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Heat–moisture treatment under mildly acidic conditions alters potato starch physicochemical properties and digestibility

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ABSTRACT

Potato starch was subjected to heat–moisture treatment (HMT; 120 °C, 3 h) under mildly acidic conditions (pH 5, 6, or 6.5 [control]) at moisture levels of 15, 20 or 25%. HMT starches exhibited significantly delayed pasting times and reduced overall paste viscosities, amylose leaching, and granular swelling characteristics relative to native starch, as well as enhanced levels of thermo-stable resistant starch (≈24%). HMT appeared to alter/enhance short-range chain associations (FT-IR) within amorphous and/or crystalline regions of starch granules. However, the extent of physicochemical change and RS enhancement during HMT was most facilitated by a mildly acidic condition (pH 6) at higher treatment moisture levels (20 or 25%). These conditions promoted limited hydrolysis of amylopectin molecules, primarily at α-(1 → 6) branch points, likely enhancing mobility and interaction of starch chains during HMT. Thus, a slightly acidic pH might reduce conditions and/or timeframe needed to impart physicochemical changes and reduced digestibility to potato starch.

1. Introduction

Heat–moisture treatment (HMT) involves heating of starch granules at low moisture levels (<35% w/w) at temperatures (84–140 °C) above that of glass transition, but below that of gelatinization, for a defined period of time (15 min–16 h) (Hoover, 2010; Jacobs & Delcour, 1998). HMT promotes the physical modification of starch chains, while in the rubbery state, by inducing structural molecular rearrangements within amorphous and/or crystalline regions of granules, retaining starch in the granular state (Hoover, 2010; Hormdok & Noomhorm, 2007; Jacobs & Delcour, 1998; Varatharajan, Hoover, Liu, & Seetharaman, 2010). Structural changes within granules resulting from HMT induce changes to granular swelling behavior, crystallinity, amylose leaching, thermal transition properties, thermal stability, and pasting behavior (Hoover, 2010; Jacobs & Delcour, 1998; Varatharajan et al., 2010). These structural and physicochemical changes incurred during HMT may also affect the susceptibility of starch granules to digestive enzymes (Hoover, 2010). From a nutritional perspective, starch may be classified as rapidly digestible starch (RDS), slowly digestible starch (SDS), or resistant starch (RS), depending on the rate and extent of glucose release and absorption during passage through the upper GI tract (Englyst, Kingman, & Cummings, 1992). SDS has been linked to potential health benefits such as diabetes management and satiety (Lehmann & Robin, 2007), while RS, due primarily to its fermentation within the colon, serves as a prebiotic substrate for growth of probiotic microorganisms, reduces risk of disease associated with the large bowel (including colon cancer), contributes an antiglycemic effect, and can favorably alter blood lipid profiles (Fuentes-Zaragoza, Riquelme-Navarrete, Sánchez-Zapata, & Pérez-Álvarez, 2010; Sajilata, Singhal, & Kulkarni, 2006). HMT represents a means for enhancing thermo-stable SDS and RS contents, which likely result from altered starch chain associations in crystalline and/or amorphous regions of granules (Chung, Hoover, & Liu, 2009; Chung, Liu, & Hoover, 2009; Shin, Kim, Ha, Lee, & Moon, 2005).

The extent of structural and physicochemical change generated during HMT is influenced by the botanical source of starch as a function of the nature, composition and organization of amylose and amylopectin chains within native granules (Hoover, 2010). For example, tuber (e.g., potato) starches have been shown to be more impacted by HMT than legume or cereal starches (Hoover & Vasanthan, 1994; Jacobs & Delcour, 1998), with conditions such as temperature, moisture content, and treatment length affecting the degree of change to starch characteristics and properties (Hoover, 2010; Shin et al., 2005). Vermeylen, Goderis, and Delcour (2006) reported that an increasing treatment temperature up to 120 °C reduced the overall long-range crystallinity of potato starch, while new crystalline structures were formed at slightly higher

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temperatures (i.e., 130 °C). At the higher temperature, thermal depolymerization of starch chains was suggested to render starch double helices sufficiently mobile to form more organized crystalline structures (Vermeylen et al., 2006).

Acid hydrolysis has been used to modify the structure and properties of granular starch via scission of glycosidic linkages (Jayakody & Hoover, 2002), with chains in amorphous regions of granules more susceptible to hydrolysis than those comprising the crystalline structure (Hoover, 2000). Consequently, pre-hydrolysis of granular starch with acid was reported to decrease the degree of polymerization of chains, and enhance the mobility and realignment of resulting chains during HMT, increasing the thermo-stable RS content (Brumovsky & Thompson, 2001; Lin, Singh, Wen, & Chang, 2011).

It was hypothesized that slightly acidic conditions during HMT might alter the molecular characteristics of starch chains within amorphous regions of granules to accelerate molecular changes during treatment without loss of granular form or excessive degradation of starch chains. The primary objective of this research was to investigate the effect of a mildly acidic condition (pH 5 or 6) during HMT on potato starch physicochemical properties, granular/molecular structural characteristics, and digestibility.

2. Materials and methods

2.1. Starch and chemical sources

Potato starch was obtained from AVEBE (Veendam, The Netherlands). Hydrochloric acid, amyloglucosidase (EC 3.2.1.3; 300 U/mL), pancreatin (Catalog No. 7545; activity 8× USP/g) and invertase (EC 3.2.1.26; 300 U/mg) were purchased from Sigma–Aldrich Corp. (St. Louis, MO, USA). A glucose assay kit (Catalog No. K-GLUC) and isoamylase (EC 3.2.1.68; 1000 U/mL) were purchased from Megazyme International Ireland Ltd. (Wicklow, Ireland). All other utilized chemicals were at minimum of analytical grade.

2.2. Starch HMT under mildly acidic conditions

Potato starch (10 g, dry basis [db]) was dispersed in distilled water (50 mL), and the resulting suspension was adjusted to either pH 5.0 or 6.0 with 1.0 N HCl; the pH of the treatment control was not adjusted (≈pH 6.5). Following pH adjustment, a given starch suspension was stirred (1 h) at ambient temperature, after which the treated starch was recovered by vacuum filtration (filter paper pore size = 1 μm, VWR, Radnor, PA, USA) and allowed to air-dry to a starch moisture content below 10%. Recovered starches were equilibrated in desiccators over saturated solutions (1000 mL) of NaCl, KNO_3, or K_2SO_4 at an ambient temperature until desired starch moisture contents (15, 20, or 25%, respectively) were achieved (Brett, Figueroa, Sandoval, Barreiro, & Müller, 2009; Saibene & Seetharaman, 2006). Equilibrated starches (10 g, db) were transferred to glass containers, tightly sealed (to inhibit moisture loss during the treatment), heated at 120 °C for 3 h, and subsequently cooled to ambient temperature. Treated starches were suspended in deionized water (40 mL), neutralized with 0.1 N NaOH, washed with deionized water (40 mL × 2 times), and washed/solvent-dried with absolute ethanol (40 mL). All HMT starches were dried at ambient temperature, and ground to pass through a No. 120 sieve.

2.3. RVA pasting properties

Pasting properties of native and HMT treated potato starches were determined via the Rapid Visco Analyser (RVA) (Newport Scientific, Warriewood, Australia) using a 7.0% (w/w) aqueous starch dispersion (2.1 g starch [db] comprising a total 30 g dispersion) under continuous shear (160 rpm). Starch suspensions were initially heated at 50 °C (1 min), heated to 95 °C (12.2 °C/min), maintained at 95 °C (2.5 min), cooled to 50 °C (11.8 °C/min), and held at 50 °C (2 min).

2.4. Light microscopy

Native and HMT starches were prepared for light microscopy by suspending granules in an excess of water on a glass slide, while starch suspensions following RVA pasting were diluted (10-fold) with deionized water, stained with 0.2% I_2/KI solution (3 mL) and transferred to a glass slide. Slides were overlaid with a cover slip, and observed on a Nikon Eclipse E600 microscope (Melville, NY, USA) equipped with a digital camera (MicroPublisher 3.3, QIMAGING, Surrey, BC, Canada).

2.5. Swelling factor determination

Swelling factors of native and HMT starches were measured at 75 °C in excess water (50 mg starch [db] in 5 mL deionized water) according to the blue dextran exclusion method of Tester and Morrison (1990), and reported as the ratio of the swollen starch granule volume to that of the dry granules.

2.6. Amylose leaching

Native or HMT starch (20 mg) was weighed into a screw cap tube (50 mL) to which deionized water (10 mL) was added, after which the capped tube was incubated in a shaking water bath (Model 406015, American Optical, Buffalo, NY, USA) at 75 °C for 30 min (160 strokes/min). Following incubation, the tube was cooled to ambient temperature and centrifuged (2000 × *g*, 10 min). The amount of liquid in the supernatant was measured and the amylose content of the supernatant was determined (Morrison & Laignelet, 1983). Amylose leaching was reported as the percentage of amylose leached per 100 g of dry starch.

2.7. X-ray diffraction (XRD)

Native or HMT potato starch (2.0 g, db) was equilibrated at ambient temperature for two weeks in a desiccator over a saturated solution (1000 mL) of NaCl to standardize moisture content. XRD patterns of moisture-equilibrated starches were obtained using a powder X-ray-diffractometer (Siemens D5000, Bruker, Madison, WI, USA) as described by Cheetham and Tao (1998). The relative crystallinity of starches was quantitatively calculated as the percent ratio of the sum of the total crystalline peak area to that of the total diffractogram (amorphous + crystalline peak area) as reported by Nara and Komiya (1983).

2.8. Fourier transform infrared spectroscopy (FT-IR)

Absorbance spectra of native and HMT starches were recorded on a Thermo Nicolet Avatar 370 spectrometer (Thermo Scientific, Waltham, MA, USA) in attenuated total reflectance (ATR) mode using a zinc selenide crystal as described by van Soest, Tournois, de Wit, and Vliegenthart (1995). After pressing starch powder onto the crystal, samples were analyzed at a resolution of 4 cm^{-1} over 64 scans. Measured spectra were baseline-corrected between 1200 and 800 cm^{-1}, while intensity measurements were performed by recording the peak heights of the absorbance bands from the baseline.