The rapid settling of starch granules in water is indicated by the rapid decrease in the interface height with respect to time (0.25 mm/min). The addition of 0.1% hydrocolloid caused the interface height to descent at a slower rate, with 0.1% CMC reducing the interface settling rate the most, (0.028 mm/min) followed by 0.1% xanthan (0.062 mm/min) and 0.1% guar (0.086 mm/min). These results suggest that CMC can minimise the rapid sedimentation of starch granules most effectively as compared to the other hydrocolloids.

3.4. Rheoscope studies

Amongst the three hydrocolloids studies, guar exerts the minimum effect on starch gelatinisation, while CMC is the most effective at reducing starch settling. While guar did not reduce the starch settling as effectively as CMC or xanthan, it was the preferred to use in the Rheoscope studies since it has the least effect on starch gelatinisation, while giving a high enough viscosity to limit starch settling during the first 10 min. After this time the sample temperature has increased enough to start starch gelatinisation, causing a large increase in viscosity. Preliminary trials demonstrated that a combination of the 0.1% guar, and the Rheoscope shear rate selected (100 s^{-1}) was sufficient to avoid starch settling throughout the entire gelatinisation process.

3.4.1. Combined rheological and microscopic measurements

The viscosity profiles for the gelatinisation of starches from different varieties in 0.1% guar solution are illustrated in Fig. 4. The trend in viscosity profile during starch gela-

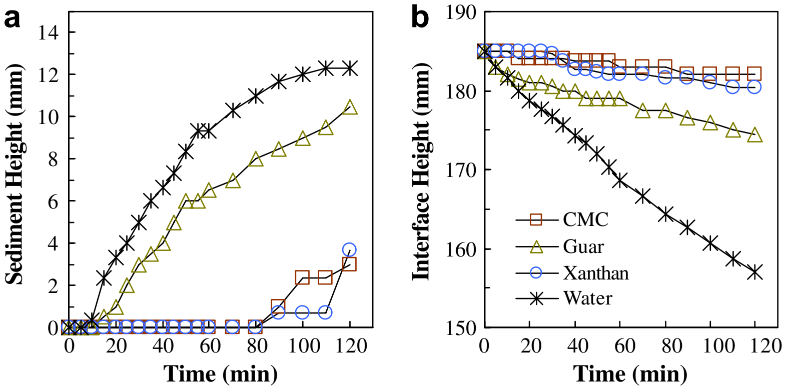

Fig. 3. The (a) sediment height and (b) interface height observed during a settling study of regular maize starch suspended in water, 0.1% xanthan, 0.1% guar and 0.1% CMC solutions.

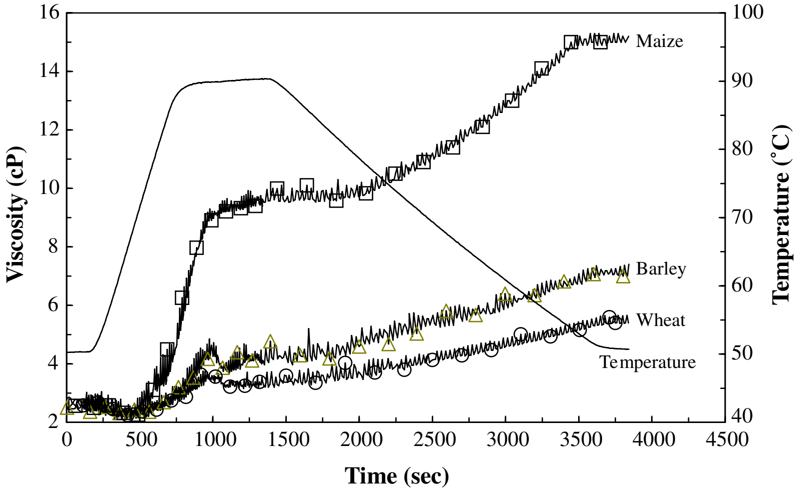

Fig. 4. Viscosity profile for starch gelatinisation in 0.1% guar solution for maize (□), wheat (○) and barley (△) starches. To improve clarity, every 20th symbol is plotted.

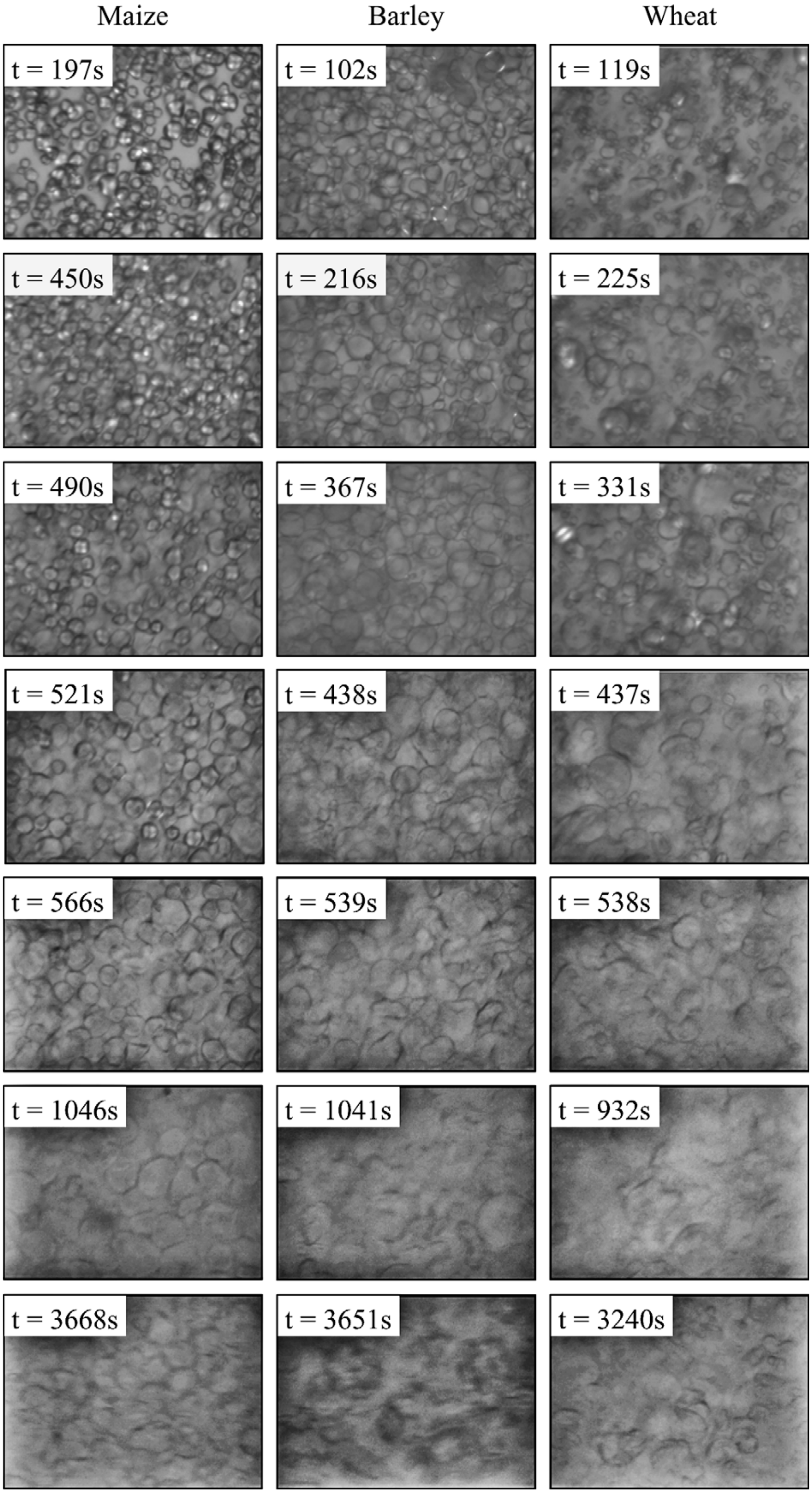

Fig. 5. Images of the gelatinisation of maize, barley and wheat starch in 0.1% guar solution captured during the gelatinisation in the Rheoscope. See Fig. 4 for details of the viscosity changes and temperature profile.

tinisation is in general similar to that observed with the RVA, where viscosity development is noted during the initial temperature ramp. However, no significant breakdown is observed in the Rheoscope viscosity profiles and the final viscosity is much higher than the peak viscosity value. This is possibly attributed to the lower concentration of starch in Rheoscope studies (2% compared to 10% in RVA) and the absence of severe shear caused by the RVA impeller. Maize starch exhibits the highest viscosity during the gelatinisation process and its viscosity develops at a faster rate when compared to those in barley and wheat starches (Fig. 4).

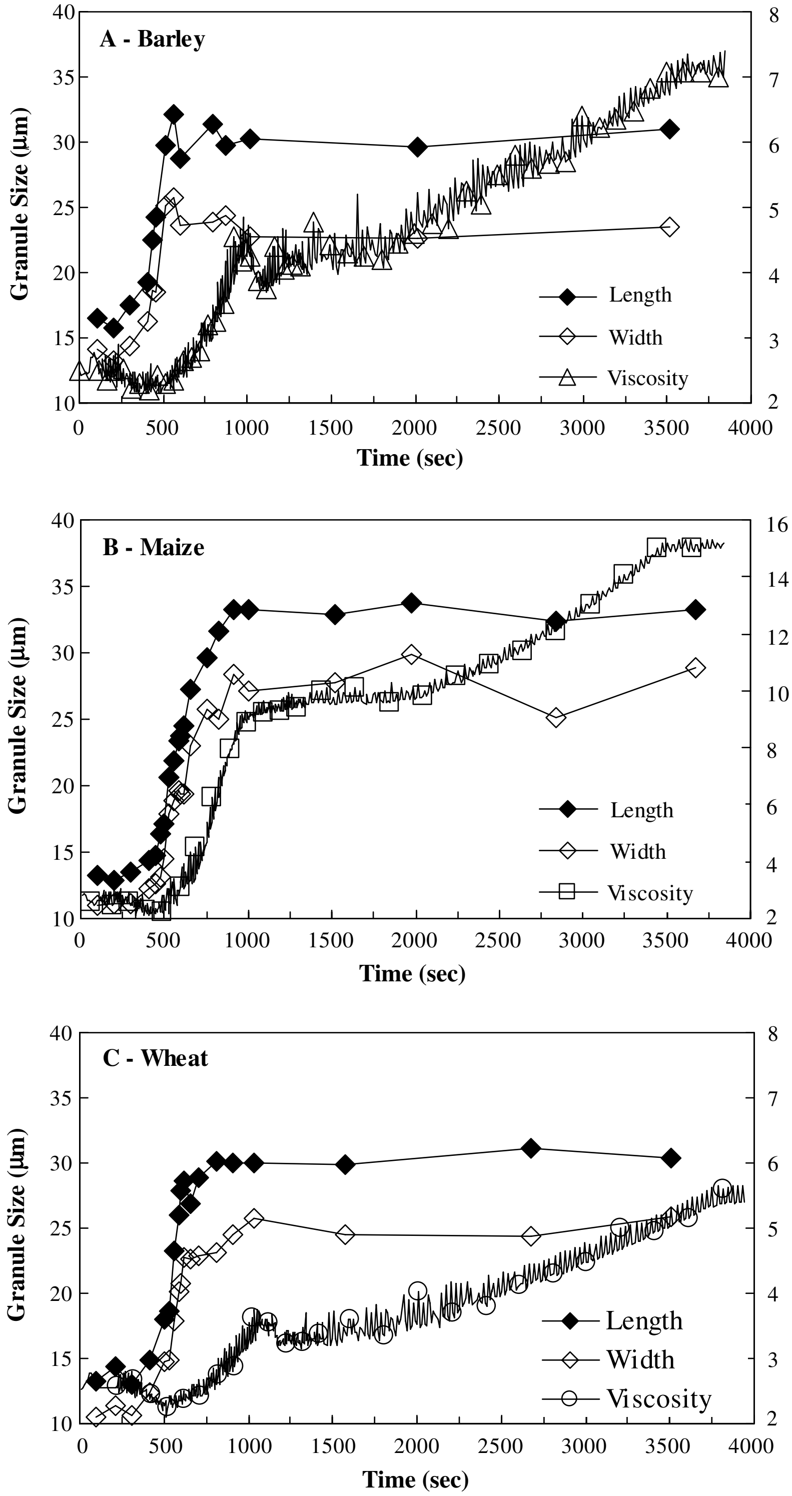

Fig. 6. The change in average granule size with time during the gelatinisation of (A) barley, (B) maize and (C) wheat starch in 0.1% guar solution. To improve clarity of the viscosity curves, every 20th symbol is plotted.

Fig. 5 shows the images of barley, maize and wheat starch granules captured at different time during the gelatinisation process. As the maize starch granules were heated, the Maltese cross of some granules began to disappear at the pasting temperature which was around 70 °C for all starches. The maize starch granules began to swell as water penetrated into the granules with further heating to 90 °C. It was noted that the larger granules began to swell earlier than the smaller granules. A rapid increase in the viscosity was observed alongside with the granule swelling, reaching a constant value as the starch–hydrocolloid solution mixtures was held at 90 °C for 8 min. A further increase in viscosity was observed as the gelatinised starch–hydrocolloid solution mixture was cooled down to 50 °C.

Barley and wheat starch showed a similar pattern of changes in appearance and viscosity. Granule swelling (particularly the larger granules) in barley and wheat starches was observed at lower temperature (around 60 °C), resulting in more deformable granules as indicated by the slight reduction in their viscosity at circa 350 s. As the temperature was further increased, the granules (both the larger and smaller size granules) continued to swell and the viscosity began to increase to maximum value at about 90 °C. The occurrence of a smaller granule population is evident in both wheat and barley starches, and the smaller granules from both wheat and barley apparently swell at higher temperature than the larger granules. The lower viscosity development in wheat starch compared to that in barley starch may be due to the presence of a larger proportion of small granules (usually termed B-type granules) in wheat starch.

Visual comparison between the granules images and viscosity profiles (Figs. 4 and 5) suggests that the observed viscosity development during heating is apparently attributable to the increase in starch granules size as a result of swelling. In addition to the granular swelling, starch granules generally changes from rigid granules to more deformable granules due to water penetrating during swelling. Since no observable changes in the granules were noted during the holding period at 90 °C and the cooling down period, the viscosity increase observed during the cooling down period is therefore attributable to the temperature dependence of viscosity.

3.4.2. Change in granule dimensions

The average size of starch granules at different times of gelatinisation was measured from these images in order to follow the changes in granule size with time (Fig. 6). As anticipated, a general increase in the average size of starch granules was observed along with the viscosity development although different rate of granular swelling is visible between the different starches. An approximately two to threefold increase in the average granule size was noted as a result of the granular swelling.

While maize starch granules swelled at a rate that was comparable to the rate of viscosity development, the rate of granular swelling for barley and wheat starches apparently did not follow the same rate as the viscosity development. Since maize starch granules consist of only one size population, the similarity between the rate of granular swelling and the rate of viscosity development for maize starch was anticipated. The notable difference between the apparent rate of granular swelling and the rate of viscosity development for barley and wheat starches can be attributed to the presence of a population of smaller granules (usually termed B-type granules, whose presence was determined from Rheoscope images) in these starches and the observation that these smaller granules only begin to swell at higher temperature. Hence, although the barley and wheat starch granules apparently swelled as much as the maize starch granules, a smaller increase in viscosity was observed due to the packing of the smaller granules

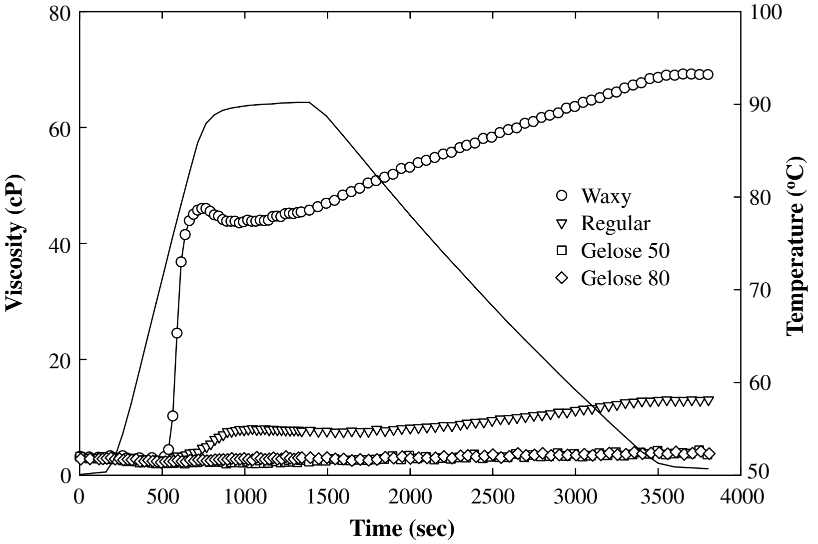

Fig. 7. Viscosity changes during the gelatinisation of maize starches with different amylose contents suspended in 0.1% guar solution.

between the interstices of larger granules reducing the overall effect of granular swelling on the viscosity development.

The variation in the rheological responses during starch gelatinisation between the different starches can thus be explained by considering the starch–guar solution as suspensions containing mixtures of swollen granules dispersed in continuous phase (composed of 0.1% guar solution and solubilised amylose). It is generally accepted that the viscosity of a suspension is strongly affected by the particle size distribution and when particles of two differing sizes are mixed, the viscosity is much lower than that for suspensions containing the same volume fraction of mono-sized particles (Larson, 1999). As indicated earlier, while maize starch granules consist of one size population, the occurrence of a population of smaller granules (B-type granules) is noted in both barley and wheat starches. The lower viscosity development observed in barley and wheat starches is therefore consistent with the trend observed generally

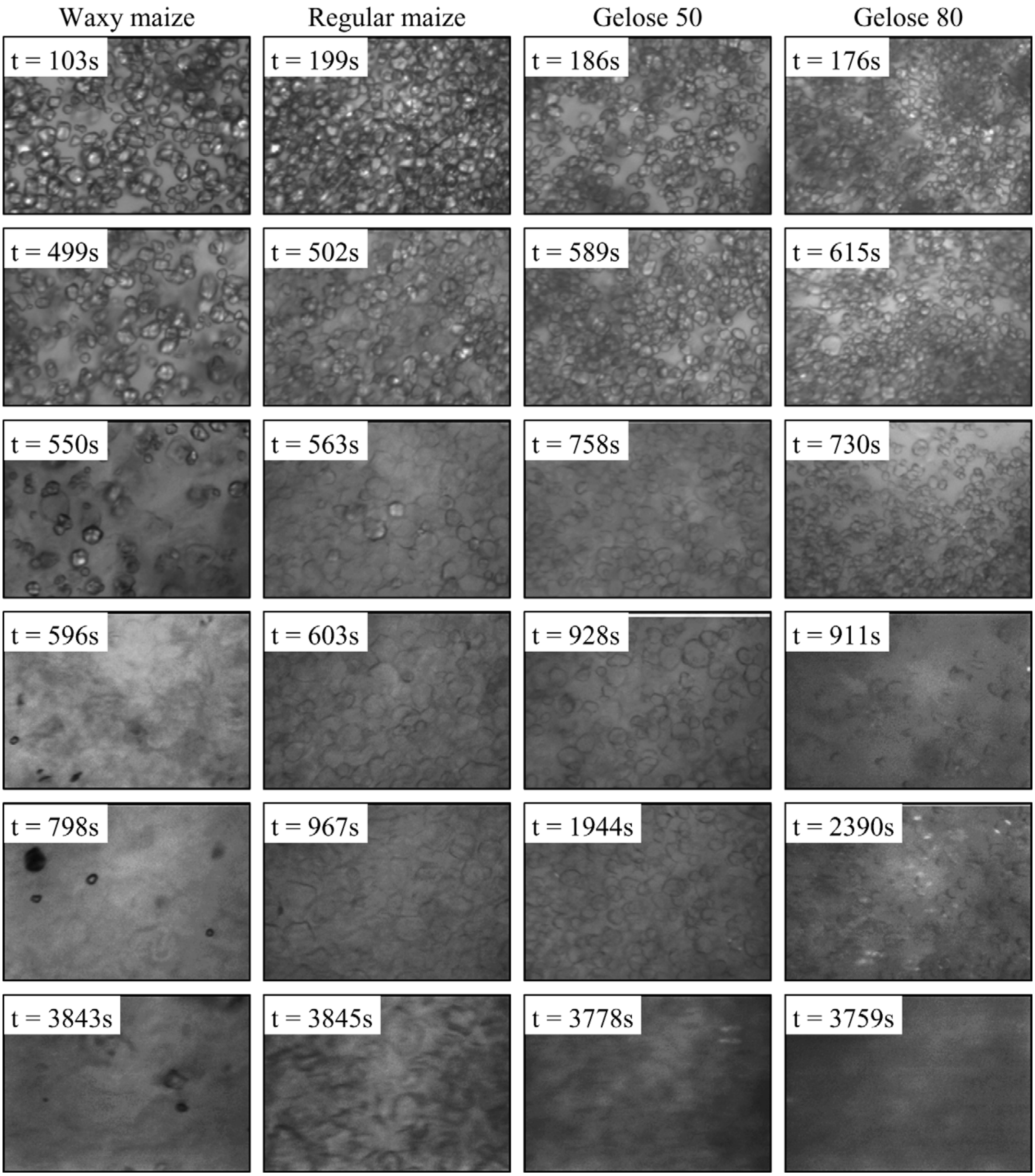

Fig. 8. Changes in the appearance of maize starch granules with different amylose contents during the gelatinisation in a 0.1% guar solution. See Fig. 7 for details of the viscosity changes and temperature profile.

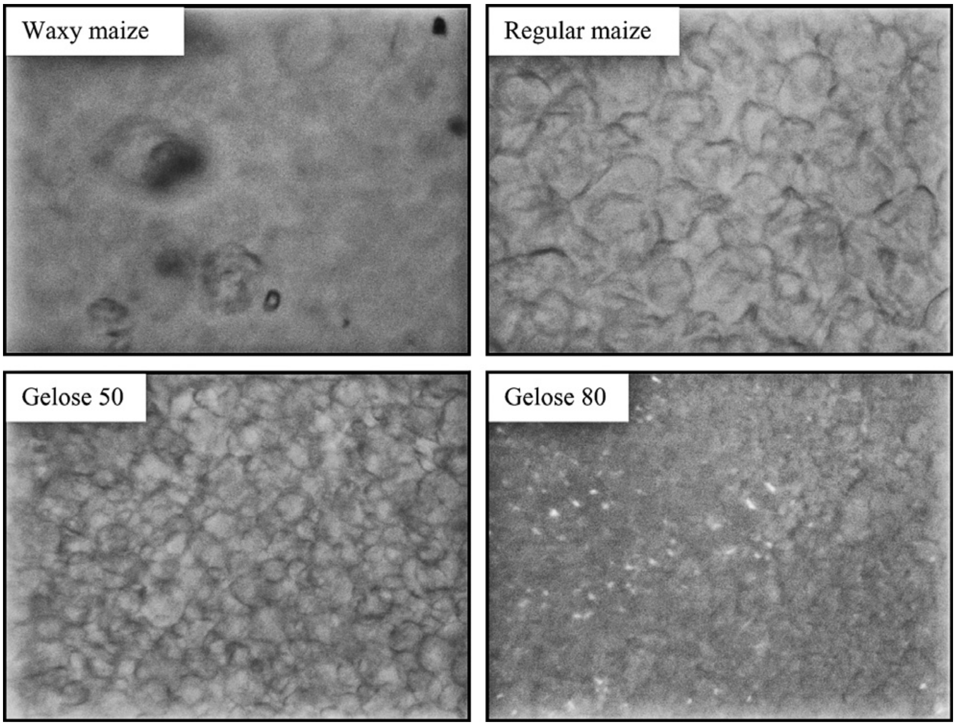

Fig. 9. Images of the resulting pastes as obtained at the end of starch gelatinisation for maize starches.

for suspensions and is a consequence of the packing of smaller granules into the interstices between the larger granules, known as the Farris effect (Larson, 1999).

3.5. Gelatinisation of starch with different amylose contents

It should also be noted that although the starch granule size distribution is an important factor in determining the starch rheological properties during gelatinisation, the ability of starch granules to swell also plays a significant role in dictating the rheological responses. This is demonstrated by comparison of the gelatinisation of maize starches with differing amylose content (0–85% amylose) (Fig. 7).

Substantial differences are noted in the viscosity profiles of maize starches with different amylose content (Fig. 7). The waxy starch exhibits the highest viscosity development and its viscosity increases most rapidly when compared to the other starches. By contrast, the high amylose maize starches do not show notable viscosity development throughout the gelatinisation process.

From comparisons of the granules images (Fig. 8), it was found that while the waxy and regular maize starch granules swelled as the Maltese cross began to disappear; the disappearance of Maltese cross in the granules of high amylose maize starches was not accompanied by the granular swelling. Hence, it is evident that the ability of starch granules to swell has a significant influence on the viscosity development. Granular swelling was not observed during gelatinisation of the high amylose starches (Gelose 50 and Gelose 80) and thus explains the lack of viscosity development in these starches. By contrast, the granules of waxy maize starch swelled substantially during the gelatinisation process, which accounted for the observed viscosity development.

The occurrence of swollen granules (also commonly known as the ghost remnants) is evident in starch pastes analysed at the end of the starch gelatinisation process (Fig. 9). The ghost remnants in gelatinised waxy starch pastes are not as obvious as those observed in regular maize starch although the reason behind such differences is still not clear at present. The granule ghosts in gelatinised high amylose starches (Gelose 50 and Gelose 80) are generally smaller in size, confirming the lack of swelling during their gelatinisation. The gelatinisation of Gelose 80 result in a more opaque paste, possibly due to the higher amylose content in Gelose 80 and hence more amylose is leached out during the gelatinisation process.

4. Conclusion

This study has demonstrated that the problem of rapid sedimentation of starch granules in Rheoscope can be successfully avoided throughout the entire gelatinisation process with minimal effect on starch gelatinisation by adding 0.1% guar. Hence, a reliable characterisation of the rheological responses of starch during gelatinisation can be obtained with the Rheoscope, which allows the simultaneous optical measurement in addition to the rheological measurement during the temperature. It was deduced that the rheological responses during starch gelatinisation can be attributed to the changes in starch granules as a result of swelling. A two to threefold increase in the size of starch granules is noted during the granular swelling for most starches except for high amylose maize starches. Additionally, the penetration of water also causes starch granules to change from rigid granules to more deformable granules. The viscosity development observed during the gelatinisation is also affected by the presence of a population of small granules (B-type granules) where the presence of significant amount of B-type granules reduces the overall viscosity increase. This consequently suggests the importance of starch granules size and their distribution in determining the rheological responses of starch during gelatinisation. In addition to the size distribution of starch granules, the swelling ability of the granules also plays a significant role in dictating starch rheological responses during gelatinisation.

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References

Biliaderis, C. G., Arvanitoyannis, I., Izydorczyk, M. S., & Prokopowich, D. J. (1997). Effect of hydrocolloids on gelatinization and structure formation in concentrated waxy maize and wheat starch gels. *Starch-Starke, 49*(7–8), 278–283.

Biliaderis, C. G., Maurice, T. J., & Vose, J. R. (1980). Starch gelatinization phenomena studied by differential scanning calorimetry. *Journal of Food Science, 45*(6), 1669–1670, 1680.

Bocharnikova, I., Wasserman, L. A., Krivandin, A. V., Fornal, J., Blaszczak, W., Schiraldi, V. Y., et al. (2003). Structure and thermodynamic melting parameters of wheat starches with different amylose content. *Journal of Thermal Analysis and Calorimetry, 74*(3), 681–695.

Cameron, R. E., & Donald, A. M. (1992). A small-angle X-ray scattering study of the annealing and gelatinization of starch. *Polymer, 33*(12), 2628–2635.

Cameron, R. E., & Donald, A. M. (1993). A small-angle X-ray scattering study of starch gelatinization in excess and limiting water. *Journal of Polymer Science: Part B: Polymer Physics, 31*(9), 1197–1203.

Carnali, J. O., & Zhou, Y. (1996). An examination of the composite model for starch gels. *Journal of Rheology, 40*(2), 221–234.

Christianson, D. D., Hodge, J. E., Osborne, D., & Detroy, W. (1981). Gelatinization of wheat starch as modified by xanthan gum, guar gum and cellulose gum. *Cereal Chemistry, 58*(6), 513–517.

Conde-Petit, B., Nuessli, J., Handschin, S., & Escher, F. (1998). Comparative characterisation of aqueous starch dispersions by light microscopy, rheometry and iodine binding behaviour. *Starch-Starke, 50*(5), 184–192.

Cooke, D., & Gidley, M. J. (1992). Loss of crystalline and molecular order during starch gelatinisation: Origin of the enthalpic transition. *Carbohydrate Research, 227*, 103–112.

Crochet, P., Beauxis-Lagrave, T., Noel, T. R., Parker, R., & Ring, S. G. (2005). Starch crystal solubility and starch granule gelatinisation. *Carbohydrate Research, 340*(1), 107–113.

Derby, R. I., Miller, B. S., Miller, B. R., & Trimbo, H. B. (1975). Visual observation of wheat–starch gelatinization in limited water systems. *Cereal Chemistry, 52*(5), 702–713.

Donovan, J. W. (1979). Phase transitions of the starch–water system. *Biopolymers, 18*(2), 263–275.

Doublier, J. L. (1987). A rheological comparison of wheat, maize, faba bean and smooth pea starches. *Journal of Cereal Science, 5*(3), 247–262.

Ellis, H. S., Ring, S. G., & Whittam, M. A. (1989). A comparison of the viscous behaviour of wheat and maize starch pastes. *Journal of Cereal Science, 10*(3), 33–44.

Evans, I. D., & Haisman, D. R. (1979). Rheology of gelatinised starch suspensions. *Journal of Texture Studies, 10*(4), 347–370.

Ferrero, C., Martino, M. N., & Zaritzky, N. E. (1996). Effect of hydrocolloids on starch thermal transitions, as measured by DSC. *Journal of Thermal Analysis, 47*(5), 1247–1266.

Fredriksson, H., Silverio, J., Andersson, R., Eliasson, A. C., & Aman, P. (1998). The influence of amylose and amylopectin characteristics on gelatinisation and retrogradation properties of different starches. *Carbohydrate Polymers, 35*(3–4), 119–134.

Genovese, D. B., & Rao, M. A. (2003). Role of starch granule characteristics (volume fraction, rigidity, and fractal dimension) on rheology of starch dispersions with and without amylose. *Cereal Chemistry, 80*(3), 350–355.

Gonera, A., & Cornillon, P. (2002). Gelatinization of starch/gum/sugar systems studied by using DSC, NMR, and CSLM. *Starch-Starke, 54*(11), 508–516.

Jay-Lin, J., & Chen, J. F. (1992). Effect of amylose molecular size and amylopectin branch chain length on paste properties of starch. *Cereal Chemistry, 69*(1), 60–65.

Jenkins, P. J., & Donald, A. M. (1998). Gelatinisation of starch: A combined SAXS/WAXS/DSC and SANS study. *Carbohydrate Research, 308*(1–2), 133–147.

Lai, V. M. F., & Lii, C. Y. (1999). Effects of modulated differential scanning calorimetry (MDSC) variables on thermodynamic and kinetic characteristics during gelatinisation of waxy rice starch. *Cereal Chemistry, 76*(4), 519–525.

Larson, R. G. (1999). *The structure and rheology of complex fluids*. New York: Oxford University Press.

Lelievre, J. (1973). Starch gelatinisation. *Journal of Applied Polymer Science, 18*, 293–296.

Lii, C. Y., Tsai, M., & Tseng, K. H. (1996). Effect of amylose content on the rheological property of rice starch. *Cereal Chemistry, 73*(4), 415–420.

Liu, H., Lelievre, J., & Ayoung-Chee, W. (1991). A study of starch gelatinization using differential scanning calorimetry, X-ray, and birefringence measurements. *Carbohydrate Research, 210*(1), 79–87.

Liu, Q., Charlet, G., Yelle, S., & Arul, J. (2002). Phase transition in potato starch–water system: I. Starch gelatinisation at high moisture level. *Food Research International, 35*(4), 397–407.

Mandala, I. G., & Bayas, E. (2004). Xanthan effect on swelling, solubility and viscosity of wheat starch dispersions. *Food Hydrocolloids, 18*(2), 191–201.

Matveev, Y. I., van Soest, J. J. G., Nieman, C., Wasserman, L. A., Prosterov, V. A., Ezernitskaja, M., et al. (2001). The relationship between thermodynamic and structural properties of low and high amylose maize starches. *Carbohydrate Polymers, 44*(2), 151–160.

McPherson, A. E., & Jane, J. (1999). Comparison of waxy potato with other root and tuber starches. *Carbohydrate Polymers, 40*(1), 57–70.

Morrison, W. R., & Laignelet, B. (1983). An improved colorimetric procedure for determining apparent and total amylose content in cereal and other starches. *Journal of Cereal Science, 1*(1), 9–20.

Nunez-Santiago, M. C., Bello-Perez, L. A., & Tecante, A. (2004). Swelling-solubility characteristics, granule size distribution and rheological behavior of banana (*Musa paradisiaca*) starch. *Carbohydrate Polymers, 56*(1), 65–75.

Paterson, J. L., Hardacre, A., Li, P., & Rao, M. A. (2001). Rheology and granule size distributions of corn starch dispersions from two genotypes and grown in four regions. *Food Hydrocolloids, 15*(4–6), 453–459.

Rao, M. A., Okechukwu, P. E., & da Silva, P. M. S. (1997). Rheological behavior of heated starch dispersions in excess water: Role of starch granule. *Carbohydrate Polymers, 33*(4), 273–283.

Rao, M. A., & Tattiyakul, J. (1999). Granule size and rheological behavior of heated tapioca starch dispersions. *Carbohydrate Polymers, 38*(2), 123–132.

Sajeev, M. S., Kailappan, R., Sreenarayanan, V. V., & Thangavel, K. (2002). Kinetics of gravity settling of cassava starch in its aqueous suspension. *Biosystems Engineering, 83*(3), 327–337.

Schuster, K. C., Ehmoser, H., Gapes, J. R., & Lendl, B. (2000). On-line FT-Raman spectroscopic monitoring of starch gelatinisation and enzyme catalysed starch hydrolysis. *Vibrational Spectroscopy, 22*(1-2), 181–190.

Shi, X., & BeMiller, J. N. (2002). Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate Polymers, 50*(1), 7–18.

Svegmark, K., & Hermansson, A. M. (1993). Microstructure and rheological properties of composites of potato starch granules and amylose: A comparison of observed and predicted structures. *Food Structure, 12*(2), 181–193.

TA Instruments. (1996). DSC 2920 *Operator's manual* (pp. C1–C76). New Castle, Delaware, USA: TA Instruments.

Tan, I. (2006). *Characterisation of novel starch materials: Structure–functionality relationship*. Brisbane, Australia, The University of Queensland. PhD.

Tan, I., Wee, C. C., Sopade, P. A., & Halley, P. J. (2004). Investigation of the starch gelatinisation phenomena in water–glycerol systems: Application of modulated temperature differential scanning calorimetry. *Carbohydrate Polymers, 58*(2), 191–204.

Tester, R. F., & Morrison, W. R. (1990). Swelling and gelatinisation of cereal starches. II. Waxy rice starches.. *Cereal Chemistry, 67*(6), 558–563.

Tester, R. F., & Sommerville, M. D. (2003). The effects of non-starch polysaccharides on the extent of gelatinisation, swelling and a-amylase hydrolysis of maize and wheat starches. *Food Hydrocolloids, 17*(1), 41–54.

Torley, P. J., Rutgers, R. P. G., D'Arcy, B., & Bhandari, B. R. (2004). Effect of honey types and concentration on starch gelatinization. *Lebensmittel Wissenschaft und Technologie, 37*(2), 161–170.

Tsai, M., Li, C. F., & Lii, C. Y. (1997). Effects of granular structures on the pasting behaviors of starches. *Cereal Chemistry, 74*(6), 750–757.

Waigh, T. A., Gidley, M. J., Komanshek, B. U., & Donald, A. M. (2000). The phase transformations in starch during gelatinisation: A liquid crystalline approach. *Carbohydrate Research, 328*(2), 165–176.

Wootton, M., & Bamunuarachchi, A. (1979). Application of differential scanning calorimetry to starch gelatinisation: III. Effect of sucrose and sodium chloride.. *Starch-Starke, 32*(4), 126–129.

Wunderlich, B., Boller, A., Okazaki, I., & Ishikiriyama, K. (1997). Heat capacity determination by temperature-modulated DSC and its separation from transition effects. *Thermochimica Acta, 305*, 125–136.

Yuryev, V. P., Kalistratova, E. N., van Soest, J. J. G., & Nieman, C. (1998). Thermodynamic properties of barley starches with different amylose content. *Starch-Starke, 50*(11–12), 463–466.

Zeng, M., Morris, C. F., Batey, I. L., & Wrigley, C. W. (1997). Sources of variation for starch gelatinization, pasting, and gelation properties in wheat. *Cereal Chemistry, 74*(1), 63–71.