

Comparison of maize and wheat starch chain reactivity in relation to uniform versus surface oriented starch granule derivatization patterns



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ABSTRACT

This study investigated whether different granular reaction patterns of starch derivatives alters the extents of reaction of different starch chain types. Maize and wheat starch granules were derivatized with the fluorescent probe 5-(4,6-dichlorotriazinyl)amino-fluorescein under different reaction conditions to obtain starches derivatized to the same level but either characterized with a surface-oriented or a rather uniform granular reaction pattern. Given the same overall extent of reaction, amylose and amylopectin chains reacted to a greater extent for the starch with a uniform granular reaction pattern, while intermediate chains [$100 \leq$ degree of polymerization (DPw) < 372] reacted to a greater extent for the starch with a surface-oriented granular reaction pattern suggesting that amylose and amylopectin chains are distributed more homogeneously throughout the granule than the intermediate chains. For both reaction patterns, it was shown that the relative reactivities of intermediate chains were 5.0–9.4 fold higher than the overall reactivity calculated across all starch chains. This study thus teaches that starch chain reactions depends on the granular reaction pattern.

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1. Introduction

Starch is a plant reserve polysaccharide laid down as granules. Its polymeric nature and ability to interact with itself or other compounds contribute to its use as thickener, stabilizer, gelling agent or filler in food systems. The industry using starch imposes high demands on its properties, which native starches do not always meet. Chemical modification is widely applied to obtain starches with desired functionalities. Even so, reaction patterns at the granular and molecular levels are not fully understood. This is probably because even subtle changes in starch molecules resulting from such modification drastically impact starch properties. Nevertheless, it has been established that the semi-crystalline nature of the starch granule architecture does impact reaction patterns of specifically amylose (AM) and amylopectin (AP) branch

chains (Hong & Huber, 2015a).

It has been recently reported that, at similar extents of overall reaction, maize starch (MS) cross-linking in 65% acetone (v/v) has a greater impact on pasting viscosity than that in 65% ethanol (v/v) (Hong, Gomand, & Delcour, 2015). This result highlights the importance of the reaction pattern on properties of the resultant starches. In starch derivatization reactions, granular reaction patterns become more uniform with increasing reagent levels (Huber & BeMiller, 2001; Kim & Huber, 2013), granule hydration (Hsieh, 2013; Kim & Huber, 2008), reaction pH, temperature (Gray & BeMiller, 2005) and contact time with the reagent prior to initiating the reaction (Hong, BeMiller, & Huber, 2016). The presence of sodium sulfate, a starch swelling inhibitor, in some reaction media causes the reaction to occur in a less uniform manner than in its absence (Gray & BeMiller, 2005). In short, the reaction pattern is controlled by various reaction parameters.

Hong and Huber (2015a, 2015b) successfully monitored the starch reaction pattern at both granular and molecular levels using a fluorescent probe as a derivatization reagent. In this approach, the distribution pattern of fluorescent signals within starch granules was studied by confocal laser scanning microscopy (CLSM). In addition, size-exclusion chromatography (SEC) equipped with both

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refractive index (RI) and fluorescence intensity (FL) detection was used to directly measure extent of reaction for amylose (AM) and amylopectin (AP) long, medium, and short chains. With these techniques, the impact of starch granule structure on AM and AP chain reactivities was investigated using a model reaction system. The reactivity of the specific starch chains (AP long chains > AM or AP medium chains > AP short chains) varied with their relative participation in the starch granule architecture. AP short chains were presumably reacted least due to their participation in the granule crystalline structure. Nevertheless, the contribution of starch intermediate material (IM) to the overall extent of derivatization was suggested to be substantial, though the reactivity of IM chains was not able to be quantitatively determined in this initial study.

IM can be precipitated from starch with isoamyl alcohol and 1-butanol, but not by 1-butanol alone (Takeda, Hizukuri, & Juliano, 1986; Whistler & Doane, 1961), and exhibits an 'intermediate' iodine binding affinity and blue value between that of AM and AP (Adkins et al., 1969). Specific molecular features of starch IM have been further described for maize (Baba & Arai, 1984; Klucinec & Thompson, 1998; Shi, Capitani, Trzasko, & Jeffcoat, 1998; Wang, White, Pollak, & Jane, 1993), wheat (Shibanuma, Takeda, & Hizukuri, 1996; Shibanuma, Takeda, Hizukuri, & Shibata, 1994; Yoo & Jane, 2002b), and rice (Lu, Chen, & Li, 1997; Takeda, Hizukuri, & Juliano, 1987; Vilaplana & Gilbert, 2010a, 2010b; Yoo & Jane, 2002a) starches. In short, IM appears to have a branched structure, and tends to elute between AM and AP fractions in gel-permeation chromatography. However, the possible location of IM within the starch granule and its function in starch modification requires further investigation.

Against this background, the aim of this study was to understand how the reaction pattern within starch granules (surface-oriented versus more homogeneously at the same modification level) impacts the reactivity of AM, IM and AP branch chains. In addition, the reactivity of IM chains was measured for the first time. To allow the detection of both granular and molecular reaction patterns, normal maize starch (MS) and wheat starch (WS) granules were derivatized with a fluorescent reagent, with reaction parameters adjusted to obtain starches with equivalent modification levels but diverse reaction patterns. The resulting MS and WS granules with either a surface-oriented versus a more uniform granular derivatization pattern were referred to as MS_{SD} and WS_{SD}, or MS_{UD} and WS_{UD}, respectively.

2. Materials and methods

2.1. Materials

Normal MS and WS were obtained from Cargill (Vilvoorde, Belgium) and Tereos Syral (Aalst, Belgium) respectively. The amylose contents of normal MS and WS were determined as 26.4% and 25.8% (on dry matter basis), respectively, by using the Megazyme amylose/amylopectin assay kit (Megazyme International Ireland, Co. Wicklow, Ireland). WS was fractionated according to Kim and Huber (2008) into A and B type granules by exploiting the difference in their sedimentation rate in 80% (w/v) sucrose. Laser diffraction Malvern (Worcestershire, UK) Mastersizer analysis showed that WS contained 92% A type granules by volume. The derivatizing agent was 5-(4,6-dichlorotriazinyl)amino fluorescein (DTAF, a fluorescent probe). Isoamylase was from *Pseudomonas* sp. ($\geq 3 \times 10^6$ units/mg, units as defined by the supplier). All reagents, solvents, chemicals and enzymes used were at least analytical grade, and were obtained from Sigma-Aldrich (Bornem, Belgium) unless indicated otherwise.

2.2. Starch derivatization in an aqueous or aqueous-acetone reaction medium

Granular starch was reacted with DTAF in aqueous sodium sulfate or in aqueous acetone as introduced by Hong et al. (2015) with slight modifications (Fig. 1). Table 1 lists the specific levels of reagents and reaction conditions. Starch granules (10.0 g, dry weight basis) were dispersed in 58.0 mL 0.8% sodium sulfate (w/v) or 69% (v/v) acetone with stirring. The amount of DTAF solution (10.0%, w/v in dimethyl sulfoxide) added was experimentally determined to result in an equal extent of overall reaction [the total area of fluorescence intensity (FL) divided by the corresponding total area of refractive index intensity (RI) in SEC chromatograms] for both media.

For starch modification in aqueous sodium sulfate, 2.0 M sodium hydroxide was added after 60 min reagent infiltration time (i.e., time allowed for reagent to infiltrate granules prior to formal initiation of the reaction) at room temperature to adjust the pH to 11.5 and initiate the reaction. Deionized water was used to bring the reaction volume to 60 mL. The reaction proceeded under stirring (400 rpm) for 20 h at room temperature. Reaction pH was monitored and maintained at 11.5 via drop-wise addition of 2.0 M NaOH (added volume <90 μ l). The reaction was terminated by decreasing the pH to 6.0 with 1.0 M HCl. For starch modification in aqueous acetone, the infiltration and reaction times were 5 and 90 min, respectively. The reaction itself took place at 45 °C and was terminated in the same fashion. All derivatizations were conducted once in the dark to minimize photo-bleaching.

Derivatized starches were collected by centrifugation (3000 g, 10 min), suspended in 35.0 mL 70% (v/v) ethanol and centrifuged as above. Washing and intermediate centrifugation was repeated until colorless supernatants were obtained. The resultant starch pellets were suspended in ethanol, vacuum-filtered through a Büchner funnel, and air-dried at room temperature (24 h). MS and WS granules derivatized in water containing 0.8% sodium sulfate (w/v) or in 67% acetone (v/v) in the corresponding reaction conditions are referred to as MS_{UD}, MS_{SD}, WS_{UD} and WS_{SD}, respectively.

2.3. Fourier transform infrared spectroscopy

Fourier transform infrared spectra (FTIR) of the materials were

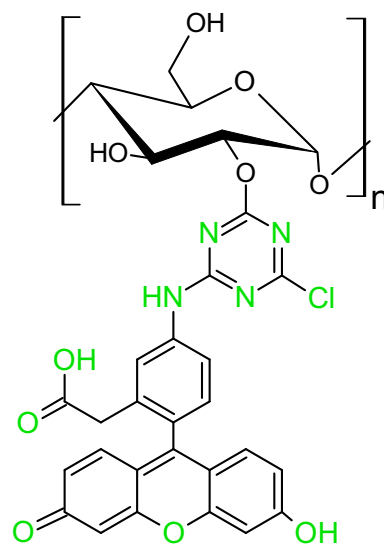


Fig. 1. Products obtained when reacting starch with 5-(4,6-dichlorotriazinyl)amino fluorescein (DTAF, a fluorescent probe).

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