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Structural changes during starch pasting using simultaneous Rapid Visco Analysis and small-angle neutron scattering

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ABSTRACT

Rapid Visco Analysis (RVA) is an industry-wide method extensively used for determining the viscous properties of starch slurries enabling information to be extracted on pasting properties; however little is known about structural changes that occur during standard protocols. A commercial RVA instrument was modified to allow the passage of a neutron beam through its heating block and paddle assembly to enable the simultaneous measurement of SANS and RVA on a variety of commercial starches. SANS measurements were made at 1 min intervals throughout a standard 13 min RVA process across a q range of 0.018–0.2 Å^{-1}. In each of the starches, the well-known lamellar structure was observed up to the point at which the viscosity began to increase markedly. At this stage, the lamellar structure transformed instantaneously; the scattering patterns are indicative of the formation of a large scale structure with no apparent semi-crystalline properties and whose spatial arrangement may be analysed in terms of a fractal-like gel. The basic building blocks of this gel, under the assumption that they are spheroidal, appear to have dimensions of approximately 1 nm across all the starches tested. The sizes of the aggregates formed are several times larger and were found to vary across the time course of the experiment.

1. Introduction

Starch is the key carbohydrate in the human diet and the major storage polysaccharide in plants. It also finds increasing use in the polymer and pharmaceutical industries, in particular biofuels. The starch granule in the native state possesses a hierarchical structure from the micron- down to the nano-scale. This directly influences a number of properties of relevance from both a physiological and industrial perspective. Viscosity, and changes thereof during the pasting process (Atwell, Hood, Lineback, Varriano-Marston, & Zobel, 1988), is one such factor although the nano-scale structural changes that accompany such transitions are poorly understood.

Starch pasting rheology has commonly been studied with a Rapid Visco Analyser (Colombo, Leon, & Ribotta, 2011; Crosbie & Ross, 2007; Gomand, Lamberts, Visser, & Delcour, 2010; Wrigley, Booth, Bason, & Walker, 1996). In this device, the rotation of a pitched paddle impeller ensures that starch slurries are suspended during a controlled heating and cooling process. During a heating and cooling cycle in excess water, several changes in the RVA profile are observed. Firstly, a sufficient number of starch granules undergo rapid swelling and partial amylose leaching, particularly following gelatinisation, that a rapid rise in viscosity is observed. Under conditions of both heat and shear, the granules are partially disrupted and the leached amylose aligns leading to a reduction in viscosity in most cases. On subsequent cooling, the hydrated polymers re-associate and the material undergoes a transition to a gel type structure observed as a 'setback' or increase in viscosity (illustrated in Fig. 3(a)). The sum of these processes can be observed in the classic RVA pasting curve. The relationship between viscosity, as measured in an RVA, and average shear rates has been described by Lai, Steffe, and Ng (2000). Putseys, Gommes, Van Puyvelde, Delcour, and Goderis (2011) recently reported on the gelation behaviour of heat treated aqueous starch, with in situ rheometry in a Couette configuration using synchrotron SAXS. They determined that the scattering patterns obtained in this configuration suggested the formation of cylindrical scattering objects, growing into larger fractal aggregates upon cooling.

Starch is deposited in granules that show considerable botanical variation in shape and size distribution; generally granules range from 2 μm to 100 μm in dimension (Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994; Perez & Bertoft, 2010). Most of the dry weight of

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the starch granule is composed of essentially linear amylose and highly branched amylopectin, the exact ratio varying considerably depending on genomic origin (Takeda, Hizukuri, Takeda, & Suzuki, 1987). The granules are further subdivided into growth ring structures, which are generally accepted to alternate between amorphous and semi-crystalline structures. This alternation is not well understood biophysically but in at least some plants may have its origin in variable diurnal deposition patterns. The semi-crystalline rings have been shown to consist of alternating 'crystalline' and 'amorphous' structures, with a repeating periodicity of approximately 90–100 Å which is readily observed using small angle neutron and X-ray scattering (SAXS/SANS) of hydrated granules (Blazek & Gilbert, 2011; Cameron & Donald, 1992; Waigh, Gidley, Komanshek, & Donald, 2000). At smaller length scales, wide angle X-ray scattering has demonstrated the existence at the molecular level of various crystal lattice types; for example, so-called A-type crystal structures being observed for cereal starches and B-type starches being observed for tubers and high amylose starches; these have monoclinic and hexagonal unit cells, respectively (Perez & Bertoft, 2010; Salman et al., 2009). There is now acceptance that there exists an intermediate level of organisation between the lamellae and growth rings. Indeed, the use of imaging techniques such as AFM on starch granules has provided some evidence for so-called blocklets; however very little is known about the details of these structures at present (see Perez & Bertoft, 2010 for review).

In general, when starch granules are heated in excess water above approximately 60 °C, the semi-crystalline structure of the starch granule is disrupted; although, in high amylose starches this occurs at higher temperature (Shi, Capitani, Trzasko, & Jeffcoat, 1998). A variety of granular, growth ring and molecular level mechanisms are thought to interplay in this process (Jenkins & Donald, 1998; Putseys et al., 2011; Vermeylen et al., 2006; Waigh et al., 2000) and the transition is irreversible. Specifically, the granules undergo a swelling process, accompanied by extensive changes in water distribution within the granule. There is also a loss of crystalline component and amylose leaching (Waigh et al., 2000). The gelatinisation behaviour of starch slurries has been studied previously using scattering techniques (I'Anson, Mile, Morris, Ring, & Nave, 1988; Jenkins & Donald, 1998; Putseys et al., 2011; Vallera, Cruz, Ring, & Boue, 1994). Cameron and Donald (1992) demonstrated that crystallinity was mainly lost during the endothermic phase of gelatinisation, after water appeared to enter the amorphous growth rings, with the crystalline regions appearing relatively unaffected during this early phase. They postulated that, beyond a critical level of swelling, stresses imposed on molecules in the semi-crystalline layers would eventually destroy the crystallinity. Vallera et al. (1994) performed SANS measurements across a wide q-range in amylose gels and concluded that the scattering spectra were not consistent with those that would be expected from true independent scattering particles such as spheres or rods; as a result, they analysed the gelation in terms of a biphasic polymer structure, with the polymer-rich phase organised into aggregated clusters that have a fractal structure. The fractal dimension of the final structures was found to be consistent with diffusion-limited aggregation.

Neutrons have several key advantages for analysing the nanostructure of food systems, in particular their relatively high penetration through dense or concentrated samples and sample environments as well as the ability to avoid beam damage relative to more intense synchrotron X-rays (Lopez-Rubio & Gilbert, 2009). We make use of these particular attributes to enable the simultaneous measurement of RVA and SANS, for the first time, to understand more fully the structural changes taking place during starch pasting.

2. Method

2.1. Small-angle neutron scattering

SANS experiments were conducted on the Quokka instrument at the Australian Nuclear Science and Technology Organisation (ANSTO) (Gilbert, Schulz, & Noakes, 2006). The instrument was operated at a wavelength, λ, of 5.078 Å with 14% wavelength resolution. All samples were prepared in D_2O at the same concentrations as typically used in RVA standard protocols as described below. Data were collected at equal source-to-sample (SSD) and sample-to-detector distance (SDD) of approximately 4 m with an aperture size = 7.5 mm yielding a q range of 0.018–0.200 $Å^{-1}$ where q is the magnitude of the scattering vector q defined as:

$$q = \frac{4\pi}{\lambda} \sin\,\theta \tag{1}$$

and 2θ is the scattering angle. One data set was also collected at longer distances of SSD ~ SDD ~ 20 m over a q range of 0.0039–0.0419 $Å^{-1}$ for tapioca starch, after completion of the RVA profile, to measure the structure of the material post-gelatinisation. Scattering from D_2O solvent sample in the RVA was collected and used as a scattering background. SANS datasets were reduced, normalised and radially averaged using a package of macros in Igor software originally written by Kline (2006) and modified to accept *HDF5* data files from Quokka. Scattering curves are plotted as absolute (SANS) intensity, I, versus q. SANS data collection was synchronised and initiated with a modification of the AACC standard 1 RVA H95 profile (AACC, 1999).

2.2. Rapid Visco Analyser

An RVA was modified to enable the simultaneous measurement of SANS. To do this a hole was drilled through the heating block to enable passage of the neutron beam. Additional borated aluminium shielding was installed to minimise activation of the RVA in addition to an upstream Cd aperture of 17.5 mm. Standard aluminium cans were used but the pitched paddle impeller was modified both to minimise scattering from the paddle itself and to ensure minimal multiple scattering (see Fig. 1). To do this, the plastic paddle, which would be a source of significant neutron scattering due to the large hydrogen content of the material, was replaced by one constructed from aluminium; the latter material has a significantly lower neutron scattering cross-section. Furthermore, a hollow, cylindrical band was incorporated into the centre of the paddle to ensure a scattering path length of 1 mm on either side between the outer surface of the paddle and the inner surface of the surrounding aluminium can. The performance of the paddle used was directly compared with the standard plastic paddle yielding highly comparable results. Samples were hydrated with D_2O instead of H_2O to significantly reduce the incoherent scattering background at a weight ratio of 3.00 g of starch–47.8 g of D_2O (equivalent to mass of 43.0 g of H_2O but taking into account the greater physical density of D_2O). Off-line comparison of H_2O and D_2O-hydrated starch shows that they are qualitatively similar (unpublished data).

A modified form of RVA Standard 1 (AACC, 1999) was used to provide a 13 min pasting profile, with maximum temperature of 95 °C. The temperature was held at a value of 25 °C for the first minute, and then allowed to ramp up to 95 °C, which was reached after an elapsed time of 4 min and 45 s. This temperature was then held until 7 min 15 s before being allowed to cool back down to 25 °C, after an elapsed time of 11 min; the device was held in this condition for a further 2 min. Samples were stirred at 960 rpm during the initial transmission measurement (2 min data collection). Thereafter, 1 min scattering runs were taken simultaneously with the RVA profile. Due to the mass of starch used in these experiments