



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



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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 B₂ chains and less short A and B₁ 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.

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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 reflect 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 affect 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.

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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 (Jeżerska, 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 $\times$ 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 $^{\circ}\text{C}/\text{min}$ from 30 to 150 $^{\circ}\text{C}$. 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 $^{\circ}\text{C}$ 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 4000g 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 $^{\circ}\text{C}$ for 3 h using a Thermomixer with continuous shaking (350 rpm). The starch suspension was then heated in a water bath (80 $^{\circ}\text{C}$) 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 $^{\circ}\text{C}$ 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 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ 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.

2.7.2. Starch size fractionation prior to OSA modification

Native potato starch was separated into three size fractions, and then modified with different OSA dosages (3%–3.5% of the dry starch basis) using the method described above. Similar DS was achieved in order to compare flowability of starches.

2.7.3. Degree of substitution

The degree of substitution (DS) was measured using the titration method as suggested by Zhang et al. (2011). The DS was calculated using the following equation:

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

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.

2.8. Confocal laser scanning microscopy (CLSM)

The OS starches (5 mg, db) were suspended in 30 mL water. Added the 1% methylene blue (MB⁺) solution into each sample when the pH was 8.0. The mixture was incubated in a shaker for 3 h at room temperature, recovered by centrifugation and then washed with methanol to remove the residual dye. The confocal microscopy was detected by a TCS SP5 CLSM (Leica, Wetzlar, Germany) with an Argon ion laser (Leica, Wetzlar, Germany). The Leica objective lens were 40×/1.25 oil, and excitation wavelength was set as 514 nm (Zhang et al., 2011).

2.9. Preparation of OS-starch-Al

OS starch was suspended in distilled water (35%, w/w) with agitation in a 35 °C water bath, then maintained pH 4 by adding HCl solution (3%, v/v). 3% Al₂(SO₄)₃ (w/v) was added to OS starch suspension as reported by Chang et al. (2014).

2.10. Determination of the repose angle

The sample was oven-dried at 105 °C for 3 h and then measured the repose angle. The repose angle was calculated by a sample geometry from the base and height of the conical heap formed using the following equation (El-Say, Tamer, Samy, & Badawy, 2010).

$$\alpha = \arctan\left(\frac{2h}{d}\right)$$

where *d* is the diameter of base, and *h* is the height of the formed conical heap.

2.11. Statistical analysis

Each experiment was performed in duplicate. Analysis of least significant difference (LSD) was performed with SPSS 13.0 for

Windows (SPSS, Inc., Chicago, IL, USA). The level of significance was set at *p* < 0.05.

3. Results and discussion

3.1. Morphological, structural and physicochemical properties

Potato starch consists of mixed populations of large, medium and small granules with a wide size distribution (1–100 μm) (Table 1, Fig. 1), in agreement with a previous report (Bechtel, Kaleikau, & Pomeranz, 1990). The scanning electron micrographs of three different size fractions are shown in Fig. 1. The granules of large-size fraction displayed a ellipsoidal shape with *d*_{3,2} of 42.37 μm (Table 1, Fig. 1P-L). The isolated medium granules displayed a spherical shape with *d*_{3,2} of about 21.38 μm (Table 1, Fig. 1P-M), and the small granules were spherical or irregular shape with *d*_{3,2} of 11.46 μm (Table 1, Fig. 1P-S). The various granule morphology may be due to the biological origin, the biochemistry of the chloroplast or amyloplast, as well as physiology of the plant (Baum & Bailey, 1987; Zhou, Robards, Glennie-Holmes, & Helliwell, 1998). Polarized light microscopic images of starch granules are shown in Fig. 1. All samples shown a characteristic birefringence pattern, indicating that the semicrystalline structure is aligned in a radial order centered at the hilum (growth center) and perpendicular to the granule surface.

X-ray diffractogram of starches is shown in Fig. 2. The unfractionated PS and P-L fraction exhibited the B-type diffraction pattern with major peaks at 5.6°, 17°, 22° and 24° 2θ, whereas the P-S fraction displayed the A-type pattern with major peaks at 15°, 17°, 18° and 23° 2θ. The P-M fraction displayed both C-type pattern characteristics, including the 23° peak and a flat shoulder at 18° 2θ (A-type feature) and the 5° peak (B-type feature). Furthermore, the P-M and P-S fractions possessed higher crystallinity (41.52%, 43.19%, respectively) compared to the P-L counterpart (35.36%). These results are consistent with a previous report, where the small size granules showed higher crystallinity (Ao & Jane, 2007).

Apparent amylose content of three different size fractions of potato starch ranged between 17.03% and 26.09% (Table 1). The large size fraction consisted of more amylose (26.09%) compared to the medium and small size fractions (18.92% and 17.03%, respectively). In general, the apparent amylose content is proportional to the granule size and maturity of starch (Jane & Shen, 1993; Pan & Jane, 2000). This is mainly attributed to the activity of granule-bound starch synthase (GBSS-I), which is responsible for amylose biosynthesis, and it is higher at the later stage of starch synthesis (Utrilla-Coello, Agama-Acevedo, Barba de la Rosa, Rodríguez-Ambríz, & Bello-Pérez, 2010).

Branch chain-length distributions of amylopectin of three size fractions and unfractionated PS are shown in Table 2. With the granular size decreasing, the average branch chain-length (CL) became shorter (P-L, 26.15; P-M, 25.18; P-S, 24.63). Branch chain-length distribution of the P-S fraction showed more short

Table 1

Particle size, amylose content and gelatinization characteristics of potato starches.

Sample	<i>d</i> _{3,2} (μm)	Amylose content (%)	Gelatinization characteristics			
			<i>T</i> ₀ (°C)	<i>T</i> _p (°C)	<i>T</i> _c (°C)	Δ <i>H</i> (J/g)
PS	37.62 ± 0.09 ^a	24.48 ± 0.51 ^a	63.45 ± 0.08 ^a	75.40 ± 0.14 ^a	79.73 ± 0.11 ^a	17.75 ± 0.34 ^{ac}
P-L	42.37 ± 0.62 ^b	26.09 ± 0.59 ^b	65.16 ± 0.03 ^b	76.31 ± 0.01 ^b	81.92 ± 0.14 ^b	15.79 ± 0.16 ^b
P-M	21.38 ± 0.28 ^c	18.92 ± 0.38 ^c	62.50 ± 0.01 ^{ac}	77.38 ± 0.28 ^c	77.04 ± 0.06 ^a	17.81 ± 0.90 ^{ac}
P-S	11.46 ± 0.12 ^d	17.03 ± 0.68 ^d	61.53 ± 0.02 ^c	77.45 ± 0.06 ^c	76.98 ± 0.04 ^a	19.62 ± 0.39 ^c

PS: potato starch; P-L: large size fraction of potato starch; P-M: medium size fraction of potato starch; P-S: small size fraction of potato starch. Values are means of duplicate determinations with standard deviation. Means in a column with different superscript letters are significantly different (*p* < 0.05) by least significant difference (LSD) test.

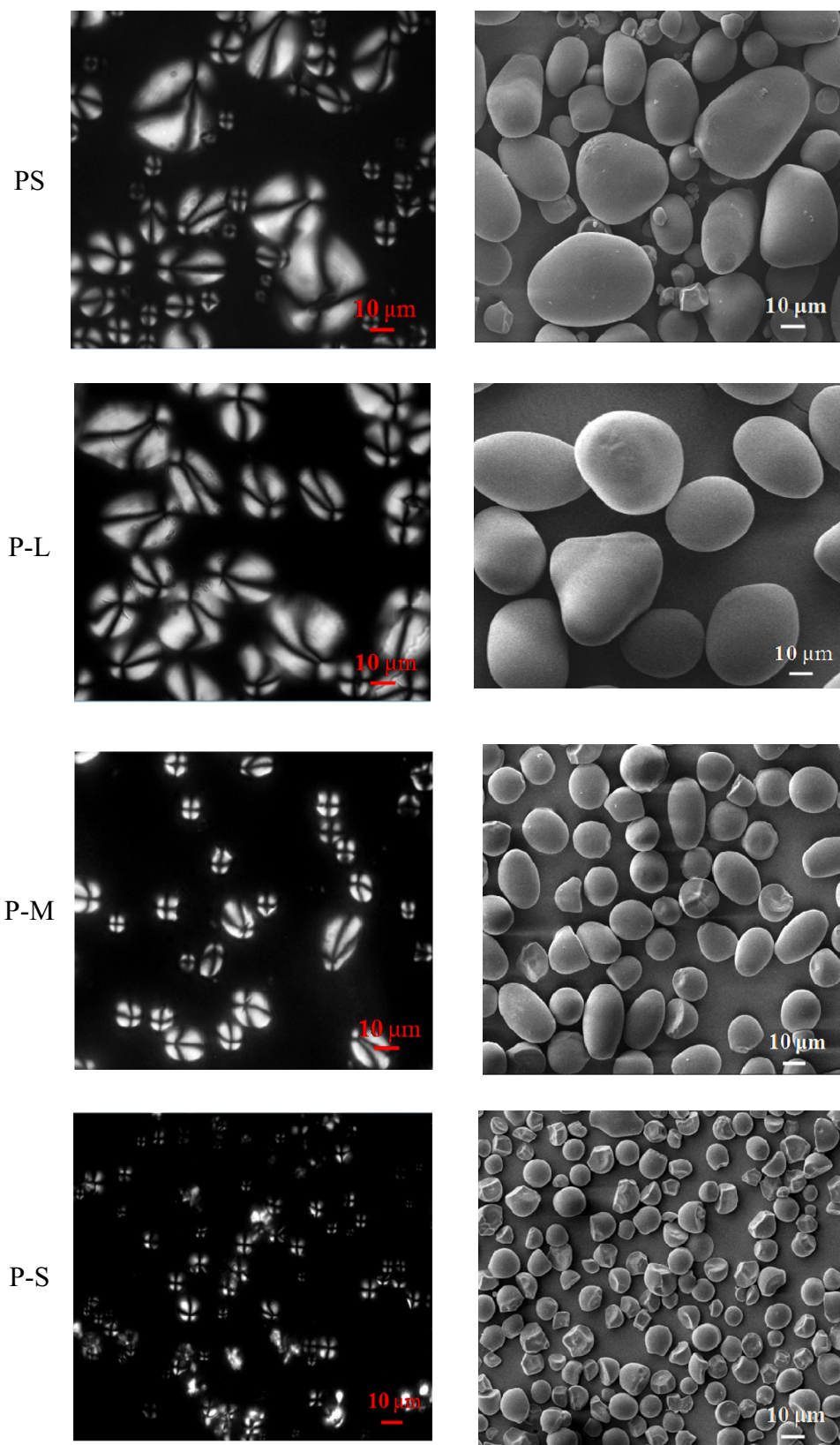


Fig. 1. Polarized light and scanning electron micrographs of size fractionated potato starches.

A and B1 chains (DP 6–12, 27.29%, and DP 14–24, 41.22%), and less long B2 chains (DP > 37) compared to the P-L fraction (DP 6–12, 22.59%; DP 14–24, 40.57%). [Peng, Gao, Båga, Hucl, and Chibbar \(2000\)](#) suggested that amylopectin molecules of the large and

small size fractions have distinct fine structure genetically controlled by starch biosynthesis enzymes during grain development.

The onset gelatinization temperature and enthalpy change of potato starches varied between 61.53 and 65.16 °C, and between

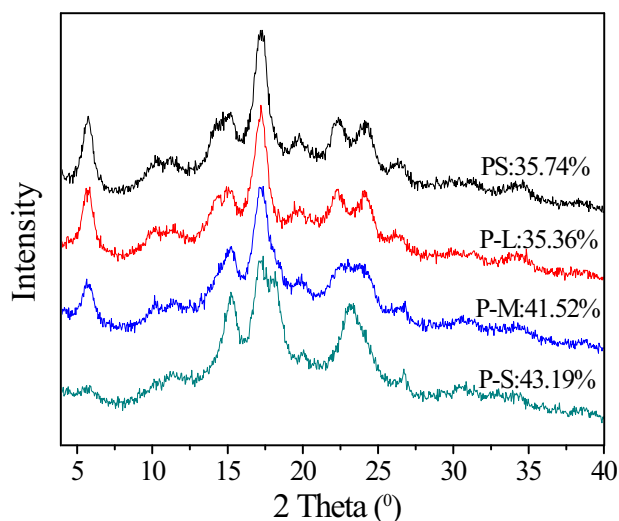


Fig. 2. X-ray diffraction of size-fractionated potato starches.

15.79 and 19.62 J/g, respectively (Table 1). Large size fraction started to gelatinize at a slightly higher temperature (65.16 °C) compared to medium (62.50 °C) and small-size fractions (61.53 °C), but with a lower enthalpy change, consistent with a previous study (Singh & Kaur, 2004). Small size fraction contains more phospholipids in comparison to the large one (Singh & Kaur, 2004), resulting in a lower gelatinization temperature (Table 2). Meanwhile, the thermal properties of starches are influenced by the branch chain length distribution of amylopectin and crystalline structure of starch granule (Noda, Takahata, Sato, Ikoma, & Mochida, 1996). Large size fraction has a significantly lower DP 6–13 chains and a higher proportion of DP > 37 chains, resulting to higher melting temperatures. The packing of helices of B-type crystal is less compact than in A-type. Furthermore, there are 36 water molecules per B-type unit cell, whereas only 4 water molecules are present in A-type unit cell. When gelatinized, the double helix forming of B-type starch would be more mobile and less energy is needed. The lower enthalpy value for the gelatinization suggested that large-granule starch have less double helix level than small-granule starch (Table 1).

Potato starch granules display ellipsoidal and spherical shapes with amylose and amylopectin molecules arranged differently in granules. The amylopectin molecules of large granules consisted more long B2 chains and less short A and B1 chains, which can be easier to align in a parallel arrangement into ellipsoidal shape. However, the amylopectin of small granules with more short A and B1 chains and less long B2 chains had a cone molecular shape, which could be radially organized into a spherical granule (Ao & Jane, 2007; Jane, 2006). The small size-fraction of potato starch has higher relative crystallinity and enthalpy values with A-type diffraction pattern compared with the B-type large size fraction.

Table 2

Branch chain-length distributions of amylopectin.

Sample	Peak DP		Average CL (DP)	CL distribution (%)			
	I	II		DP 6–13	DP 14–24	DP 25–36	DP ≥ 37
PS	13	48	26.09 ± 0.57 ^a	24.38 ± 0.33 ^a	39.33 ± 0.45 ^a	13.86 ± 0.19 ^a	20.38 ± 0.23 ^{ab}
P-L	13	48	26.15 ± 0.36 ^a	22.59 ± 0.44 ^b	41.97 ± 0.57 ^a	13.97 ± 0.31 ^a	21.46 ± 0.69 ^a
P-M	13	46	25.18 ± 0.37 ^{ab}	25.38 ± 0.72 ^a	41.15 ± 0.23 ^a	13.66 ± 0.11 ^{ab}	19.81 ± 0.84 ^{bc}
P-S	12	46	24.63 ± 0.04 ^b	28.29 ± 0.29 ^c	39.01 ± 0.20 ^b	13.20 ± 0.18 ^b	19.49 ± 0.09 ^c

CL: chain length; DP: Degree of Polymerization. Values are means of duplicate determinations with standard deviation. Means in a column with different superscript letters are significantly different ($p < 0.05$) by least significant difference (LSD) test.

3.2. Effects of granule size on OSA modification

The DS values of size-fractionated OSA modified potato starch are shown in Table 3. The DS values of potato starch granules increased with the size decreasing: P-S > P-M > PS > P-L. In other words, the small-size fraction was easier to react with OSA molecules than the large ones. Bertolini, Souza, Nelson, and Huber (2003) investigated the crosslink reactivity of isolated wheat A- and B-granule fractions, showing that the smaller wheat B-granules displayed a greater degree (6–16%) than the larger wheat A-granules. In this study, there is a mixture of OSA droplets and dissolved OSA molecules in water due to poor solubility of OSA. With larger specific surface area, the small granules have more opportunities to react with OSA droplets/molecules. So the small granule starch showed a higher DS value.

The fractionated starches were modified with OSA, and the distribution of OS groups in the starch granules was investigated using CLSM (Fig. 3). All OS starch granules had uniform bright fluorescence, especially on the surface. The granular surface can react with OSA droplets as well as with dissolved OSA molecules (Shogren, Viswanathan, Felker, & Gross, 2000), so the granular surface of OS starch has a higher DS than the bulk. Compared with the large size-fraction of OS potato starch, the interior of small size fraction showed stronger fluorescence intensity, which implied OS groups were more homogeneously distributed in small size granule. Since OSA reacted rapidly before penetrating and permeating evenly throughout the starch granules, OSA droplets started reaction at the periphery first and then proceeded to the core of the large size-fraction potato starch granules. It was reported that A-type starch consisted of large population of short branch-chains (A and B1 chains), which are less stable and more susceptible for the rearrangement in the crystalline structure to generate more loosely packed areas of voids (Jane, 2006). The B-type polymorphic starches (e.g., large size potato starch fraction) have more long B chains, which extend through two or more clusters and stabilize the internal structures of granules (Jane, 2006). The OSA droplets might be easier to penetrate into the bulk of the granule, when the size of starch granule was smaller as P-S fraction.

3.3. Effects of granule size on flowability

When particle size is less than 100 µm, interparticle adhesion forces (such as van der Waals forces) exceed the gravitational forces by several orders of magnitude, and resulting in a poor flowability (Tomas & Kleinschmidt, 2009). Thus, flowability of many particle products is a scientific and technological problem. In order to reduce the van der Waals forces, some flow additives have been used to promote the surface roughness of particles. The application of additives could improve the discharge of powders, resulting in a good flowability of the particles (Tomas & Kleinschmidt, 2009).

Flowability of native and OSA modified starches was characterized by the repose angle, and shown in Table 3. Small size-fraction of potato starch showed the highest flowability (repose angle

Table 3

Effect of granular size on the DS values and flowability of OS potato starches.

Sample	After OSA modification		Repose angle (°)	
	DS ^A	DS ^B	Native starch	OS-starch-Al ^C
PS	0.0171 ± 0.0004 ^a	0.0171 ± 0.0004 ^a	27.31 ± 0.51 ^a	22.56 ± 1.07 ^a
P-L	0.0147 ± 0.0002 ^b	0.0178 ± 0.0050 ^a	28.78 ± 1.28 ^a	18.98 ± 0.26 ^b
P-M	0.0205 ± 0.0009 ^c	0.0180 ± .00041 ^a	17.11 ± 1.06 ^b	10.09 ± 0.32 ^c
P-S	0.0219 ± 0.0001 ^c	0.0181 ± 0.0072 ^a	8.47 ± 0.31 ^c	4.73 ± 0.70 ^d

Values are means of duplicate determinations with standard deviation. Means in a column with different superscript letters are significantly different ($p < 0.05$) by least significant difference (LSD) test.

^A Starches modified with OSA, and then fractionated to measure DS.

^B Fractionated the starch, and then modified with OSA.

^C Fractionated the starch, then modified with OSA and $\text{Al}_2(\text{SO}_4)_3$.

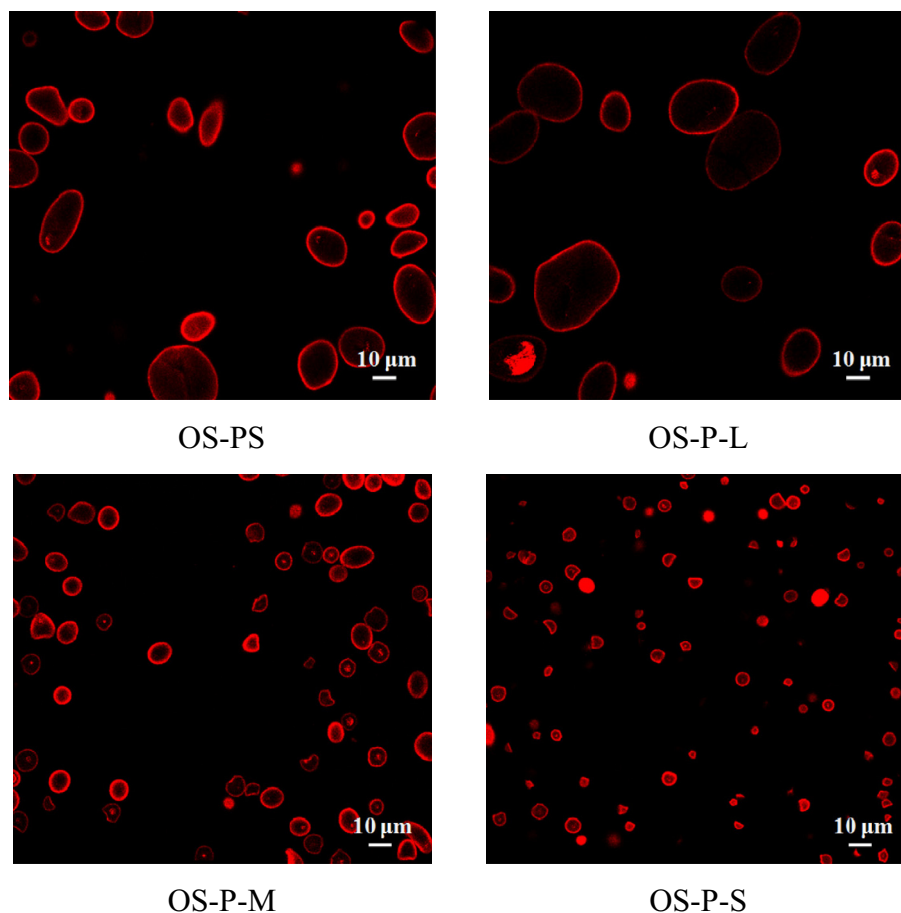


Fig. 3. The CLSM optical sections of OS potato starches (OS-PS, OSA modified potato starch; OS-P-L, OSA modified large size fraction of potato starch; OS-P-M, OSA modified medium size fraction of potato starch; OS-P-S, OSA modified small size fraction of potato starch).

8.47°) among the three size fractions. After OSA and $\text{Al}_2(\text{SO}_4)_3$ modification, the flowability of all samples have been improved. The repose angle of the modified P-L and P-S samples were 18.98° and 4.73° respectively. Unfractionated potato starch with OSA modification showed the highest repose angle value, probably due to the uneven esterification reaction of starch granules with different sizes.

Higher degree of contact area is normally associated with more compact particles and stronger intermolecular forces (Kuakpetoon, Flores, & Milliken, 2001). The large potato starch granules were ellipsoidal to cause the larger contact surface between the granules, which could improved the particle adhesion force between the granules and decreased the flowability of starch granules. However, the contact surface of small granules was lower with

the spherical morphology, showing a better flowability. After OSA modification, hydrophobic OS groups were crosslinked by aluminium ions, the surface of the starch granule screened by hydroxyl group to reduce the cohesive forces among starch granules (Chang et al., 2014). The remarkable improvement of the flowability of small size potato starch may have potential applications in pharmaceutical, food, cosmetic and printing industries.

4. Conclusions

The morphological, structural and physicochemical properties of starch granules vary with granule size. The large potato starch fraction with more long B2 chains displayed ellipsoidal shape,

whereas small-size fraction with short A and B1 chains is in spherical shape. Large granules showed B-type crystalline structure, whereas small size fraction displayed A-type pattern. We also found that the small size fraction has higher relative crystallinity and enthalpy values, less apparent amylose content compared with the large size fraction. Furthermore, the differences of granular size of starches affected the OSA modification, OS group distribution and flowability. In general, small size fraction of potato starch more readily reacts with OSA droplets/molecules, and shows higher flowability compared with large granules with or without OSA modification.

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