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The impact of single and dual hydrothermal modifications on the molecular structure and physicochemical properties of normal corn starch

Hyun-Jung Chung[a], Ratnajothi Hoover[b], Qiang Liu[a,*]

[a] Guelph Food Research Centre, Agriculture and Agri-Food Canada, 93 Stone Road West, Guelph, ON N1G 5C9, Canada
[b] Department of Biochemistry, Memorial University of Newfoundland, St. John's, NL A1B 3X9, Canada

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ABSTRACT

Effect of single and dual hydrothermal modifications with annealing (ANN) and heat-moisture treatment (HMT) on molecular structure and physicochemical properties of corn starch was investigated. Normal corn starch was modified by ANN at 70% moisture at 50 °C for 24 h and HMT at 30% moisture at 120 °C for 24 h as well as by the combination of ANN and HMT. The apparent amylose content and swelling factor (SF) decreased on ANN and HMT, but amylose leaching (AML) increased. These changes were more pronounced on dual modification. The crystallinity (determined by X-ray diffraction), the gelatinization enthalpy (determined by differential scanning calorimetry) and ratio of 1047 cm^{-1}/1022 cm^{-1} (determined by Fourier transform infrared spectroscopy) slightly increased on ANN and decreased on HMT. The ANN and subsequent HMT (ANN-HMT) resulted in the lowest crystallinity, gelatinization enthalpy and ratio of 1047 cm^{-1}/1022 cm^{-1}. The gelatinization temperature range decreased on ANN but increased on HMT. However, the gelatinization range of dually modified starches (ANN-HMT and HMT-ANN) was between ANN starch and HMT starch. Birefringence remained unchanged on ANN but slightly decreased on HMT as well as dual modification. Average chain length and amount of longer branch chains (DP ≥ 37) remained almost unchanged on ANN but decreased on HMT and dual modifications (ANN-HMT and HMT-ANN). HMT and dual modifications resulted in highly reduced pasting viscosity. ANN and HMT as well as dual modifications increased RDS content and decreased SDS and RS content.

1. Introduction

Starch has been used in a wide variety of products, either as a food ingredient or as an industrial material. Total annual world production of starch is approximately 60 million MT [1]. Corn supplies over 80% of the world starch market [2], followed by potato, cassava and wheat. Starch digestibility has been known to vary among different starchy foods, which have been ascribed to various factors, including botanical source [3], food processing [4], particle size [5], amylose/amylopectin ratio [6], type of crystalline polymorphic (A, B or C) form [7], and presence of amylose–lipid complexes [8,9]. For nutritional purposes, starches are classified on the basis of their rate of enzymatic digestion into three categories: rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS) [10]. RDS is the starch fraction that causes a sudden increase in blood glucose level after ingestion, and SDS is a starch fraction that is digested completely in the small intestine at a lower rate as compared to RDS. RS is the starch portion that cannot be digested in the small intestine, but is fermented in the large intestine.

Native starches usually do not meet industrial needs in which starch should be able to withstand high shear rates and shear forces during processing, low acidity and high and low temperatures. Consequently, starches have been modified physically (heat-moisture treatment, annealing, pre-gelatinization, high pressure treatment) and chemically (cross-linking, substitution, acid hydrolysis, oxidation) in order to extend the range of starch applications in food, textiles, paper and pharmaceuticals [11]. At the present time, there is great interest in the use of hydrothermal treatment such as heat-moisture treatment (HMT) and annealing (ANN) which modify starch structure and properties without destroying its granular structure. Both HMT and ANN involve incubation of starch at a specific temperature and at a certain moisture level during a certain time period. The term HMT is used when low moisture levels (<35%, w/w) are applied, whereas, ANN refers to treatment of starch in excess water (<65%, w/w) or at intermediate water (40–55%, w/w). Both HMT and ANN occur below the onset temperature of gelatinization and have been shown to modify the structural arrangement of starch chains within the amorphous and crystalline domains to different extents [12,13]. ANN has been shown to increase granular stability, crystalline perfection and gelatinization

* Corresponding author. Tel.: +1 519 780 8030; fax: +1 519 829 2600.
E-mail address: liuq@agr.gc.ca (Q. Liu).

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transition temperatures, and to decrease granular swelling, amylose leaching and the gelatinization temperature range. However, depending on the starch source and ANN conditions, crystallinity, amylose–lipid interactions, and susceptibility towards acid and enzyme hydrolysis have been shown to increase, decrease or remain unchanged on ANN [12–16]. Regardless of starch origin, increase in gelatinization transition temperatures, widening of the gelatinization temperature range, decrease in granular swelling and amylose leaching and an increase in thermal stability have been shown to occur on HMT. However, depending on botanical origin and treatment conditions, changes to the X-ray pattern (B to A + B), formation of amylose–lipid complexes, disruption of crystallinity, and increase or decrease in enzyme susceptibility have been shown to occur on HMT [12,17–20]. Although many studies have investigated the effect of ANN and HMT on starches individually, there is a dearth of information on the impact of dual hydrothermal treatment (ANN followed by HMT [ANN-HMT] and HMT followed by ANN [HMT-ANN]) on starch structure and properties. Stute [21] studied the effect of dual modification (ANN-HMT and HMT-ANN) on the gelatinization transition temperatures, X-ray pattern, pasting properties and sorption isotherm of potato starch (B-type unit cell). The above study showed that structural alterations on ANN are reversible when ANN potato starch is subjected to HMT and also that HMT potato starch can be annealed, since in addition to the structural changes in the elementary cell the interaction between the crystallites and the amorphous parts can still be modified under ANN conditions. However, it is difficult to interpret the data on the above study, due to lack of information on changes to amylopectin chain length distribution, crystallinity, amylose leaching and gelatinization enthalpy. Thus, the objective of this study was to determine to what extent the molecular structure and physicochemical properties of normal corn starch (A-type unit cell) can be modified when subjected to single (ANN and HMT) and dual (ANN-HMT and HMT-ANN) modification. The results of this study may provide an alternative route for improving the thermal stability, shear stability, freeze–thaw stability and digestibility of corn starch. Research geared to hydrothermal treatment is important, since it is highly unlikely that any new chemical or genetic modification be allowed to alter the functional properties of existing commercially based starches.

2. Materials and methods

2.1. Materials

Normal corn starch (cat. no. S-4126), pancreatin from porcine pancreas (cat. no. P-7545, activity 8 × USP/g) and invertase (ED 3.2.1.26) grade VII from Bakers yeast (355 U/mg) were purchased from Sigma Chemical Company (St. Louis, MO, USA). Amyloglucosidase (EC 3.2.1.3., 3300 U/ml) and glucose oxidase-peroxidase assay kit (cat. no. K-GLUC) were purchased from Megazyme (Megazyme International Ireland Ltd., Bray, Ireland).

2.2. Hydrothermal treatment

2.2.1. Annealing

Starches were subjected to one step annealing. Native corn starch (30 g, db) and distilled water (70 ml) were placed in a 125 ml glass container, sealed, and incubated at 50 °C for 24 h in a water bath. At the end of the incubation period, samples were centrifuged (2000 *g*) for 10 min and supernatant was decanted. The annealed starches were washed once with deionized water and air dried at 40 °C.

2.2.2. Heat-moisture treatment

Starch samples (30 g, db) were weighed into 125 ml glass containers. The moisture content of starch was brought to 30% by adding the appropriate amount of distilled water. The starch samples were mixed thoroughly during the addition of water. The containers were sealed, kept for 24 h at ambient temperature, and then placed in a forced air oven at 120 °C for 24 h. Afterwards the containers were opened and the starch samples air dried to uniform moisture content (∼10%).

2.2.3. Dual modification

Annealed corn starch samples prepared by the annealing procedure (Section 2.2.1) were weighed into glass containers. The moisture content was adjusted to 30%, followed by heat-moisture treatment (Section 2.2.2). This treatment procedure is abbreviated as ANN-HMT in the text.

Heat-moisture treated corn starch samples (Section 2.2.2) were weighed into glass containers. The starch slurries were prepared by adding water (starch:water = 3:7), followed by annealing (Section 2.2.1). This treatment procedure is abbreviated as HMT-ANN in the text.

2.3. Polarized light microscopy

Birefringence of native and modified corn starch granules was observed under polarized light with a binocular microscope (DME, Leica Canada, Mississauga, ON, Canada) equipped with real time viewing (Micropublisher 5.0, QImaging, Surrey, BC, Canada). The images were recorded at the same magnification (400×) for all starch samples (1.0% starch suspension).

2.4. Apparent amylose content

Apparent amylose content of native and modified starches was determined by a colorimetric method [22].

2.5. Swelling factor (SF)

The swelling factor of native and modified corn starches when heated in the range 60–90 °C in excess water was measured according to the method of Tester and Morrison [23]. The SF is reported as the ratio of the volume of swollen granules to the volume of the dry starch.

2.6. Amylose leaching (AML)

Starches (20 mg) in water (10 ml) were heated in the range 60–90 °C in sealed tubes for 30 min with continuous shaking. The tubes were then cooled to room temperature and centrifuged at 2000 *g* for 10 min. The supernatant (1.0 ml) was withdrawn and its amylose content was determined as described by Williams et al. [22]. AML was expressed as percentage of amylose leached per 100 g of dry starch.

2.7. X-ray diffraction

X-ray diffractograms of native and modified corn starches (∼10% moisture content) were obtained from a Rigaku RPT 300 PC X-ray diffractometer (Rigaku-Denki Co., Tokyo, Japan) at 40 kV and 100 mA with 3–35° scanning range and 2.0°/min scan speed. The crystallinity of the starches was quantitatively estimated following the method of Nara and Komiya [24] using the Origin 6.0 software (Microcal Inc., Northampton, MA).

2.8. Fourier transform infrared spectroscopy (FTIR)

Infrared spectra of native and modified starches were recorded on a Digilab FTS 7000 spectrometer (Digilab USA, Randolph, MA) equipped with a thermoelectrically cooled deuterated tri-glycine