

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

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Abstract

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

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1. Introduction

Starch gelatinisation is commonly defined as an irreversible order–disorder transition of starch granules from a structured state to a disordered state (starch pastes) upon heating in the presence of plasticisers. The normal sequence of events during gelatinisation process include granular swelling, loss of birefringence, loss of molecular orders and crystallinity, heat uptake, marked increase in viscosity and the polysaccharides (amylose) solubilisation (Cooke & Gidley, 1992; Derby, Miller, Miller, & Trimbo, 1975;

Donovan, 1979). These events underlie the technologically important properties of starch pasting and retrogradation, and are undoubtedly relevant to starch processing, its suitability for particular end uses as well as the final product properties (Cooke & Gidley, 1992).

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

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

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

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

The unique rheological responses noted during starch gelatinisation can be attributed to the changes in starch granular sizes and their overall distributions, changes in the granules concentration (volume fraction of the granules as they swell), the granules deformability as a result of water penetration and the presence of solubilised starch macromolecules in the continuous phase (Carnali & Zhou, 1996; Ellis et al., 1989; Evans & Haisman, 1979; Genovese & Rao, 2003; Paterson et al., 2001; Rao et al., 1997; Rao &

Tattiyakul, 1999; Svegmarm & Hermansson, 1993). These hypotheses were deduced by comparing results obtained in separate studies of granule sedimentation, swelling characteristics and size distribution measurements and subsequently relating these results to the rheological properties (Carnali & Zhou, 1996; Ellis et al., 1989; Evans & Haisman, 1979; Genovese & Rao, 2003; Paterson et al., 2001; Rao et al., 1997; Rao & Tattiyakul, 1999; Svegmarm & Hermansson, 1993).

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

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

2. Experimental methods

2.1. Materials

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

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