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Structure and physicochemical properties of octenyl succinic esters of sugary maize soluble starch and waxy maize starch

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ABSTRACT

The structure and physicochemical properties of octenyl succinic anhydride (OSA) starches prepared from sugary maize (SMSS) and waxy maize (WMS) were studied and compared. The degree of substitution (DS) increased linearly with the amount of OSA, while the DS of OSA-SMSS was higher than that of OSA-WMS using equivalent modification conditions. FT-IR analysis indicated that two characteristic peaks, at 1725 and 1570 cm^{-1}, were observed for OSA-starch. The weight-average of the molar mass (M_w) and z-root mean square radius of gyration (R_z) of SMSS increased with increased OSA esterification substitutions, whereas M_w was reduced and R_z was nearly constant for WMS. The zeta-potential and emulsifying activity increased with DS for starch modified with OSA. OSA-SMSS (DS of 0.0192) was the best material for stable oil-in-water emulsion preparation. The increase of DS in OSA-starch resulted in a substantial reduction of RDS content with an accompanying increase of SDS and RS. This study revealed the potential application of OSA-SMSS as a particle stabilizer of oil-in-water emulsion, which would allow encapsulate and protect functional food components.

1. Introduction

Diabetes, obesity and cardiovascular diseases have become major public health concerns worldwide, and the number of cases has increased exponentially in recent years (Aston, 2006; Manuel-y-Keenoy & Perez-Gallardo, 2012). The multi-factorial etiology of this worldwide epidemic and the idea that diet may be contributing is now well recognised (WHO/FAO, 2002). New developments in food and nutritional science indicate that controlled release bioactive food ingredients in the gastrointestinal tract can increase the effectiveness and potential physiological benefits (McClements, Decker, Park, & Weiss, 2009; Wang et al., 2011). With a properly designed food-grade controlled-release delivery system, the functional component is released at the desired site and time at the desired rate. However, the work is still relatively challenging due to the difficulty in attaining accurate control-release of bioactive food factors in the human digestive system.

Starch is the most abundant polysaccharide reserve in cereals, roots and tubers and provides the metabolic energy required for the sustenance of life. It is composed of a mixture of two distinct macromolecules with an α-D-glucopyranosyl unit: amylose, a linear fraction linked by α-(1→4) bonds with a small number of long-chain branches, and amylopectin, a highly branched fraction linked by α-(1→4) and α-(1→6) linkages (Calvert, 1997). Starch is currently used for a variety of purposes, including thickening, gelling, increasing process stability and replacing or extending costly ingredients. Native starches are inherently unsuitable for most industrial applications and often tailored by chemical or physical modification to develop desirable functional properties, such as solubility, pasting properties, dispersion or digestibility (BeMiller & Whistler, 2009; Miao, Jiang, Zhang, Jin, & Mu, 2011; Sweedman, Tizzotti, Schäfer, & Gilbert, 2013; Tharanathan, 2005; Wolf et al., 2001). The modified starch derivatives are obtained through glucosidic bond cleavage, the formation of new functional groups, the substitution of free available hydroxyl groups, or the bridging of molecular chains by a cross-linking reagent (Tharanathan, 2005). The chemical modification of starch with octenyl succinic anhydride (OSA), achieved through a standard esterification reaction, was first patented by Cadwell and Wurzburg (1953). OSA-starch as an amphiphilic derivative is an effective stabilizer in water in oil emulsions as well as some oil-in-water systems due to hydrophobic and steric contribution (Sweedman et al., 2013; Wang et al., 2011). It has been used in a range of industrial areas, particularly in food production due to its good filming properties and excellent emulsion-stabilizing properties. Since 1972, the United States Food and Drug Administration (FDA) has approved the use of modified starch with 3.0% OSA (degree of substitution is approximately 0.02) in foods. Therefore, OSA-starch is expected to be a potential controlled release carrier material in

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beverage delivery systems; however, earlier research on OSA-starch was performed with corn, wheat, rice, and potato starches, and little work has been reported on the structure and properties of the OSA modification of sugary maize soluble starch. The objective of this study was to investigate the reaction of OSA with starch from different maize varieties, to study the structure and physicochemical properties, and to determine whether there is any advantage to starting with soluble starch and waxy starch.

2. Materials and methods

2.1. Materials

Fresh sugary-1 maize kernels were purchased from the Chinese Academy of Agricultural Sciences (Beijing, China). The waxy maize starch (WMS) was a gift from Changchun Dacheng Industrial Group Co. Ltd. (Jilin, China). 2-Octen-1-ylsuccinic anhydride (Cat. No. 416487, 97%) and α-amylase from porcine pancreas (Cat. No. A3176, Type VI-B, ⩾10 units/mg solid) were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO, USA). Amyloglucosidase (EC 3.2.1.3., 3300 U/ml) and glucose oxidase–peroxidase assay kits (Cat. No. K-GLUC) were purchased from Megazyme International Ireland Ltd. (Wicklow, Ireland). All chemicals were reagent grade and were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

2.2. Isolation of sugary maize soluble starch

The sugary maize soluble starch (SMSS) was isolated from sugary maize in the laboratory following the methods of as described in a previous study (Miao et al., 2014). The sugary-1 maize fresh kernels were dehulled, endosperm was separated from germ and soaked in 5 times their weight of deionised water at 20 °C overnight. The softened grains were ground in a laboratory blender. The mixture was filtered through 100-mesh sieves and then centrifuged at 10,000*g* for 10 min. The supernatant was collected, and the sediment was extracted twice with deionised water. The resulting decantate was heated in a boiling water bath for 30 min to denature the protein. After centrifugation, one volume of liquid was measured and three volumes of ethanol were added to precipitate the soluble starch. The precipitate was then collected and placed in a fume hood to remove the residual ethanol. The dried solid was ground to form a powder, which was then used for further studies within the next few months.

2.3. Octenyl succinic anhydride modification

The isolated SMSS and commercial WMS were chemically modified with OSA to various DS using the method of He, Liu, and Zhang (2008) with some modifications. The starch (10 g, dry weight) was suspended in distilled water (30%, w/w) with agitation. 2-Octen-1-ylsuccinic anhydride (OSA) was diluted 5 times with isopropanol, and added in 2 h at levels of 0.5–3% while the pH was maintained at 8.5 using 0.3% NaOH solution. After the esterification reaction at 35 °C for 8 h, the pH was adjusted to 6.5 using 2.5 M HCl. The reaction mixture was centrifuged (3000*g*) and washed 3 times with distilled water and 3 times with 70% ethanol. The collected material was oven-dried at 40 °C for 24 h and then ground to form a powder (100 mesh) for further analysis.

2.4. Determination of the degree of substitution

The degree of substitution (DS) was measured using the titration method as suggested by Kweon, Choi, Kim, and Lim (2001) with some modifications. The OSA-modified starch sample (0.5 g) was acidified by stirring for 30 min in 3 ml of HCl solution (2.5 M). Ten milliliters of 90% aqueous isopropanol (v/v) was added and stirred for an additional 10 min. The suspension was filtered and the residue was washed with 90% aqueous isopropanol until no chloride ions were present, as determined by the addition 0.1 M $AgNO_3$; no chloride was present when a white haze of AgCl was no longer observed upon addition. The residue was re-dispersed in distilled water (30 ml) and heated in a boiling water bath for 30 min. The mixture was titrated with a 0.1 M NaOH solution using phenolphthalein as the end-point indicator. The DS was calculated using the following formula:

$$\mathrm{DS} = \frac{0.162 \times (A \times M)/W}{1 - [0.210 \times (A \times M)/W]}$$

where A was the titration volume of NaOH solution, M was the molarity of NaOH solution, and W was the dry weight of sample.

The reaction efficiency (RE) was calculated as follows:

$$\mathrm{RE} = \frac{\text{Actual DS}}{\text{Theoretical DS}} \times 100\%.$$

The theoretical DS was calculated by assuming that all the added OSA reacted with starch to form the ester derivative. Each sample was analysed in triplicate.

2.5. Fourier transform infrared spectroscopy (FT-IR)

The FT-IR spectrum was recorded on a Nicolet Nexus 470 FT-IR spectrometer (Thermo Electron Corporation, Waltham, MA, USA) at room temperature following the method of Zhang et al. (2011). The sample powder was blended with KBr powder at a 1:100 ratio and pressed into tablets before measurement. A region from 400 to 4000 cm^{-1} was used for scanning at 4 cm^{-1} resolution with 32 scans.

2.6. Molecular weight distribution profiles

The weight-average molar mass (M_w) and z-root mean square radius of gyration (R_z) were determined using the methods of Gidley et al. (2010) and Miao et al. (2014) with a slight modification. The OSA-starch samples (10 mg) were added to 5 ml of deionised water and boiled for 15 min to completely dissolve the samples using DMSO with 50 mM LiBr at a concentration of 2% (w/v). The dissolved samples were filtered through 5 μm cellulose acetate filters (Whatman, Maidstone, UK) and injected into a high performance size exclusion column chromatography system with multi-angle laser light scattering detector and a refractive index detector (HPSEC-MALLS-RI) (Wyatt Technology, Santa Barbara, CA, USA). Two series tandem columns (300 × 8 mm, Shodex OH-pak SB-806 and 804, Showa Denko K.K., Japan) with a OH-pak SB-G guard column, a DAWN HELEOS II laser photometer fitted with a He–Ne laser (λ = 632.8 nm) with a K-5 flow cell and a OPTILAB® T-rEX Interferometric Refractometer were used. The flow rate was set at 0.5 ml/min with a mobile phase of distilled–deionised water (pH 6.8, 18.2 MΩ cm) containing 0.02% NaN_3. A dn/dc value of 0.138 was used in the molecular weight calculation, and data processing was performed using ASTRA software (Version 5.3.4.14, Wyatt Technology). M_w (g/mol) and R_z (nm) were obtained using the second-order Berry method. The molecular density (ρ, g/mol nm^3) was calculated as M_w/R_z^3.

2.7. Zeta-potential and particle size

Zeta-potential and particle size analysis was conducted using a Zetasizer Nano ZS (Malvern Instruments Ltd., Malvern, UK) at room temperature. The sample powder (0.01%, w/v) was suspended in