



Structure and pasting properties of alkaline-treated phosphorylated cross-linked waxy maize starches



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ARTICLE INFO

Article history:

Received 24 December 2015

Received in revised form 27 May 2016

Accepted 5 July 2016

Available online 6 July 2016

Keywords:

Cross-linked waxy maize starch

Starch phosphates

Structural property

Pasting property

ABSTRACT

The objectives of this study were to determine the stability of cross-linked bonds of starch at different pH values and their effects on the pasting property of waxy maize starch cross-linked by 0.05% and 3% sodium trimetaphosphate/sodium tripolyphosphate. The cross-linked waxy maize starch (CLWMS) was slurried (40%, w/w) and subjected to alkali treatments of pH 9, 10, 11, and 12 at 40 °C for 4 h. The phosphorus in 3% CLWMS decreased with increasing pH and remained unchanged in 0.05% CLWMS for all pH treatments. Decreased settling volumes indicated the reduction of swelling power for the alkali-treated CLWMS at pH 11 and 12. The ³¹P NMR spectra of 3% CLWMS at pH 12 showed decreased cyclic monostarch phosphate, monostarch monophosphate, and monostarch diphosphate, but significantly increased distarch monophosphate. Alkali treatments of phosphorylated cross-linked starches offer a way to manipulate the rheological properties of cross-linked starch for desired food applications.

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1. Introduction

Phosphorylation, or cross-linking of starch, is a well-known starch modification method (Paschall, 1964; Wurzburg, 2006). The main purpose of starch cross-linking is to eliminate the shortcomings of native starch and make starch paste stable at high acidity and high shear. These processing conditions are common in the food industry and are normally associated with the rupturing of swollen granules and fragmentation that lead to decreased viscosity and development of the stringy and cohesive texture of native starch, especially waxy starch (Rutenberg & Solarek, 1984). The detrimental effects on starch can be minimized or prevented by introducing cross-linking groups in the starch molecules by binding the neighboring anhydrous glucose units (AGU) in the amorphous regions. Cross-linking suppresses the swelling of starch granules due to covalent bonds between starch chains, thus developing a short and non-cohesive paste texture and improved

viscosity (Wurzburg, 2006). The enhanced rheological and texture properties of starch paste can be achieved with a very low level of modifications.

Starch is chemically phosphorylated with sodium trimetaphosphate (STMP), sodium tripolyphosphate (STPP) or phosphoryl chloride to produce ester derivatives (Sang, Prakash, & Seib, 2007; Sang & Seib, 2006; Solarek, 1995; Woo & Seib, 2002). Ester derivatives produced are monostarch phosphates and/or distarch phosphates. The ratio of monostarch to distarch phosphates depends mainly on the phosphorylating agents used, concentration, and reaction conditions (Sang & Seib, 2006; Sang et al., 2007; Woo & Seib, 2002). Monostarch phosphates are formed by the esterification of a phosphate to the hydroxyl group of one AGU, whereas distarch phosphates are produced when hydroxyl groups of two AGUs are esterified to the same phosphate group via cross-linking (Landerito & Wang, 2005). Unlike distarch phosphates, which are formed by starch reaction with polyfunctional phosphorylating agents, monostarch phosphates are produced using monofunctional reagents (Thomas & Atwell, 1999). Monostarch phosphates are produced with a higher substitution of phosphates on starch than distarch phosphates (Lim & Seib, 1993). Distarch phosphates result in improved starch texture with a very low phosphorus (P) content (0.04%), whereas monostarch phosphates require significantly higher total P (0.1–0.4%) to improve appearance, hygroscopicity, transparency, swelling, and

Abbreviations: AGU, anhydrous glucose units; ANOVA, analysis of variance; CLWMS, cross-linked waxy maize starch; cyclic-MSMP, cyclic-monostarch phosphate; db, dry basis; DSC, differential scanning calorimeter; DSMP, distarch monophosphate; MSDP, monostarch diphosphate; MSMP, monostarch monophosphate positioned at C3 and C6; P, phosphorus; NMR, nuclear magnetic resonance; Pi, inorganic phosphate; sb, starch basis; STMP, sodium trimetaphosphate; STPP, sodium tripolyphosphate; wb, wet basis; WMS, waxy maize starch.

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viscosity (Rutenberg & Solarek, 1984). Furthermore, Woo and Seib (2002) used a combination of 12% STMP and STPP at pH 11.5 to produce resistant starch that contained up to 0.4% total P. The *in vitro* enzymatic testing method and digestion mechanism of highly cross-linked wheat starch have been studied and reported (Shukri, Seib, Maningat, & Shi, 2013; Shukri, Zhu, Seib, Maningat, & Shi, 2015).

The pH during the starch phosphorylation process directly influences the concentration of mono- and di-esters in cross-linked starches. Early research showed that phosphate monoesters were produced using mixtures of orthophosphates at the pH of 5.0–6.5, whereas use of STPP required pH of 5.0–9.0 (Kerr & Cleveland, 1947). A combination of 2% STMP and 5% STPP at pH 9.5 produced cross-linked starch with better heat and shear resistance (Lim & Seib, 1993). Understanding the structural changes of cross-linked starch caused by pH is crucial to gain knowledge of the altered functional properties. Holding phosphorylated wheat starch (0.37% P) at pH 12 for four hours reduced the level of substituted phosphate esters (cyclic-monostarch monophosphate, monostarch diphosphate, and monostarch monophosphate) about 22%, but increased distarch monophosphate esters (cross-linked bonds) about 18% (Sang, Seib, Herrera, Prakash, & Shi, 2010). The increase in cross-linking content explained the retention of total dietary fiber in the alkali-treated starch. The previous study (Sang et al., 2010) focused on the digestibility profile of the alkali-treated cross-linked starch and did not reveal any data on alteration of pasting properties. High alkaline treatment on cross-linked starch, particularly with a low level of phosphorylation, may have a significant effect on the pasting property. In addition, alkali treatments on cross-linked starch may have potential in manipulating the pasting property of cross-linked starch to the desired outcome. Thus, the objective of this study was to determine the stability of cross-linked bonds in starch at different pH levels of aqueous sodium hydroxide and their effects on the pasting property of cross-linked waxy maize starch.

2. Materials and methods

2.1. Materials and chemicals

Waxy maize starch (Amioca) was obtained from Ingredion Inc. (Bridgewater, NJ). STMP was purchased from MP Biomedicals LLC (Solon, CA). STPP, sodium sulfate, sodium hydroxide, and hydrochloric acid were purchased from Fisher Scientific (Bridgewater, NJ). Thermally stable α -amylase (activity of 10,000 unit (U)/mL on soluble starch) and amyloglucosidase (3300 U/mL on soluble starch) were obtained from Megazyme International Ireland Ltd. (Wicklow, Ireland). One U of α -amylase at pH 4.5 and 40 °C is defined as the amount of enzyme required to release one micromole of D-glucose per minute from soluble starch. One U of amyloglucosidase at pH 4.5 and 40 °C is defined as the amount of enzyme required to release one micromole of D-glucose per minute from soluble starch. All chemicals were reagent grade.

2.2. General methods

The P content was assayed by the method of Smith and Caruso (1964). Moisture content was determined by AACC method 44-15 (American Association of Cereal Chemists, 2000), drying a sample in an oven at 130 °C for one hour.

2.3. Preparation of cross-linked waxy maize starch (CLWMS)

CLWMS was prepared using the method of Woo and Seib (2002). Two levels of cross-linking were prepared using 0.05%

(starch basis, sb) and 3% (sb) combination of STMP and STPP (99:1) as phosphorylating agents, and these two products are labeled as 0.05% CLWMS and 3% CLWMS, respectively, throughout the paper. Preparation of 0.05% CLWMS involved mixing waxy corn starch (50.0 g, dry basis, db), distilled water (70.0 mL), STMP (0.02475 g, 0.0495%, sb), STPP (0.00025 g, 0.0005%, sb), and sodium sulfate (5 g, 10%, sb). The pH of the slurry was adjusted to 11.5 by slowly adding 1.0 M sodium hydroxide into the stirred mixture to avoid gelatinization of starch. The slurry was stirred continuously and held at 45 °C for a three-h reaction in a water bath. The pH of the slurry was then adjusted to 6.5 by adding 1.0 M hydrochloric acid. The starch was centrifuged and washed with 150 mL distilled water for seven times to remove any unreacted chemicals, dried in an oven overnight at 40 °C, and ground. The same procedure was repeated with 3% STMP/STPP to obtain a higher level of cross-linking.

2.4. Alkaline treatment of CLWMS

The treatment was done based on the method described by Sang et al. (2010). CLWMS (50.0 g, db) was mixed with water (70.0 mL) in five different beakers. The pH for one of the slurries was left unadjusted so it could act as the control, but the pH levels of the other slurries were adjusted to 9, 10, 11, and 12 using 1.0 M sodium hydroxide. The covered beakers containing the slurries were held at 40 °C for 4 h. After cooling to 25 °C, slurries were adjusted to 6.5 using 1.0 M hydrochloric acid. The starch was centrifuged (1500×g, 10 min), supernatant was discarded, and starch was washed four times with distilled water, dried overnight at 40 °C, and ground.

2.5. Conversion of CLWMS to phosphodextrins and ^{31}P nuclear magnetic resonance (^{31}P NMR) spectroscopy

CLWMS was converted to phosphodextrins and analyzed by ^{31}P NMR based on the method by Sang et al. (2010).

2.6. Pasting properties of the CLWMS

Pasting properties of the CLWMS were determined using a Micro Visco-Amylograph (Brabender, Duisburg, Germany). CLWMS was added to distilled water to prepare 8% and 15% suspensions (dry weight basis, w/w) for 0.05% CLWMS and 3% CLWMS, respectively. The heating and cooling cycles were programmed by heating the suspension from 50 °C to 90 °C (heating rate of 5 °C/min), holding at 90 °C for 6 min, and cooling to 50 °C (cooling rate of 5 °C/min). The viscosity of the starch suspension was expressed in Brabender Units (BU).

2.7. Settling measurement of the CLWMS

Settling measurement of the CLWMS was determined by a method from Tayal, Shariff, and Whaley (2004) with slight modifications on the amount of slurry used (changed from 5 g to 20 g). CLWMS (5 g, db) was stirred constantly in water (100 mL) and placed in water bath at 95 °C for 30 min. After the slurry was cooled to 25 °C, slurry (20 g, wb) was transferred to 100 mL graduated cylinder containing water (80 g, wb) and allowed to settle at the bottom of the graduated cylinder. The settling volume of the CLWMS was taken after 24 h.

2.8. X-ray diffraction

The alkali-treated CLWMS was hydrated to 15% moisture content by placing samples in a 100% relative humidity chamber. The X-ray diffraction patterns of the hydrated starch samples were

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