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Settling volume and morphology changes in cross-linked and unmodified starches from wheat, waxy wheat, and waxy maize in relation to their pasting properties

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ABSTRACT

Normal wheat, waxy wheat and waxy maize starches were cross-linked with 0.01, 0.03 and 0.06% (sb) phosphorus oxychloride. The objective of this study was to correlate the morphology changes and settling volume to the pasting properties of those cross-linked and unmodified starches. Pasting and microscopic data for waxy maize starch and its cross-linked products was similar to waxy wheat starch, except changes occurred at ~5 °C higher in temperature. At 6% solids, waxy wheat starch cross-linked with 0.01% $POCl_3$ had a greater settling volume and a higher pasting viscosity than the cross-linked waxy maize starch, but at 7 and 8% solids, waxy maize starch cross-linked with 0.03% and 0.06% $POCl_3$ had a higher pasting viscosity. At 6% starch solids, particle volume fraction appeared to be the dominant factor controlling consistency, but at higher starch solids contents, the deformability (rigidity) of swollen granules became important in controlling viscosity.

1. Introduction

Waxy wheat is a specialty wheat (Chibbar & Chakraborty, 2005; Graybosch, 2005, Graybosch & Hansen, 2016) that can be dry- and wet-milled into valuable products, including waxy wheat starch (WWS) and vital wheat gluten (Guan, Seib, Graybosch, Bean, & Shi, 2009; Sayaslan, 2002; Sayaslan, Seib, & Chung, 2005). Wheat gluten and its modifications are well-established ingredients in an array of foods for humans and pets (Day, Augustin, Batey, & Wrigley, 2006). Compared to normal wheat starch (NWS), WWS granules swell more extensively when heated in water and give a higher peak viscosity; however, the swollen granules are fragmented at high temperatures, resulting in more breakdown in viscosity (Garimella Purna, Shi, Guan, Wilson, & Graybosch, 2015).

Waxy wheat starch gelatinizes and begins to swell in excess water at a temperature 5–7 °C below that of waxy maize starch (WMS) (Reddy & Seib, 2000). Traditionally, WMS is the preferable base-starch that is modified to produce thickeners for food. The decreased cooking temperature needed to gelatinize WWS increases its marketing potential as a thickener in microwaved foods, and the reduced cooking temperature saves energy during food processing.

To be used as a thickener in foods, starch is often chemically modified to improve the thickening power and the texture and stability of its paste. A few studies regarding chemical modification of WWS have been reported. Reddy and Seib (2000) compared modified WWS with modified WMS, and found that cross-linked WWS possesses improved freeze-thaw stability over similarly modified WMS. In addition, cross-linked and hydroxypropylated or acetylated WWS produced non-stringy pastes of almost equal consistency compared to similarly modified WM. Graybosch and Hansen (2016) studied the pasting properties of chemically modified WWS and of partial waxy wheats. Those authors reported that with both the native and modified starches, the pasting curves of partial waxy wheat starches displayed consistencies intermediate between those of a pure waxy and its wild-type.

There is an unexplained difference in the pasting (7.5% starch solids) behavior of cross-linked starches from WWS and WMS when those starches are treated with an increasing level (0.01–0.05% based on starch) of $POCl_3$ (Reddy & Seib 2000). In the case of WWS, the higher the level of $POCl_3$, the greater the decrease in paste consistency of its cross-linked product. A level of 0.018% $POCl_3$ on WWS gave a high-viscosity, non-cohesive (non-stringy) paste. However, in the case of cross-linking of WMS with 0.03–0.05% $POCl_3$, the paste consistency of its modified starches proceeded through an optimum level of ~0.04% $POCl_3$. That level of 0.04% was twice the level of reagent needed to

Abbreviations: sb, dry starch basis; CL, cross linked; DSC, differential scanning calorimetry; MVA, Micro Visco-Amylograph; NWS, normal wheat starch; WWS, waxy wheat starch; WMS, waxy maize starch

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generate the most viscous paste from cross-linked WWS. We hypothesize that the pasting viscosity is dependent on the swelling and rigidity of starch granules (Steeneken, 1989; Tayal, Shariff, & Whaley, 2004), and cross-linked and unmodified starches from wheat, waxy wheat and waxy maize have different swelling powers and rigidities. At a low concentration, the viscosity is governed by the volume fraction of swollen granules, and a low swelling starch has a low viscosity. However, at a high concentration, the viscosity is governed by the rigidity of swollen granules, and thus a low swelling starch (e.g. a cross-linked starch) has a high viscosity (Steeneken, 1989; Tayal et al., 2004).

In this study, we examined the pasting properties of the cross-linked and unmodified starches at different solids contents (6–8%), and determined the settling volume and morphology changes of those starches during heating. Our objective was to correlate the morphology changes and settling volume to the pasting properties of those starches. Specific experiments were performed to: (1) prepare cross-linked starches with three levels (0.01, 0.03 and 0.06%, sb) of phosphoryl chloride from wheat, waxy wheat, and waxy maize starches, (2) determine the pasting properties of the cross-linked and unmodified starches at different solids contents (6–8%) and different rates of heating, (3) record the changes in granule structure continuously on a hot-stage microscope during heating, and (4) determine the settling volume of cross-linked and unmodified starches at 25 °C and after being heated to 80 °C and 95 °C. In addition, differential scanning calorimetry (DSC) was used to determine gelatinization properties of the cross-linked and the unmodified starches, and extent of re-association of the gelatinized starches at 4 °C.

2. Materials and methods

2.1. Materials

NWS with the commercial name Midsol 50 was obtained from MGP Ingredients Inc (Atchison, KS). WMS was obtained from Ingredion Inc (Bridgewater, NJ). One advanced waxy hard wheat (cultivar Mattern) was provided by Dr. Robert Graybosch (USDA/ARS, University of Nebraska). Phosphorus oxychloride (99%) and sodium sulphate were purchased from Fisher Scientific (Fair Lawn, NJ).

2.2. Isolation of waxy wheat starch (WWS)

Wheat kernels were tempered to 16.0% moisture (wet basis) for 24 h at 25 °C then roller-milled into straight-grade flour on an experimental mill (Buhler Co., Uzwil, Switzerland). Starch was isolated from the flour by the AACC gluten hand-washing Method 38-10 with the slight modification described by Guan et al. (2009). The purified starch was oven-dried at 40 °C for 24 h, and gently ground with a mortar and pestle. The yield of the isolated WWS was 61% of flour weight, and its contamination with normal wheat starch granules was less than 0.5% as determined microscopically after staining with a solution of I_2/KI.

2.3. Cross-linking of starches

Starch (90 g, dry solids) was stirred in water (135 mL) at 25 °C. Sodium sulphate (1.8 g) was added to the slurry followed by dropwise addition of 0.75 M sodium hydroxide to pH 11.5 monitored by a pH electrode. Phosphoryl chloride (5.5 μL, 16.5 μL or 33.0 μL, respectively, equal to 0.01, 0.03 or 0.06 wt% based on dry starch) was added with stirring. After 60 min, the slurry was adjusted to pH 5.5 with 1 M hydrochloric acid, and the cross-linked starch was isolated by vacuum filtration. The starch was washed with deionized water (200 mL) three times, isolated by centrifugation (3500 × *g*, 10 min), then oven-dried at 40 °C for 24 h. The dried starch was ground gently with a mortar and pestle.

2.4. Microscopic observation of starch granules

2.4.1. Unmodified starch granules

Starch (0.03 g) was added to distilled water (3 mL) and dispersed on a vortex mixer. A small amount of high-vacuum grease (Dow Corning Corporation, Midland, MI) was spread evenly in a thin layer around the edge of a square-shaped cover-slip. One drop of the starch suspension (about 15 μL) was transferred onto a glass microscope slide, and the drop was topped by the cover-slip. The starch was viewed with an Olympus BX51 microscope (Olympus America Inc., Melville, NY) equipped with a STC200 hot stage. Images and photographs were captured with a 40X objective lens using the SPOT Insight Camera and SPOT 4.6 software (Diagnostic Instrument Inc., Sterling Heights, MI, USA), operating on Microsoft Windows. The heating rate was set at 5 °C/min with temperature controlled by a temperature-controller with hot stage software Wintemp (Instec Inc., Boulder, CO, USA) on a Windows system.

2.4.2. Modified starch granules

Starch (0.03 g) was added to distilled water (3 mL) and mixed using a magnetic stirrer in a water bath at 25, 70, 80 or 90 °C for 20 min. The dispersion was stained with 10 μL of 0.5 M iodine in KI, and 15 μL of the stained slurry was placed on a microscope slide and topped with a cover-slip. The starch was viewed with the Olympus BX-51 microscope using the 40X objective lens. Unmodified starches were set as a control.

2.5. Pasting properties

The pasting properties of the three unmodified starches were determined using a Micro Visco-Amylograph (C.W. Brabender Instruments Inc., South Hackensack, NJ). Starch (8.05 g, db) was suspended in water (106.95 mL) to give a slurry with 7.0% starch solids. The mixture was heated from 40 °C to 95 °C at a rate of 6.0 °C/min, held at 95 °C for 5 min, cooled to 50 °C at 6.0 °C/min, and held at 50 °C for 2 min. In another set of experiments, the same temperature profile was used at a heating rate of 12 °C/min. Pasting properties of cross-linked starches (6.90 g, 8.05 g and 9.20 g, equal to 6.0, 7.0 and 8.0 wt%, respectively, starch solids in a total aqueous mixture of 115.0 g) were recorded by heating from 40 °C to 95 °C at a rate of 6.0 °C/min, holding at 95 °C for 5 min, cooling to 50 °C at 6.0 °C/min, and holding at 50 °C for 2 min. Cohesiveness (stringiness) of a cooked and cooled paste was judged visually using a glass rod.

2.6. Settling volume

The settling volume was determined using the method of Shukri and Shi (2015) with slight modification. Starch (1.2 g, db) was stirred continually in 118.8 mL distilled water (total weight 120.0 g) in a water bath at 25, 80 or 95 °C for 30 min. The slurry was cooled, if need be, to room temperature with constant but gentle stirring, and 100 mL of the slurry was transferred into a 100-mL graduated cylinder. The cylinder was held at room temperature for 24 h, and the volume of sediment was determined visually.

2.7. DSC of starch/water mixtures

The thermal properties of starches were measured on a differential scanning calorimeter (Q200, TA instrument, Schaumburg, IL) as previously described by Zhu, Liu, Sang, Gu, and Shi (2010). The ratio of starch (~8 mg) to water was 1:2 (w/w) and high-volume stainless-steel pans were used. Gelatinization was determined by heating a starch-water mixture in a DSC pan from 10 °C to 140 °C at a heating rate of 10 °C/min. The onset (T_o), peak (T_p), and conclusion (T_c) temperatures of gelatinization, and the enthalpy (ΔH) of the transition were determined by DSC software (TA Instruments, Schaumburg, IL, USA). To determine the re-association of a gelatinized starch, the gelatinized