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Chemical composition, digestibility and emulsification properties of octenyl succinic esters of various starches

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ABSTRACT

Octenyl succinate starches are commonly used as emulsifiers and texturizing agents in many food-systems. Rice, tapioca, corn, wheat and potato starches were modified with octenyl succinic anhydride (OSA) at 3% level. Structural characterization, molecular weight, starch digestibility and physical properties of starch granule stabilized emulsions were studied for modified starches. Modified potato (0.022) and wheat (0.018) starches had the highest and lowest degrees of OSA substitution, respectively. For all starches, amylose and amylopectin molecular mass was significantly ($P < 0.05$) lower for OSA starches. OSA modification may have hydrolyzed the small amylose and amylopectin chains, or caused rearrangement of the starch molecules. Although the starch modification improved emulsification properties, botanical source showed more influence on this parameter. Overall, botanical source had more influence on functional properties than degree of substitution. Further studies on OSA group distribution and fine molecular structure of amylopectin and relationship with functional properties will be important.

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1. Introduction

Starch in its native form often has limited use as an ingredient in food-systems. For this reason, starch may be modified to improve its functional properties, especially to enhance emulsification and nutritional properties. Such modification alters the physical and chemical characteristics of the native starch (Shih & Daigle, 2003). Chemical modification with octenyl succinic anhydride (OSA) is one type of starch modification used in the food industry (Ai, Nelson, Birt, & Jane, 2013). OSA esterification enhances emulsification properties of starch by incorporating hydrophobic alkenyl groups from OSA into the hydrophilic starch molecule. The incorporation of the hydrophobic groups results in surface active properties which are useful in stabilizing emulsions (Shogren, Viswanathan, Felker, & Gross, 2000; Song, He, Ruan, & Chen, 2006). OSA esterified starches have been widely used as emulsion stabilizers in molecular form (Nilsson & Bergenståhl, 2006), as surface active hydrocolloids and more recently in the form of intact granules producing Pickering type emulsions (Rayner et al., 2014; Timgren, Rayner, Dejmek, Marku, & Sjöö, 2013). Pickering emulsions are stabilized by solid particles in the size range of tens of nm to tens of μm. Adsorption of the oil water interface occurs at the surface of these particles due to their partial dual wettability for aqueous and non-aqueous phases. After adsorption of the oil water interface at the particle surface, the particles are essentially trapped at the oil water interface creating a thick interfacial barrier (Aveyard, Binks, & Clint, 2003; Dickinson, 2006).

Pickering emulsions in the context of food products have received increasing research interest due to the high degree of stability provided by the particle layer at the oil water interface, which prevents coalescence, even for large droplets. Other research has shown that Pickering emulsions may also act to reduce Ostwald ripening (Yusoff & Murray, 2011), improve barrier properties and freeze thaw stability (Marefati, Rayner, Timgren, Dejmek, & Sjöö, 2013; Matos, Timgren, Sjöö, Dejmek, & Rayner, 2013; Rayner et al., 2014), and in some cases decrease the rate of oxidation (Kargar, Fayazmanesh, Alavi, Spyropoulos, & Norton, 2012). The use of starch to create Pickering emulsions is very attractive as there is large natural variation with respect to granule size, shape and functional properties among various botanical sources (Jane, Kasemsuwan, Leas, Zobel, & Robyt, 1994). Furthermore, OSA esterified starch has been reported to have distinctive digestibility properties. The rate and extent of the starch digestion of OSA esterified starches are reduced when compared to native starches, resulting in high levels of slowly digestible starch and moderately resistant starch content (Ai et al., 2013; Han & BeMiller, 2007). The capacity of the OSA esterified starch to stabilize emulsions and its resistant starch content make it an ideal material for the encapsulation of bioactive compounds in targeted delivery systems (Li et al., 2012).

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The properties of OSA esterified starch depend on the level of OSA substitution (degree of substitution, DS) (Ai et al., 2013; Bai, Shi, Herrera, & Prakash, 2011) and the hydrophobic and hydrophilic character of the OSA groups (Bao, Xing, Phillips, & Corke, 2003). However, OSA esterified starch properties are greatly dependent on the botanical source of the starch. The amylose and amylopectin from starches of different botanical sources vary substantially in molecular weight and fine structure. The OSA starch properties will be affected by amylose/amylopectin ratio, crystallinity and molecular packing (Bertoft, 2013). OSA substitution has previously been determined to occur mostly in the amorphous region without affecting the crystallinity and, that OSA groups were found primarily in the periphery of the starch granule in maize and potato starches (Shogren et al., 2000; Wang et al., 2013). At the molecular level, it has been suggested that OSA substitution occurs close to the branching points of the amylopectin (Bai, Kaufman, Wilson, & Shi, 2014; Bai et al., 2011; Shogren et al., 2000). Therefore, because there are differences in fine structure of starches of different botanical sources, it will be of interest to study OSA esterified starches from several botanical sources which receive the same level of modification under the same modification conditions and the effect on the chemical and emulsification properties. In this study OSA starches were prepared using rice, corn, wheat, tapioca and potato starches, representing the top sources of starch around the world and their structure, digestibility and emulsification properties after OSA modification was studied.

2. Materials and methods

2.1. Material

Native wheat, corn, rice and potato starches were obtained from Sigma-Aldrich and tapioca starch was acquired as a gift from Ingredion. Octenyl succinic anhydride (OSA) was purchased from Dixie Chemical Company. Medium chain triglyceride oil (Miglyol 812) was purchased from Sasol AG, Germany.

2.2. Esterification with octenyl succinic anhydride

Starches (100 g, dry basis, db) were dispersed in water (225 mL) with stirring. The pH of the slurry (at ~25 °C) was adjusted to 8.5–9.0 with 1 M NaOH. Octenyl succinic anhydride (OSA, 3% of the weight of the starch) was added during continuous stirring at room temperature (~25 °C), while maintaining the pH at 8.5. A burette was used to add the OSA in a slow steady stream of approximately 0.1 ml/min. After 6 h, the starch slurry was neutralized to pH 7.0 with 1 M HCl. The modified starch was centrifuged (2500 rpm, 15 min). The residue was washed three times with water and once with acetone, and air-dried (40 °C, 24 h) (Han & BeMiller, 2007).

2.3. ^{1}H nuclear magnetic resonance spectroscopy

Before conducting the nuclear magnetic resonance (NMR) spectroscopy experiments, the starch samples were purged with deuterium oxide (D_2O) three times, lyophilizing between each purge. The samples were dissolved in D_2O (0.6 ml, 85 °C, 2 h) and placed in NMR tubes (8 in., 5 mm, thin wall). ^{1}H spectra were taken using a Bruker 400 MHz NMR (Billerica, USA). The analysis was conducted at 25 °C for 64 scans with a delay time of 1 s. The degree of substitution (DS) was calculated according to the method reported by Shih and Daigle (2003). The internal standard was considered to be the equatorial proton of the anhydroglucose unit (AGU) of starch (5.2–5.4 ppm). The extent of OSA substitution was determined by integration of the methyl protons of the OSA (0.8–0.9 ppm). Thus, the $DS = A_{0.8–0.9} / (3 \times A_{5.10–5.26})$, where A is the integral value of the peak assigned.

2.4. Fourier transform-infrared spectroscopy (FT-IR)

During the esterification, hydroxyl groups of starch molecules were substituted by carbonyl groups of OSA which can be confirmed by FTIR (Wang et al., 2013). A Fourier transform infrared spectrometer (FTIR, Nicolet 8700 Thermo Scientific) was used to obtain the IR spectrum of native and OSA starches. Approximately 1.5 mg of sample was ground with potassium bromide (KBr) and pressed to form a pellet disc. The disc was placed in the sample compartment before the spectra was obtained. The samples were scanned over the wavelength range from 400 to 4000 cm cm^{-1}.

2.5. Molecular weight of amylose and amylopectin

For the determination of starch molecular mass and apparent amylose content, the starch was prepared according to the method of Grant, Ostenson, and Rayas-Duarte (2002). The starch was dissolved in a 1:10 (v/v) solution of 6 M urea and 1 M KOH and heated for 90 min at 100 °C. The samples were then neutralized using 1 M HCl and filtered through 0.45 μm nylon syringe filters before analysis by high performance size exclusion chromatography (Simsek, Whitney, & Ohm, 2013) (HPSEC, Agilent Technologies, USA) with multi-angle light scattering (MALS, Wyatt Technology, USA). The dn/dc value for calculation of the starch molecular mass was 0.146 (You & Lim, 2000). The Debye model with a fit degree of one was used for calculation of the molar mass. The results were fitted to a first order polynomial model.

2.6. Starch digestibility

In vitro starch digestibility of native and OSA starches was analyzed using the method described by Englyst, Kingman, and Cummings (1992). The samples (0.3 g) with 0.1 M sodium acetate buffer (20 mL, pH 5.2) were gelatinized in boiling water for 30 min and put in a water bath (37 °C) with agitation (100 strokes/min). Guar gum (50 mg) and 5 glass beads were added to each tube. One blank and glucose standard tubes were prepared. Five milliliters of enzyme solution was added to each tube at 1 min intervals. The enzyme solution was prepared as follows: amyloglucosidase solution (70 U/mg, 24 mg in 12 mL of deionized water), invertase solution (≥300 U/mg, 60 mg in 8 mL of deionized water), pancreatin solution (3 g in 20 mL of deionized water, stirred for 10 min at 4 °C and centrifuged). The pancreatin solution (108 ml) was mixed with the invertase and amyloglucosidase solutions, and was freshly prepared for the digestion analysis. Aliquots (0.5 mL) of the samples were taken at 20 min intervals over a total of 180 min and were mixed with 5 mL of absolute ethanol and centrifuged. The glucose released was measured at 510 nm in parallel with a standard curve of glucose using the glucose oxidase assay (Megazyme International Ireland). The rapidly digestible starch (RDS), slowly digestible starch (SDS) and resistant starch (RS) were determined as expressed in percentage (%). RDS is considered the portion of the starch hydrolyzed from 0 to 20 min, SDS is the starch hydrolyzed between 20 and 120 min and the RS is the starch remaining after 120 min of digestion (Englyst et al., 1992). The hydrolysis index (HI) was obtained by dividing the area under the hydrolysis curve of the sample by the area obtained for white bread (hydrolysis curve 0 min to 180 min). The estimated glycemic index (eGI) of the samples was calculated using the equation described by Granfeldt, Bjorck, Drews, and Tovar (1992):

$$eGI = 8.198 + 0.862 * HI.$$

2.7. Emulsion preparation

Emulsions were prepared in glass tubes using starch granules as stabilizers. Medium chain triglyceride oil as dispersed phase and