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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.

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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 ΔH_{ungel}. The fraction of the starch that did not gelatinize during the isothermal step was equal to $\Delta H_{ungel}/\Delta H_{tot}$.

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

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