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Processing of waxy starch/xanthan gum mixtures within the gelatinization temperature range

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ABSTRACT

Pasting experiments of waxy potato and waxy maize starch systems were set up in which temperatures close to the gelatinization temperature were selected (67.5, 70 and 72.5 °C). DSC measurements showed that under these conditions small fractions of the starches remained ungelatinized. During the pasting process two different shear rates were imposed ($50\,s^{-1}$ and $150\,s^{-1}$) to investigate the shear stability of the different starch containing systems. Swelling of the granules occurred in a more controlled manner and granule breakdown during pasting could be limited. As a result of these heating conditions more swollen granules are present, as confirmed by laser light diffraction. This positive effect was clearly noticeable in the flow curves of the cooled pastes. Xanthan gum addition could further reduce breakdown either by restricting the swelling or by stabilizing the granules. At higher starch contents the former is most likely dominating.

1. Introduction

When starch granules are heated in excess water, they undergo a process called gelatinization. The hydrogen bonds in amorphous regions are disrupted and water, which acts as a plasticizer, is absorbed. This endothermic transition causes swelling of the starch granules and can be observed microscopically by the loss of their birefringence. Starch macromolecules (primarily amylose) leach from the swollen granules. The process of pasting follows gelatinization and occurs with continued heating and shearing of starch granules in the presence of excess water and involves continued granule swelling, additional leaching of dissolved starch polymer molecules, and disruption of the fragile, swollen granules. The resulting paste consists of a dispersed phase of swollen granules, granule ghosts, and granule fragments within a continuous aqueous phase of dissolved starch polymer molecules. The rheological properties of the paste are governed by the size and the shape of the particles in the discontinuous phase, the composition and nature of the continuous phase and interactions between the two phases (BeMiller, 2011; Hermansson & Svegmark, 1996). In food products such as sauces and puddings containing disintegrated starch granules, the texture becomes long or slimy. In this case the rheological properties are governed by the continuous phase (Hermansson & Svegmark, 1996). Native starches cannot withstand the stringent processing conditions which lead to abundant granule disruption and undesirable product properties. Furthermore their stability and water holding capacity is unsatisfactory. They are used in the food industry for instance in dry mixes or products like buttermilk or salad dressings where a slightly long texture is acceptable, but most often native starches are chemically modified to improve their functionality (BeMiller & Whistler, 2009). Also, a combination with a suitable hydrocolloid can overcome shortcomings of native starches, as they can protect against shear during cooking, improve product texture/rheology, hold moisture and protect against syneresis (BeMiller, 2011).

Because of its unique rheological properties, xanthan gum is often applied to starch based foodstuffs. This extracellular polysaccharide is produced by fermentation of *Xanthomonas campestris* and 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 (Imeson, 2010). In most food systems, xanthan gum exists in a rigid, rodlike conformation. Furthermore xanthan can engage in non-covalent molecular entanglements (Capron, Alexandre, & Muller, 1998; Mohammed, Haque, Richardson, & Morris, 2007; Rodd, Dunstan, & Boger, 2000). Both of these unique characteristics cause a strong shear thinning behavior with high viscosities at low shear rates and low viscosity at high shear rates, which is a behavior often desired in non-gelled foodstuffs.

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Non-starch hydrocolloids in general and xanthan gum in particular are known to affect the granule swelling and degradation during pasting. At high starch contents swelling of the starch is reduced in the presence of xanthan, probably as a consequence of restricted water availability. In most of these cases the peak viscosity is reduced (Kruger, Ferrero, & Zaritzky, 2003; Song, Kim, & Shin, 2008; Song, Kwon, Choi, Kim, & Shin, 2006; Tester & Sommerville, 2003; Weber, Clerici, Collares-Queiroz, & Chang, 2009). At lower starch concentrations (<6%) the granule swelling is often enhanced by xanthan gum, making them more vulnerable for breakdown (Chaisawang & Suphantharika, 2005, 2006; Chaisawang & Suphantharika, , 2006; Mandala & Bayas, 2004; Samutsri & Suphantharika, 2012). Shi and BeMiller (2002) attributed this to an interaction between xanthan and amylose in the continuous phase, causing increased amylose leaching, which in turn leads to a higher water absorption. In more anionic starches (e.g. potato) an opposite effect was observed due to the repelling forces between the xanthan molecules and the starch polymers, leading to reduced swelling and lower viscosities (Cai, Hong, Gu, & Zhang, 2011; Shi & BeMiller, 2002; Sikora, Kowalski, & Tomasik, 2008). Combinations of xanthan and waxy starches, which are essentially free of amylose, are much less studied. Xanthan is reported to reduce their (relative) breakdown during pasting (Achayuthakan & Suphantharika, 2008) and to induce larger granule diameters (Achayuthakan, Suphantharika, & Rao, 2006). Possibly this can be related to its ability to enwrap the surface and hence stabilizing the granule (Abdulmola, Hember, Richardson, & Morris, 1996; Achayuthakan & Suphantharika, 2008; Achayuthakan et al., 2006; Gonera & Cornillon, 2002). This property might be an interesting feature to improve the stability of native starches.

It is generally known that sufficiently swollen starch granules, with limited breakdown, yield products with a good sensory perception. When granule breakdown becomes predominant undesired textures are formed. Few studies suggest that when heated at temperatures slightly higher than the gelatinization temperature, granule swelling is incomplete, but their rigidity is preserved (Bagley & Christianson, 1982; Jacquier, Kar, Lyng, Morgan, & McKenna, 2006; Li & Yeh, 2001; Mandala & Bayas, 2004; Nayouf, Loisel, & Doublier, 2003; Rao, Okechukwu, Da Silva, & Oliveira, 1997). Chemically modified waxy maize and potato starches are used very often in the food industry, because the native variants are highly unstable during shear and heat treatments (BeMiller & Whistler, 2009). The purpose of our experimental setup was to investigate whether the use of temperatures within the gelatinization range (67.5, 70 and 72.5 °C) during pasting along with the addition of xanthan gum, could lead to a more controlled swelling and a more limited breakdown of the granules of native starches.

2. Materials and methods

2.1. Materials

Xanthan gum (Satiaxane CX911, further denoted as 'X') was acquired from Cargill Texturizing Solutions (Ghent, Belgium). Its pyruvic acid content was >1.5%. Native waxy maize starch (Merizet 300) and waxy potato starch (Eliane 100) were provided by Tate & Lyle Benelux and AVEBE (Veendam, The Netherlands), respectively. Because both starch types are from a waxy variety the denomination 'waxy' will further not be repeated throughout the paper.

2.2. Preparation of xanthan gum solutions

Xanthan gum powder was dispersed in deionised water, whilst continuously stirring with a magnetic stirrer. The premix was placed in an Ekato Unimix LM3 laboratory mixer (EKATO Rühr- und Mischtechnik GmbH, Schopfheim, Germany), a mixing apparatus equipped with a temperature control system, a paravisc agitator and a colloid mill homogenizer. To further dissolve the xanthan gum the premix was homogenized for 15 min at 5000 rpm and stirred at of 150 rpm. The resultant xanthan solutions (0.8%) were then diluted with NaCl solutions to 0.4% xanthan and a salt content of 0.01 M NaCl. An additional heating step was applied by means of the Ekato Unimix (85 °C 10 min) to obtain full dissolution and hydration. 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.

2.3. Starch/xanthan systems

Starches were dispersed at room temperature in salt solutions (references) of 0.01 M NaCl and 0.1 M NaCl or in xanthan solutions prepared as described higher. Samples from this premix were either transferred to DSC-pans or to the starch pasting cell. The starch:solvent ratio was always 5:100, except for the last part of the experimental setup where ratios of 3:100 and 7:100 were used as well.

2.3.1. DSC Measurements

About 10–15 mg of suspension was accurately weighted in a DSC pan and hermetically sealed. An empty pan was used as reference. 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). To determine the gelatinization parameters, the samples were heated from 20 °C to 99 °C at a heating rate of 3 °C/min. The total enthalpy of the gelatinization is denoted as ΔH_{tot}. Within the same starch type, the ΔH_{tot} of the different compositions were not significantly different, as verified by ANOVA. Therefore one single averaged value of ΔH_{tot} was calculated. Isothermal gelatinization was also performed by heating (3 °C/min) to the desired setpoint temperature, holding this isothermally for 10 min. Next a rapid cooling step (20 °C/min) to 45 °C was introduced and after holding for 5 min, the remaining gelatinization was determined by heating to 99 °C at a ramp of 3 °C/min. The enthalpic transition during this second ramp is denoted by $\Delta H_{\mathrm{ungel}}$. The fraction of the starch that did not gelatinize during the isothermal step was equal to $\Delta H_{\mathrm{ungel}}/\Delta H_{\mathrm{tot}}$.

2.3.2. 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 presheared at 100 s^{-1} for 2 min and then heated to the desired holding temperature (67.5, 70 or 72.5 °C) at a heating rate of 3 °C/min, held isothermal for 10 min and then cooled down to 20 °C (5 °C/min). Throughout the heating and cooling steps a shear rate of either 150 or 50 s^{-1} was maintained. The maximum viscosity was attained during the heating or the isothermal step, depending on the setpoint temperature. The relative breakdown was calculated as the difference between the maximum viscosity and the viscosity at the end of the isothermal step, divided by the maximum viscosity (expressed as percent). The cooled samples were recollected and stored for 24 h in the refrigerator (5 °C) for further analysis.

2.4. Statistical analysis

IBM SPSS Statistics software (version 20, SPSS inc., Chicago, USA) was used for statistical comparison of the 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.

2.5. Particle size determination

The particle size distribution of the cooled starch pastes were 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 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 set to 0.1 (Tecante & Doublier, 1999; Zhu, Gayin, Chatel, Dewettinck, & Van der Meeren, 2009).

2.6. Flow curves of cooled pastes

The flow curves of the cooled pastes were recorded using cross hatched aluminum plate-plate geometry with solvent trap. The gap was set at 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}.The absence of wall slip was verified by comparing different gap sizes (1000, 2000 and 3000 μm) for some randomly selected samples as suggested by Barnes (1995). 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). The resulting data 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 $\dot{\gamma}$, the parameters σ_0, k and n represent the yield stress, the consistency index and the flow behavior index, respectively. Flow curves of the maize starch systems were fitted over a shear rate range of 0.01 s^{-1} to 100 s^{-1}, and those of the potato starch systems were fitted from 0.1 s^{-1} to 100 s^{-1} to obtain a better match with the model.

3. Results and discussion

3.1. Determination of processing temperatures and isothermal gelatinization

DSC experiments were performed to determine the most optimal temperatures for the pasting experiments. For the maize system, gelatinization was not influenced by the xanthan content, as there were no statistical differences between the gelatinization temperatures and gelatinization enthalpy of the samples when heated in a continuous ramp to 99 °C, as demonstrated in our preceding paper (Heyman, De Hertogh, Van der Meeren, Depypere, & Dewettinck, in press). Between the two NaCl contents there is a difference in gelatinization temperatures of about 3 °C. The average temperature between the gelatinization onset and the gelatinization peak of the systems at 0.01 M NaCl and 0.1 M NaCl, i.e. 70 °C and 72.5 °C respectively, were chosen as processing temperature for the isothermal step. In order to control the size of the experimental setup, only discrete temperature steps of 2.5 °C were considered. The fraction of the starch that remained ungelatinized was also quantified by DSC. These experiments revealed that after heating at 70 °C for 10 min, about 11% of the starch is ungelatinized for the xanthan free system and 17% for the xanthan containing system at the lowest salt content (Fig. 1). This illustrates that particularly under these low temperature conditions xanthan gum might affect the gelatinization process, probably by restricting water diffusion into the amorphous regions of the starch. At the highest salt content (0.1 M), the ungelatinized fraction was about 63%, meaning that the larger part of the granules remained ungelatinized. The gelatinization occurs over a quite broad temperature range, and the preceding isothermal step caused a fractionation between the granules gelatinizing at the lowest temperatures and the ones gelatinizing at the higher temperatures. After an isothermal step of 72.5 °C, the systems with a salt content of 0.01 M were fully gelatinized, whereas about 20% remained ungelatinized in the presence of 0.1 M NaCl.

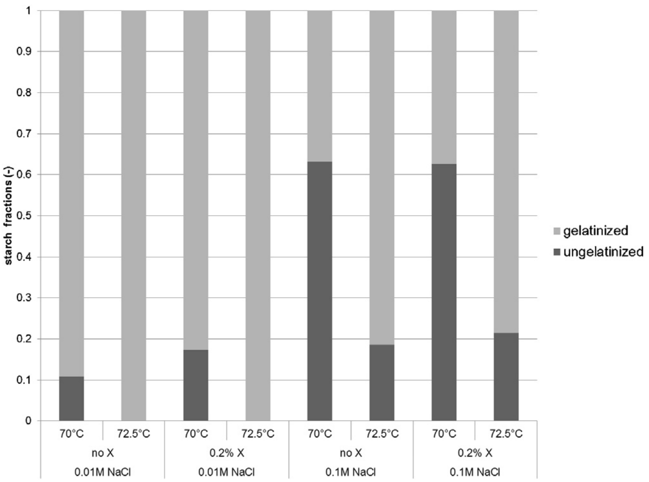

Fig. 1. Fractions of gelatinized and ungelatinized waxy maize starch/xanthan systems after isothermal steps at 70 °C and 72.5 °C.

For the waxy potato starch, the differences in salt content seemed to have a less strong effect on the gelatinization temperatures, only a slight shift of less than 1 °C was detected when increasing the salt content from 0.01 to 0.1 M (Heyman et al., in press). A temperature of 67.5 °C was chosen as isothermal processing temperature, along with 70 °C. All samples appeared to be fully gelatinized after an isothermal step at 70 °C, but this was not the case at 67.5 °C. For the xanthan-free system 12% of the starch was ungelatinized at the lowest salt content and 22% for the systems with 0.1 M NaCl. In the case of the xanthan containing dispersions, this was 16% and 24%, respectively (data not shown).

The selected processing temperatures clearly offered the opportunity to work at different degrees of gelatinization. These selected temperatures were used as maximum temperatures of the pasting experiments.

3.2. Influence of processing conditions on pasting of starch/xanthan systems

When heated above the gelatinization temperature, swelling of starch granules becomes significant (Choi & Kerr, 2004; Jacquier et al., 2006; Li & Yeh, 2001; Zhu et al., 2009). In food applications heating is usually performed at temperatures well above the gelatinization temperature which can be important for microbial stability, but these temperatures are not necessarily optimal for starch functionality, particularly because starch degradation might occur. Therefore, in most commercial applications crosslinked starches are used, which can withstand or even require more elevated temperatures and higher levels of shearing. Native waxy starches swell quickly when heated above the gelatinization

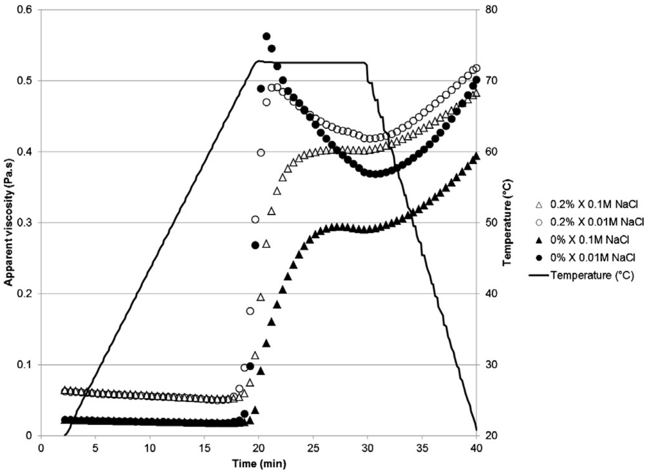

Fig. 2. Pasting behavior of waxy maize starch at 72.5 °C and shear rate of 150 s^{-1}.

temperature as demonstrated by Jacquier et al. (2006). This rapid swelling is at least partially responsible for their high shear sensitivity. In this setup temperatures were kept as closely as possible to the gelatinization temperature to avoid excessive swelling and consequently rupture of the granules. The heating rate was kept relatively low (3 °C/min) to allow an equal temperature distribution all over the sample and to avoid local temperature overshoot. Pasting experiments were performed at two different shear rates (50 s^{-1} and 150 s^{-1}) to evaluate the shear tolerance of the samples. At too low shear rates sedimentation of starch granules could occur, particularly in the xanthan-free systems. High shear rates (>200 s^{-1}) appeared to be too destructive for some of the samples.

Fig. 2 depicts the pasting behavior of the maize starch systems at a temperature of 72.5 °C and a shear rate of 150 s^{-1}. Peak viscosities and breakdown derived from the different pasting experiments are represented in Table 1. For maize starch it is clear that the limited amount of gelatinization of the samples with 0.1 M NaCl at 70 °C led to a largely incomplete swelling of the starch granules. For the lowest salt contents a significant viscosity increase indicated a fair extent of granule swelling at this temperature. When processed at a shear rate of 50 s^{-1} no breakdown took place, and the xanthan containing sample did not even show breakdown at the highest shear rate. When pasting was performed at 72.5° C, all samples at the lowest salt content exhibited breakdown. However, this parameter was clearly lower when xanthan was present. At this temperature the samples containing 0.1 M salt showed a significant swelling. When sheared at 50 s^{-1} no equilibrium viscosity was attained during the isothermal step. Conversely, plateau values were recorded at a shear rate of 150 s^{-1}. Similar to the processes at 70 °C, there was no or significantly less breakdown of the systems when xanthan gum was present.

The differences in gelatinization temperature between the highest and the lowest salt content were much lower for the potato starch systems. Nonetheless at 67.5 °C the systems at 0.1 M NaCl showed (curves not represented) an incomplete swelling when processed at 50 s^{-1} as indicated by the continuously increasing viscosity, but at higher shearing (150 s^{-1}) plateau values (xanthan containing paste) and even breakdown (xanthan free paste) was observed. Elevating the temperature to 70 °C allowed more granules to gelatinize and swell at 0.1 M NaCl, whereas the samples with the lowest salt content became more sensitive to breakdown as illustrated for the sample without xanthan at 50 s^{-1} and for both samples at 150 s^{-1} (Table 1).

These results clearly demonstrate that the pasting behavior of shear sensitive starches can be better controlled at low temperatures. By selecting a processing temperature slightly higher than the gelatinization onset, breakdown can clearly be limited. Furthermore an increased shear rate facilitated the viscosity build-up at slowly swelling conditions, similar to crosslinked starches (Nayouf et al., 2003), but could lead to breakdown at higher temperatures. In practice operation temperatures can be chosen slightly lower when higher shear rates are applied and vice versa. Nonetheless a correct choice of the operating temperature appears to be most decisive.

Xanthan gum can clearly play a mediating role in starch granule swelling at these moderate temperatures. Breakdown was significantly reduced for all investigated samples. DSC experiments suggested that at these temperature conditions gelatinization is partially inhibited by xanthan. This could imply a more restricted swelling of the granules and consequently a more reduced breakdown. Particularly at the lowest salt content pasting viscosities of the xanthan containing samples are lower than for the xanthan free systems. As it was demonstrated in our preceding paper (Heyman et al., in press), this marked viscosity reduction is not caused by a more restricted swelling, but appears to be the result of two complex phenomena: a reduced viscosity of the continuous xanthan

Table 1
Pasting properties of different starch/xanthan mixtures as influenced by temperature and shear rate.

Starch type	Isothermal step (°C)	NaCl (M)	Conc. xanthan	Shear rate 50 s^{-1}		Shear rate 150 s^{-1}	
				Maximum viscosity (Pa.s)	Relative breakdown (%)	Maximum viscosity (Pa.s)	Relative breakdown (%)
Maize	70	0.01	0%	0.787 ± 0.007^{E}	0.0	0.373 ± 0.005^{D}	7.5
			0.2%	0.657 ± 0.004^{D}	0.0	0.376 ± 0.005^{D}	0.0
		0.1	0%	0.021 ± 0.000^{A}	0.0	0.036 ± 0.000^{A}	0.0
			0.2%	0.136 ± 0.004^{B}	0.0	0.119 ± 0.003^{B}	0.8
	72.5	0.01	0%	1.210 ± 0.014^{G}	15.9	0.564 ± 0.012^{F}	34.1
			0.2%	1.062 ± 0.015^{F}	3.3	0.492 ± 0.003^{E}	14.6
		0.1	0%	0.499 ± 0.028^{C}	0.0	0.295 ± 0.016^{C}	1.7
			0.2%	0.694 ± 0.008^{D}	0.0	0.403 ± 0.014^{D}	0.5
Potato	67.5	0.01	0%	1.886 ± 0.033^{C}	0.0	0.862 ± 0.009^{C}	14.2
			0.2%	1.126 ± 0.033^{A}	0.0	0.624 ± 0.002^{A}	1.1
		0.1	0%	1.230 ± 0.179^{A}	0.0	0.700 ± 0.010^{B}	3.7
			0.2%	1.408 ± 0.025^{B}	0.0	0.729 ± 0.018^{B}	1.1
	70	0.01	0%	2.201 ± 0.047^{D}	9.2	1.034 ± 0.014^{E}	29.5
			0.2%	1.329 ± 0.070^{B}	0.0	0.727 ± 0.021^{B}	4.1
		0.1	0%	1.884 ± 0.006^{C}	0.8	0.946 ± 0.022^{D}	18.6
			0.2%	1.901 ± 0.004^{C}	0.5	0.878 ± 0.004^{C}	13.4

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

Table 2
Average granule diameters as influenced by pasting conditions.

NaCl (M)	Conc. xanthan	Shear rate (s^{-1})	Maize		Potato	
			D(0.1)	D[4,3]	D(0.1)	D[4,3]
			70 °C		67.5 °C	
0.01	0%	50	15.2 ± 0.2	34.0 ± 0.7	46.0 ± 2.0	144.1 ± 3.5
		150	12.5 ± 0.1	29.3 ± 0.5	37.1 ± 0.3	123.1 ± 2.2
	0.2%	50	15.9 ± 0.4	35.7 ± 2.2	60.0 ± 0.7	175.0 ± 1.8
		150	14.3 ± 0.2	34.6 ± 1.1	48.2 ± 0.8	149.6 ± 1.5
0.1	0%	50	13.1 ± 0.4	28.0 ± 0.5	47.7 ± 1.3	148.9 ± 2.4
		150	12.8 ± 0.2	27.9 ± 0.3	35.3 ± 0.6	110.3 ± 1.1
	0.2%	50	12.6 ± 0.3	27.4 ± 0.3	49.3 ± 1.0	156.3 ± 4.0
		150	12.3 ± 0.9	27.0 ± 1.2	38.4 ± 2.3	122.6 ± 5.7
			72.5 °C		70 °C	
0.01	0%	50	13.8 ± 0.1	34.0 ± 0.6	45.3 ± 0.8	140.5 ± 1.1
		150	11.3 ± 1.0	29.0 ± 0.6	37.3 ± 1.1	124.1 ± 2.4
	0.2%	50	14.7 ± 0.6	36.8 ± 1.6	52.4 ± 1.4	175.1 ± 12.0
		150	11.0 ± 0.2	33.0 ± 0.7	43.1 ± 0.4	136.9 ± 2.5
0.1	0%	50	15.2 ± 0.1	32.6 ± 0.8	42.9 ± 0.8	134.6 ± 2.1
		150	13.4 ± 0.1	29.9 ± 0.2	32.1 ± 0.7	108.3 ± 4.8
	0.2%	50	14.6 ± 0.1	32.1 ± 0.6	48.6 ± 3.2	148.5 ± 8.3
		150	14.5 ± 1.0	32.3 ± 0.1	36.6 ± 1.7	121.0 ± 7.3
			85 °C		85 °C	
0.01	0%	50	9.6 ± 0.2	29.9 ± 0.5	44.3 ± 0.1	143.8 ± 0.0
	0.2%	50	9.4 ± 0.7	37.8 ± 2.0	46.4 ± 0.6	145.3 ± 1.8

phase and a modified granule interaction as caused by xanthan gum. When xanthan gum is heated at low salt contents, its rigid helical structure transforms to a random coil with much lower viscosity (Capron, Brigand, & Muller, 1998; Choppe, Puaud, Nicolai, & Benyahia, 2010; Milas & Rinaudo, 1986). At higher salt contents this transition does not take place, which explains the differences between the two salt contents. Furthermore xanthan gum most likely can change the manner in which particles interact during the pasting process. It was suggested before that xanthan gum is capable of enwrapping the starch granules (Cai et al., 2011; Chaisawang & Suphantharika, 2006; Gonera & Cornillon, 2002). This envelope might physically stabilize the particle by acting as a lubricating layer. Another explanation might be that an increased viscosity in the presence of xanthan in the continuous phase reduces the turbulence in the starch pastng cell and hence the Reynolds number, which leads to a lower collision rate of the granules (Walstra, 2003). These phenomena might explain why systems, even with the same extent of granule swelling, can exhibit lower viscosities when xanthan gum is present. These observations suggest that a restriction in swelling, if it occurs, is probably not the only reason for the stabilizing effect of xanthan gum, but a reduced intergranular impact might cause this as well.

3.3. *Particle size distributions of the cooled pastes*

Particle size distributions of the cooled pastes were determined after 24 h of storage at 5 °C. Two different derived diameters were taken into consideration. Besides the volume–weighted mean diameter D[4,3] the 10th percentile of the volume–weighted particle size distribution D(0.1) was considered. The latter is a measure for the smaller fragments as a consequence of granule breakdown, as 10% (*V*) of the particles have a diameter smaller than this one. It is interesting to consider both values together as the obtained average diameters are usually the result of granule swelling and granular breakdown. The derived diameters are summarized in Table 2.

For the maize starch systems processed at 70 °C, differences in particle diameters could only be observed at the lowest salt content (Table 2). In these cases the granule size was lower when pasted at a shear rate of 150 s^{-1}. However this reduction was much less pronounced when xanthan gum was present. Similar trends are observed for the pastes prepared at 72.5 °C. At a salt content of 0.1 M the xanthan containing system exhibited larger diameters when pasted at 150 s^{-1} whereas there was no noticeable difference at the lowest shear rate. In general these results confirm the findings of the pasting experiments, because some clear correlations exist between the measured breakdown and the corresponding granule size diameters. In this manner the stabilizing properties of xanthan gum were demonstrated. Granules of samples where swelling was limited or incomplete, and breakdown seemed not to occur, appeared not to be influenced by xanthan gum. This could prove that xanthan gum does not restrict swelling of the granules at the concentrations considered here. Although it should be noted that – based on the DSC measurements – xanthan gum might reduce the number of granules that can gelatinize and swell in the given conditions. This does not necessarily mean that the ones that are capable of swelling adopt smaller diameters. As the volume-weighted mean diameter D[4,3] is dominated by the size of the fully swollen granules, the contribution of the unswollen granules might be overlooked.

Comparable results were obtained for the potato starch system, although the differences between both shear rates were more distinct, even in the presence of xanthan gum (Table 2). In all of these systems the average diameters were much lower when processed at 150 s^{-1}, indicating a stronger shear sensitivity than for the maize starch. Again the granules of the xanthan containing pastes always proved to be larger compared to the gum free systems. In this case the effect of xanthan gum appears to be much more pronounced at the lowest salt content. This might be related to the xanthan transition or by a higher electrostatic repulsion at low salt concentrations. The xanthan transition as such did not seem to have a distinct effect in the case of the maize system because comparable effects could be noted at the lowest as well as the highest salt content. Of course comparison between systems with high and low salt content was not straightforward given their difference in gelatinization temperature. In Table 2 the diameters of starches pasted at 85 °C are represented as well. These results demonstrate the positive effects of processing near the gelatinization temperature: the number of small granule fragments is reduced (higher D(0.1) values), as a result of the reduced starch breakdown.

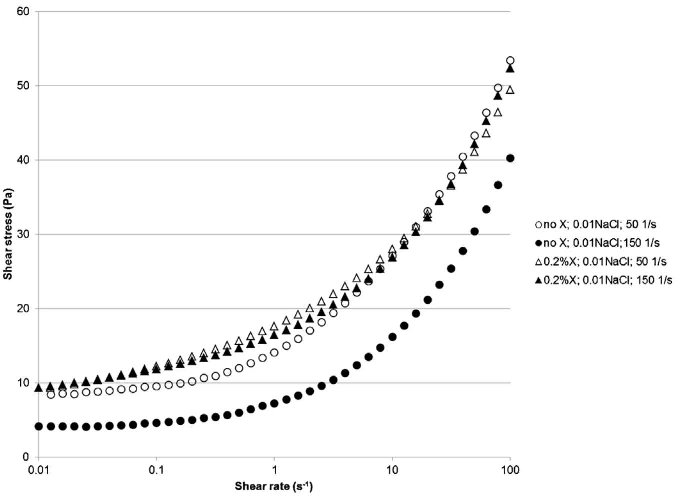

Fig. 3. Flow curves of cooled waxy maize starch pastes as influenced by pasting conditions (all pasted at 70 °C).

3.4. Flow curves of the cooled pastes

Flow curves of the cooled maize starch pastes prepared at 70°C 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. Only the samples with a NaCl concentration of 0.01 M were considered. Granule swelling was too limited at 0.1 M, resulting in a watery suspension of largely ungelatinized starch granules. Table 3 summarizes the derived Herschel–Bulkley parameters for all the investigated systems. In the xanthan free systems, the higher shear during pasting, and consequently the higher extent of granule degradation, shifts the flow curves to lower values, which is translated in lower values of the yield stress and consistency index. Samples in which more disruption took place, are also characterized by a higher flow behavior index. Most likely the increased values of the yield stress and the consistency index, cannot solely be attributed to differences in granular preservation, but the properties of the continuous phase might play a role as well. In dilute systems, the rheological behavior is governed by the properties of the continuous phase, e.g. the dissolved hydrocolloids, as well as the volume occupied by the swollen starch granules. In this manner highly swelling starches induce higher viscosities. At higher starch contents when granules are more closely packed, the rigidity of the granules dominates the rheological behavior (Steeneken, 1989). At the given concentrations, the maize starch occupies a volume of about 20% which is far below close packing (calculation based on the volume equivalent average diameter D[3,0] of the swollen and unswollen granules). So it can be assumed that the continuous phase, which contains xanthan gum, still strongly influences the rheological behavior. However, Abdulmola et al. (1996) stated that even below close packing swollen starch granules interact and influence the small deformation rheology. Most likely the starch granules dominate the rheological behavior at low shear rates, whereas the influence of the continuous phase is more noticeable at higher shear rates.

The Herschel–Bulkley model appeared to be less suitable to fit the flow curves of the potato starch systems. Therefore, the low shear data (<0.1 s^{-1}) were omitted in the fit. Consequently the differences between σ_0 and k values suggest larger differences than would be expected from the location of the flow curves. Because of the strong correlation between both fitted parameters, higher values of k give rise to lower values of σ_0 and vice versa. Empirically the differences between the sums of the yield stress and consistency index correspond well with the differences seen in

Table 3
Herschel–Bulkley parameters of cooled starch pastes (20 °C), prepared at different pasting conditions.

Conc. NaCl (M)	Conc. xanthan	Shear rate (s^{-1})	Maize				Potato				
			σ_0	k (Pa s^n)	n (−)	R^2	σ_0	k (Pa s^n)	n (−)	Sum $\sigma_0 + k$	R^2
			70 °C				67.5 °C				
0.01	0%	50	5.9 ± 0.3	8.8 ± 0.3	0.37 ± 0.01	0.997	16.6 ± 0.5	9.0 ± 0.5	0.39 ± 0.01	25.7	0.996
		150	3.1 ± 0.4	4.4 ± 0.4	0.47 ± 0.02	0.977	14.6 ± 0.3	6.3 ± 0.2	0.48 ± 0.01	20.9	0.998
	0.2%	50	6.5 ± 0.2	11.0 ± 0.2	0.29 ± 0.00	0.999	3.6 ± 0.5	16.5 ± 0.5	0.25 ± 0.01	20.1	0.999
		150	8.3 ± 0.3	8.0 ± 0.3	0.37 ± 0.01	0.994	16.6 ± 0.4	6.1 ± 0.4	0.42 ± 0.01	22.7	0.994
0.1	0%	50	Not determined				4.8 ± 1.0	5.7 ± 0.9	0.40 ± 0.03	10.5	0.966
		150	Not determined				8.3 ± 0.4	5.0 ± 0.4	0.45 ± 0.02	13.2	0.992
	0.2%	50	Not determined				0.2 ± 0.5	14.1 ± 0.5	0.27 ± 0.01	14.3	0.999
		150	Not determined				13.2 ± 0.8	10.3 ± 0.8	0.31 ± 0.01	23.5	0.992
			72.5 °C				70 °C				
0.01	0%	50	7.9 ± 0.2	9.8 ± 0.3	0.40 ± 0.01	0.998	30.6 ± 0.6	6.1 ± 0.5	0.51 ± 0.02	36.7	0.990
		150	6.3 ± 0.1	4.3 ± 0.1	0.56 ± 0.01	0.999	22.6 ± 0.3	4.0 ± 0.2	0.58 ± 0.01	26.6	0.996
	0.2%	50	12.6 ± 0.4	9.0 ± 0.4	0.39 ± 0.01	0.989	13.2 ± 0.4	11.8 ± 0.4	0.32 ± 0.01	25.0	0.998
		150	9.8 ± 0.5	6.3 ± 0.5	0.44 ± 0.02	0.981	22.1 ± 0.5	5.3 ± 0.4	0.47 ± 0.02	27.3	0.991
0.1	0%	50	3.9 ± 0.3	6.0 ± 0.4	0.39 ± 0.01	0.989	18.8 ± 1.1	7.8 ± 1.0	0.43 ± 0.03	26.6	0.979
		150	2.4 ± 0.1	4.1 ± 0.1	0.48 ± 0.00	0.999	16.8 ± 0.1	4.7 ± 0.1	0.54 ± 0.00	21.5	1.000
	0.2%	50	5.3 ± 0.2	9.2 ± 0.2	0.33 ± 0.00	0.998	10.9 ± 1.3	15.9 ± 1.3	0.30 ± 0.01	26.8	0.991
		150	5.1 ± 0.3	12.1 ± 0.3	0.29 ± 0.00	0.998	20.4 ± 1.2	12.9 ± 1.2	0.33 ± 0.02	33.3	0.988

the location of the flow curves. For the xanthan free systems, flow curves of systems pasted at 150 s^{-1} were systematically located below the curves of pastes prepared at 50 s^{-1}. When xanthan gum is present, the location of the flow curves appeared more difficult to predict based on the pasting degradation and particle size distributions. At 0.01 M NaCl pasting experiments and particle size distributions showed less granule disruption when xanthan was present, but when processed at 50 s^{-1} flow curves of the these systems were lower than their gum free counterparts. When pasted at 150 s^{-1} their differences were less pronounced. At 0.1 M NaCl, the addition of xanthan gum shifted the flow curves upwards, which was expressed as higher values of the yield stress and the consistency index. For all samples processed at 50 s^{-1}, the addition of xanthan gum led to a significant reduction of the yield stress, an increased consistency index, and a lower flow behavior index. This distinct behavior may suggest a specific interaction between starch and xanthan, that modifies the way particles interact, so the flow behavior cannot be predicted solely based on the granule size as it was also observed during the pasting experiments. Although data are lacking to draw general conclusions, still electrostatic interactions are most likely influencing this behavior. A number of researchers have suggested an electrostatic incompatibility between xanthan gum and the potato starch which has an anionic nature due to its high degree of phosphorylation (Cai et al., 2011; Shi & BeMiller, 2002; Sikora et al., 2008). This repulsion might in turn be (partially) shielded by the present ions, explaining the differences between both salt contents. Furthermore the interpretation of the flow behavior of these potato starch systems is complicated by the fact that they cannot be considered as simple particles imbedded in a continuous phase of dissolved xanthan gum. Potato starch granules swell to relatively large dimensions, even when processed at moderate temperatures, they take in large effective volume fractions. Therefore they are likely to deform and even break up within a flow field.

3.5. Effect of varying starch concentrations

The previous results showed the beneficial effects of both moderate temperature processing and xanthan gum on the stabilization of waxy starch granules during pasting at a fixed starch:water ratios of 5:100. The differences observed between maize starch and potato starch, might be attributed to their completely different swelling power and hence their effective volume fraction in the dispersion. At higher starch volumes, the particle-particle collisions are increased during shear and consequently the mutual impact. Therefore it might be possible that the aforementioned positive effects, namely the higher degree of starch granule preservation, are cancelled out at higher starch contents. To examine this, pasting experiments were compared at different starch contents. For maize starch an isothermal temperature of 70 °C was selected and for potato starch this was 67.5 °C. At these temperatures the systems exhibited satisfactory results for a salt content of 0.01 M. Fig. 4 represents the pasting behavior of the different potato starch systems. These results demonstrate that at higher starch contents there is some breakdown, but it still remains limited, presumably as a result of restricted swelling at a moderate temperature. Similar results were observed for the maize starch system at a ratio of 7:100 (data not represented). Furthermore the positive effects of xanthan gum are clearly demonstrated as no breakdown could be observed for all systems. A possible consequence might be that swelling is more restricted, especially at the higher starch contents, water might be limiting and competition with xanthan gum could result in less water imbibition. This is demonstrated as a clearly less steep viscosity increase during pasting. For the maize starch systems, the differences in particle size remained limited. Only a slight influence of xanthan gum can be observed at higher starch ratios. There is also no pronounced difference in granule diameter by increasing the starch content. So swelling should not be restricted by water limitation. In the case of potato starch, some clear differences exist between all concentrations (Fig. 5). Potato starch has a high swelling power and in these systems, the higher concentration clearly limits granule swelling. When xanthan gum was present, higher diameters were measured, most likely due to less granule degradation. An exception could be observed at the lowest starch content where the average diameter of the xanthan containing system was lower than its counterpart. In these dilute systems it is very likely that starch granules swell freely to high dimensions without breaking down. In a more viscous medium this expansion of the granule might be more limited.

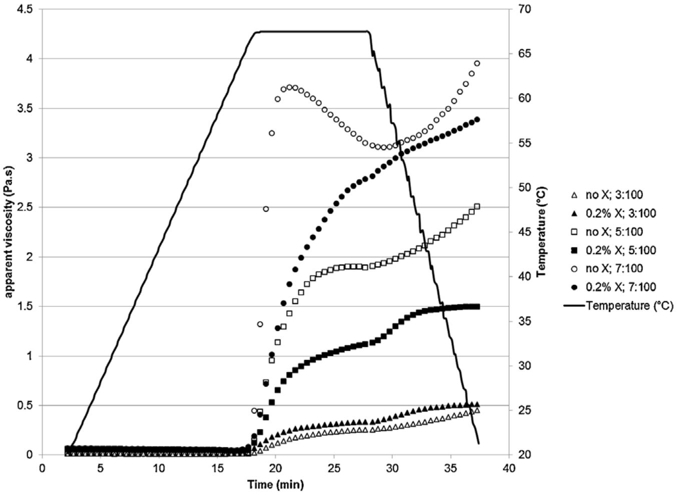

Fig. 4. Effect of xanthan gum on pasting behavior of waxy potato starch at different concentrations (67.5 °C; 0.01 M NaCl; shear rate 50 s^{-1}).

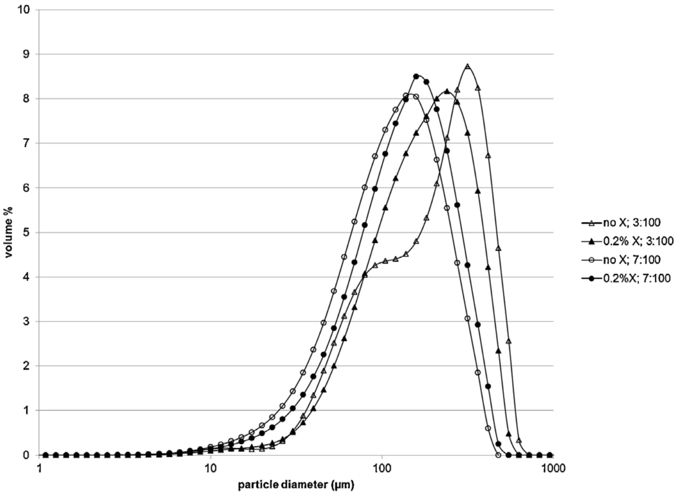

Fig.5. Influence of xanthan gum on particle size distributions of two different concentrations (3:100 and 7:100 dry starch:continuous phase) of waxy potato starch (pasted at 67.5 °C, shear rate 150 s^{-1}, 0.01 M NaCl).

4. Conclusions

When native waxy starches (maize or potato) are pasted at temperatures slightly higher than the gelatinization onset temperature, their swelling can be more controlled, but a limited fraction of the starch will remain ungelatinized. Under these conditions granule breakdown can be limited and a higher shear rate can even be beneficial in the development of the viscosity. The optimal temperature is therefore a critical point in the process. When the temperature is too low, swelling will be incomplete and at more elevated temperature breakdown will start. In the latter case the presence of xanthan can help to stabilize the granule, probably by altering the impact between the granules. Processing at temperatures within the gelatinization range, combined with the addition of xanthan gum can therefore improve the performance of native starches in food systems.

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