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Understanding starch gelatinization: The phase diagram approach

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ABSTRACT

By constructing a detailed phase diagram for the potato starch–water system based on data from optical microscopy, synchrotron X-ray scattering and differential scanning calorimetry, we show that gelatinization can be interpreted in analogy with a eutectic transition. The phase rule explains why the temperature of the gelatinization transition (G) is independent on water content. Furthermore, the melting (M1) endotherm observed in DSC represents a liquidus line; the temperature for this event increases with increasing starch concentration. Both the lamellar spacing and the inter-helix distance were observed to decrease with increasing starch content for starch concentrations between approximately 65 wt% and 75 wt%, while the inter-helix distance continued decreasing upon further dehydration. Understanding starch gelatinization has been a longstanding challenge. The novel approach presented here shows interpretation of this phenomenon from a phase equilibria perspective.

1. Introduction

Starch is a biopolymer of immense importance composed of the two α-D-glucose based polysaccharides amylose and amylopectin. While amylose is essentially linear, amylopectin is highly branched (Buléon, Colonna, Planchot, & Ball, 1998a; Hoover, 2001, Pérez & Bertoft, 2010; Tester, Karkalas, & Qi, 2004). Starch is synthesized in nature as granules with alternating semi-crystalline and amorphous domains in concentric growth rings. The semi-crystalline domains mainly consist of amylopectin whereas the amorphous parts are composed of amylose and non-crystalline amylopectin. The crystalline regions consist of short amylopectin side-chains which adopt either A (Imberty, Chanzy, Pérez, Buleon, & Tran, 1988), B (Imberty & Pérez, 1988) or C type crystallinity, where the C type is a mixture of A and B (Buléon, Gerard, Riekel, Vuong, & Chanzy, 1998b). The type of crystalline polymorph depends on the length of the short chain fraction in amylopectin: shorter chains, found in e.g. cereal grains, favor formation of A type crystallites whereas longer chains, found in e.g. tubers, typically form B type crystallites. It has also been found that, when a transition from one crystallite type to another is possible, increased hydration favors B type crystallinity (Carlstedt, Wojtasz, Fyhr, & Kocherbitov, 2014). When sufficiently hydrated, the inter-crystalline amorphous regions are plasticized which allows the crystalline regions to be ordered into a lamellar structure with a repeat distance of approximately 9 nm (Waigh et al., 1997). Water thus has both plasticizing and structuring roles in starch (Paris, Bizot, Emery, Buzaré, & Buléon, 1999).

When heated in the presence of water, starch undergoes a transition termed gelatinization where the ordered native granules swell and form a viscous solution (Jenkins & Donald, 1998; Ratnayake & Jackson, 2007; Vermeylen et al., 2006a,b; Waigh, Gidley, Komanshek, & Donald, 2000; Wang & Copeland, 2012; Wang, Li, Yu, Copeland, & Wang, 2014). Since native starch granules do not dissolve in cold water it is necessary to gelatinize starch for most applications. Understanding starch gelatinization is a longstanding challenge that has been extensively investigated. Several starch gelatinization theories and models have been proposed. Among the gelatinization theories are the so-called semi-cooperative (Marchant & Blanshard, 1978), water availability (Donovan, 1979), crystallite stability (Evans & Haisman, 1982), sequential phase transitions (Nakazawa, Noguchi, Takahashi, & Takada, 1984) and three-stage phase transition theories (Biliaderis, Page, Maurice, & Juliano, 1986); however, none of these can fully explain the gelatinization mechanisms (Ratnayake & Jackson, 2009). For a deeper understanding of starch gelatinization and in order to be able to fully control the various processes for applications involving starch–water systems, further studies are needed.

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A phase diagram contains a large collection of experimental data. Constructing phase diagrams has been a very successful approach in order to understand the interactions in complex colloidal systems. With a few exceptions, this approach has not been exploited for starch systems (Carlstedt et al., 2014; Sciarini et al., 2015; van der Sman & Meinder, 2011). Starch–water is a very complicated system for several reasons. One major complication with starch–water systems is the non-equilibrium nature of the gelatinization process and it must be understood that once starch has gelatinized the granules will not return to their original shape or structure. Furthermore, most starches are composed of both amylose and amylopectin which makes phase diagrams particularly difficult to construct if the constituents are considered as different components in the thermodynamic sense; for practical reasons it is convenient to treat starch–water as a pseudo-binary system. Finally, since each starch granule is unique with respect to size and composition all phase transitions occur over rather a wide range of temperature.

With the aim to resolve the gelatinization process, we used a combination of optical microscopy, synchrotron radiation X-ray scattering techniques and differential scanning calorimetry to investigate mixtures of native potato starch and water. Moreover, our data was used to construct the first, to the very best of our knowledge, full pseudo-binary temperature versus composition phase diagram for the native potato starch–water system.

2. Material and methods

2.1. Materials

Native potato starch was obtained from Lyckeby Starch AB (Kristianstad, Sweden). Before use, the starch was dried overnight in vacuum at room temperature in the presence of 3 Å molecular sieves. Pregelatinzed potato starch was prepared by heating aqueous native potato starch suspensions of varying concentration to 80 °C in closed vials and holding at that temperature for 20 min. Mixtures of starch and water were prepared by adding the required mass of liquid water to the dried starch (for starch concentrations $\leq$ 75 wt%) or by equilibrating the dried starch at room temperature at various relative humidities (between 11.3 and 97.3% RH) using saturated salt solutions (Greenspan, 1976). We used LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl, KCl, and K_2SO_4, all with a purity $\geq$99%, from Sigma. All samples were left to equilibrate for at least one week at room temperature before measurement. The water used for the experiments and for preparing the saturated salt solutions was purified using an Elga Flex 2 system.

2.2. Optical microscopy

A Nikon OptiPhot optical microscope equipped with a DS-U1 digital camera and cross-polarizers together with a Linkam Analysa-LTS350 temperature controlled stage were used. Samples were placed on glass slides cleaned with 99.5% ethanol. A cover glass together with silicone grease was used to seal the sample in order to avoid water evaporation.

2.3. Small/wide-angle X-ray scattering (SAXS/WAXS)

All SAXS and WAXS experiments were performed at beamline I911-SAXS at the MAX IV Laboratory in Lund, Sweden (Labrador, Cerenius, Svenssson, Theodor, & Plivelic, 2013). The q-ranges for SAXS and WAXS experiments were approximately 0.1–8.5 nm^{-1} and 0.5–22 nm^{-1}, respectively. The wavelength of the beam was 0.91 Å and the sample to detector distance was between 1360 and 1370 mm (SAXS) or 320 mm (WAXS). A temperature program in which the temperature was stepwise increased from 25 °C to a maximum of 85 °C (the limit of the present set-up) was used. After the maximum temperature was reached the samples were cooled down to 25 °C and measured again at this temperature. The software Fit2d was used for data evaluation (Hammersley, 1997). Background subtraction (empty solid sample holder or capillary) as well as peak integration and slope analysis were performed using software written in Matlab.

2.4. Differential scanning calorimetry (DSC)

A DSC1 from Mettler Toledo International Inc., Switzerland, was used to analyze mixtures of starch and water. The samples were prepared in 40 μl aluminum crucibles which were directly hermetically sealed after the addition of the required masses of starch and water. In a typical experiment, the sample was cooled down to −50 °C and subsequently heated to 100 °C at a scanning rate of either 1 °C min^{-1} or 10 °C min^{-1}. For a few selected sample compositions several lower scanning rates were also used in order to extrapolate the endset of melting of ice to zero scan rate (endset temperatures were used). The extrapolated value was then subtracted from the ice melting temperatures recorded for all other compositions. For a selected starch–water composition, scans with much slower cooling rates were performed in order to be able to determine the glass transition just below ice melting. Indium was used as a calibrant and an empty aluminum crucible (40 μl) was used as a reference. A dry nitrogen gas flow of 80 ml min^{-1} was used to purge the furnace chamber of the DSC instrument. No weight loss of the samples was detected after the experiments.

3. Results and discussion

We investigated the effects of hydration and temperature on the properties of native potato starch with a particular emphasis on the mechanism of gelatinization of starch. Below we report optical microscopy, SAXS and DSC results obtained at different water contents of the starch–water system, then in Section 3.4 we summarize these findings to explain the mechanism of gelatinization.

3.1. Optical microscopy

Microscopy images of native potato starch in water (0.5–1 wt%) were collected at different temperatures in order to visually follow gelatinization. Two different methods were used: continuous scanning from low to high temperature and constant temperature observations. We collected both bright field and cross polarized light images. It was observed that starch granules started to swell and lose their birefringence at approximately 50 °C and that all granules had gelatinized at approximately 70 °C. The swelling was substantial: assuming an ellipsoidal geometry, starch granules were swollen to approximately 50–150 times their original volume. Assessing swelling from microscopy images can sometimes be a bit misleading because of surface roughness (Wojtasz, Carlstedt, Fyhr, & Kocherbitov, 2015), however, it gives an idea of the order of swelling. Starch granules need time to swell. Approximately 5 min at a constant temperature was needed for an individual starch granule to reach maximum swelling. Microscopy images of starch granules in water at different temperatures are shown in Fig. 1: at 25 °C a two-phase system comprising native starch granules in water; at 60 °C gelatinized starch granules coexist with native granules in water (three-phase system), whereas at 75 °C a two-phase system of gelatinized starch granules in liquid is observed. Additional images are shown in Figure S1, Supplementary data.