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Corn starch granules with enhanced load-carrying capacity via citric acid treatment

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ABSTRACT

This research investigated conditions by which maize starch granule porosity and load-carrying capacity (LCC) might be enhanced via treatment with varying citric acid concentrations (0.5–1.5 M), temperatures (40–60 °C), and lengths of treatment (1–8 h). At the lowest temperatures (40 and 50 °C), citric acid treatment induced minimal physicochemical changes to granules. In contrast, both aqueous and oil LCCs of starches treated at 60 °C (0.5 M citric acid, 2 h) were almost doubled (15.69 and 14.48 mL/10 g starch, respectively), recovering 92% of the granular starch after treatment. Such treatment increased starch hydration capacity (0.97–1.91) and reduced gelatinization enthalpy (10.6–7.4 J/g). More severe treatment conditions adversely impacted aqueous LCC (due to excessive granule swelling), but improved oil absorption. The basis for LCC enhancement by citric acid treatment was ascribed to leaching of starch material from granules and partial disruption of the granule crystalline structure, as opposed to starch hydrolysis or chemical substitution.

1. Introduction

Highly porous materials possessing exceptional specific surface areas find use as catalysts, sorbents, plating/carrying agents, etc. with surface structure being a primary factor determining their functionality and efficiency in technological applications (Szymonska & Wodnicka, 2005). Compared with inorganic porous materials such as mesoporous silica (Zhang et al., 2010), clay particles (Zhang et al., 2010) and lipid-inorganic hybrids (Tan, Simovic, Davey, Rades, & Prestidge, 2009), starch-based porous biomaterials offer the distinct advantages of non-toxicity, biocompatibility, biodegradability, renewability, and low cost (Wu et al., 2011). Thus, porous starch particles find extensive use in food, pharmaceutical, agricultural, cosmetic, pulp/paper, and other aligned industries (Glenn et al., 2010; Qian, Chang, & Ma, 2011).

Starch granules of certain botanical origin (i.e., maize, sorghum, millet, wheat, etc.) possess native internal channels, many of which extend inward from the external granule surface to the central cavity at the granule hilum (Huber & BeMiller, 2000). Both cavity and channel structures within starch granules may be enlarged to further increase granular porosity via limited erosion/hydrolysis of amorphous regions within starch granules using amylolytic enzymes (α-amylase, glucoamylase, etc.) under varied experimental conditions (Uthumporn, Zaidul, & Karim, 2010; Zhao, Madson, & Whistler, 1996). A higher degree of hydrolysis produces channels and cavities of greater size, but also decreases the ultimate recovery of porous starch material, due to more extensive erosion or removal of starch from granules (Qian, Chen, Ying, & Lv, 2011; Uthumporn, Zaidul, & Karim, 2010; Zhao, Madson, & Whistler, 1996). Alternatively, hydrolysis of starch within granules via lintnerization may also enhance porosity of corn starch granules, with preferential attack occurring within granule amorphous regions (Jayakody & Hoover, 2002). Chabot, Allen, and Hood (1978) observed two primary patterns of action for acid hydrolysis within waxy maize starch granules, one in which hydrolysis proceeded from the inner hilum region outward (most likely facilitated by channel structures), and the other in which the hydrolysis front progressed from the external granule surface inward. As the starch granule matrix is reported to be permeable to molecules possessing a hydrodynamic radius less than 0.6 nm (Planchot, Roger, & Colonna, 2000), the extent of diffusion (as well as hydrolytic action) within the granule matrix was suggested to be greater for mineral acid treatment relative to that of amylolytic enzymes (Jayakody & Hoover, 2002). Nevertheless, porous starch materials generated by either amylolytic enzyme or mineral acid hydrolysis must be labeled as modified food starch within the U.S. Though modified starches prepared for food use are considered both functional and safe ingredients (Singh, Kaur, & McCarthy, 2007), consumer demand for 'clean label' ingredients has renewed efforts to develop alternative starch products.

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One possible approach for generating alternative porous starch materials involves treatment of starch granules with organic acids, such as citric acid. Citric acid is common to citrus fruits, and is further utilized as a GRAS ingredient (e.g., acidulant, preservative) within processed foods. Hirashima et al. (2004) reported differing effects of citric acid on the pasting behaviors of corn starch granules depending on treatment conditions. Below pH 3.5, citric acid treatment induced fracture or collapse of starch granules, as well as extensive hydrolysis of starch chains, resulting in reduced pasting viscosities. Conversely, at less acidic pH values ($3.6 < pH < 5.5$), citric acid treatment promoted enhanced leaching of starch chains from granules (during heating/gelatinization), leading to increased pasting viscosities. In short, citric acid has potential to cleave glucose chains within starch granules (similar to common mineral acid or enzymatic hydrolysis) and/or accelerate leaching of starch chains from granules during heating. Based on the fact that the granule hilum is reported to be the least organized region within the granule (Baker, Miles, & Helbert, 2001), and that the hilum has direct access to the external granule environment via interconnected channels within corn starch granules (Huber & BeMiller, 1997, 2000), it was hypothesized that citric acid treatment could induce preferential erosion and/or leaching of starch from amorphous regions of granules to enhance granule porosity. Nevertheless, there are no prior reports detailing preparation of porous starch particles via citric acid treatment.

The primary objective of this research was to investigate the potential for increasing the load-carrying capacity of normal maize starch granules, utilizing multiple concentrations of citric acid in conjunction with varied treatment temperatures and times.

2. Materials and methods

2.1. Starch source and chemicals

Normal maize starch (Pure-Dent B700) was provided by Grain Processing Corporation (Muscatine, IA, USA). Citric acid was purchased from Sigma–Aldrich Corp. (St. Louis, MO, USA). Isoamylase (EC 3.2.1.68; 1000 U/mL) was purchased from Megazyme International Ireland Ltd. (Wicklow, Ireland). Mercury dibromofluorescein (disodium salt, merbromin) was purchased from Fluka (Seelze, Germany). All other utilized chemicals were at minimum of analytical grade.

2.2. Citric acid treatment

Normal maize starch was treated with citric acid according to a factorial experimental design ($3 \times 3 \times 5$) consisting of three concentrations of citric acid solution (0.5, 1.0, or 1.5 M), three levels of temperature (40, 50, or 60 °C), and five lengths of treatment (1, 2, 3, 5, or 8 h). Normal maize starch (10 g, dry basis [db]) was dispersed in the appropriate concentration of citric acid solution (100 mL), and the dispersion was incubated at the designated temperature with stirring (440 rpm) for a set length of time (as defined by the factorial design). After citric acid treatment, treated starch was collected by centrifugation ($3000 \times g$, 10 min), and neutralized with 0.1 N NaOH. Neutralized starch was washed with 70% aqueous ethanol (100 mL × 2 times) followed by washing with absolute ethanol (100 mL) to remove residual citric acid and dehydrate the starch. Treated starch was dried in a vacuum oven (50 °C, 70 kPa, 8 h), and ground to pass through a No. 120 sieve. Control starch was prepared according to the same procedure (without addition of citric acid) as a reference. Recovery of starch material following citric acid treatment was calculated according to the equation below:

$$\text{Recovery}\,(\%) = \frac{\text{Weight of starch after citric acid treatment}}{\text{Weight of starch before citric acid treatment}} \times 100$$

2.3. Load-carrying capacity (LCC) of starches

Load-carrying capacity (LCC) of starch granules was assessed in both water and oil media using ASTM Standard Method D281-95. In general, starch (10 g, db) was transferred to a glass beaker (150 mL), after which a sufficient aliquot of water or oil was mixed into the starch with a spatula to yield a homogeneous powder. Additional water or oil was added to the starch (with further stirring) until a stiff, continuous, putty-like paste was formed (the endpoint was a continuous paste that did not break with stirring). If the paste became flowable (i.e., too much liquid had been added), the obtained value was discarded and the test was repeated. Load-carrying capacity was calculated as the total volume of fluid added to the starch and reported as mL of liquid per 10 g of starch (db).

2.4. Scanning electron microscopy (SEM)

Native, control, and citric acid-treated starch granules were mounted directly onto double-sided carbon tape attached to aluminum stubs. Mounted starches were carbon-coated, and viewed using scanning electron microscopy (SEM) (Amray 1830 Scanning Electron Microscope, Amray Inc. Bedford, MA, USA) at 10 kV.

2.5. Optical microscopy

Starch granules were placed in distilled water or immersion oil on a glass slide, overlaid with a cover slip, and observed with a Nikon Eclipse E600 microscope (Melville, NY, USA).

2.6. Merbromin treatment and fluorescence microscopy

Interior channels and cavities of native maize, treatment control and citric acid-treated starch granules were flooded with a methanolic solution of merbromin as described by Kim and Huber (2008). Merbromin solution was prepared by dissolving merbromin (0.1 g) in methanol (100 mL). Starch granules (200 mg, db) were dispersed in methanolic merbromin solution (20 mL) with stirring (440 rpm) for 4 h in the dark at ambient temperature. Merbromin-treated starch granules were recovered by vacuum filtration, lightly washed on the filter with ethanol (merbromin is insoluble in ethanol) to fix merbromin to starch granule surfaces, and allowed to air-dry.

Merbromin-treated starch granules were placed in immersion oil on a glass slide, overlaid with a glass cover slip, and observed with an Olympus upright BX51 microscope (Melville, NY, USA) equipped with a fluorescence source (excitation at 450–550 nm).

2.7. Hydration capacity of starch granules

Hydration capacity of starch granules was measured as described by AACC Method 56-20 (AACC, 2000). Starch (2.0 g, db) was suspended in distilled water (40 mL) and shaken vigorously to fully disperse the starch. The starch suspension was allowed to stand (10 min), during which time tubes were inverted after 5 and 10 min. After the 10 min suspension period, the dispersion was centrifuged ($1000 \times g$, 15 min), the supernatant was decanted, and the sediment was weighed. Hydration capacity of starch granules was calculated according to the equation below:

$$\text{Hydration capacity} = \frac{(\text{Weight of tube} + \text{sediment}) - (\text{weight of tube})}{\text{Sample weight}\,(\text{db})}$$

2.8. Differential scanning calorimetry (DSC)

Thermal transition properties of starch granules were carried out using differential scanning calorimetry (DSC) (2920