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Substituent distribution changes the pasting and emulsion properties of octenylsuccinate starch

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ABSTRACT

An improved preparation method of octenylsuccinate (OS) starch under high shear condition was described in this study. The distribution of OS substituents at the granular and molecular levels was assessed by confocal laser scanning microscopy (CLSM), β-amylase hydrolysis, chromatographic and ^{1}H NMR techniques. We found that the OS group distribution could change the pasting and emulsion properties of OS starches. Specifically, more uniform OS group distribution was identified in the central region of OS starch granules prepared under high shear condition (H–OS–starch), and OS groups were located both near the branching points and the non-reducing ends. More OS groups exposed outside of non-reducing ends would access the interface between oil and water and give more stabilized emulsion.

1. Introduction

Shortcomings of non-modified starches limit their use in many commercial applications, such as the breakdown of starch granules during cooking especially exposed to high shear or low pH condition (Wurzburg, 1986). Chemically modified starches with enhanced the pasting and emulsion properties are widely adopted in food and industrial products. Octenylsuccinic anhydride (OSA) modified starch is one of the most important chemically modified starches which is achieved by octenylsuccinate (OS) group substitution (Bai, Kaufman, Wilson, & Shi, 2014; Sweedman, Tizzotti, Schafer, & Gilbert, 2013a). OS starch contains both hydrophilic and hydrophobic groups, and extensively used as emulsifiers in the food, pharmaceutical, personal care, and biodegradable plastic industries (Jane, Robert, Nidolov, & Roque, 1991; Trubiano, 1986). The physiochemical properties of OS starches such as paste viscosity can be designed by changing reaction condition and group distribution (Bhosale & Singhal, 2007; Ruan, Chen, Fu, Xu, & He, 2009; Song, He, Ruan, & Chen, 2006; Zhang et al., 2011). Huber and BeMiller (2009) proposed that the structure of substituted starches could be characterized at three levels: universal, granular and molecular. At the universal level, the overall extent of substitution, or DS, can be determined by titrimetric, nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FT-IR) or high performance liquid chromatographic (HPLC) methods reported elsewhere (Bai & Shi, 2011; Shih & Daigle, 2003; Shogren, 2003; Qiu, Bai, & Shi, 2012). At the granular level, substitution reactions occur primarily in amorphous regions, and do not change the crystalline pattern of starches at a low DS value (Bai & Shi, 2011; Shogren, Viswanathan, Felker, & Gross, 2000; Song et al., 2006). The distribution of OS groups is not uniform either among individual starch granules or within a single granule. OS groups were located mainly on the granule surface which was indicated by FT-IR (Bai, Shi, & Wetzel, 2009; Wetzel, Shi, & Reffner, 2010), confocal Raman spectroscopy (Wetzel, Shi, & Schmidt, 2010), X-ray photoelectron spectroscopy and CLSM (Huang et al., 2010; Shogren, 2003; Zhang et al., 2011). With the probes of CLSM and surface gelatinization, recently we found that the A-type polymorphic maize starch with pinholes and channels displayed much more homogeneous on OSA reaction pattern compared with B-type potato starch (Wang et al., 2013). At the molecular level, OS substitution was found to occur primarily at O2 and O3 (Bai, Shi, Herrera, & Prakash, 2011). Bai et al. (2014) reported that at a lower substitution value (DS 0.018), most OS groups are located near branching points of the amylopectin,

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Abbreviations: CLSM, confocal laser scanning microscopy; DB, degree of branching; DS, degree of substitution; *D* [3,2], volume-surface average diameter; FT-IR, Fourier transform infrared spectroscopy; NMR, nuclear magnetic resonance; HPLC, high performance liquid chromatography; H–OS–starch, homogenized OS starch; OS, octenylsuccinic; OSA, octenylsuccinic anhydride; RE, reaction efficiency.

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whereas products with a higher substitution value (DS 0.092) occur both near branching points and non-reducing ends.

Revealing the substituent distribution within starch granules is a powerful tool to understand the changes of functional properties after modification. For example, OS starch prepared with the aid of ultrasound showed higher pasting temperatures, lower peak viscosity, hot pasting viscosity and final viscosity, possibly due to a more even substituent distribution (Chen, Huang, Fu, & Luo, 2014). In addition, Chen et al. (2004) found that the amylose populations isolated from smaller size fractions of acetylated potato starch were less susceptible to enzymic digestion than was that isolated from large potato starch granules, even though the DS values were similar. The authors suggested that the acetyl groups were distributed more heterogeneously and located nearer to the non-reducing ends of amylose originating from smaller size granules than lager size granules.

The reaction rate of OSA with starch granules is often retarded, due to the poor penetration of the big oily OSA droplets into solid granules in an aqueous suspension. Dissolved or some fully dispersed OSA molecules could penetrate the entire A-type polymorphic starch granules via the channels (0.07−0.1 μm) to the central cavity, only allowing <100 nm droplets to be accessible (Zhang, Dhital, & Gidley, 2013). High-speed shear, which is widely used in food industry, provides a high shear, cavitation and collision force, making the material be blended, disintegrated, dispersed, homogenized and emulsified. In our previous study, we found that there is no significant change in melting temperature and crystalline structure of native and OS starch granules when shear rate was less than 1.0×10^4 rpm (Wang, He, Fu, Luo, & Huang, 2015). High-speed shear decreased the size of OSA droplets (Wang et al., 2013) and promoted more homogenous substitute group distribution in starch granule (Wang et al., 2015). However, reports about the effect of substituent distribution on the properties of OS starch are limited. The objective of this study was to understand whether the OS group distribution of starch granules can be regulated by high shear homogenization during the chemical synthesis, and also how the structure changes the pasting and emulsion properties.

2. Materials and methods

2.1. Materials

Waxy maize starch was purchased from Dacheng Company (Changchun, China). OSA, the product of Vertellus Specialties Inc., was obtained from Nanjing Golden Chemical Co., Ltd (Nanjing, China). β-Amylase (Type II-B, from barley) was obtained from Megazyme International Ltd. (Co. Wicklow, Ireland), and the activity was 10,000 Betamyl units/mL. Other chemicals were commercial products of analytical grade.

2.2. Preparation of OS starches

A series of OS waxy maize starch products with various DS values were prepared. Three groups DS were prepared. The OSA reaction was performed as previously described (Zhang et al., 2011). In detail, waxy maize starch was suspended in distilled water (35%, w/w) at 10,000 rpm with the high-speed homogenizer (FJ200-SH, Shanghai specimen and model factory, China), and a control sample was treated at 500 rpm using a mechanical stirrer. The pH of the suspension was adjusted to 8.0–9.0 by adding 3% NaOH solution (w/w) monitored by a pH meter, and the temperature was controlled at 35 °C. Various amounts of OSA (1–8%, dry starch basis) were added slowly within 1 h and the reaction was allowed to proceed for a total of 2 h. After reaction, the pH was adjusted to 6.5 with 3% (w/w) HCl solution. The mixture was washed two times with distilled water and two times with ethanol. The starch samples were oven-dried at 40 °C for 24 h, and then passed through a 100 mesh nylon sieve.

2.3. Structure analysis

2.3.1. Determination of the degree of substitution

The OS starch sample (5 g, dry weight) was accurately weighed and suspended by stirring for 30 min in 25 mL of HCl–isopropyl alcohol solution (2.5 M). 100 mL 90% (v/v) aqueous isopropyl alcohol solution was added, and the slurry was stirred an additional 10 min. The suspension was filtered through a glass filter (1.5–2.5 μm) and the residue was washed with 90% isopropyl alcohol solution until no Cl^- could be detected (using 0.1 M $AgNO_3$ solution). The starch was re-dispersed in 300 mL distilled water, and then the dispersion was heated in a boiling water-bath for 20 min with stirring. The starch solution was titrated with 0.1 M standard NaOH solution, using phenolphthalein as an indicator. A blank was simultaneously titrated with native starch as a control (Zhang et al., 2011). The DS was calculated by the following equation:

$$\mathrm{DS} = \frac{0.162 \times (A \times M)/W}{1 - [0.209 \times (A \times M)/W]}$$

where A is the titration volume of NaOH solution (mL); M is the molarity of NaOH solution; and W is the dry weight (g) of the OS starch. 162 is the molecular weight of anhydroglucose unit and 209 is the molecular weight of octenylsuccinic anhydride-1.

2.3.2. Confocal laser scanning microscopy

Confocal laser scanning microscopy was performed using an A TCS SP5 with an Argon ion laser (Leica, Wetzlar, Germany), following the method of Zhang et al. (2011).

2.3.3. Beta-amylase hydrolysis

Waxy maize starch or OS starch (0.5 g) was dispersed in 20 mL acetate buffer (0.01 M, pH 5.5), and the mixture was heated in a boiling water bath at 100 °C for 1 h. After cooling to 55 °C, β-amylase (1 wt% based on the weight of starch,) was added, and the digestion was incubated 24 h at 55 °C followed by heating in a boiling water bath for 30 min to denature the enzymes (Bai et al., 2014). The resulting solution was freeze-dried for high performance liquid chromatography analysis.

The method of removing maltose is described elsewhere (Sweedman, Hasjim, Tizzotti, Schäfer & Gilbert, 2013b). The freeze-dried starch was dissolved in 5 mL DMSO solution containing 0.5% (w/w) LiBr at 80 °C overnight, and then precipitated with 20 mL ethanol followed by centrifugation at 3000 × g for 10 min. The precipitate was further washed twice with ethanol to remove maltose. The precipitate was dried 12 h at 60 °C for ^{1}H NMR analysis.

2.3.4. Determination of molecular size distribution

The whole molecule size distribution of starch hydrolysates was obtained using an Agilent 1260 size-exclusion chromatography system (Agilent Technologies, US) equipped with a refractive index detector. The freeze-dried starch was mixed with 5 mL of hot water, heated in a boiling water bath for 30 min, filtered through a 2 μm filter (Millipore, Bedford, MA), then injected to a Shodex OHpak SB-806 MHQ column (Tosoh Co., Japan) with a Shodex OHpak SB-G guard column. The eluting solvent was distilled water, and the flow rate was 1 mL/min. The column oven temperature was controlled at 70 °C. The amount of liberated maltose was used to calculate its β-limit value as follows:

$$\beta\text{-limit value} = \frac{\text{Weight of maltose in the hydrolysate} \times 0.95}{\text{Weight of starch}} \times 100\%$$