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Influence of xanthan transition on the rheological properties of waxy starches

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ABSTRACT

The effects of xanthan gum on the properties of waxy starch systems were investigated with a particular focus on the conformational transition of xanthan. Different types of starches were used in this setup: maize, potato, chemically modified maize and rice. Under dilute conditions, xanthan gum and its transition did not affect the gelatinization of the starches. However, significant effects on the pasting behavior were observed, where the xanthan transition caused a significant reduction of the viscosity. It was demonstrated that xanthan can limit the breakdown of sensitive starch granules and that this effect might be enhanced by the xanthan transition. Flow curves of the cooled pastes showed that granule integrity is a prerequisite for optimal xanthan functionality, but the granule stabilizing effect of xanthan was too limited under these pasting conditions to significantly influence the flow behavior.

1. Introduction

Combinations of starch and non-starch hydrocolloids have been studied extensively in literature. Food gums prove to be very useful additives when combined with starches. In many cases they act synergistically and the gums are known to improve the rheological properties and stability of many starch based systems like sauces and dressings (Arocas, Sanz, & Fisman, 2009; Dolz, Hernandez, & Delegido, 2006; Heyman, Depypere, Delbaere, & Dewettinck, 2010; Sikora, Badrie, Deisingh, & Kowalski, 2008). Moreover the suggestion is made that gums can compensate the shortcomings of native starches, hence reducing the need for chemically modified starches (BeMiller, 2011). One particular hydrocolloid of great interest is xanthan gum. This extracellular polysaccharide is produced by fermentation of *Xanthomonas campestris*. Xanthan consists of 1,4-linked β-D-glucose residues having a trisaccharide side chain attached to O-3 of alternate D-glucosyl residues. The side chains are (3 → 1)-α-linked D-mannopyranose, (4 → 1)-β-D-mannopyranose and (2 → 1)-β-D-glucuronic acid, which account for the anionic properties of xanthan gum. Compared to other polysaccharides, the shear-thinning behavior of xanthan gum is much more extreme, exhibiting high viscosities at low shear rates and very low viscosities at high shear. This unique flow behavior enhances sensory qualities in food products and guarantees easy mixing, pumping and pouring of otherwise viscous liquids. Its low-shear viscosity enables its use as a stabilizer for colloidal suspensions. Although xanthan solutions exhibit weak gel-like properties at low shear rates, they do not form true gels at any concentration or temperature (Imeson, 2010). These advantages are responsible for its wide use in the food industry.

In the presence of salt and at low temperatures, xanthan molecules in solution adopt an ordered conformation where the side chains are folded-down and associated with the backbone by non-covalent interactions. Its high rigidity compared to other polysaccharides is the basis for the distinct rheological behavior and consequently the commercial value of xanthan. This secondary structure shows a temperature induced transition T_m, to a disordered structure, where the side chains project away from the backbone. This temperature is dependent on the ionic strength of the solution, the nature of the electrolyte, the pH, depending less on acetyl and pyruvate acetal contents (Capron, Brigand, & Muller, 1997; Capron, Brigand, et al., 1998; Milas & Rinaudo, 1986). The temperature and ionic strength induced transitions in xanthan from an ordered to disordered structure are well documented but the nature of the secondary structure is still a subject to debate. Some authors claim the existence of two different ordered states: native and renatured. The native form is the conformation under which it appears in the unpasteurized fermentation broth. Renatured xanthan is obtained after heating above the transition temperature and subsequent cooling of native or already renatured xanthan. The distinction between the native and renatured

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conformation is important since commercially available xanthan gum is often heat treated and thus sold under its renatured form (Choppe, Puaud, Nicolai, & Benyahia, 2010). The details of its ordered conformations, as well as the number of chains involved have been discussed by many authors but still remain controversial. There is some general agreement that the ordered structures are helical whereas the disordered structure can be described as a broken or imperfect helices (Camesano & Wilkinson, 2001; Capron et al., 1997; Capron, Alexandre, et al., 1998; Katzbauer, 1998; Li, Rief, Oesterhelt, & Gaub, 1999; Liu, Sato, Norisuye, & Fujita, 1987; Matsuda, Biyajima, & Sato, 2009)

A lot of differing effects of hydrocolloids on starch based systems are described in literature. As pointed out by BeMiller (2011), hydrocolloids strongly vary in structure and consequently also their functionality. Furthermore, starches originating from different botanical sources, also show distinct structural characteristics. This natural variability combined with differences in preparation methods makes it hard to draw general conclusions. Particularly regarding the addition of xanthan gum to starch systems, diverging results are abundant. Increases in peak viscosity, breakdown and swelling power are very often reported (Achayuthakan & Suphantharika, 2008; Chaisawang & Suphantharika, 2005; Chantaro & Pongsawatmanit, 2010; Christianson, Hodge, Osborne, & Detroy, 1981; Korus, Juszczak, Witczak, & Achremowicz, 2004; Pongsawatmanit, Temsiripong, Ikeda, & Nishinari, 2006; Viturawong, Achayuthakan, & Suphantharika, 2008). The exact opposite conclusions are found as well (Cai, Hong, Gu, & Zhang, 2011; Sikora, Kowalski, & Tomasik, 2008; Song, Kim, & Shin, 2008; Weber, Clerici, Collares-Queiroz, & Chang, 2009). Most of these discrepancies originate from differences in the concentrations used as well as the content and the modifications (e.g. anionic starch) of amylose. As pointed out by Samutsri and Suphantharika (2012), aside from their contribution, few or no publications focus on the influence of salts on ionic hydrocolloid/starch mixtures. Furthermore, the effect of the xanthan gum transition on the functionality of the combined waxy starch/xanthan gum system is to our knowledge never studied. Some authors explicitly mention the use of high salt contents to stabilize the ordered conformation and to avoid the complication of the xanthan denaturation (Abdulmola, Hember, Richardson, & Morris, 1996; Alloncle & Doublier, 1991). The aim of this research was to investigate the effects of this transition at different salt contents on the rheological properties of the xanthan gum as such and its indirect effects on the waxy starch functionality. Concentrations were chosen within ranges typically used in food systems. From a practical point of view waxy starches are very interesting because their chemically modified counterparts are very often used in combination with xanthan gum. As they are essentially free of amylose, they do not form strong gels upon cooling, which makes them suited for application in sauces and dressings. Furthermore the interpretation of the results is not complicated by amylose–xanthan interactions in the continuous phase of the dispersion.

2. Materials and methods

2.1. Materials

Xanthan gum (Satiaxane CX911, abbreviated as ‘X’ throughout the paper) was acquired from Cargill Texturizing Solutions (Ghent, Belgium). Its pyruvic acid content was denoted as >1.5%. The supplier indicates a molecular weight between 2 and 4×10^6 Da, an order of magnitude that is also mentioned by other authors (Benna-Zayani, Kbir-Ariguib, Trabelsi-Ayadi, & Grossiord, 2008; Viturawong et al., 2008). Native waxy maize starch (Merizet 300) and adipate crosslinked acetyl substituted waxy maize starch (Resistamyl 347, further denoted as ‘modified maize’) was supplied by Tate & Lyle Benelux. Native waxy rice starch (Remyline xs) and waxy potato starch (Eliane 100) were provided by Beneo-Remy (Wijgmaal, Belgium) and AVEBE (Veendam, The Netherlands), respectively. Because all starch types used here are of a waxy type, the denomination ‘waxy’ will not be further repeated throughout the paper.

2.2. Preparation of xanthan solutions

Xanthan gum powder was dispersed in deionised water, whilst continuously stirring with a magnetic stirrer. Next, the premix was put in an Ekato Unimix LM3 laboratory mixer (EKATO Rühr- und Mischtechnik GmbH, Schopfheim, Germany), a mixing apparatus equipped with a temperature control system, paravisc agitator with revolving blades and a colloid mill homogenizer. To fully dissolve the xanthan gum the premix was homogenized at room temperature for 15 min at 5000 rpm and stirred at an agitation speed of 150 rpm. During homogenization the unimix system was placed under vacuum to limit air inclusion. The obtained xanthan solutions (0.8%) were then diluted with NaCl solutions to the desired xanthan and salt content. An additional heating step could be introduced to solutions containing 0.4% xanthan and 0.01 M NaCl by means of the Ekato Unimix (85 °C 10 min). These samples were afterwards diluted to 0.2% X with salt solutions to obtain a final salt concentration of 0.1 M or 0.01 M. Preheated xanthan solutions are indicated by ‘HX’ and not-preheated solutions by ‘UHX’.

2.3. Rheology of xanthan solutions

Rheological measurements of xanthan solutions (0.2 and 0.4%) were performed on an AR2000 and AR2000ex rheometer (TA Instruments, New Castle, USA), using 28 mm conical concentric cylinders (gap of 500 μm between the inner and outer cylinder) with solvent trap to limit evaporation. A sample size of approximately 20 g was used.

To determine the linear visco-elastic region, strain sweeps were performed. First, equilibration was allowed for 2 min, at a temperature of 20 °C. Next, a strain sweep step was performed: strain was varied from 0.1 to 100% (measuring 10 points per decade), at a constant frequency of 1 Hz. A strain of 20% was found to be a valid parameter for several xanthan solutions tested, with both low and high salt concentrations. This strain was further used in all oscillatory measurements.

To assess the xanthan transition from ordered to disordered conformation, a temperature ramp was imposed to the unheated xanthan solutions. The temperature was increased from 20 °C to 85 °C at a rate of 3 °C/min, held for 10 min and cooled down (3 °C/min) to 20 °C. Hereby, the strain was held constant at 20% and the frequency was 1 Hz for samples containing 0.4% (w/w) xanthan gum and 0.5 Hz for samples containing 0.2% (w/w) xanthan gum. The transition temperature T_m was calculated by means of the sudden drop of the complex modulus $|G^*|$. The temperature at which the change in slope between the 4 preceding and the 4 succeeding data points was maximal, was selected as T_m.

Before and after this heating step, flow curves of the xanthan solutions were recorded. After 2 min of equilibration at 20 °C, samples were subjected to a stepped flow step: shear rate was varied from 0.01 to 100 s^{-1} (with 10 measuring points per decade).

2.4. Starch/xanthan systems

Starches were dispersed cold in salt solutions (references) of 0.01 M NaCl and 0.1 M NaCl or in xanthan solutions prepared as described above. Either heated xanthan solutions (HX) or unheated xanthan solutions were used (UHX). The dry starch:continuous phase weight-ratio was always 5:100. Samples from this premix were either transferred to DSC-pans or to the starch pasting cell.

2.4.1. DSC measurements

About 10-15 mg of suspension was accurately weighted in an alodined DSC pan (TA Instruments, New Castle, USA) and hermetically sealed. An empty pan was used as reference. The samples were heated from 20 °C to 99 °C at a heating rate of 3 °C/min. The onset (T_o), peak (T_p) and conclusion (T_c) temperature of gelatinization, as well as the corresponding enthalpy (ΔH) were calculated by means of the Universal Analysis 2000 Software (TA Instruments, New Castle, USA). A DSC Q1000 (TA Instruments, New Castle, USA) was used for all measurements. The instrument was calibrated with Indium (TA Instruments, New Castle, USA) for melting enthalpy and temperature. Additional temperature calibrations were performed with azobenzene (Sigma–Aldrich, Bornem, Belgium) and *n*-undecane (Acros Organics, Geel, Belgium).

2.4.2. Pasting experiments

The pasting behavior was studied using a starch pasting cell mounted to a controlled stress rheometer AR2000 (TA Instruments, New Castle, USA). Starch suspensions were preheated at 100 s^{-1} for 2 min and then heated to 85 °C at a heating rate of 5 °C/min, held isothermal for 10 min and then cooled down (5 °C/min) to 20 °C. Throughout the heating and cooling steps a shear rate of 50 s^{-1} was maintained. The cooled samples were recollected and stored for 24 h in the refrigerator (5 °C) for further analysis.

2.5. Particle size determination

The particle size distribution of the cooled starch pastes was determined by laser light diffraction using a Malvern Mastersizer S (Malvern, UK) equipped with a 300 mm reversed Fourier lens and a MSX-17 sample dispersion unit. To measure the starch particle size in the cold paste samples, 4 g of paste was diluted to 20 g with deionized water and gently shaken manually. Pumping and stirring speeds were put on 30% of the maximum values and the background was measured. The optical model used was the 3OHD with real refractive index 1.5295 and 1.33 for starch and the continuous phase, respectively. The imaginary refractive index was fixed at 0.1.

2.6. Flow curves of cooled pastes

The flow curves of the cooled pastes were recorded using 40 mm cross hatched steel plate-plate geometry with solvent trap. To prevent drying of the sample, 1 ml of water was brought in the solvent trap compartment. The gap was set to 1000 μm. After 15 min of equilibration at 20 °C, a steady state flow step was performed by logarithmically increasing the shear rate from 0.001 s^{-1} to 100 s^{-1}. At very low shear rates (<0.01 s^{-1}) unreliable data is obtained, resulting from the sample not reaching steady state or signals below the transducer limit of the instrument and the corresponding stresses are believed to be lower than the yield stress (Walls, Caines, Sanchez, & Khan, 2003). Flow curves were fitted to the Herschel–Bulkley model with the SigmaPlot 10 Software (Systat Software Inc., San Jose, USA).

$$\sigma_s = \sigma_0 + k\dot{\gamma}^n \tag{1}$$

In this equation which relates the shear stress σ_s with the shear rate $\gamma^{\cdot}$, the parameters σ_0, k and n represent the yield stress, the consistency index and the flow behavior index, respectively. All flow curves were fitted from shear rate 0.01 s^{-1} to 100 s^{-1}, except for the potato starch systems (0.1 s^{-1} to 100 s^{-1}) to obtain a better match with the model.

Table 1
Transition temperature T_m (°C) as a function of xanthan concentration and salt content.

NaCl (M)	0.2%X	0.4%X
0.01	60.0 ± 2.4^A	62.6 ± 1.6^A
0.02	69.6 ± 1.8^B	73.2 ± 0.4^B
0.03	77.0 ± 2.3^C	78.9 ± 0.6^C
0.04	80.8 ± 1.3^C	82.7 ± 0.8^D

Superscripts A–D indicate significant differences ($p < 0.05$) between data within a same column.

2.7. Statistical analysis

IBM SPSS Statistics Software (version 20, SPSS Inc., Chicago, USA) was used for statistical comparison of the DSC and pasting data. All the reported values are the average of three replicates. Homoscedasticity was verified by the Levene test. Analysis of variance was carried out to determine significant differences between the results, followed by Tukey's post hoc test for pairwise comparisons. All tests were performed at a 95% significance level.

3. Results and discussion

3.1. Determination of the xanthan transition

Because of their viscosity enhancing properties, xanthan gum and other biopolymers are usually dosed at low concentrations (<1%). This makes rheology a very useful technique to determine temperature induced conformational changes (Capron, Brigand et al., 1998; Choppe et al., 2010; Milas & Rinaudo, 1986). Oscillatory temperature ramps can be imposed to the system to monitor the conformational change. The transition temperature is accompanied by a reduction in both moduli, G' and G'', whereas the phase angle delta increases. The sudden drop in $|G^*|$ (not depicted) was used to derive the transition temperature T_m (Fig. 1). These experiments were performed at two concentrations (0.2% and 0.4% of xanthan) and at 5 salt concentrations (0.01, 0.02, 0.03, 0.04, 0.1 M NaCl). Table 1 indicates that the transition temperature is shifted to higher values when the salt content is increased. Rheological data show that at a salt content of 0.04 M the reduction of G' is limited, most likely because a fraction of the xanthan molecules remains in the ordered state at 85 °C. The transition temperatures do not increase linearly with increasing salt content, as the difference between T_m at 0.01 M and 0.02 M NaCl is much larger than the difference between 0.02 M and 0.03 M. For the highest salt content, 0.1 M, no transition could be observed rheologically within the studied temperature range. Salts shield the negative charges of the polymer molecules and hence the rodlike shape of the gum is stabilized, counteracting the thermal energy which forces the molecules to expand. Our data reveal slightly higher transition temperatures at a xanthan concentration of 0.4%, although this could not be proven statistically. This effect might be explained by a slightly higher salt content, originating from the xanthan powder or a slower heat transfer within a more viscous solution.

The highly branched, anionic nature of xanthan makes it susceptible to the presence of salt, but the distinct effects depend on the xanthan concentration. At lower concentrations, (approximately up to 0.2%), monovalent and divalent salts are reported to cause a decrease in viscosity. For higher concentrations the addition of salt results in a significant increase in viscosity (Wyatt & Liberatore, 2009, 2010; Wyatt, Gunther, & Liberatore, 2011). At low xanthan concentrations, salt causes a screening of the anionic charges, leading to a lower hydrodynamic volume and viscosity. At higher xanthan contents and when charges are shielded, hydrogen bonds can be formed between molecules causing an increase in viscosity. On the contrary, in this setup, no remarkable

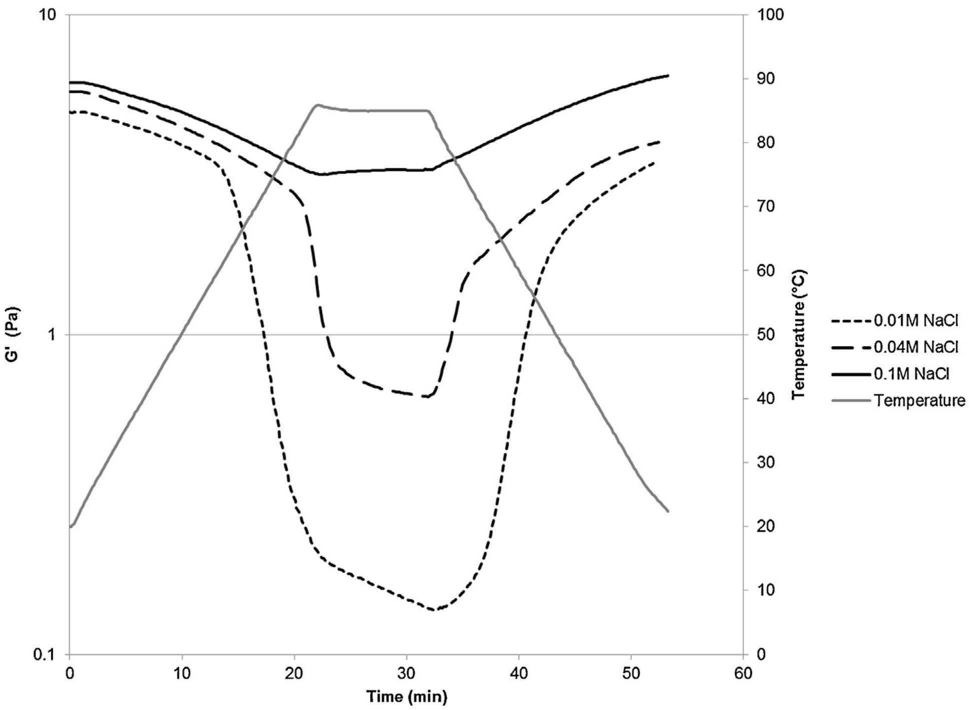

Fig. 1. Xanthan transition in a 0.4% (w/v) xanthan solution determined by oscillatory rheology as influenced by salt content.

differences in flow behavior of the unheated xanthan solutions could be observed between the different salt contents, not even at 0.4% which is much higher than the critical concentration of 0.2% (data not represented). It must be stated that in the before mentioned publications high salt contents (>0.1 M) are compared with salt free systems in which xanthan gum might adopt a random coil conformation already at low temperature. Furthermore preference was given here to a commercial xanthan sample, which is used as such in the food industry. No additional purification steps were performed, possibly causing a behavior different from more idealized solutions.

Flow curves of the xanthan solutions were compared at 20 °C before and after the heating step (data not represented). Except for the xanthan solutions with 0.1 M NaCl, a marked viscosity reduction was observed. These results indicate that following a thermal transition, the molecular conformations and/or associations are different compared to those in the unheated solutions. The commercial xanthan gum used in this setup was pasteurized after fermentation, so it can be assumed that the renatured form was present, not the native conformation. Consequently, differences before and after heating were expected not to be so pronounced. However Capron et al. (1997) claim that both single and double stranded structures coexist in commercial samples, which are often only partially renatured. The thermal treatment of the crude fermentation broth of xanthan and the conditions under which it is applied, have a pronounced influence on the final properties of the molecules. At a concentration below about 1%, double stranded native xanthan could dissociate, but at a higher concentration of molecules, they can only partly dissociate due to steric effects (Born, Langendorff, & Boulenguer, 2005; Capron et al., 1997). So it can be assumed that in our diluted solutions further dissociation of double stranded molecules is taking place. Furthermore, polysaccharides tend to form aggregates in solution that can mask the behavior of individual macromolecules (Camesano & Wilkinson, 2001). Presumably these agglomerates are also stabilized by salts, but are disrupted by additional heating above the denaturation temperature, which may explain the quite pronounced differences observed here. To exclude these effects, both preheated as well as unheated xanthan solutions were used in combination with the starches. When heating, a concentration of 0.4% xanthan was used at a salt concentration of 0.01 M to obtain full hydration/dissociation. These samples were diluted after cooling to 0.2% xanthan and the salt content was adjusted.

3.2. Influence of xanthan gum on the gelatinization properties of the starches

Two salt contents were selected for this setup: 0.01 M and 0.1 M. As indicated in the previous section no xanthan transition occurs at the highest salt content, whereas a marked transition is observed for the lowest salt content. The temperature onset, peak and conclusion of gelatinization derived from the DSC experiments are summarized in Table 2. The gelatinization temperatures are greatly influenced by the salt content. For the samples with 0.1 M NaCl, the gelatinization temperatures are shifted to higher values, but the gelatinization enthalpy is not significantly influenced.

At the relatively low NaCl contents used in this setup, the effects of salt on the gelatinization can probably not be related to the water binding effects and hence an induced water limitation. A more plausible explanation is based on the Hofmeister series, which states that the structure of water is modified by its solutes, like salts (Zhu, Gayin, Chatel, Dewettinck, & Van der Meeren, 2009). The Hofmeister series ranks the relative influence of ions on the physical behavior of macromolecules. Salts in the upper end of the Hofmeister lyotropic series, called kosmotropes, or water structure makers have strong electrostatic interactions with water molecules. They thus reduce the fraction of free water and increase the gelatinization temperature. On the other hand, ions with low charge densities, called chaotropes, or water structure breakers, increase the fraction of free water by breaking or weakening hydrogen bonds, hereby decrease the gelatinization temperature. The salts which are located in the middle of the lyotropic series, like NaCl, show an increase with low concentrations where higher concentrations induce a decrease the gelatinization temperature (Chiotelli, Pilosio, & Le Meste, 2002; Zhang & Cremer, 2006).

Table 2
Effect of xanthan addition and NaCl concentration on the gelatinization parameters of different starches at a ratio 5:100 (starch:continuous phase).

Starch type	Conc. NaCl (M)	Xanthan	T_o (°C)	T_p (°C)	T_c (°C)	ΔH (J/dry starch)
Maize	0.01	No X	67.03 ± 0.29^{A}	73.02 ± 0.06^{A}	78.68 ± 0.12^{A}	12.76 ± 1.28^{A}
		0.2% HX	67.28 ± 0.08^{A}	73.16 ± 0.09^{A}	78.93 ± 0.40^{A}	13.50 ± 1.00^{A}
	0.1	No X	70.04 ± 0.20^{B}	75.72 ± 0.19^{B}	81.00 ± 0.11^{B}	12.37 ± 0.33^{A}
		0.2% HX	70.29 ± 0.08^{B}	76.04 ± 0.18^{B}	81.53 ± 0.28^{B}	12.93 ± 1.04^{A}
Potato	0.01	No X	64.94 ± 0.22^{A}	70.53 ± 0.16^{A}	76.88 ± 0.21^{A}	12.75 ± 0.69^{A}
		0.2% HX	64.99 ± 0.13^{A}	70.64 ± 0.04^{A}	77.01 ± 0.13^{A}	13.59 ± 0.99^{A}
	0.1	No X	65.93 ± 0.23^{B}	71.34 ± 0.16^{B}	77.55 ± 0.21^{B}	12.15 ± 1.52^{A}
		0.2% HX	65.93 ± 0.17^{B}	71.43 ± 0.12^{B}	77.98 ± 0.19^{B}	13.35 ± 0.38^{A}
Rice	0.01	No X	61.07 ± 0.21^{A}	68.40 ± 0.13^{A}	74.92 ± 0.06^{A}	10.25 ± 0.09^{A}
		0.2% HX	60.80 ± 0.44^{A}	68.44 ± 0.25^{A}	74.07 ± 0.41^{A}	10.19 ± 1.11^{A}
	0.1	No X	64.17 ± 0.91^{B}	71.44 ± 0.23^{B}	77.91 ± 0.41^{B}	10.34 ± 1.70^{A}
		0.2% HX	64.47 ± 0.71^{B}	71.63 ± 0.39^{B}	77.36 ± 0.47^{B}	9.63 ± 0.95^{A}
Modified maize	0.01	No X	62.01 ± 0.10^{A}	68.54 ± 0.08^{A}	74.31 ± 0.29^{A}	12.06 ± 0.16^{A}
		0.2% HX	61.73 ± 1.40^{A}	68.89 ± 0.54^{A}	75.31 ± 1.31^{A}	13.18 ± 1.43^{A}
	0.1	No X	64.86 ± 0.54^{B}	71.22 ± 0.16^{B}	77.02 ± 0.36^{B}	11.68 ± 0.98^{A}
		0.2% HX	65.43 ± 0.28^{B}	71.28 ± 0.18^{B}	77.59 ± 0.60^{B}	11.90 ± 0.27^{A}

For each starch type, superscripts A–B indicate significant differences within columns ($p < 0.05$).

Xanthan gum did not significantly affect the gelatinization temperatures of the different starches. This conclusion was also drawn by other researchers (Chantaro & Pongsawatmanit, 2010; Samutsri & Suphantharika, 2012; Viturawong et al., 2008). A reduction of the gelatinization enthalpy was reported by some authors, but their setups dealt with amylose-containing starches (Aguirre-Cruz, Mendez-Montealvo, Solorza-Feria, & Bello-Perez, 2005; Chaisawang & Suphantharika, 2006; Viturawong et al., 2008). Gelatinization temperatures can be affected as well, but generally at high starch concentrations, where hydrocolloids are believed to restrict hydration of the amorphous regions (Aguirre-Cruz et al., 2005; Tester & Sommerville, 2003). In general it should be noted that the gelatinization of all starches investigated in this setup, is not influenced by the presence of xanthan gum and consequently not by the xanthan transition that is occurring.

3.3. Influence of xanthan transition on the pasting properties

Pasting curves of the rice and native maize starch systems are depicted in Fig. 2. The pasting temperatures (i.e. temperature of onset in viscosity increase), peak/maximum viscosity and breakdown of the different systems were calculated and listed in Table 3. Pasting temperatures are mostly very close to the gelatinization onset temperatures. In the case of maize and potato starch, pasting seems to start even at lower temperatures, although this is uncertain considering standard deviations of both parameters, and the different heating mechanisms in DSC (small volume, no shear) and starch pasting cell (large volume, with shear). DSC measurements demonstrated that – except for potato starch – the gelatinization temperature of all starches differed about 3-3.5 °C between both salt contents, a difference that was also observed in the pasting temperatures of the xanthan free systems. Similar to the DSC-measurements, xanthan gum did not significantly affect the pasting temperature at a given salt concentration. Although it cannot be proven statistically, a slightly higher pasting temperature is suggested for maize and potato starch in the presence of unheated xanthan at the lowest salt content. A similar delay for pasting of waxy maize starch was observed by Achayuthakan and Suphantharika (2008) and Weber et al. (2009). This might be caused by competition for the available water, because these starches have the tendency to swell rather quickly.

Except for the potato starch system, the pasting curves of the xanthan free systems exhibit a similar behavior at both salt contents. This however is strongly changed when xanthan is present. In all cases the peak viscosities of starch/xanthan systems with 0.01 M NaCl are significantly lower than the corresponding systems with 0.1 M NaCl. Furthermore in the case of native maize and potato starch, peak viscosities of the xanthan containing systems are lower (0.01 M) or similar (0.1 M) to their gum free counterparts. This clearly demonstrates a strong influence of xanthan gum on the rheological properties of the mixed systems, but the exact effects differ between the different starch types. The most obvious explanation for the reduced peak viscosity observed in the potato and maize starch system would be a restriction in swelling behavior. However, as will be demonstrated further, xanthan gum does not negatively influence the starch dimensions in the given concentrations (except for a slight restriction of rice starch swelling). At least a partial explanation may be found in the xanthan transition. After converting to the random coil shape, the viscosity of the continuous xanthan phase is greatly reduced. Logically more work is required to move granules past each other when the viscosity of the medium is higher. Because xanthan gum exhibits a much lower viscosity in the random coil conformation, this might explain the differences between both salt contents of the mixed xanthan/starch systems. Assuming similar granule swelling in both xanthan free and xanthan containing media, this theory does not explain why peak viscosities can be higher in a xanthan free system. Hongsprabhas, Israkarn, and Rattanawattanaprakit (2007) suggested that the increase in peak viscosity could arise just from the friction of stabilized swollen granules moving past each other. Most likely this theory is valid at high starch volume fraction with strongly interacting starch granules, whereas the solvent has a decisive influence on the rheological properties of more dilute systems. Therefore it is likely that xanthan modifies the manner in which particles interact or collide during pasting. Another explanation might be that xanthan enwraps the granules as illustrated by Chaisawang and Suphantharika (2006) and Gonera and Cornillon (2002). This layer associated with the granules might act as a stabilizing, lubricating film. The distinct behavior of potato starch was previously attributed to an incompatibility with xanthan gum. Because of its high degree of phosphorylation potato starch is anionic, which could repel the anionic xanthan molecules (Cai et al., 2011; Shi & BeMiller, 2002). Similar effects were observed with phosphorylated corn starch (Shi & BeMiller, 2002). The effect seems to be more pronounced at low salt content, which could be explained by partial shielding at higher salt contents.

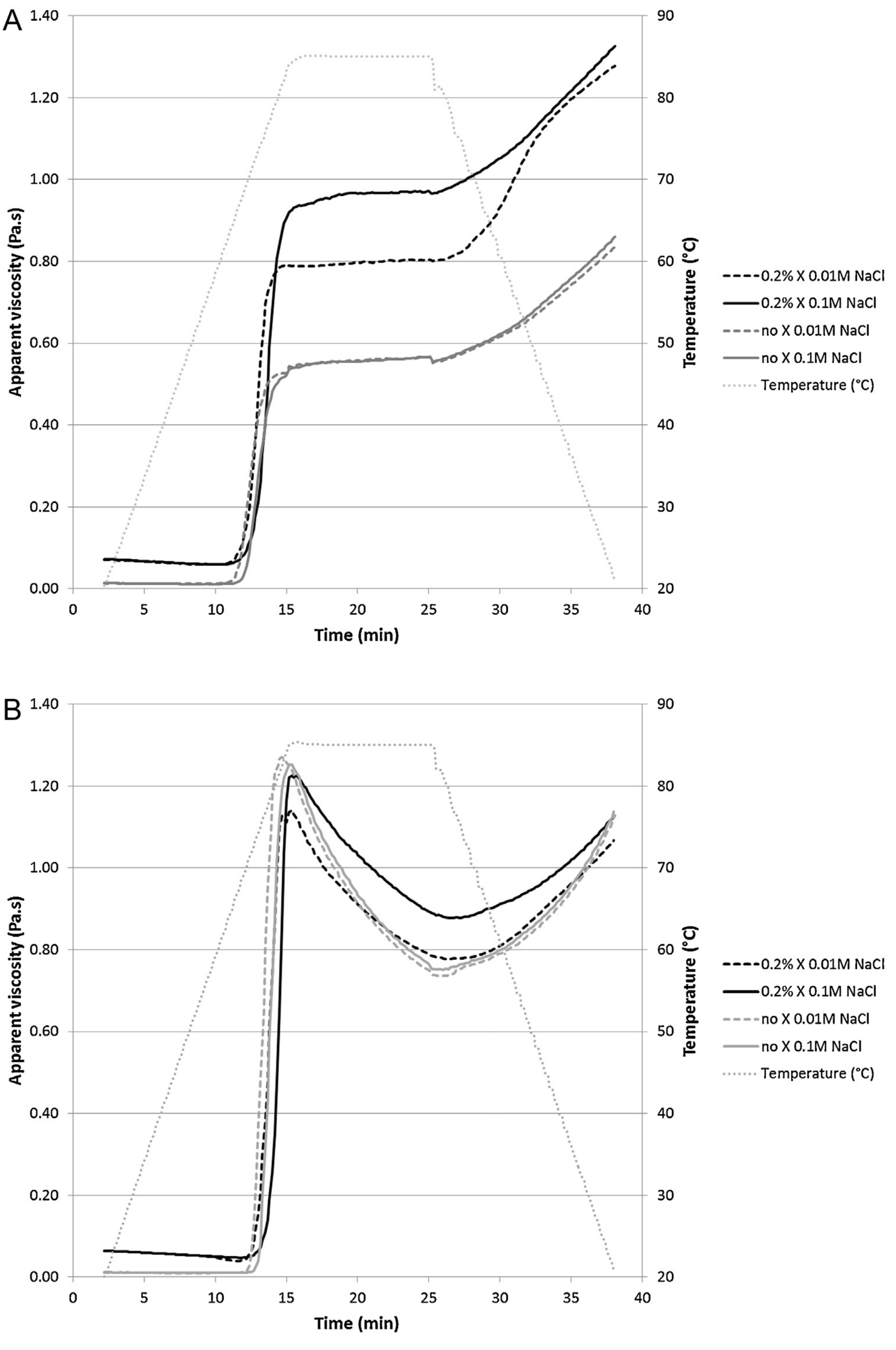

Fig. 2. Pasting properties of waxy rice starch (A) and native waxy maize starch (B) as influenced by salt content and xanthan gum.

The presence of xanthan gum increased the pasting viscosities of the rice starch and the modified maize starch systems, as demonstrated for rice starch in Fig. 2. For these starches the effect of the continuous phase is more noticeable. For the system with 0.01 M NaCl the viscosity was again significantly lower due to the xanthan transition. Furthermore, the difference in viscosity of the preheated and the unheated xanthan solutions also became apparent in the pasting viscosities at the highest salt content.

Breakdown was not observed in the case of rice starch or modified maize, but was relatively high for native maize and potato starch (Table 3). In the xanthan-free potato starch systems breakdown was significantly higher at the lowest salt content, whereas with native maize starch systems no differences between systems of low versus high salt content were noticed. On the other hand the presence of xanthan gum significantly reduced the breakdown for both maize and potato starch. Again this might be attributed to a reduced interaction or friction during pasting or a more controlled swelling which makes the granules less susceptible to breakdown. Particle size measurements should help to further clarify the observed phenomena.

Table 3
Influence of xanthan gum (0.2%) and salt content on the pasting parameters of different starches at a ratio 5:100 (starch:continuous phase).[a]

Starch type	Conc. NaCl (M)	Xanthan	Maximum viscosity (Pa s)	Breakdown (Pa s)[b]	Pasting temperature (°C)
Maize	0.01	No X	1.27 ± 0.01^{C}	0.52 ± 0.01^{C}	67.1 ± 0.0^{A}
		0.2% HX	1.14 ± 0.01^{A}	0.36 ± 0.00^{A,B}	67.3 ± 0.4^{A,B}
		0.2% UHX	1.15 ± 0.00^{A}	0.35 ± 0.00^{A,B}	68.4 ± 0.0^{B}
	0.1	No X	1.25 ± 0.02^{B,C}	0.49 ± 0.02^{C}	70.0 ± 0.7^{C}
		0.2% HX	1.23 ± 0.00^{B}	0.34 ± 0.00^{A}	70.0 ± 0.0^{C}
		0.2% UHX	1.28 ± 0.01^{C}	0.37 ± 0.01^{B}	70.0 ± 0.0^{C}
Potato	0.01	No X	2.18 ± 0.01^{C}	0.89 ± 0.01^{D}	63.6 ± 0.9^{A}
		0.2% HX	1.56 ± 0.03^{A}	0.22 ± 0.03^{A}	63.7 ± 0.9^{A}
		0.2% UHX	1.56 ± 0.02^{A}	0.22 ± 0.01^{A}	64.6 ± 0.6^{A}
	0.1	No X	1.93 ± 0.09^{B}	0.61 ± 0.06^{C}	64.9 ± 0.2^{A}
		0.2% HX	1.97 ± 0.03^{B}	0.49 ± 0.03^{B}	64.0 ± 0.4^{A}
		0.2% UHX	1.99 ± 0.01^{B}	0.49 ± 0.00^{B}	65.1 ± 0.1^{A}
Rice	0.01	No X	0.57 ± 0.01^{A}	N.D.	61.7 ± 0.6^{A,B}
		0.2% HX	0.80 ± 0.00^{B}	N.D.	61.1 ± 0.0^{A}
		0.2% UHX	0.79 ± 0.01^{B}	N.D.	62.2 ± 0.5^{A,B,C}
	0.1	No X	0.56 ± 0.01^{A}	N.D.	64.6 ± 0.0^{D}
		0.2% HX	0.96 ± 0.01^{C}	N.D.	63.5 ± 1.0^{C,D}
		0.2% UHX	1.04 ± 0.01^{D}	N.D.	63.0 ± 0.6^{B,C,D}
Modified Maize	0.01	No X	0.68 ± 0.01^{A}	N.D.	63.9 ± 0.3^{A}
		0.2% HX	0.77 ± 0.01^{B}	N.D.	62.4 ± 0.6^{A}
		0.2% UHX	0.76 ± 0.00^{B}	N.D.	63.6 ± 0.1^{A}
	0.1	No X	0.70 ± 0.01^{A}	N.D.	66.4 ± 0.3^{B}
		0.2% HX	1.14 ± 0.00^{C}	N.D.	65.7 ± 0.4^{B}
		0.2% UHX	1.24 ± 0.02^{D}	N.D.	66.0 ± 1.1^{B}

[a] For each starch type, superscripts A–D indicate significant differences within columns.

[b] N.D. indicates parameters that were not detectable.

3.4. Granule size determination

In many cases, the swelling power of starches and starch/gum systems is determined by centrifugation. Unfortunately there are some disadvantages to this approach. In the presence of gums, centrifugation may be inefficient and influence the results (Song, Kwon, Choi, Kim, & Shin, 2006). Furthermore the starch concentrations are generally low and no shear is applied during heating, which makes it hard to relate with pasting experiments. In our setup, the samples were recollected after pasting, stored for 24 h and particle size distributions were determined. Table 4 summarizes the derived volume weighted equivalent diameters *D*[4,3]. Particle size distributions of pasted starch granules are generally influenced by two phenomena: granule swelling and granule disruption. Pasting data of modified maize starch and rice starch showed no breakdown, so in these cases the first effect is assumed to be predominant. Modified maize starch seems to be only slightly influenced by the presence of xanthan gum and salts. Rice starch swelling appears to be inhibited by xanthan gum, as well as by salt. Rice starch granules have a low swelling power, and are often present as associated granules in raw starch powder. Agglomerated granules dissociate when they start to swell. In this case the water binding properties of xanthan gum might restrict the water imbibition of the rice starch granules. The diameters of the maize starch appeared to be clearly higher when xanthan gum is present. This corresponds with the findings from the pasting experiments. In general, no differences could be observed between the unheated and the preheated xanthan solutions. The lowest salt content resulted in the highest average diameters for the xanthan containing system, which can suggest a beneficial effect of the xanthan transition. It can be hypothesized that the low pasting viscosity – and hence the reduced friction – led to less granule breakdown. Furthermore because of these higher diameters, the hypothesis of a more restricted swelling caused by xanthan gum, seems more unlikely. On the other hand it cannot be fully excluded because the average diameters are always the result of a combined swelling and breakdown effects, whereby it is difficult to distinguish between both phenomena.

Similar trends although not significant, are suggested at the lowest salt content for potato starch. This starch is much more influenced by the salt content as such, so an indirect effect of xanthan transition is harder to derive. Furthermore it should be remarked that the diverging pasting results caused by xanthan, strongly contrast with the limited differences observed in the particle size distributions of potato starch. This could indicate an electrostatic incompatibility between the potato starch, which contains phosphoryl groups and the anionic xanthan gum, as stated before. One should therefore be cautious when interpreting pasting data solely on swelling/degradation phenomena, as these results prove their complexity.

3.5. Flow curves of the cooled starch pastes

Some characteristic flow curves recorded after 1 day of cold storage are represented in Fig. 3. All samples are shear thinning, the upward curvature at higher shear rates is due to the logarithmic scaling of the shear rate axis. The derived Herschel–Bulkley parameters of all systems are summarized in Table 5. When the data of the different systems are compared, it is clear that the presence of xanthan gum causes a more distinct change in flow behavior of the rice starch and the modified maize starch. In these samples breakdown was not observed and the pastes consist of intact granules. The rheological properties of swollen non-degraded starch granules depend largely on their volume fraction as well as their rigidity (Steeneken, 1989). In dilute starch based systems the volume fraction of the starch as well as the rheological properties of the continuous phase (e.g. dissolved polysaccharides) strongly influence the rheology, whereas in more concentrated dispersions particle–particle interactions dominate. In this case the rigidity of the granules plays an important role. For the rice and modified maize starch the increase of yield stress and consistency index by the addition of xanthan cannot be attributed to an enhanced swelling of the granules, as demonstrated by particle size distributions. In the case of rice starch even a reduction of the average granule diameter was observed. Therefore the enhanced

Table 4
Volume weighted equivalent diameters $D[4,3]$ (μm) of different starches as influenced by salt concentration and xanthan.

Conc. NaCl (M)	Xanthan	Maize	Potato	Rice	Modified maize
0.01	No X	29.89 ± 0.51	143.76 ± 0.04	23.96 ± 0.28	40.11 ± 1.45
	0.2% HX	37.79 ± 2.04	145.35 ± 1.81	21.04 ± 0.32	41.63 ± 1.02
	0.2% UHX	36.14 ± 0.35	149.12 ± 1.49	20.78 ± 0.36	41.75 ± 0.94
0.1	No X	30.08 ± 1.35	130.97 ± 0.07	22.15 ± 0.53	39.94 ± 1.37
	0.2% HX	32.72 ± 0.25	128.21 ± 4.25	19.46 ± 0.25	40.09 ± 0.42
	0.2% UHX	32.64 ± 0.14	139.60 ± 3.77	19.45 ± 0.27	40.12 ± 0.10

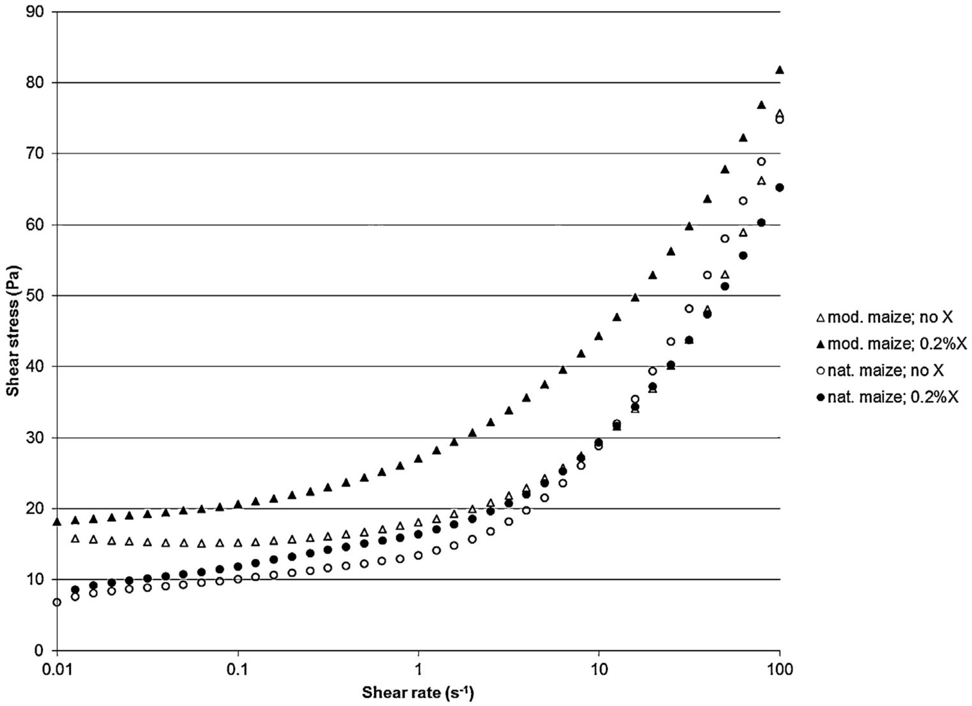

Fig. 3. The effect of xanthan addition on flow curves (20 °C) of modified and native starch pastes (0.01 M NaCl).

Table 5
Herschel–Bulkley parameters fitted to the flow curves of the cooled pastes (20 °C).

Starch type	Conc. NaCl (M)	Xanthan	σ_0 (Pa)	k (Pa s^n)	n (–)	R^2
Maize	0.01	No X	7.22 ± 0.23	6.83 ± 0.23	0.505 ± 0.008	0.997
		0.2% HX	8.48 ± 0.21	7.81 ± 0.22	0.433 ± 0.006	0.998
		0.2% UHX	8.09 ± 0.35	7.34 ± 0.39	0.415 ± 0.011	0.992
	0.1	No X	6.17 ± 0.37	7.94 ± 0.38	0.468 ± 0.010	0.994
		0.2% HX	3.86 ± 0.42	13.36 ± 0.47	0.326 ± 0.007	0.996
		0.2% UHX	4.18 ± 1.06	15.09 ± 1.19	0.307 ± 0.016	0.981
Potato	0.01	No X	24.82 ± 0.84	6.86 ± 0.69	0.508 ± 0.022	0.987
		0.2% HX	25.21 ± 0.36	7.32 ± 0.32	0.460 ± 0.009	0.998
		0.2% UHX	24.36 ± 0.49	6.69 ± 0.43	0.453 ± 0.013	0.994
	0.1	No X	27.17 ± 0.91	7.69 ± 0.76	0.491 ± 0.021	0.987
		0.2% HX	31.81 ± 0.83	7.78 ± 0.74	0.432 ± 0.020	0.988
		0.2% UHX	32.59 ± 0.65	6.33 ± 0.57	0.455 ± 0.019	0.990
Rice	0.01	No X	10.64 ± 0.34	4.88 ± 0.33	0.504 ± 0.015	0.988
		0.2% HX	12.01 ± 0.22	12.93 ± 0.25	0.344 ± 0.004	0.999
		0.2% UHX	11.92 ± 0.09	11.61 ± 0.11	0.352 ± 0.002	0.999
	0.1	No X	7.89 ± 0.27	4.50 ± 0.27	0.498 ± 0.014	0.990
		0.2% HX	11.71 ± 0.78	12.13 ± 0.88	0.370 ± 0.015	0.983
		0.2% UHX	12.30 ± 0.42	11.93 ± 0.47	0.357 ± 0.008	0.995
Modified Maize	0.01	No X	14.97 ± 0.08	3.34 ± 0.06	0.627 ± 0.004	0.999
		0.2% HX	15.40 ± 0.17	11.80 ± 0.18	0.377 ± 0.003	0.999
		0.2% UHX	15.99 ± 0.16	11.50 ± 0.17	0.381 ± 0.003	0.999
	0.1	No X	16.61 ± 0.11	3.70 ± 0.09	0.634 ± 0.005	0.999
		0.2% HX	18.28 ± 0.26	12.11 ± 0.28	0.409 ± 0.005	0.998
		0.2% UHX	19.67 ± 0.28	13.05 ± 0.31	0.388 ± 0.005	0.997

rheological properties are likely to be attributed to direct or indirect effects of the xanthan gum. Abdulmola et al. (1996) stated that even at relatively low concentrations, swollen starch granules can interact and that this interaction can be increased by the presence of xanthan gum. They attributed this to either bridging or depletion flocculation. The modified maize system in particular is very interesting because all systems showed very similar particle size distributions, but some distinct effects of the salt content could be observed when xanthan was present.

In general there were no or only limited effects of preheating the xanthan solutions on the rheological properties of the cooled pastes. As mentioned above, the viscosity of the (starch-free) unheated xanthan samples is higher than the viscosity of the heated solutions. At the highest salt content, when no transition can occur, the stabilizing action of the ions should preserve this difference during pasting. Nevertheless this effect probably fades in the presence of starch, as indicated by the similar flow curves of starch pastes containing either unheated or preheated xanthan. Therefore differences between the flow curves at low or high salt content, e.g. in the case of modified maize starch, are most likely due to indirect effects on the starch interactions, rather than a direct effect on the viscosity of xanthan in the continuous phase. Salts can reduce the hydrodynamic volume and the intermolecular repulsion of the molecules and can in turn affect bridging and depletion flocculation.

The rheological behavior of the native maize and potato starch systems was even more complex. For these systems some marked differences in granule sizes were observed. Nonetheless it appears that the effects of xanthan gum on the final rheological behavior were rather limited. It can be assumed that despite the stabilizing action of xanthan gum, the majority of the granules is still disrupted and the remaining ones are highly swollen and consequently have lost their rigidity. Microstructurally these systems exist as a discontinuous phase of still intact granules and granule remnants within a continuous watery phase of amylopectin mixed with xanthan gum. Hermansson and Svegmark (1996) stated that the rheological behavior of overcooked starch pastes is dominated by the continuous phase, which is a complex macromolecular solution. In this case polymer compatibility between xanthan gum and starch polymers becomes important. Insights regarding their phase behavior might help to explain some of the phenomena observed here. Unfortunately there is little or no information available regarding this aspect.

4. Conclusions

At the investigated concentrations the xanthan transition did not influence the gelatinization of waxy starches but it affected the pasting behavior. When starch/xanthan systems were heated above the xanthan transition temperature, the conformational change of xanthan in the continuous phase gave rise to reduced pasting viscosities. This might explain some of the discrepancies seen in literature. Furthermore the gum is capable of reducing the breakdown of shear sensitive waxy starches. Different mechanisms were proposed: restriction of the swelling, physical stabilization by enwrapping the granules and/or reduction of the impact between granules during pasting. This stabilizing action might be enhanced by the xanthan transition but further research is required to confirm this.

The effect of the xanthan transition is not directly noticeable in the flow behavior of the cooled pastes. For the given processing conditions, the granule protecting effect of xanthan gum only had a limited effect on the flow behavior. The most likely explanation is that a large fraction of the native maize and potato starch granules were still broken down, causing a complex macromolecular solution. Xanthan gum on the other hand had a large influence on the flow behavior of the starches with a large extent of granule preservation. Therefore granule integrity appears to be a prerequisite for optimal xanthan functionality.

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