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Physicochemical properties and amylopectin structures of large, small, and extremely small potato starch granules

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Abstract

The physicochemical properties and amylopectin structures of large (L), small (S), and extremely small (ES) potato starch granules, which were produced by air-classification in a local factory, were investigated. The content of phosphorus, calcium, magnesium, potassium, and sodium manifestly increased as the granule size decreased. Smaller granule size was associated with lower values of peak viscosity and breakdown and higher values of peak viscosity temperature. The hydrolysis rate of raw starch by glucoamylase became distinctly higher as the granule size decreased. In contrast, the granule size did not have a large influence on the amylose content and DSC gelatinization properties. Amylopectins resembled each other in the distributions of phosphorylated unit-chains (PUCs) as well as total (neutral and phosphorylated) unit-chains.
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Keywords: Potato starch; Phosphorus content; Granule size; Pasting properties; Amylopectin

1. Introduction

In chilly regions, the potato is the key crop grown for starch production. In Hokkaido, the northernmost island of Japan, local factories produce potato starch. Starch has small amounts of monoesterified phosphate groups in amylopectin molecules. Compared to other starches, potato has a higher phosphorus content (Hizukuri, Tabata, & Nikuni, 1970), which provides unique viscosity properties (Blennow, Bay-Smidt, Leonhardt, Bandsholm, & Madsen, 2003; Noda et al., 2004b,c; Suzuki, Shibanuma, Takeda, Abe, & Hizukuri, 1994; Veselovsky, 1940; Wiesenborn, Orr, Casper, & Tacke, 1994). It has been reported that the phosphate group is attached to longer unit-chains with DP>20 of amylopectin (Takeda & Hizukuri, 1982). In addition, phosphoryl-oligosaccharides, which have received much attention concerning their functional properties, are produced in the digestion of potato starch by amylase (Kamasaka et al., 1995). Enhancing the phosphorus content of starch is desirable for the production of phosphoryl-oligosaccharides. Therefore, we attempted to screen potato starch with much higher phosphorus content. Potato starch has a wide distribution of granule size, ranging from 5 to 100 μm. Small starch granules fractionated from starch granules of potato tubers have been reported to have higher phosphorus content (Chen, Schols, & Voragen, 2003; Kainuma, Yamamoto, Suzuki, Takaya, & Fuwa, 1978). In a few factories in Hokkaido, potato starch is separated into several different sizes of granules. Thus, potato starch composed of extremely small granules would be cheap and easily available and would have a remarkably high content of phosphorus.

The article describes the molecular structures of amylopectins, including the distributions of phosphorylated unit-chains (PUCs), as well as some physicochemical properties of large, small, and extremely small potato starch granules produced in a local factory in Hokkaido.

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2. Materials and methods

2.1. Starch samples

Large (L), small (S), and extremely small (ES) potato starch granules, which were produced by air-classification at the Nakashari Starch Factory, Shari Agricultural Cooperative Association, Shari, Hokkaido, Japan, during 2001–2003, were used in this study. Nine samples were examined. They are referred to as L (-01, -02, and -03), S (-01, -02, and -03), and ES (-01, -02, and -03).

2.2. Physicochemical properties of starch

Some starch properties, namely, the content of amylose and total phosphorus, the granule size distribution, the RVA paste viscosity, and the DSC thermal properties, were determined as described previously (Noda et al., 2004c). The determination of amylose content was done in triplicate. The analyses of the granule size distribution, phosphorus content, RVA paste viscosity, and DSC thermal properties were carried out in duplicate. The content of phosphorus attached to C-6 of the glucose residue was measured using glucose 6-phosphate dehydrogenase (Hizukuri et al., 1970), and the determination was done in duplicate. The cation content of starch was measured as follows. For the determination of the content of calcium and magnesium, each starch (5 g) was ashed in a muffle furnace for 1–5 h at 500 °C, and the ash was refluxed in 2.5 ml of 20% HCl. Distilled water was then added to the extraction to give an HCl concentration of 1%. Solution was added to the extraction to give a sodium strontium concentration of 0.5% only for the determination of the magnesium content. The calcium content of the solution was measured by ICP atomic emission spectroscopy (Vist-Pro, Varian, Inc.) at 317.9 nm. The magnesium content of the solution was determined by atomic absorption spectrophotometry (AA890, Nippon Jarrrell-Ash Co., Ltd., Japan) with an air/acetylene flame at 285.2 nm. For the determination of the content of sodium and potassium, each starch (5 g) was extracted with 1% HCl with stirring for 30 min and kept for one night. After centrifugation (1500 g, 5 min), the sodium content of the supernatant was analyzed by atomic absorption spectrophotometry (Spectr AA640, Varian, Inc.) with an air/acetylene flame at 589.6 nm, and the potassium content of the supernatant was determined by atomic absorption spectrophotometry (AA890, Nippon Jarrrell-Ash Co., Ltd., Japan) with an air/acetylene flame at 766.5 nm. The estimations of the content of calcium, magnesium, potassium, and sodium were performed only once. The enzymatic digestibility of the raw starch by the crystalline glucoamylase of *Rhizopus niveus* was evaluated for 4 h at 40 °C with a substrate concentration of 2% (Noda et al., 2004a). The determination of amylase digestibility was done in triplicate.

2.3. Amylopectin structures

Amylopectins were fractionated from L-03, S-03, and ES-03 granules by the method of Lansky, Kooi, and Schoch (1949) with modifications (Takeda, Hizukuri, & Juliano, 1986). Prior to amylopectin analysis, each amylopectin was debranched with *Pseudomonas* isoamylase (Hanashiro, Abe, & Hizukuri, 1996). Phosphorylated unit-chains (PUCs) were separated by DEAE- Sephadex A-50 chromatography (Takeda & Hizukuri, 1982). Fluorescent labeling and subsequent size-exclusion HPLC (HPSEC) analysis of PUC as well as the total (neutral and phosphorylated) unit-chains in the amylopectin molecules were carried out according to Hanashiro, Tagawa, Shibahara, Iwata, and Hizukuri (2002).

2.4. Statistical analysis

The averages and Duncan-*t*-test were computed to measure the variations in the parameters of the physicochemical properties of starches with various granule sizes.

3. Results

The median granule size and the content of amylose and phosphorus of L, S, and ES potato starch granules are given in Table 1. The median granule size was 39.9–43.7, 20.3–23.4, and 13.2–14.0 μm for L, S, and ES granules, respectively. The amylose content, calculated from the blue values at 680 nm, ranged from 18.5 to 22.5%, but no significant difference in the mean value of amylose content was found among L, S, and ES granules. A large difference in phosphorus content (715–1128 ppm) was observed among the starch samples examined. The mean value of

Table 1
Median granule size and the content of amylose and phosphorus of large (L), small (S), and extremely small (ES) potato starch granules produced in 2001, 2002 and 2003

	Median granule size (μm)	Amylose content (%)	Phosphorus		
			Total content (ppm)	P-6[a] (ppm)	P-6[a]/ organic (%)
L-01	43.7	20.5	764	523	68.4
L-02	43.2	21.5	790	541	68.5
L-03	39.9	20.2	715	545	76.2
L-mean ($n=3$)[b]	42.3a	20.7a	756c	536c	71.0a
S-01	23.4	20.6	990	665	67.2
S-02	21.2	19.9	1011	727	72
S-03	20.3	19.4	935	692	74
S-mean ($n=3$)[b]	21.6b	20.0a	979b	695b	71.1a
ES-01	14	19.6	1128	727	64.5
ES-02	13.5	22.5	1090	785	72
ES-03	13.2	18.5	1125	785	70
ES-mean ($n=3$)[b]	13.6c	20.2a	1114a	766a	68.8a

[a] P-6, phosphorus bound at C-6 of the glucose residue.
[b] Values followed by the same letter in the same row within the same parameter are not significantly different ($P<0.05$).

the total phosphorus content was as high as 1114 ppm for ES granules, while the values for L and S granules were 0.679 and 0.879 times the value of ES granules, respectively. The ranking of the content of phosphorus bound at C-6 of the glucose residue among L, S, and ES granules was similar to that of total phosphorus. About 70% of total phosphorus was attached to C-6 of the glucose residue for L, S, and ES granules. The cation content of L, S, and ES potato starch granules is presented in Table 2. The potassium content was remarkably higher (683–1061 ppm) than the content of calcium (104–177 ppm), magnesium (85–140 ppm), and sodium (57–84 ppm). The effect of granule size on the cation content was significant. The mean values of the content of potassium, calcium, magnesium, and sodium were the highest for ES granules, intermediate for S granules, and lowest for L granules.

The RVA pasting properties of L, S, and ES potato starches are listed in Table 3. Wide ranges of peak viscosity (217–322 RVU), breakdown (92–228 RVU), and peak viscosity temperature (73.4–87.2 °C) were recognized among the starch samples examined, whereas the range of the pasting temperature was narrow (67.0–68.2 °C). The peak viscosity, breakdown, and peak viscosity temperature were greatly influenced by the granule size. The peak viscosity and breakdown manifestly decreased as the granule size decreased. A smaller granule size was closely associated with higher values of peak viscosity temperature. In contrast, there was no significant difference in the mean value of the pasting temperature among L, S, and ES granules. Thermal properties were analyzed by DSC, and the results are summarized in Table 4. Onset temperature (T_o), peak temperature (T_p), and enthalpy (ΔH) varied within the range of 59.7–61.5 °C, 64.4 to 67.0 °C, and 19.1–20.9 J/g, respectively. ES granules gave significantly higher mean value of T_p (66.8 °C) than L (65.1 °C) and S (65.8 °C) granules; however, the difference was small. No significant differences in the mean values of T_o and ΔH were observed among L, S, and ES granules. The digestibility of raw starches by crystalline glucoamylase is also presented in Table 4. A remarkable difference in the hydrolysis rate (0.37–1.35%) was found among the starch samples examined. Starch granules were more easily digested by glucoamylase as the granule size decreased. Namely, the mean value of the hydrolysis rate for the ES granules was 1.21%, which was 2.69- and 1.61-fold greater than those for L and S granules, respectively.

The isoamylase-digested potato amylopectin contains a large amount of neutral unit chains and a very small amount of phosphorylated unit-chains (PUCs); first, the total (neutral and phosphorylated) unit-chains were analyzed. The distribution of the total unit-chains of the representative amylopectin (L-03), which was analyzed by HPSEC after debranching with isoamylase followed by fluorescent labeling of unit-chains, is shown in Fig. 1. All three

Table 2
The cation content of L, S, and ES potato starch granules produced in 2001, 2002 and 2003

	Calcium content (ppm)	Magnesium content (ppm)	Potassium content (ppm)	Sodium content (ppm)
L-01	105	85	683	58
L-02	104	87	740	57
L-03	108	88	696	58
L-mean ($n=3$)[a]	106c	86c	706c	57c
S-01	142	113	841	70
S-02	140	122	944	68
S-03	144	116	851	70
S-mean ($n=3$)[a]	142b	117b	879b	70b
ES-01	177	130	906	77
ES-02	172	131	1007	73
ES-03	154	140	1061	84
ES-mean ($n=3$)[a]	168a	134a	991a	78a

[a] Values followed by the same letter in the same row within the same parameter are not significantly different ($P<0.05$).

Table 3
RVA pasting properties of L, S, and ES potato starch granules produced in 2001, 2002 and 2003

	Peak viscosity (RVU)	Breakdown (RVU)	Pasting temperature (°C)	Peak viscosity temperature (°C)
L-01	321	215	68.2	75
L-02	322	223	67.9	73.4
L-03	306	208	67.5	74.1
L-mean ($n=3$)[a]	316a	215a	67.9a	74.2c
S-01	283	165	67.8	77.8
S-02	277	158	67.7	78.7
S-03	265	150	67	78.2
S-mean ($n=3$)[a]	275b	158b	67.5a	78.2b
ES-01	225	104	67.8	84.6
ES-02	217	92	67.5	87.2
ES-03	220	93	67.8	86.3
ES-mean ($n=3$)[a]	221c	96c	67.7a	86.0a

[a] Values followed by the same letter in the same row within the same parameter are not significantly different ($P<0.05$).

Table 4
DSC gelatinizaiton properties and enzymatic digestibility of L, S, and ES potato starch granules produced in 2001, 2002 and 2003

	DSC gelatinization properties			Hydrolysis rate of starch granules (%)
	T_o (°C)	T_p (°C)	ΔH (J/g)	
L-01	61.5	65.6	19.2	0.37
L-02	60.9	65.3	19.2	0.49
L-03	60.2	64.4	20	0.49
L-mean ($n=3$)[a]	60.9a	65.1b	19.5a	0.45c
S-01	61	66.2	20.3	0.59
S-02	60.9	66	19.1	0.88
S-03	60.5	65.2	20.1	0.78
S-mean ($n=3$)[a]	60.8a	65.8b	19.8a	0.75b
ES-01	59.7	67	19.4	1.02
ES-02	59.9	66.7	20.9	1.27
ES-03	60.7	66.8	20.3	1.35
ES-mean ($n=3$)[a]	60.1a	66.8a	20.2a	1.21a

[a] Values followed by the same letter in the same row within the same parameter are not significantly different ($P<0.05$).

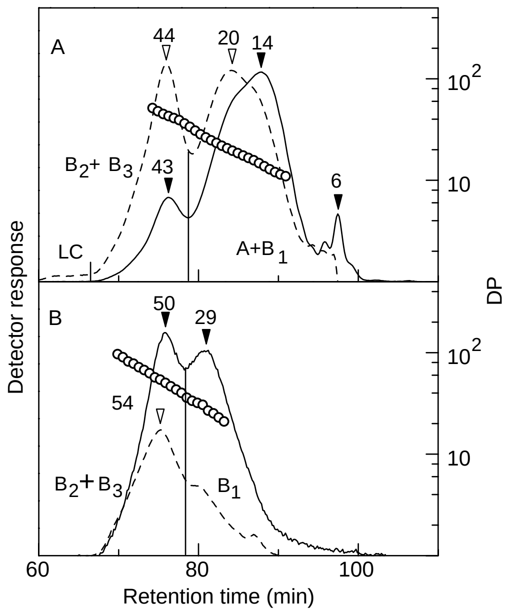

Fig. 1. Weight- and molar-based distributions of total (A) and phosphorylated (B) unit-chains of amylopectins of L, S, and ES potato starch granules produced in 2003. Solid line, fluorescence response; dash, RI response; circle, DP; number with an arrowhead, DP at the position.

amylopectins examined (L-03, S-03, and ES-03) exhibited a biomodal distribution profile, with the first peak around DP ~43 and the second peak around DP ~14 on a molar basis, irrespective of the granule size. Furthermore, for all amylopectins, extremely short chains with DP 6 and 7 were apparent, and very small amounts of long unit-chains (LC) with DP > 100 were observed. As reported by Hizukuri (1986), amylopectin unit-chains can be fractionated into B_3, B_2, B_1, and A chains. The A chain carries no chains, and the B chain carries other chains. A and B_1 chains are localized to one cluster. B_2 and B_3 are defined as B chains that span two and three clusters, respectively. The second peak from gel-permeation HPLC seems to be B_2+B_3, and the first peak is likely to be $A+B_1$. The number-average chain length (CLn) and the weight and molar proportions for each fraction are listed in Table 5. Similar values of the CLn of the whole chain (21–22), $A+B_1$ (16–17), and B_2+B_3 (48–49) were obtained for L-03, S-03, and ES-03 granules, respectively. In addition, the molar ratios of $A+B_1$ to B_2+B_3 for the differently sized starch granules examined were the same (5.3). Second, PUCs were separated by ion-exchange chromatography and analyzed. The distribution of PUCs of the representative amylopectin (L-03) measured by a fluorescent labeling/HPSEC method is also presented in Fig. 1. The distribution profiles of the PUCs of amylopectins of L-03, S-03, and ES-03 granules are shown in Table 6. There was not a large difference in the distribution of PUCs among the starch samples examined. All PUCs were distributed in B_1, B_2, and B_3 chains with two peaks around DP ~50 and ~30. Short unit-chains at retention times of approximately 90 min (DP below 12), which corresponds to the A chain, were hardly detected in all cases. The amounts of the B_2+B_3 fraction were estimated at around ~70 and ~50% on a weight and molar basis, respectively, not showing large differences among differently sized granules.

Table 5
The distributions of total unit-chains of amylopectins of L, S, and ES potato starch granules produced in 2003

	L-03	S-03	ES-03
Weight (%)			
LC	0.7	0.5	0.5
B_2+B_3	35.7	36.3	36.2
$A+B_1$	63.6	63.2	63.3
Mole (%)			
B_2+B_3	16	16	16
$A+B_1$	84	84	84
Molar ratio			
$(A+B_1)/(B_2+B_3)$	5.3	5.3	5.3
CLn			
LC	22	22	21
B_2+B_3	49	49	48
$A+B_1$	17	16	16

Table 6
The distributions of phosphorylated unit-chains (PUCs) of amylopectins of L, S, and ES potato starch granules produced in 2003

	L-03	S-03	ES-03
Weight (%)			
B_2+B_3	66	72	69
B_1	34	28	31
Mole (%)			
B_2+B_3	44	52	47
B_1	56	48	53
CLn			
	40	40	44
B_2+B_3	58	54	66
$A+B_1$	24	23	26

4. Discussion

Starch has a wide distribution in granule size in general. Barley and wheat starches, especially, have a biomodel distribution of A-type (large) and B-type (small) granules. Potato starch displays a normal distribution in granule size, but the range of the size distribution is wide (5–100 μm). Studies have been performed concerning the properties of classified starch granules differing in granule size in potato (Chen et al., 2003; Cottrell, Duffus, Paterson, & Mackay, 1995; Fujita, Sugimoto, & Fuwa, 1983; Geddes, Greenwood, & Mackenzie, 1965; Kainuma et al., 1978) as well as in barley (Kang, Sugimoto, Kato, Sakamoto, & Fuwa, 1985; MacGregor & Ballance, 1980; MacGregor & Morgan, 1984; Takeda, Takeda, Mizukami, & Hanashiro, 1999) and wheat (Peng, Gao, Abdel-Aal, Hucl, & Chibbar, 1999; Soulaka & Morrison, 1985). We have analyzed the physicochemical properties of differently sized potato starch granules (L, S, and ES granules) obtained by air-classification at a local factory. Granule size had significant effects on the content of phosphorus and cation, the RVA parameters (peak viscosity, breakdown, and peak viscosity temperature), and digestibility by glucoamylase. In contrast, few differences in amylose content, gelatinization properties, and amylopectin structures were observed among L, S, and ES granules.

Several researchers have investigated the amylose content in A- and B-types of barley (Kang et al., 1985; Takeda et al., 1999) and wheat (Peng et al., 1999; Soulaka & Morrison, 1985) starch granules. A-type granules have been reported to contain more amylose than B-type granules. Similarly, a larger granule size was associated with a higher amylose content in differently sized potato starch granules separated by sedimentation (Geddes et al., 1965). Contrary to this, none or only slight differences in amylose content were observed among differently sized potato starch granules (Chen et al., 2003; Fujita et al., 1983; Kainuma et al., 1978), which agrees with the present data.

Potato starch is distinct from other starches in that it has a higher concentration of covalently bound phosphate in the amylopectin molecules. In addition, potato starch contains metal cations, such as potassium and calcium, bound to starch phosphate esters by ionic forces. The phosphate groups are attached to amylopectin molecules as monoesters at C-6 (about 70%) and C-3 positions (about 30%) of the glucose residues (Hizukuri et al., 1970). Chen et al. (2003) and Kainuma et al. (1978) indicated that fractionated small potato starch granules had a higher phosphorus content than large ones. They also revealed that the content of potassium, calcium, magnesium, and sodium was higher in small granules than in large granules. The present experiments confirmed these results. Furthermore, this study added to the new knowledge that the ratio of phosphorus bound at C-6 of the glucose residue to total phosphorus was almost constant (about 0.7) irrespectively of the granule size. It would be important to screen potato starch with extremely high phosphorus content because phosphoryl-oligosaccharides, which are easily obtainable after digestion of starch with a high phosphorus content, have recently been identified as functional compounds. For example, they have an inhibitory effect on the formation of calcium phosphate precipitate (Kamasaka et al., 1995) and a large potential for improving the remineralization of enamel (Kamasaka et al., 2002). Previous studies (Chen et al., 2003; Kainuma et al., 1978) as well as ours indicate that small-sized fractions of potato starch contain high levels of phosphorus. The results obtained in this study, in particular, those showing that the phosphorus content of ES potato starch granules produced over three years had more than 1000 ppm of phosphorus content, suggest that ES granules are easily available sources of starches with a markedly high phosphorus content and have the potential for application in the production of phosphoryl-oligosaccharides.

Kainuma et al. (1978) analyzed the pasting properties of differently sized potato starch granules using amylography and observed low values of peak viscosity and breakdown in small granules and high values of peak viscosity temperature; these results are consistent with those obtained from RVA. Starch-bound phosphate is an important factor for determining the starch viscosity characteristics. Several results have been obtained that demonstrate that a higher starch phosphorus content is closely associated with higher viscosity in potato (Blennow et al., 2003; Noda et al., 2004b, c; Suzuki et al., 1994; Veselovsky, 1940; Wiesenborn et al., 1994). However, these studies were performed using non-fractionated starch samples from different potato cultivars. Thus, it should be noted that starch phosphorus content is not positively correlated with peak viscosity and breakdown when classified small potato starch granules are included, as found in this study.

Granule size is a critical factor in determining the digestibility of raw starch by amylase. The larger starch granules have a reduced surface area than the smaller ones, and the smaller surface area of the substrate in the larger starch granules decreases the opportunity for amylase to absorb. Thus, classified small starch granules have been digested faster than large granules in barley (Kang et al., 1985; MacGregor & Ballance, 1980) and potato (Cottrell et al., 1995; Kainuma et al., 1978), which is in good agreement with the present results. Furthermore, the digestibility of raw starch by amylase is generally altered according to the plant origin of the starch. Potato starch has the largest granule size of commercial starches, and this is in part responsible for its reduced susceptibility to the action of amylase. Supporting this, manifestly higher hydrolysis rates were found in 30 sweet potato starches (1.97–7.34%) (Noda, Takahata, & Nagata, 1993), 8 wheat starches (16.1–51.7%) (Mangalika, Miura, Yamauchi, & Noda, 2003), and 11 rice starches (23.4–38.6%) (Noda, Nishiba, Sato, & Suda, 2003) under the same conditions for enzyme reaction that were applied in this study.

Much information has been obtained on thermal properties measured by DSC of size-fractionated starch granules. Reports have provided evidence that granule size has no or only slight influence on T_o and T_p in barley (Kang et al., 1985), wheat (Peng et al., 1999; Soulaka & Morrison, 1985), and potato (Fujita et al., 1983). The present data on T_o and T_p agrees with these previous findings. Smaller starch granules have been reported to have lower ΔH in barley (Kang et al., 1985), wheat (Peng et al., 1999; Soulaka & Morrison, 1985), and potato (Fujita et al., 1983). Contrary to these results, the present data shows that granule size has no influence on ΔH.

The structures of amylopectin from size-fractionated starch granules have been studied to some extent. In barley, no or only slight differences in the structure of amylopectin were found among differently sized starch granules (Kang et al., 1985; Macgregor & Morgan, 1984; Takeda et al., 1999). In potato, the gel filtration pattern of debranched starch implied that the chain-length distributions of amylopectins from differently sized starch granules were similar (Fujita et al., 1983; Kainuma et al., 1978). Supporting this, this study demonstrated that there is no difference in the ratio of the short-chain fraction ($A+B_1$) to the long-chain fraction (B_2+B_3) in the amylopectin molecules among differently sized potato starch granules. The ratio of $A+B_1$ to B_2+B_3 is altered according to the botanical source. Potato amylopectins have been reported to have lower values of the ratio (5.4–6.5) than those of wheat (12.3–12.9), rice (10.1–10.8), maize, and sweet potato (9.5–10.1) (Hanashiro et al., 2003). The results obtained here of the ratio of $A+B_1$ to B_2+B_3 (5.3) for differently sized potato starches were in agreement with their data. High phosphorus content is a notable characteristic of potato amylopectin. Therefore, we analyzed the PUCs of amylopectin to have a better understanding of the fine structure of amylopectin. According to the reports of Takeda and Hizukuri (1982) and Blennow, Bay-Smidt, Wischmann, Olsen, and Møller (1998), the phosphate groups are located mostly in the long B-chains in potato amylopectin. Similar results have been reported in amylopectins from edible canna (Thitipraphunkul, Uttapap, Piyachomkwan, & Takeda, 2003), arrow root (Blennow et al., 1998), and curcuma (Blennow et al., 1998; Hanashiro et al., 2003). In this investigation, using differently sized potato starches, new knowledge was obtained that shows that, regardless of the granule size, phosphates were attached to the B_1, B_2, and B_3 chains and the molar ratio of B_2+B_3 to B_1 was about 1. From these results, it is clear that, in potato, granule size has no effect on the molecular structures of amylopectin, namely, the size distributions of PUCs, as well as the total unit-chains in amylopectin molecules.

5. Conclusions

The physicochemical properties and amylopectin structures of size- fractionated potato starches were analyzed. Overall, the results showed that several starch properties, namely, the content of phosphorus and cation, pasting properties, and digestibility by amylase, varied greatly according to the granule size. In contrast, no or only slight differences in amylose content and gelatinization properties were observed among the differently sized starch granules. Furthermore, the molecular structures of amylopectins, including the distributions of PUCs, were similar, irrespectively of the granule size. The information obtained in this study should be useful to the food and related industries that make use of potato starch granules of varying sizes.

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