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Granular size of potato starch affects structural properties, octenylsuccinic anhydride modification and flowability

Chan Wang, Chuan-He Tang, Xiong Fu, Qiang Huang *, Bin Zhang *

School of Food Science and Engineering, South China University of Technology, Guangzhou 510640, PR China

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ABSTRACT

Native potato starch (PS) granules were separated into three size fractions: larger than 30 μm (P-L), 15–30 μm (P-M), and smaller than 15 μm (P-S). The morphological and crystalline structure of fractionated potato starches were investigated by light and scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC). The P-L fraction showed ellipsoidal shape and B-type X-ray pattern, whereas the P-S fraction had spherical shape and A-type pattern. The fluorophore-assisted capillary electrophoresis data showed that the P-L fraction had more B_2 chains and less short A and B_1 chains than the P-S counterparts. Smaller granules with larger specific surface area had higher degree of substitution when reacted with octenylsuccinic anhydride (OSA), and showed more uniform distribution of octenylsuccinate substituents. Both OSA modified and unmodified P-S samples showed higher flowability compared with the P-L counterparts.

1. Introduction

Starch is a major kind of carbohydrate reserve in higher plant tissues. Starches from different organs including leaves, seeds, fruits, stems and roots vary widely with respect to the molecular structure, morphological and physicochemical properties (Li, 2006). At different growth stages, the termination of starch granule synthesis could cause various particle structure and properties. Granule size of starch could reflects biosynthetic age, small-size granules were considered as the immature granules that are unable to develop into fully full-size granules, whereas the large granules were completely developed granules (Pan & Jane, 2000).

The size of starch granules affects the physicochemical properties such as pasting profiles, as well as the distribution of modified groups of starch granules. It was reported that large-size potato starch fractions showed slightly higher amylose content, lower swelling power compared to the small-size granules (Singh & Kaur, 2004). Small size granule fractions of either potato or sweet potato starch showed higher degree of substitution (DS) with more heterogeneous acetyl group distribution (Chen, Schols, & Voragen, 2004). Further, Dhital, Shrestha, Hasjim, and Gidley (2011) studied the chemical composition, molecular structure and physicochemical properties of size fractionated maize and potato starch granules. Results suggested that both large size granules have a lower lipid, protein, and mineral contents than that of small size maize and potato starch granules, but a higher apparent amylose contents. In addition, it was reported that granule size could affected the DS of cross-linked and hydroxypropylated sweet potato starches and their physicochemical properties. Both large-size

Abbreviations: CL, chain length; CLSM, confocal laser scanning microscopy; $d_{3,2}$, volume-surface average diameter; DS, degree of substitution; DP, degree of polymerization; DSC, differential scanning calorimetry; ΔH, enthalpy change; LSD, least significant difference; PS, potato starch; OSA, octenylsuccinic anhydride; OS-PS, OSA modified potato starch; OS-P-L, OSA modified large size fraction of potato starch; OS-P-M, OSA modified medium size fraction of potato starch; OS-P-S, OSA modified small size fraction of potato starch; OS-starch-Al, starch aluminium octenylsuccinate; P-L, large size fraction of potato starch; P-M, medium size fraction of potato starch; P-S, small size fraction of potato starch; XRD, X-ray diffraction; SEM, scanning electron microscopy; T_c, conclusion temperature; T_o, onset temperature; T_p, peak temperature.

* Corresponding authors.
E-mail addresses: fechoh@scut.edu.cn (Q. Huang), zhangb@scut.edu.cn, zhangb24@gmail.com (B. Zhang).

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native and modified starch fractions showed a lower transition temperatures, enthalpy changes and syneresis than that of small-size starch granules, but a higher paste viscosity (Zhao et al., 2015).

The flowability of powders depends on a series of physical characteristics and environmental conditions, including pre-consolidation, particle size and morphology, distribution of surface asperity, surface humidity, chemical and mineral composition, as well as temperature (Tomas & Kleinschmidt, 2009). It was reported that starch improved flowability of the spruce sawdust, and reduced the impact of friction forces on the contact stainless material (Jezerska, Zajonc, Rozbroj, Vyletělek, & Zegzulka, 2014). However, native starches have many disadvantages for applications, such as hydrophilicity, poor mechanical properties, and poor process capability. The addition of hydrophobic reagents on the surface of the starch granules through physical or chemical modification improves the flowability of starch granules (Cai, Li, Shen, Ma, & Xing, 2009). In our previous study, aluminium starch octenylsuccinate (OS-starch-Al) was prepared to promote flowability and hydrophobicity (Chang, He, Fu, Huang, & Qiu, 2014).

Potato starch granules isolated from potato tubers show a unimodal and wide particle size distribution (Dhital et al., 2011). Little work has been reported on the structural differences, OS group distribution and flowability of various size fractions before and after OSA modification. In this study, we fractionated the potato starch by granular size, and investigated the molecular, crystalline and morphological structures of all size fractions. In addition, we also investigated granule size effects on OS group distribution and flowability of the OS potato starches.

2. Materials and methods

2.1. Materials

Potato starch was obtained from Dacheng Company (Changchun, China). Apparent amylose content was determined using the iodine colorimetric method reported elsewhere (Hoover & Ratnayake, 2001). OSA was purchased from Nanjing Golden Chemical Co., Ltd (Nanjing, China). Other chemicals used in the study were commercial products of analytical grade.

2.2. Fractionation of potato starch granules and particle size measurement

Potato starch was separated into three size fractions through two test sieves (15 μm and 30 μm opening, respectively): larger than 30 μm (P-L, 80.5%, w/w), 15–30 μm (P-M, 11.3%, w/w) and smaller than 15 μm (P-S, 8.2%, w/w), respectively. Particle size was measured by Mastersizer 2000 (Malvern Instruments Ltd., UK) using the method reported elsewhere (Wang, He, Huang, Fu, & Liu, 2013).

2.3. Light and scanning electron microscopy (SEM)

Light microscopy was performed using an Olympus BX-51 light microscope (Tokyo, Japan) under normal and polarized light, and the images were recorded at 500× magnification. Images of starches were performed under an EVO18 scanning electron microscope (Carl Zeiss, Germany) as previously described (Wang et al., 2013).

2.4. Differential scanning calorimetry

A Diamond-1 differential scanning calorimeter (Perkin-Elmer, Norwalk, CT, USA) with an intra cooler was used to examine the thermal properties of starch samples. Starch samples (10–20 mg) were mixed with de-ionized water (moisture level 70%) and hermetically sealed in high-pressure stainless steel pans (PE No. BO182901) with a gold-plated copper seal (PE No. 042-191758). After equilibrating for 24 h at room temperature, samples were scanned at a heating rate of 5 °C/min from 30 to 150 °C. The enthalpy change (ΔH), onset (T_o), peak (T_p), and conclusion (T_c) temperature of starch gelatinization were calculated by using a Pyris software (Perkin-Elmer, Norwalk, CT, USA) (Zhang et al., 2011).

2.5. X-ray diffraction (XRD)

The crystalline structure and relative crystallinity of starches were identified and quantified by a D/Max-200 X-ray diffractometer (Rigaku Denki Co. Ltd., Tokyo, Japan), following a published method (Wang, He, Fu, Luo, & Huang, 2015).

2.6. Amylopectin branch chain-length distribution

All starch samples were extracted and dissolved in DMSO solution with 0.5% (w/w) LiBr (DMSO/LiBr) in a shaking thermomixer running at 80 °C and 350 rpm for 20 h, following a method described elsewhere (Wu, Li, & Gilbert, 2014). The suspension was occasionally inverted by hand to ensure no clumps of the precipitate adhere to the tube wall in the first 2 h. The solubilized starch was precipitated by washing with 10 mL absolute ethanol and centrifuged at 4000*g* for 10 min to remove non-starch components (proteins, lipids, and non-starch polysaccharides). This was repeated to further remove residual non-starch components and solvent.

The extracted starch (~4 mg, dry basis, db) was dispersed using 0.9 mL of warm deionized water and incubated in boiling water for 30 min. The sample was cooled to room temperature, added 0.1 mL of 0.1 M acetate buffer (pH 3.5), 5 mL of 4% sodium azide solution (w/v), and 2.5 mL of isoamylase (Megazyme EISAMY), finally mixed and incubated at 37 °C for 3 h using a Thermomixer with continuous shaking (350 rpm). The starch suspension was then heated in a water bath (80 °C) for 2 h after being neutralized with 0.1 M NaOH solution, and then freeze-dried overnight. The freeze-dried sample was labeled using 8-aminopyrene-1,3,6,trisulfonic acid (APTS) following a previously reported method (Wu et al., 2014). And then the APTS labeled debranched starch molecules were separated using an N-CHO coated capillary (50 μm diameter, 40 cm in length) in a PA-800 Plus System (Beckman-Coulter, Brea, CA, SA), coupled with a solid-state laser-induced fluorescence (LIF) detector using an argon-ion laser as the excitation source. Pressure injection (3 s at 0.5 psi) was performed to inject samples into the capillary. A carbohydrate separation buffer (Beckman Coulter) was used as the separating medium, and the separation was carried out at 25 °C using a voltage of 30 kV.

2.7. Preparation of OS starches

2.7.1. Modified starch prior to size fractionation

Potato starch (100.0 g, db) was suspended in distilled water (35%, w/w) with agitation. A weighed quantity of OSA (3% of the dry starch basis) was added dropwise from a burette slowly within 1 h while maintaining the pH at 8.5 by NaOH solution (3%, w/w) with a pH meter. After the esterification reaction for 2 h at 35 °C, the pH was adjusted to 6.5 with the diluted HCl solution. The mixture was filtrated and washed twice with distilled water and ethanol (90%, v/v). The OS starches were dried in an oven at 45 °C for 24 h, and then passed through a 100 mesh nylon sieve (Zhang et al., 2011). The OSA modified potato starch was separated into three size fractions for degree of substitution measurement.