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Phase transition and swelling behaviour of different starch granules over a wide range of water content

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ABSTRACT

The relationship between swelling behaviour and thermal transitions of starch was investigated by differential scanning calorimetry (DSC) in combination with swelling power of starch. Sodium dodecyl sulphate (SDS)-treated wheat, waxy maize and potato starches showed increasing swelling power with increasing water/starch ratio. In contrast, swelling power of untreated wheat and high-amylose maize starches increased initially with increasing water/starch ratio, and then remained essentially unchanged above a certain ratio. The main endotherm *G* of native and SDS-treated wheat starch broadened progressively with increasing water/starch ratio up to 10:1. SDS-treated wheat, waxy maize and potato starches showed a typical endotherm over the whole range of water/starch ratios from 0.33:1 to 25:1, but the maximum enthalpy change occurred at different water/starch ratios. Our results indicate that thermal transition behaviour of starch granules is a very complex process, which involves swelling and leaching of starch polymer molecules rather than the dissociation of double helices or melting of crystallites.

1. Introduction

When heated in excess water, starch granules undergo an irreversible phase transition, referred to as gelatinization, in which the highly ordered structure is disrupted. Starch gelatinization has been broadly defined as the "collapse (disruption) of molecular orders (breaking of hydrogen bonds) within the starch granule manifested in irreversible changes in properties such as water uptake, granular swelling, crystallite melting, unwinding of double helices, loss of birefringence, starch solubilisation and viscosity development"(Atwell, 1988; BeMiller, 2011; Biliaderis, 2009). This definition implies that at least three distinct changes occur during gelatinization: granule swelling, disruption of ordered structures (crystalline and molecular) and solubilisation of starch molecules (Wang & Copeland, 2012a). The extent to which these changes occur is a major determinant of the functional properties of starch, including its susceptibility to enzymatic digestion, and depends on the type of starch and the moisture and heating conditions during hydrothermal processing (Biliaderis, 2009; Goldstein, Nantanga, & Seetharaman, 2010).

Starch gelatinization has been studied extensively using a variety of techniques, of which DSC is accepted widely as most suitable for quantitative and qualitative analyses following pioneering work of Stevens and Elton (1971) and Donovan (1979). Other techniques including wide angle X-ray diffraction (WAXD), small angle X-ray scattering (SAXS), ^{13}C nuclear magnetic resonance (NMR), FTIR, and microscopy (light microscopy, electron microscopy and transmission microscopy) have also been used directly or in combination with DSC, to examine multiple aspects of starch gelatinization simultaneously (Biliaderis, 2009; Ratnayake & Jackson, 2009; Wang & Copeland, 2013a, 2013b; Derycke et al., 2005; Jenkins & Donald, 1998; Le Bail et al., 1999; Vermeylen et al., 2006a; Vermeylen et al., 2006b).

Donovan's pioneering work considered the effect of water content on thermal transitions of starch granules (Donovan, 1979). He observed a single constant endotherm (called endotherm *G*) with potato starch at a water/starch ratio of 1:1.5 or greater, which was assumed to represent the complete gelatinization of starch (Donovan, 1979). However, other studies have obtained different DSC profiles, indicating that Donovan's observations and conclusions for potato starch, which is known to have granules with a

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typical swelling property, do not apply generally. Increasing experimental evidence is showing that the endotherm *G* at a water/starch ratio above 1.5 shifts to higher temperature with increasing water/starch ratio and does not represent the full gelatinization of starch granules (Cruz-Orea, Pitsi, Jamée, & Thoen, 2002; Liu, Yu, Xie, & Chen, 2006; Randzio, Flis-Kabulska, & Grolier, 2002; Tananuwong & Reid, 2004; Wang & Copeland, 2012a, 2012b). In addition to water content, the surface proteins and lipids were shown to influence the swelling behaviour and thermal properties of starch granules (Debet & Gidley, 2006; Wang et al., 2014). Sodium dodecyl sulphate (SDS) solution has been proven to remove proteins and lipids from surface of starch granules sufficiently (Debet & Gidley, 2006).

In a previous study (Wang & Copeland, 2012a), we investigated the effect of water content on the thermal transitions of pea starch granules over a wide range of water/starch ratios. The endothermic transition of pea starch granules was proposed to reflect the swelling behaviour of starch during DSC heating, and not complete gelatinization. The present study is aimed at determining how generally this relationship between DSC thermal transitions and swelling behaviour, as observed for pea starch, applies, thereby increasing our understanding of what the DSC endothermic transitions for starch actually represent. To this end, the swelling power and DSC profiles of wheat starch, waxy maize starch, potato starch and high-amylose maize starch were investigated over a wide range of water/starch ratios (from 0.33:1 to 25:1 or 30:1). To our knowledge, this is the first study to investigate the thermal transitions of different starches over such a wide range of water/starch ratios.

2. Materials and methods

2.1. Materials

Wheat, potato, and waxy maize starches were obtained from commercial sources, with amylose content of 27%, 25% and 3%, respectively. High-amylose maize starch (85% amylose) was obtained from the National Starch and Chemical Company (Shanghai, China). The starches were used without further purification. To investigate the influence of surface proteins and lipids on starch swelling and thermal transition, wheat starch was treated with 2% sodium dodecyl sulphate (SDS) solution at room temperature for 24 h to remove surface proteins and lipids (Debet & Gidley, 2006). All other chemicals were analytic grade from Sigma–Aldrich Chemical Corporation (Shanghai, China).

2.2. Sample preparation

To understand the swelling behaviour of starches during the DSC heating, the water:starch ratios used in the DSC measurements were largely consistent with those used in the swelling power test, which can be seen in Figs. 1–5. For direct comparison of the effect of water/starch ratio on swelling power and DSC thermal transition, the water/starch ratio used in Figures of DSC thermal transition parameters was adjusted correspondingly.

2.3. Swelling power and starch solubility

Swelling power and solubility of starch were determined in triplicate according to the method described elsewhere (Wang & Copeland, 2012c) as follows. Exactly 40 mg (wet basis) of starch were weighed into a 2 ml screw cap plastic test tube and water was added. After the lid was screwed on tightly, the starch-water mixtures were heated in a water bath at 92.5 °C for 30 min with regular shaking. The samples were cooled at 20 °C for 3 min and

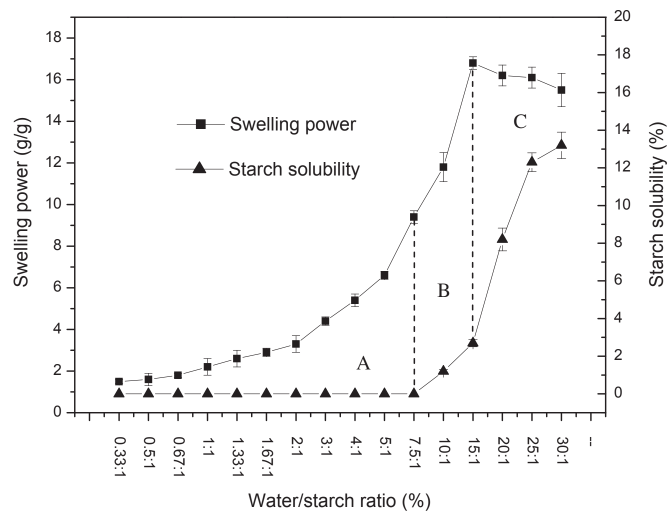

Fig. 1. Effect of water/starch ratio (40 mg of starch was used) on swelling power and solubility of wheat starch granules. The zones marked A, B and C correspond to the stages of swelling discussed in the text, namely A: limited swelling without leaching; B: incomplete swelling with some leaching; C: complete swelling with continuous leaching.

centrifuged at 13, 000 × *g* for 10 min. When a supernatant was obtained, it was transferred carefully to a glass evaporating dish, evaporated to dryness on a steam bath, and dried further for 24 h at 80 °C. SDS-treated wheat starch, potato starch and waxy maize starch formed a soft gel, making it difficult to separate a clear supernatant even after centrifugation. For these starches, the starch solubility was considered to be zero. The sedimented, swollen granules and dried soluble fraction were weighed to determine swelling power (g H_2O absorbed/g dry starch) and solubility (% of dry starch) using the following formulae:

$$\text{Solubility, } S = [\text{weight of solubles}] / \times [\text{dry weight of original starch}]$$

$$\text{Swelling power, } SP = [\text{weight of swollen granules}] / \times [\text{dry weight of original starch}]$$

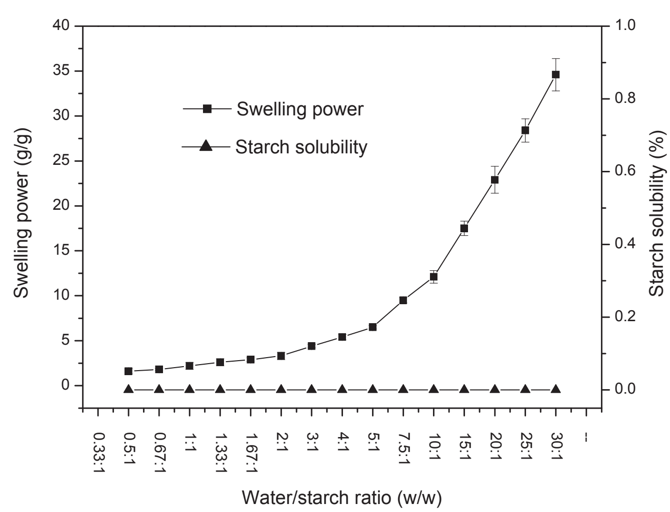

Fig. 2. Effect of water/starch ratio on swelling power and starch solubility of SDS-treated wheat starch.