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Influence of reaction conditions on the location of reactions in waxy maize starch granules reacted with a propylene oxide analog at low substitution levels

Jonathan A. Gray[1], James N. BeMiller*

Whistler Center for Carbohydrate Research, Purdue University, Food Science Building, 745 Agriculture Mall Drive, West Lafayette, IN 47907-2009, USA

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Abstract

A constant amount of an anionic propylene oxide analog was reacted with waxy maize starch under conditions in which temperature, pH, and swelling-inhibiting salt type and concentration were varied. Reaction sites were located utilizing a reflectance confocal laser scanning microscopy (R-CLSM) method. Results confirm that uniformity of reaction within granules and molar substitution (MS) levels are a function of reaction conditions. In most cases, increasing pH from 10.7 to 11.7 increased the extent of reaction. Changes in temperature between 44 and 54 °C had little effect. Reactions carried out in the presence of NaCl produced more derivatization than did reactions carried out in the presence of Na_2SO_4 under identical conditions. More reaction was observed in the presence of a lower concentration (0.395 m) of Na_2SO_4 as compared to a higher concentration (0.527 m). Salt concentration effects were not discernible when reactions were done in the presence of NaCl (0.471 and 0.629 m).

Keywords: Hydroxypropylstarch; Starch; Hydroxypropylation; Waxy maize

1. Introduction

Development of improved modified starch products is likely limited to the use of currently allowed reagents and conditions. Patterns of reaction in granules are important since one avenue available for the development of novel products in granular form is control of the location of reactions within granules (BeMiller, 1997). Assuming that reaction efficiency is a function of granule swelling, it is theoretically possible to control the location of reactions by changing granule swelling conditions. Verification requires reliable methods to locate reactions in granules. Two such methods are now available (Gray & BeMiller, 2004; Huber & BeMiller, 2001).

The objective of this research was to determine the effect, if any, of modification conditions related to granule swelling on location of derivatization in waxy maize starch granules reacted with an anionic propylene oxide analog at a low substitution level using one of these methods (Gray & BeMiller, 2004). Waxy maize starch was chosen for these experiments for two reasons: (1) to avoid loss of starch polymer molecules as much as possible (the primary material that leaches from hydroxypropylated starch granules during reaction and/or work-up appears to be amylose (Shi & BeMiller, 2002)) and (2) to minimize the background (waxy maize starch contains less protein, which forms silver salts, the basis of the method for locating reactions sites to be used, than does normal corn starch (Han & Hamaker, 2002)). All reaction-related variables in derivatization reactions, viz. pH, temperature, type of swelling-inhibiting salt, and concentration of swelling-inhibiting salt, potentially impact granule swelling, so all were selected for study. Representative industrial reaction conditions for hydroxypropylation were chosen as the midpoints; higher and lower temperatures, pH values, and salt concentrations were utilized to provide insight as to the effect of each on the efficiency of reaction.

* Corresponding author. Tel.: +1 765 494 5684; fax: +1 765 494 7953.
E-mail address: bemiller@purdue.edu (J.N. BeMiller).
[1] Nestle Research and Development, Connecticut, New Milford, CT 06776, USA

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1.1. Impact of swelling on starch granule reactivity

Hauber, BeMiller, and Fannon (1992) concluded that, in order for reactions with granular starch to take place, granule swelling must first occur. That granule swelling has an effect on granule reactivity is supported by the finding that about 1.8 times more propylene oxide was needed to achieve the same MS when Na_2SO_4 was replaced by potassium citrate (a more effective swelling inhibitor) (Shi & BeMiller, 2000). Also, solutions of fluorescent amides of C_6, C_8, and C_{10} fatty acyl molecules were less able to penetrate common corn, waxy maize, and potato starch granules in the presence of sodium citrate than in the presence of Na_2SO_4 (Gray & BeMiller, 2001).

The importance of granule swelling to reactions with starch can be explained using base-catalyzed derivatization as an example. Formation of nucleophilic alkoxide ions is crucial for reactions to occur and is associated with dissipation of hydrogen bonds that hold the granule structure together. Thus, starch polymers, while becoming more reactive, become more flexible and amorphous regions become more hydrated and more swollen (Jenkins & Donald, 1997). As regions become more derivatized, they swell even more, eventually pulling apart crystallites.

1.2. Factors affecting starch granule swelling under derivatization conditions

Factors affecting starch swelling include temperature, starch:H_2O ratio, pH, presence or absence of a swelling-inhibiting or swelling-promoting salt, and the concentration of the salt. In addition, derivatization disrupts hydrogen bonding permanently, mostly by a steric effect, and makes further granule swelling more facile.

Because reaction of ethylene oxide with alkaline solutions is slower inside starch granules than in the extragranular phase, van Warners, Stamhuis, and Beenackers (1994) recommended that hydroxyethylation of starch be conducted at as high a starch/water ratio as possible. The reaction rate of starch with ethylene oxide increases with increasing moisture content of the starch because the rate of absorption of ethylene oxide increases exponentially with the moisture content of starch granules (van Warners, Lammers, Stamhuis, & Beenackers, 1990).

In theory, an increase in media pH (by the addition of NaOH, for example) causes swelling of starch granules via ionization of starch hydroxyl groups, which disrupts hydrogen bonding of chains and thereby effectively makes the starch molecules more flexible. Another explanation for the effect of base addition on granule swelling is that alkoxide ions repel one another, opening the spaces between starch chains (BeMiller & Pratt, 1981). Starch buffers changes in pH (Oosten, 1990) and can support pH levels up to at least pH 11 with little apparent structural change (BeMiller & Pratt, 1981; Hauber et al., 1992), even though the buffering effect means that starch hydroxyl groups are being converted into alkoxyl groups.

The impact of salts on gelatinization of granules is not completely clear. Swelling-inhibiting salts, particularly Na_2SO_4 and NaCl, are important to starch modification reactions because they prevent starch molecule leaching and inhibit gelatinization (Oosten, 1990; Pratt, 1975). Salts affect starch gelatinization according to their position in the Hofmeister (lyotropic) series. For example, Na_2SO_4, high on the lyotropic series, increases the gelatinization temperature (T_{gel}) of starch granules, while salts on the low end (NaI, for example) decrease the T_{gel} (some cause gelatinization at room temperature) (Sandstedt, Kempf, & Abbott, 1960). Salts in the middle of the series, such as NaCl, increase the onset temperature of gelatinization at low concentration (<1.5 M), but at concentrations >1.5 M lower the onset temperature (Evans & Haisman, 1982; Jane, 1993; Lii & Lee, 1993; Sandstedt et al., 1960; Wootton & Bamunuarachchi, 1980).

It appears that the impact of salts on starch gelatinization is controlled by two effects: (a) altering the structure of water (For example, ions with high charge density have been postulated to stabilize both the molecular structure of water and starch granules, while ions of low charge density both break water structure and destabilize granule structure (Jane, 1993)) and (b) affecting electrostatic interactions between starch and salt ions. (The starch granule is a weak-acid ion exchanger (Oosten, 1990), and thus attracts cations into the granule, and repels anions. Cations stabilize the granule to gelatinization, whereas anions disrupt hydrogen bonds (Oosten, 1982, 1983).) It has been postulated that salts not only change the T_{gel} of granules, but also the mechanism of gelatinization (Sandstedt et al., 1960).

The complexity of competing effects of salts (anion vs. cation) has been attributed to ion charge densities and overall salt concentrations (Jane, 1993), as well as to pH and temperature (Oosten, 1982, 1983). When sodium hydroxide is added to starch solutions containing NaCl or Na_2SO_4, gelatinization temperature increases. Perhaps this is due to the influx of sodium ions into the granule, which results in a higher Donnan potential that excludes anions from the granule (Oosten, 1979, 1982, 1983). However, above a critical pH value, anions are able to enter the granule and effect gelatinization. Heat, which effects a lowering of the Donnan potential, allows faster anion entry and thus accelerates the gelatinization process (Oosten, 1982, 1983).

1.3. Hydroxypropylation of starch

Reactions of starch with propylene oxide are generally conducted at 38–52 °C (100–125 °F) in the presence of sodium hydroxide. Swelling-inhibiting salts are added to prevent pasting. Reaction takes about 24 h to complete, and reaction efficiency is generally about 60% (Tuschoff, 1986).