



Effect of heat-moisture treatment under mildly acidic condition on fragmentation of waxy maize starch granules into nanoparticles



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ABSTRACT

Waxy maize starch was modified by a heat-moisture treatment (HMT) under acidic conditions followed by homogenization to create starch nanoparticles. Waxy maize starch was heated at 130 °C for 3, 5, or 8 h under mildly acidic conditions (0.00, 0.10, or 0.15 N sulfuric acid solution) and homogenized for up to 60 min. The crystalline, molecular, and granular structures of starch were effectively changed without severe loss of starch substance (less than 25%) by the HMT under acidic conditions. The HMT under acidic conditions enhanced short-range order of starch granules based on the results of FT-IR but decreased the proportion of amylopectin long chains. The data suggest that the amorphous region of the starch granule was readily hydrolyzed by the acidic condition during the HMT. Moreover, homogenization after the HMT (0.15 N for 8 h) induced fragmentation of starch granules into nano-sized particles with diameters less than 40 nm.

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1. Introduction

Starch has been used for many purposes, such as in food, cosmetics, and pharmaceuticals, as it is an abundant, natural, renewable, and biodegradable polymer. Moreover, starch is involved in nanotechnology to make crystalline platelet-like particles with nanoscale dimensions (Dufresne, 2015; LeCorre, Bras, & Dufresne, 2010). The preparation of certain starch nanoelements is based on the structure of starch granules, which consist of alternating crystalline and amorphous concentric layers. Semicrystalline growth rings of starch granules are composed of blocklets (20–50 nm) that include amorphous and crystalline lamellae (9 nm) (Gallant, Bouchet, & Baldwin, 1997). The amorphous regions of granules are more susceptible to chemical or enzymatic hydrolysis, so the acid hydrolysis of native starch selectively disrupts the organization of the granules and releases highly crystalline particles called starch nanocrystals (Dufresne, 2015). On the molecular scale, acid hydrolysis can cleave the α -(1 → 4) and α -(1 → 6) linkages of starch chains, and it induces a series of changes in granular structure: (i) erosion of the surface, (ii) collapse of the wall of starch granules, and (iii) fragmentation of the growth rings

(LeCorre, Bras, & Dufresne, 2011). Changes in both granule structure and the molecular structure of starch may generate starch nanocrystals. When waxy maize, normal maize, high-amylose maize, potato, and mungbean starches were hydrolyzed using 3.16 M H₂SO₄ solution, round or oval shaped nanocrystals with diameters ranging from 40 to 70 nm were produced (Kim, Lee, Kim, Lim, & Lim, 2012).

A two-stage acid hydrolysis pattern has been observed in all starches. A faster hydrolysis rate during the first 8 days and a slower hydrolysis rate between 7 and 12 days were observed in maize, waxy maize, high-amylose maize, wheat, potato, oat, rice and legume starches (Hoover, 2000). The faster acid hydrolysis stage is attributed to the hydrolysis of the more amorphous parts of the starch granule, whereas the subsequent slower hydrolysis is associated with the slow degradation of the crystalline materials in starch (Hoover, 2000). LeCorre et al. (2011) reported that starch nanocrystals were not generated at the end of the acid hydrolysis procedure but were continuously formed over course of the acid hydrolysis period. At the initial stage of acid hydrolysis, starch nanocrystals were formed and mixed together with micro-sized starch particles; however, the nanocrystals formed at the initial stage may have transformed into soluble sugar by the end of the batch acid hydrolysis procedure and could have caused a low yield for starch nanocrystals (LeCorre et al., 2011). Although acid

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hydrolysis has been commonly used to prepare nanoparticles, the optimized condition has previously resulted in a yield of 14.69% and required a relatively long duration of acid hydrolysis (Angellier, Choinsard, Molina-Boisseau, Ozil, & Dufresne, 2004). Alternative strategies to prepare starch nanoparticles include a combination of acid hydrolysis paired with physical treatment or enzyme treatment, which has been reported to overcome the limitation of the traditional acid hydrolysis procedure. Ultrasonication during the acid hydrolysis of waxy maize starch prevented the aggregation of nanoparticles and increased the yield of starch nanoparticles (Kim, Han, Kweon, Park, & Lim, 2013). Enzymatic pretreatment (α -amylase, β -amylase, and glucoamylase) of starch granules prior to acid hydrolysis facilitated the acid penetration during acid hydrolysis and subsequently reduced the duration of hydrolysis (LeCorre, Vahanian, Dufresne, & Bras, 2012).

Heat-moisture treatment (HMT) involves the heating of starch granules at low moisture levels (<35% w/w), at temperatures above glass transition but below gelatinization (84–140 °C), for a defined period of time (15 min–16 h) (Hoover, 2010). The HMT induces structural changes within the amorphous and/or crystalline regions of granules resulting in changes in granular swelling behavior, crystallinity, amylose leaching, thermal transition properties, thermal stability, and pasting behavior. Dual modification of starch granules using the HMT and acid hydrolysis can induce changes in both the granular and molecular structure of starch. When HMT starch was hydrolyzed using a 2.2 N HCl solution, acid hydrolysis decreased slightly in HMT starch (Hoover & Manuel, 1996). In the HMT starch, after acid hydrolysis, the enzymatic resistance was increased, possibly due to improved molecular mobility and order during the HMT treatment. Kim and Huber (2013) reported that in simultaneous dual modification of the HMT and acid hydrolysis, the HMT under mildly acidic conditions promoted limited hydrolysis of amylopectin molecules, with branch points enhancing the mobility and interaction of starch chains. Considering the molecular and granular changes during the acid hydrolysis for preparation of the nanocrystals, it was hypothesized that under mildly acidic conditions, the HMT may also induce similar effects on starch granules, such as collapsing of the wall of starch granules and fragmentation of the growth rings. The limited moisture content during the HMT under acidic condition may inhibit loss of soluble sugar during the treatment, and the relatively higher temperature for the HMT possibly accelerate rate of acid hydrolysis. Consequently it was expected that the HMT under mildly acidic condition may improve a process for preparation of starch nanoparticles in terms of yield and treatment period. The primary objective of this study was to determine the effect of HMT under mildly acidic conditions on the fragmentation of maize starch and to evaluate molecular and crystalline structures of the fragmented starch. Among the genotype of starch, waxy type starch are readily susceptible to acidic degradation compared to normal and high amylose starch (Angellier et al., 2004), so waxy maize starch was chosen for this study.

2. Materials and methods

2.1. Materials

Waxy maize starch was provided by Samyang Genex, Inc. (Seoul, South Korea). Isoamylase (EC 3.2.1.68; 1000 U/mL) was purchased from Megazyme International Ireland Ltd. (Wicklow, Ireland). All other chemicals were analytical grade at minimum.

2.2. HMT under mildly acidic conditions

Starch was modified by the HMT under mildly acidic conditions

(Kim & Huber, 2013). An aliquot of a 0.00 (control), 0.10, 0.15 or 0.20 N sulfuric acid solution (6 mL) was added to starch dispersion (15 g starch, dry basis [db]/150 mL distilled water). The mixtures were stirred for 1 h at an ambient temperature and then the starch was recovered using vacuum filtration (Whatman filter paper 40, GE Healthcare Life Science, Piscataway, NJ, USA). The starch was dried at 35 °C for 12 h and ground to pass through a No. 120 sieve. The starch was stored in a thermo-hygrostat (TH-ME, Jeio Tech, Daejeon, South Korea) at 35 °C and a relative humidity (RH) of 95% to reach 20% moisture levels in starch samples. After reaching the moisture equilibrium, the samples (10 g, db) were moved to a Teflon PFA (perfluoroalkoxy) jar (Cowie Technology Corp., Wilmington, DE, USA), and then the jar was hermetically closed and heated to 130 °C for 3, 5, or 8 h and cooled to ambient temperature. The treated starch was dispersed in 50% EtOH (40 mL), neutralized with 0.1 N NaOH, washed with 50% EtOH (40 mL \times 2 times), and washed and solvent-dried with 40 mL of absolute ethanol. The treated starch was dried at ambient temperature and ground to pass through a No. 120 sieve. A phenol-sulfuric acid method (DuBois, Gilles, Hamilton, Rebers, & Smith, 1956) was used to measure the total carbohydrate content in the washing solvents, and the yield of the starch was calculated according to the equation below:

$$\begin{aligned} \text{Yield}(\%) &= (\text{Weight of starch} \\ &\quad - \text{total carbohydrate in the solvent}) \\ &\quad \times / \text{Weight of starch} \times 100 \end{aligned}$$

2.3. Fragmentation of starch granules

Untreated starch granules and HMT starch granules (35 mg) were dispersed in distilled water (3.5 mL) and each resulting suspension was treated in an ice bath using a homogenizer (Silent Crush M with Tool 8DF, Heidolph Instruments, Schwabach, Germany) at 23,000 rpm up to 60 min. The homogenized sample was collected or freeze-dried for further analyses.

2.4. Fourier transform-infrared spectroscopy (FT-IR)

The moisture of the starch samples (2.0 g, db) was equilibrated at 30 °C and RH 75% for 24 h in a thermo-hygrostat (TH-ME, Jeio Tech, Daejeon, Korea), and the samples (untreated, HMT and homogenized starch) were measured to determine the absorbance spectra using a Frontier spectrometer (PerkinElmer, Waltham, MA, USA) containing a zinc selenide crystal and in attenuated total reflectance (ATR) mode (van Soest, Tournois, de Wit, & Vliegthart, 1995).

2.5. X-ray diffraction (XRD)

X-ray diffraction was performed for the untreated, HMT and homogenized (lyophilized) starch samples (Cheetham & Tao, 1998). Moisture of starch samples (2.0 g, db) was equilibrated at 30 °C and RH 75% for 24 h in a thermo-hygrostat (TH-ME, Jeio Tech, Daejeon, Korea). The XRD patterns of the moisture-equilibrated starches were obtained using a powder X-ray-diffractometer (X'Pert PRO MPD, PANalytical, Almelo, Netherlands).

2.6. Starch intact molecular profile

Native or HMT starch was dispersed in 90% dimethyl sulfoxide (DMSO) and was precipitated in absolute ethanol as described by

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