



Research Paper

Reaction pattern differences impact physical properties of starches derivatized to the same extent in a model cross-linking system



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ABSTRACT

This study investigated the physical properties of maize (MS) and wheat (WS) starches derivatized with 5-(4,6-dichlorotriazinyl)aminofluorescein (model cross-linking system) to have the same overall fluorescence intensity on starch molecules, but reacted either more uniformly throughout granules (UD) or more at granule surfaces (SD). Both MS and WS derivatives had lower swelling powers (SP) at 90 °C than their respective native starches. The UD derivatives had lower SP (90 °C) and greater retrogradation enthalpies than did SD derivatives, consistent with their lower peak and higher setback pasting viscosities. Also, SD starches were less soluble and retained a greater degree of granular integrity than UD starches in time-lapse, hot-stage light microscopy studies (50–95 °C), likely due to a greater concentration of cross-links at the granule surface. The results confirm that derivatization patterns impact the physical properties of modified starches. Thus, varying derivatization patterns can be a strategy to tailor modified starch properties.

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1. Introduction

Chemical modification of starch can enhance its cold storage/freeze-thaw stability, paste consistency and clarity, film formation, and adhesion characteristics. However, due to regulatory constraints, only a limited number of novel chemical reagents and modification techniques have been introduced in the last several decades. This observation itself indicates the need for better understanding and control of existing modification practices to more effectively manipulate starch functionality (BeMiller, 1997).

Starch modification practices can be better understood when monitoring derivatization patterns at the granular and molecular levels. Han and BeMiller (2006) reported that an increased reaction pH promotes starch derivatization by propylene oxide. The uniformity of derivatization within the granule is enhanced at

higher pH under otherwise comparable reaction conditions (Gray & BeMiller, 2005). Uniformity also increased as the time (0–60 min) during which reagent (fluorescent probe) was allowed to diffuse into starch granules prior to the initiation of reaction (*i.e.*, addition of base) was increased (Hong, BeMiller, & Huber, 2016). A longer reagent infiltration time resulted in an increased overall extent of derivatization and a greater reduction in pasting viscosity, suggesting a greater effect of cross-linking for the more uniformly reacted starch granules.

However, in contrast, only minute differences in properties were observed for normal and waxy maize and wheat starches modified either traditionally (reagent and base added together at the beginning of the reaction) or by first allowing the reagent to penetrate into granules for a three hour period prior to initiating the reaction (Sui, Huber, & BeMiller, 2013; Sui, Huber, & BeMiller, 2015). Evaluated reagents included phosphorous oxychloride, sodium trimetaphosphate, and carboxylic acid anhydrides. Hirsch and Kokini (2002) noted a higher pasting viscosity, yet a lower swelling potential (*i.e.*, the amount of intragranular water) for starch cross-linked with phosphorous oxychloride compared to that cross-linked with sodium trimetaphosphate or epichlorohydrin. They suggested that this difference might be due to the concentration of cross-links at the surfaces of granules (forming a hard shell) when using phosphorous oxychloride, and more diffuse

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cross-linking when using sodium trimetaphosphate or epichlorohydrin. Regretfully, Hirsch and Kokini (2002) did not provide overall extents of derivatization in their report, making comparison of the physical properties of the modified starches in this study difficult. Indeed, although the majority of studies on this topic (Gray & BeMiller, 2005; Han & BeMiller, 2006; Hirsch & Kokini, 2002; Hong, BeMiller et al., 2016) have demonstrated that reaction patterns impact the physical properties of modified starches, it is not clear whether these variations are due to differences in uniformity of the reaction pattern or to the overall extent of derivatization (molar substitution or degree of substitution).

Recently, Hong, Gomand, Huber, and Delcour (2016) generated two different reaction patterns when modifying starches with a fluorescent reagent [5-(4,6-dichlorotriazinyl)aminofluorescein, DTAF] under precisely controlled reaction conditions. In the first case, derivatization occurred primarily at the surfaces of starch granules (SD), including the granular periphery and within channels and cavities. In the second case, a more uniform distribution of derivatization (UD) was achieved throughout the granules. For both scenarios, granular reaction patterns were confirmed by confocal laser scanning microscopy (Fig. 1). These two different reaction patterns were successfully achieved by controlling reaction conditions – the UD was conducted in an aqueous medium at a slower reaction rate [0.8% aqueous Na₂SO₄ (w/v) medium, at 20 °C for 20 h], whereas the SD was reacted under limited moisture conditions [69% (v/v) aqueous acetone medium, at 45 °C for 1.5 h]. The fluorescent reagent, DTAF, is capable of forming cross-linked distarch and/or substituted monostarch derivatives through the two chlorinated carbons of the *s*-triazine ring (Warren, Reid, & Hamalainen, 1952). The level of DTAF addition was adjusted for the UD and SD reactions to achieve the same total fluorescence intensity (*i.e.*, overall extent of derivatization), which was assessed by size-exclusion chromatography equipped with fluorescence (FL) and refractive index (RI) detectors (SEC-RI-FL).

The starch derivatives were enzymatically debranched and chromatographically categorized into amylose (AM1 and AM2), intermediate (IM1 and IM2), and amylopectin (AP1, AP2, and AP3) fractions, which enabled comparison of their relative extents of derivatization (Hong, Gomand et al., 2016). Given equivalent extents of overall derivatization, intermediate chains (IM), a fraction in-between amylose (AM) and amylopectin (AP) fractions, tended to be more derivatized in the SD derivative, whereas the UD derivative showed greater extents of AM and AP derivatization. An increased degree of derivatization for AM has also been observed for starches produced with a longer reagent infiltration time prior to formally initiating the reaction (Hong, BeMiller et al., 2016). Thus, these findings indicated that the granular reaction pattern can alter the relative extents of derivatization for different starch chain populations.

The above studies suggest that both granular and the molecular reaction patterns co-determine the physical characteristics of modified starches. Thus, the starch derivatives generated by Hong, Gomand et al. (2016) are useful for further investigating the effect of granular derivatization patterns on starch physical properties, as both starches have equivalent overall extents of derivatization. As an extension of the previous study of Hong, Gomand et al. (2016), we here set out to contrast the swelling powers (SP), solubilities, and gelatinization/pasting/retrogradation properties of SD and UD starch derivatives. In addition, we utilized time-lapse microscope observations to relate temperature-induced changes in starch granule integrity (*i.e.*, retention of starch granular structure) to observed starch physical characteristics. Overall, this study focused on physical property differences between starch derivatives possessing a uniform (UD) or surface-oriented (SD) granular reaction pattern.

2. Materials and methods

2.1. Materials

Normal maize (MS) and normal wheat (WS) starches and their derivatives from a previous study (Hong, Gomand et al., 2016) were directly utilized for analysis of starch physical properties. Derivatization with 5-(4,6-dichlorotriazinyl)aminofluorescein (DTAF) resulted in MS_{UD} and MS_{SD}, as well as WS_{UD} and WS_{SD} (Fig. 1). As introduced in Section 1, the overall extents of derivatization for the two types of derivatization patterns (SD versus UD) for a given starch source were not statistically different from each other. The overall extents of derivatization were reported as 0.64 and 0.67 for MS_{UD} and MS_{SD}, and 0.65 and 0.66 for WS_{UD} and WS_{SD}, respectively in the previous study. These values were calculated as the ratio of the total FL peak area to the corresponding RI peak area in SEC-RI-FL chromatograms. All reagents, solvents, and chemicals used were at least analytical grade, and were obtained from Sigma-Aldrich (Bornem, Belgium) unless indicated otherwise.

2.2. Close packing concentration, swelling power and solubility

C*, SP, and solubility characteristics of native and derivatized starches were investigated. C* is the concentration (C) at which swollen granules fully occupy the total volume of the starch suspension at a given temperature (Eerlingen, Jacobs, Block, & Delcour, 1997; Evans & Haisman, 1980). In contrast to C*, swelling power (SP) is the ratio of swollen granules to the starch dry matter, taking into account dissolved material that occupies only part of the volume of the system (Steeneken, 1989). C* and SP for native and derivatized starches were determined as in Eerlingen et al. (1997) with slight modification. Starch suspensions (0.1 g in 9.0 mL deionized water) prepared in screw-capped glass tubes (98 × 12 mm) were heated for 30 min at 50, 70, or 90 °C in a water bath, with intermittent shaking every 5 min. Starch suspensions were cooled for 5 min and centrifuged (1000g, 30 min, 20 °C). The sediments were weighed and the supernatants transferred to fresh glass tubes. Carbohydrate leaching (CHL) analysis of the supernatants was conducted by the phenol-sulfuric acid colorimetric method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). C* and SP were determined according to the following equations:

$$C^* (\%) = \frac{\text{dry matter starch weight (g)} \times 100}{\text{sediment weight (g)}}$$

$$SP (\text{g/g}) = \frac{\text{sediment weight (g)} \times 100}{\text{dry matter starch weight (g)} \times (100 - \% \text{CHL})}$$

The supernatants obtained following incubation at 90 °C were oven-dried at 120 °C for 120 min and weighed as in Xiao, Lin, Liu, and Yu (2012). Starch solubility at 90 °C was calculated as follows:

$$\text{Solubility (\%)} = \frac{\text{dried supernatant weight (g)}}{\text{dry matter starch weight}} \times 100$$

2.3. Differential scanning calorimetry

Starch gelatinization properties were analyzed in triplicate by differential scanning calorimetry (DSC) using a Q2000 DSC (TA Instruments, Newcastle, DE, USA) as in Gomand et al. (2010). Starch and deionized water were accurately weighted in aluminum pans (Perkin Elmer, Waltham, MA, USA) to obtain a starch:deionized water ratio of 1:3 (w/w, 3–4 mg of starch dry weight basis). Pans were hermetically sealed and held for 30 min at room temperature. The heat flow of the samples was monitored from 20 °C to 120 °C at 4 °C/min. An empty aluminum pan was used as a reference, and

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