Impact of physical and enzymatic cell wall opening on the release of pre-gelatinized starch and viscosity forming potential of potato flakes

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ABSTRACT

Potato flakes (PFs) are used in instant foods. They contain pre-gelatinized starch which readily develops viscosity upon hydration. We here provide the first report on factors influencing their viscosifying potential. Swelling power (SP) ($r = 0.719$, $p < 0.01$) and mean particle size ($r = -0.704$, $p < 0.05$) mainly determine instant viscosity development of PF suspensions while short extractable extracellular amylose molecules [degree of polymerization between 150 and 1500 (EE-AM₁₅₀₋₁₅₀₀)] positively impact their cold paste viscosity (CPV) ($r = 0.717$, $p < 0.01$) in Rapid Visco Analyzer (RVA) models. Cell wall opening by ball milling or cellulase treatments increased PF SP resulting in up to 75% higher RVA peak viscosity readings. Furthermore, the release of EE-AM₁₅₀₋₁₅₀₀ molecules increased CPV by about 30% since they readily associated upon cooling. Partial cell wall opening thus improves the viscosifying potential of PFs and expands their applicability in instant foods.

1. Introduction

The use of starch as functional ingredient in food systems in many instances relies on its ability to bind large amounts of water. When heated in water above a characteristic temperature, i.e. the gelatinization temperature, the molecular order of the native starch granules is irreversibly lost (Tan, Wee, Sopade, & Halley, 2004; Tester & Morrison, 1990). Upon gelatinization, starch crystallites melt and granules swell. This results in a large viscosity increase of the aqueous starch suspensions and progressive solubilization of starch molecules (Delcour & Hoseney, 2010).

An alternative to heat treatment during food processing is to use pre-gelatinized starches as these have cold-water swelling properties (Dries, Knaepen, Goderis, & Delcour, 2017). Cold-water swelling starches can be used in instant and convenience foods such as soups, sauces and puddings (Anastasiades, Thanou, Loulis, Stapatoris, & Karapantsios, 2002; Majzoobi, Kaveh, Blanchard, & Farahnaky, 2015; Mason, 2009). Pre-gelatinized starches are traditionally precooked, drum-dried and ground prior to their use in food applications (Chiu & Solarek, 2009). One of the major drawbacks of such starches is that they

have lower thickening ability upon heating in excess water than do their native counterparts (Anastasiades et al., 2002; Chiu & Solarek, 2009). This has mainly been attributed to the loss of granular structure during their production (Rajagopalan & Seib, 1992). Aqueous alcohol treatments at elevated temperature produce granular cold-water swelling starches with a V-type crystalline structure (Dries, Gomand, Goderis, & Delcour, 2014; Dries, Gomand et al., 2017; Zhang, Dhital, Haque, & Gidley, 2012). Such starches have superior thickening ability since the granular structure is preserved (Jane & Seib, 1991).

Starch mainly consists of two α -(1,4)-D-glucose polymers, the quasi linear amylose (AM) and the highly branched [5–6% α -(1,6) linkages] amylopectin (AP) (Buléon, Colonna, Planchot, & Ball, 1998; Tester, Karkalas, & Qi, 2004). Potato AM has a molecular weight (MW) of about 10^6 and a degree of polymerization (DP) on a number average basis (DP_n) of 4920 (Gomand, Lamberts, Derde et al., 2010; Takeda, Shirasaka, & Hizukuri, 1984). Potato AP is much larger (MW 1.7×10^8) with a DP_n value of 11,200 (Gomand, Lamberts, Derde et al., 2010; Takeda, Shibahara, & Hanashiro, 2003). Starch swelling is mainly determined by AP (Tester & Morrison, 1990). A unique feature is that, in contrast to what is the case for cereal starches, potato starch AP

Abbreviations: AP, amylopectin; AM, amylose; C*, close packing concentration; CPV, cold paste viscosity; DP, degree of polymerization; EE-AP, extractable extracellular amylopectin; EE-AM, extractable extracellular amylose; EE-AM₁₅₀₋₁₅₀₀, extractable extracellular amylose with degree of polymerization between 150 and 1500; EE-AM_{>1500}, extractable extracellular amylose with degree of polymerization > 1500; EE-S, extractable extracellular starch; HPSEC, high performance size exclusion chromatography; MW, molecular weight; DP_n, number average degree of polymerization; PV, peak viscosity; PF, potato flake; RVA, rapid visco analyzer; SP, swelling power

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contains a relatively high level of phosphate monoesters (0.2–0.4% of the AP glucose units) (Takeda & Hizukuri, 1982) which cause repulsion between adjacent chains (Berghaller, 2004). This leads to rapid hydration, swelling, and high viscosity during heating. As a consequence, pre-gelatinized potato starches are highly suitable for instant applications (Yadav, Guha, Tharanathan, & Ramteke, 2006).

Dehydrated potato (*Solanum tuberosum* L.) derivatives contain pre-gelatinized starch (Alvarez & Canet, 1999; Gisaw, Asquith, Lai, Villagran, & Cole, 2003; Villagran, Beverly, & Williamson, 2011). They are produced by steam peeling, boiling, and mashing potatoes and subsequent drying (Lamberti, Geiselmann, Conde-Petit, & Escher, 2004). During boiling, starch gelatinizes within the potato tissue (Kim & Kim, 2015b). Although completely gelatinized, the starch granules are not fully disintegrated since the cell walls of the parenchyma cells in which they are embedded restrict their swelling during gelatinization (Lamberti et al., 2004). Boiling partially solubilizes the potato cell walls which mainly contain pectin [50–60% of cell wall dry matter (dm)] and cellulose (30% of dm). Blanching prior to boiling reduces the degree to which starch leaches from potato cells as it strengthens the parenchyma cell walls (van Dijk, Fischer, Beekhuizen, Boeriu, & Stolle-Smits, 2002).

Dehydrated potato products thus contain cold-water swelling starch which readily develops viscosity upon hydration. They are available either as drum-dried potato flakes (PFs) or air-dried potato granules and are used in the production of instant potato soups, instant mashed potatoes and fried or extruded potato snacks (Alvarez & Canet, 1999; Kim & Kim, 2015a; Villagran et al., 2011). However, the parenchyma cell walls may retard or inhibit instant swelling upon hydration and hamper leaching of starch from potato cells (Kim & Kim, 2015a, 2015b). PFs have a substantial portion of broken cells (40–60%) since the cell walls are partially ruptured due to the shear during drum-drying (Villagran et al., 2011). In the process, part of the disintegrated starch granules enter the extracellular space (Alvarez & Canet, 1999; Lamberti et al., 2004). Upon hydration, suspensions of PFs thus consist of potato cells and fragments thereof that are embedded in an extracellular starch matrix (Lamberti et al., 2004). These characteristics are believed to determine the functionality of PFs during food processing. However, to date, little is known about the composition of the extracellular starch fraction of PFs and its impact on gel formation.

Against this background, the present work not only set out to unravel the viscosifying properties of PFs in Rapid Visco Analyzer (RVA) model systems and, hence, their potential functionality in instant food systems but also to provide a rational basis for improving their viscosity development. Our effort includes physical and enzymatic treatments that disrupt the potato cells to impact on the release of pre-gelatinized starch and the pasting properties of PFs. The results provide a knowledge base for optimizing current and developing further applications of PFs in instant foods.

2. Materials and methods

2.1. Materials

Commercial PFs were kindly supplied by Clarebout (Nieuwerkerke, Belgium), Lamb Weston/Meijer (Kruiningen, The Netherlands), Agrarfrost (Wildeshausen, Germany) and Farm Frites (Lommel, Belgium). All chemicals were at least of analytical grade and from Sigma-Aldrich (Bornem, Belgium) unless indicated otherwise. Isoamylase was from *Pseudomonas* sp. (0-8124), cellulase from *Trichoderma reesei* (C-8546), and the following peptidases were used: trypsin from porcine pancreas (T-4799), pepsin (P-6887) and papain (P-3125). No pectinase side-activity was present in the cellulase. Furthermore, neither the cellulase nor the peptidases did contain α -amylase side-activities (results not shown). Enzyme units (EU) mentioned are as defined by the supplier.

2.2. Standard analyses

Moisture and ash contents were measured according to AACC methods 44-15a and 08-12 (1999), respectively. PF protein contents ($N \times 6.24$) were determined by the Dumas combustion method, an automated protein analysis system (EAS, VarioMax N/CN, Elt, Gouda, The Netherlands) in line with AOAC Official Method 990.03 (1995). Starch contents were calculated as 0.9 times the glucose contents, which were determined by gas chromatography of alditol acetates obtained by acid hydrolysis, reduction and acetylation of the resulting glucose units as in Courtin, Van den Broeck, and Delcour (2000). Differential scanning calorimetry analysis and wide angle X-ray diffraction were executed as in Bosmans et al. (2012) and Dries et al. (2014), respectively, and showed that none of the PFs still contained ungelatinized starch (results not shown). Dietary fiber content was analyzed according to AOAC Official Method 991.43 (1995). The total uronic acid content of PFs was determined after acid hydrolysis as in Ahmed and Labavitch (1978). Hydrolysis of the pectin in PF samples (500.0 mg) was with concentrated sulfuric acid (8.0 mL, 95%, VWR International, Leuven, Belgium) for 240 min in ice-water. To quantify the extractable uronic acids, PFs (500.0 mg) were suspended in deionized water (10.0 mL), shaken (150 min^{-1} , 30 min, 60 °C) and then centrifuged (2000 g, 15 min, 20 °C). Total and extractable uronic acid contents were then analyzed as in Blumenkrantz and Asboe-Hansen (1973) using the chromogenic reagent meta-hydroxydiphenyl (0.15% w/v) in 125 mM NaOH. Extinctions were measured at 520 nm. A galacturonic acid calibration curve (0–0.5 $\mu\text{mol/mL}$) was used to quantify the uronic acids. All analyses were performed in triplicate.

2.3. Ball milling of potato flakes

PFs (180 g) were ball milled in triplicate [500 revolutions per min (rpm)] for 5, 15, 30 or 60 min using a Retsch PM 100 planetary ball mill (Haan, Germany) equipped with a 500 mL stainless steel grinding jar and 6 stainless steel grinding balls (20 mm in diameter). After every 5 min of actual milling, a 5 min rest was introduced to avoid extensive heat build-up in the jar. All analytical measurements were carried out for each technical replicate.

2.4. Particle size distribution

The cumulative volumetric particle size distributions (PSDs) of untreated and ball milled PFs were determined using a Malvern 2000 Mastersizer (Goffin/Meyvis, Hoeilaart, Belgium) which detects particles with diameters between 0.38 μm and 2.000 mm. The volumetric PSDs were calculated from the intensity of the scattered light based on the Fraunhofer theory (de Boer, de Weerd, Thoenes, & Goossens, 1987). Average particle sizes were calculated in terms of the volume mean diameter, essentially as in Tzoumaki, Moschakis, Kiosseoglou, & Biliaderis (2011).

2.5. Microscopic analysis

Cell walls in untreated and ball milled PFs (200 mg) were stained with Congo red (1.0% w/v) essentially as in Kim and Kim (2015a). Cellular structures were then studied with an Eclipse 80i epifluorescence microscope equipped with a digital sight DS-U2 camera and an Intensilight C-HGFI lamp (Nikon, Melville, NY, USA). Images were analyzed with Nikon NIS-Elements BR software.

2.6. Swelling power

The swelling properties of PFs were determined as in Eerlingen, Jacobs, Block, & Delcour (1997). PFs suspended in deionized water (0.25% w/v) were heated at 60 °C [representing the consumption temperature of some instant food products such as soups and sauces

(Kim & Yoo, 2014)] for 30 min with intermittent shaking every 5 min. The suspensions were then centrifuged (1000 g, 15 min, 20 °C), the supernatants transferred to small test tubes and the sediments weighed. Carbohydrates in the supernatant were quantified by the method of Dubois, Gilles, Hamilton, Rebers, & Smith (1956) using a glucose calibration curve (0–1.1 μmol/mL) and expressed as starch ($0.9 \times \text{glucose}$). The close packing concentration (C^*) and swelling power (SP) at 60 °C were then calculated as follows:

$$C^* = \frac{\text{sample weight(dm)}}{\text{sediment weight}} \times 100$$

$$SP = \frac{\text{sediment weight}}{\text{sample weight(dm)} \times (100 - \% \text{solubilized carbohydrates})} \times 100$$

2.7. Content and chromatographic separation of extracellular starch

Starch was extracted by continuous shaking (150 min^{-1}) for 30 min at 60 °C from untreated or ball milled PFs (300.0 mg) suspended in 10.0 mL 200 mM sodium phosphate buffer (pH 8.0) and is further referred to as extractable extracellular starch (EE-S). After cooling to room temperature, the suspensions were centrifuged (2000 g, 15 min, 20 °C) and the carbohydrate contents of the supernatants determined according to Dubois et al. (1956) as outlined above.

2.7.1. Protein degradation and starch debranching

Since a refractive index detector (RID) would detect protein extracted along with the starch, a peptidase treatment was carried out prior to the chromatographic separation. Peptidase solution (100 μL) containing 5.88% w/v trypsin, 0.40% w/v pepsin and 0.65% w/v papain in sodium phosphate buffer (pH 8.0, 200 mM) was added to 4.5 mL extract containing EE-S. To this mixture, 0.5 mL 100 mM ethylene diamine tetraacetic acid (EDTA) disodium salt (VWR International) was added. It was then incubated for 5 h at 25 °C. In a next step, the peptidases were inactivated by heating (10 min, 100 °C). To 1.0 mL of the resulting samples, 0.9 mL 1.0 M acetic acid (VWR International) was added to adjust the pH to 4.0. Starch was then debranched with isoamylase (400 EU) at 40 °C for 48 h, essentially as in Dries, Gomand, Delcour, and Goderis (2016), to allow separating long AM chains from short AP chains (Wang, Hasjim, Wu, Henry, & Gilbert, 2014). After the first 24 h of incubation, 400 U of isoamylase was again added to ensure complete debranching. After enzyme inactivation by heat treatment (10 min, 100 °C), samples were filtered (0.45 μm, Thermo Scientific, Rockwood, TN, USA) and immediately analyzed by High Performance Size Exclusion Chromatography (HPSEC).

2.7.2. Chromatographic separation

HPSEC was used to determine the relative AM and AP levels and to study the chain length distribution of the debranched AM fraction. Debranched samples (50 μL) were injected (SIL-HT_C Auto sampler, Shimadzu, Kyoto, Japan) into three TSK gel columns (G6000 PW_{XL}, G4000 PW_{XL} and G3000 PW_{XL}) (Tosoh, Stuttgart, Germany) mounted in series on a modular Shimadzu SIL-HT_C unit equipped with a LC-20AT pump, a DGU-20A5 degasser, a 10A RID operating at 40 °C and a column oven (CTO-20A, Shimadzu) at 60 °C. The flow rate was 0.5 mL/min and the eluent was a 10:9 (v/v) mixture of 200 mM sodium phosphate buffer (pH 8.0) containing 9.8 mM disodium EDTA and 1.0 M acetic acid. Shodex P-82 pullulan standard solutions (1.0 mg/mL) (Showa Denko, Tokyo, Japan) with following MWs and corresponding DPs were injected (50 μL): 5.9×10^3 (DP 35), 11.8×10^3 (DP 70), 22.8×10^3 (DP 140), 47.3×10^3 (DP 290), 112×10^3 (DP 690), 212×10^3 (DP 1310), 404×10^3 (DP 2490), 788×10^3 (DP 4860) and 1600×10^3 (DP 9880). A third order polynomial relation was fitted between the logarithm of the MWs of the standards and the elution times. The HPSEC weight distribution chromatograms were divided into 3 regions based on the DP of the eluting molecules (Li, Fitzgerald,

Prakash, Nicholson, & Gilbert, 2017). Components with DP < 150 were defined as AP branches, while molecules with DP > 150 were defined as AM chains. The relative amounts of AM and AP in the EE-S were determined as the area under the elution curve and expressed in arbitrary units (AU). The distribution of AM molecules was further divided into 2 regions with DP limits being: 150–1500 and > 1500 (Gomand, Lamberts, Derde et al., 2010). Each HPSEC analysis run included a reference PF sample for quality control reasons.

2.8. Pasting properties

The pasting of PF suspensions was studied with an RVA Super 4 (Perten Instruments, Hägersten, Sweden). PFs (2.0 g dm) were premixed with 540 μL 95% (v/v) ethanol (Chem-Lab, Zedelgem, Belgium) to avoid excessive swelling prior to analysis. Deionized water was then added to obtain a total sample mass of 25.0 g (dm content of 8.0%). The PF suspensions were equilibrated for 5 min at 50 °C, heated to 95 °C at 9 °C/min, held at 95 °C for 8 min, cooled to 50 °C at 9 °C/min and held at 50 °C for 5 min. The stirring speed was 160 rpm.

2.9. Cellulase treatment

PFs (150.0 mg) suspended in 10.0 mL 100 mM sodium acetate buffer (pH 5.0) were incubated in triplicate with cellulase (0.10 U per mg dm flakes) at 40 °C for 1, 2, 4 and 6 h while stirring at 130 rpm to hydrolyze cellulose in PF cell walls. After centrifugation (2000 g, 15 min, 20 °C), the samples were heated (10 min at 100 °C) to inactivate cellulase. The same treatments were also executed without cellulase addition. Quantification and chromatographic separation of the EE-S was executed essentially as in 2.7. The SP of PFs in the presence of cellulase was determined essentially as in 2.6. PFs were suspended in 100 mM sodium acetate buffer (pH 5.0) and kept at 40 °C for 30 min. When studying the impact of cellulase on PF pasting, no ethanol was added to the PFs prior to RVA analysis and, instead of deionized water, 100 mM sodium acetate buffer (pH 5.0) was added to the PFs to obtain a total sample mass of 25.0 g. Pasting properties were determined in duplicate. PF suspensions without cellulase served as control for analysis of SP and pasting properties.

2.10. Statistical analysis

All statistical analyses were conducted using JMP Pro 12 (SAS Institute, Cary, NC, USA). Data were analyzed with one-way analysis of variation (ANOVA) and Tukey multiple comparison test (significance level $p < 0.05$) to verify whether mean values were significantly different. Pearson correlation coefficients (r) were calculated to determine correlations between PF physico-chemical properties. Principal component (PCA) and hierarchical cluster analysis (HCA) were used to select representative PF samples.

3. Results and discussion

3.1. (Physico-)chemical characterization of potato flakes

Table 1 gives a summary of the chemical composition, SP, level and composition of EE-S, and pasting properties of 12 untreated PF samples (numbered from 1 to 12). Starch (77.2%–81.5% of dm), protein (7.4%–9.8% of dm), dietary fiber (6.7%–8.6% of dm) and ash (2.7%–3.7% of dm) contents differed somewhat amongst the PFs investigated and were in line with published data (Kim & Kim, 2015b; Yadav et al., 2006). The mean particle sizes of PFs, their SPs and peak viscosities at 50 °C in the RVA model system (PVs) ranged from 241 to 427 μm, from 27.9 to 34.0 g/g dm, and from 1045 to 1755 mPa.s, respectively. The latter were significantly related to SP ($r = 0.719$, $p < 0.01$) as well as to mean particle size ($r = -0.704$, $p < 0.05$) (Supplementary data Fig. 1). In general, PFs with a relatively small

Table 1
Chemical composition [% dry matter (dm)], extractable extracellular starch (EE-S) content (% dm), relative extractable extracellular amylose (EE-AM) [divided in regions with degree of polymerization (DP) > 1500 and 150–1500] and amylopectin (EE-AP) contents [arbitrary units (AU)], mean particle size (μm), swelling power (SP) and peak and cold paste viscosity (PV and CPV) of 8.0% dm suspensions of 12 untreated potato flakes (PFs).

PF	Starch (% dm)	Protein (% dm)	Ash (% dm)	Dietary Fiber (% dm)	EE-S content (% dm)	Relative EE-AM content (AU)	150 < DP ≤ 1500 (AU)	DP > 1500 (AU)	Relative EE-AP content (AU)	Mean particle size (μm)	SP (g/g dm)	PV (mPa s)	CPV (mPa s)
1	80.7 (0.9) ^a	7.4 (0.1) ^c	3.2 (0.1) ^d	7.2 (0.2) ^{bc}	14.7 (0.3) ^f	14.5 (0.2) ^a	7.3 (0.3) ^{bc}	7.2 (0.4) ^a	31.5 (1.2) ^c	350 (4) ^e	31.2 (0.7) ^{bc}	1470 (20) ^c	790 (5) ^b
2	80.1 (2.1) ^a	8.1 (0.1) ^b	3.5 (0.1) ^b	7.6 (0.2) ^b	17.6 (0.1) ^{bc}	12.3 (0.8) ^{bcd}	6.4 (0.6) ^{cde}	5.7 (0.3) ^{bc}	31.5 (0.5) ^c	365 (4) ^{de}	33.4 (1.2) ^{ab}	1530 (75) ^{bc}	670 (5) ^d
3	80.6 (1.6) ^a	8.0 (0.1) ^d	3.3 (0.1) ^c	6.7 (0.1) ^c	16.9 (0.1) ^{cd}	13.8 (0.2) ^{ab}	7.6 (0.3) ^{abc}	6.2 (0.2) ^b	35.5 (0.9) ^b	388 (8) ^c	34.0 (0.3) ^a	1445 (75) ^c	745 (15) ^c
4	80.3 (0.9) ^a	7.8 (0.1) ^d	2.9 (0.1) ^e	7.3 (0.3) ^{bc}	16.1 (0.4) ^{de}	13.9 (0.8) ^{ab}	7.9 (0.5) ^{ab}	6.0 (0.3) ^b	27.2 (1.7) ^d	427 (1) ^a	27.9 (1.8) ^d	1080 (125) ^d	795 (20) ^b
5	80.8 (1.2) ^a	7.9 (0.1) ^d	2.9 (0.1) ^e	7.3 (0.4) ^{bc}	15.3 (0.2) ^{ef}	14.5 (1.0) ^a	8.8 (0.5) ^a	5.7 (0.5) ^{bc}	29.2 (1.6) ^{cd}	408 (3) ^b	33.1 (0.6) ^{ab}	1045 (130) ^d	800 (20) ^b
6	81.5 (1.8) ^a	8.1 (0.1) ^d	2.7 (0.1) ^f	7.3 (0.1) ^{bc}	15.1 (0.3) ^{ef}	13.4 (0.7) ^{abc}	7.2 (0.4) ^{bcd}	6.2 (0.4) ^b	28.1 (0.1) ^d	395 (3) ^{bc}	33.6 (1.7) ^{ab}	1400 (60) ^c	845 (10) ^a
7	79.4 (1.5) ^a	9.6 (0.1) ^{ab}	3.3 (0.1) ^c	7.0 (0.1) ^{bc}	13.2 (0.3) ^g	11.1 (0.5) ^{de}	6.7 (0.5) ^{bcd}	4.4 (0.1) ^{de}	24.0 (0.6) ^e	371 (7) ^d	29.1 (0.5) ^{cd}	1085 (45) ^d	790 (10) ^b
8	78.1 (0.5) ^a	9.3 (0.1) ^b	3.3 (0.1) ^c	8.6 (0.1) ^a	12.6 (0.2) ^g	13.6 (0.7) ^{ab}	7.8 (0.5) ^{ab}	5.8 (0.2) ^{bc}	27.0 (1.4) ^d	241 (6) ^b	34.0 (0.9) ^a	1715 (65) ^{ab}	855 (5) ^a
9	79.8 (2.0) ^a	9.8 (0.4) ^b	3.2 (0.1) ^d	7.0 (0.3) ^{bc}	13.0 (0.5) ^g	9.4 (0.8) ^{ef}	5.5 (0.6) ^{fg}	3.9 (0.2) ^e	26.2 (0.7) ^{de}	284 (4) ^g	33.6 (1.1) ^{ab}	1755 (5) ^a	775 (40) ^{bc}
10	77.7 (2.6) ^a	9.3 (0.1) ^b	3.3 (0.1) ^c	7.1 (0.1) ^{bc}	18.9 (0.4) ^a	11.0 (0.3) ^{de}	5.9 (0.2) ^{def}	5.1 (0.2) ^{cd}	41.7 (0.4) ^a	319 (5) ^f	29.7 (0.6) ^{cd}	1200 (30) ^d	580 (5) ^f
11	79.1 (0.8) ^a	8.7 (0.1) ^c	3.2 (0.1) ^d	7.2 (0.2) ^{bc}	18.3 (0.4) ^{ab}	11.5 (0.8) ^{cd}	5.3 (0.6) ^{fg}	6.2 (0.2) ^b	39.1 (0.9) ^a	365 (9) ^{de}	33.5 (0.6) ^{ab}	1445 (25) ^c	645 (5) ^{de}
12	77.2 (0.7) ^a	9.5 (0.1) ^{ab}	3.7 (0.1) ^a	7.3 (0.1) ^{bc}	16.5 (0.3) ^d	7.9 (0.6) ^f	4.0 (0.5) ^g	3.9 (0.3) ^e	35.9 (0.6) ^b	369 (4) ^d	29.6 (0.5) ^{cd}	1150 (30) ^d	620 (5) ^{ef}

Standard deviations are given between brackets. Mean values in the same column differ significantly ($p < 0.05$, Tukey's test) when not sharing the same letter. Means and standard deviations of 3 analytical replicates are shown.

mean particle size and high SP exhibited enhanced instant viscosity development. The RVA profiles of PF suspensions also showed a viscosity peak during heating which originated from a second starch swelling due to (1) the higher water binding capacity of starch at higher temperatures (Gomand, Lamberts, Visser, & Delcour, 2010), and (2) partial cell wall breakdown of potato cells during heating under continuous shear (van Marle et al., 1997). Cold paste viscosities (CPVs) ranged from 580 to 855 mPa.s and were not related to PV values. The formation of a continuous gel network when cooling starch suspensions is dictated by AM gelation (Delcour & Hoseney, 2010; McGrane, Mainwaring, Cornell, & Rix, 2004). Although the PFs in the present study had similar total starch contents, their EE-S contents ranged from 12.6% to 18.9% dm. Moreover, HPSEC separation of EE-S into extractable extracellular amylose (EE-AM) and extractable extracellular amylopectin (EE-AP) showed that relative EE-AM and EE-AP contents ranged from 7.9 to 14.5 AU and from 26.4 to 41.7 AU, respectively. Although it has been suggested that the extracellular starch fraction mainly consists of AM (Escher, Rotach, Schweingruber, & Solms, 1979; Lamberti et al., 2004), we here clearly showed that it contained substantial amounts of AP. Potato AP has a relatively high solubility in water due to it being partly phosphorylated (Singh, Singh, Kaur, Sodhi, & Gill, 2003; Svegmarm & Hermansson, 1991). Last but not least, the relative contents of EE-AM molecules with DP 150–1500 (EE-AM₁₅₀₋₁₅₀₀) and DP > 1500 (EE-AM_{>1500}) ranged from 4.0 to 8.8 AU and from 3.9 to 7.2 AU, respectively.

We here further observed that the EE-AM₁₅₀₋₁₅₀₀ contents were positively ($r = 0.717$, $p < 0.01$) correlated with CPV (Supplementary data Fig. 1) while EE-AM_{>1500} contents were not. Thus, higher levels of shorter EE-AM chains increased PF gel formation. It has earlier been reported that short AM chains have a high rate of AM association and, hence, gel formation (Chung & Liu, 2009; Gidley & Bulpin, 1989). The extractable AM chains with relatively high MW that are present in the extracellular space are probably less mobile during cooling and thereby limit the degree to which AM associates (Chung & Liu, 2009).

To provide a rational basis for improving the viscosifying potential of PFs, HCA and PCA were combined to first select representative PF samples based on the above-mentioned characteristics (Supplementary data Fig. 2). HCA grouped the samples of PFs in four well-defined clusters. Next, a PCA plot was constructed based on three uncorrelated principal components of linear combinations of PF physico-chemical properties. It explained 83% of the total variation in PF characteristics. PFs 1, 4, 8 and 10 occurred in a different cluster (HCA) and covered the variation in PF characteristics (PCA). This subset of PF samples was here used to study the impact of additional cell wall breakdown by physical (ball milling) and enzymatic (cellulase) treatments on the release of starch (especially AM) and the pasting and gelation properties of PF suspensions in RVA models.

3.2. Milling induced changes in potato flake morphology

Both untreated and ball milled PFs had a unimodal particle size distribution (Supplementary data Fig. 3). Fig. 1 shows the cumulative particle size distributions. Ball milling PFs for 60 min significantly reduced their mean particle size from 350 μm to 152 μm, from 427 μm to 125 μm, from 241 μm to 130 μm and from 319 μm to 154 μm for PF 1, 4, 8 and 10, respectively. The resultant PF dimensions approximated the size of individual potato cells (150 μm) (Bordoloi, Kaur, & Singh, 2012). Microscopic images (Fig. 2) clearly showed that ball milling physically damaged the cells. As a result of 60 min of ball milling, the soluble uronic acid contents were 8–25% higher (Table 2). Taken together, ball milling disrupted the potato cells and partially solubilized their cell wall material.

3.3. Swelling power

Fig. 3 shows that ball milling caused the SP of PFs to be significantly

Fig. 1. Particle size distribution of untreated and ball milled potato flakes (PFs) expressed as the cumulative amount of particles (volume%) as a function of the particle diameter (μm).

Fig. 2. Light microscopy images of (A) untreated and (B) ball milled (60 min) potato flakes (PFs) stained with Congo red (1.0%, w/v). (For interpretation of the references to colour in this Figure legend, the reader is referred to the web version of this article.)

higher. As a result of 60 min of milling, the SP of PFs 1, 4, 8 and 10 had increased from 31.2 to 35.3 g/g dm, from 27.9 to 37.3 g/g dm, from 34.0 to 36.1 g/g dm and from 29.7 to 31.6 g/g dm, respectively. Note the pronounced increase for PF 4. Kim and Kim (2015b) earlier suggested that intact parenchyma cell walls retard or limit swelling of pre-

gelatinized starches when entrapped in their cellular matrix. We here indeed showed that partial opening of the PF cell walls by ball milling effectively improved their SP.

To further study the impact of cell wall breakdown on PF SP, the cellulose fraction was enzymatically hydrolyzed. Note that the SPs of

Table 2

Total and soluble uronic acid content [% dry matter (dm)], relative extractable extracellular amylose (EE-AM) [divided in regions with degree of polymerization (DP) > 1500 and 150–1500] and amylopectin (EE-AP) content [arbitrary units (AU)], and peak and cold paste viscosity (PV and CPV) of 8.0% dm suspensions of untreated and ball milled (5, 15, 30 and 60 min) potato flakes (PFs).

PF		Total uronic acid content (% dm)	Soluble uronic acid content (% dm)	Relative EE-AM content (AU)	150 < DP ≤ 1500 (AU)	DP > 1500 (AU)	Relative EE-AP content (AU)	CPV (mPa s)
1	Untreated	2.02 (0.09)	0.56 (0.02) ^b	14.5 (0.2) ^a	7.3 (0.3) ^a	7.2 (0.4) ^a	31.5 (1.2) ^b	790 (5) ^b
	60 min		0.77 (0.03) ^a	14.6 (0.1) ^a	7.3 (0.3) ^a	7.3 (0.8) ^a	44.7 (0.6) ^a	865 (15) ^a
4	Untreated	1.52 (0.12)	0.40 (0.01) ^b	13.9 (0.8) ^b	7.9 (0.5) ^b	6.0 (0.3) ^b	27.2 (1.7) ^b	795 (20) ^b
	60 min		0.54 (0.04) ^a	20.8 (0.9) ^a	12.8 (0.5) ^a	8.0 (0.4) ^a	37.1 (2.1) ^a	1040 (5) ^a
8	Untreated	2.35 (0.06)	0.65 (0.01) ^a	13.6 (0.7) ^a	7.8 (0.5) ^a	5.8 (0.2) ^a	27.0 (1.4) ^b	855 (5) ^b
	60 min		0.71 (0.01) ^a	13.3 (0.3) ^a	7.7 (0.2) ^a	5.6 (0.5) ^a	34.5 (0.8) ^a	900 (5) ^a
10	Untreated	1.84 (0.04)	0.59 (0.02) ^b	11.0 (0.3) ^b	5.9 (0.2) ^b	5.1 (0.2) ^a	41.7 (0.4) ^b	580 (5) ^b
	60 min		0.77 (0.02) ^a	12.1 (0.5) ^a	6.5 (0.2) ^a	5.6 (0.4) ^a	56.2 (2.4) ^a	610 (5) ^a

Standard deviations are given between brackets. Mean values from the same sample in the same column differ significantly ($p < 0.05$, Tukey's test) when not sharing the same letter. Means and standard deviations of 3 analytical replicates are shown.

Fig. 3. Peak viscosity values (primary axis) and swelling power (secondary axis) of untreated and ball milled potato flakes (PFs). Mean values for the same sample differ significantly ($p < 0.05$, Tukey's test) when not sharing the same upper (swelling power) or lower case (peak viscosity) letter.

the control samples (Table 3, analyzed at 40 °C and pH 5.0 for ensuring optimal cellulase activity) in this experiment were considerably lower (15.9–17.7 g/g dm) than those of the untreated samples shown in Fig. 3 (27.9–34.0 g/g dm, analyzed at 60 °C in deionized water). Cellulase treatment significantly increased PF SP by 7.1% (PF 8) to 14.9% (PF 10).

Taken together, physical and enzymatic cell wall breakdown improved starch and, hence, PF swelling properties.

3.4. Extracellular starch

Since the properties of the extracellular starch matrix dictate PF gelation (see 3.1), we here studied the impact of physical or enzymatic treatments on the EE-S contents and properties of PFs. Fig. 4 shows that increasing extents of ball milling resulted in gradually increasing EE-S contents. After 60 min of milling, the EE-S content of PFs 1, 4, 8 and 10 had significantly increased from 14.7 to 19.0% dm, from 16.1 to 22.7% dm, from 12.6 to 15.7% dm and from 18.9 to 24.9% dm, respectively.

Table 3

The effect of cellulase treatment on potato flake (PF) swelling power (SP) and peak and cold paste viscosity (PV and CPV) of 8.0% dry matter (dm) suspensions of PFs were studied by adding 0.10 U per g dm cellulase to the flake suspensions. Relative extractable extracellular amylose (EE-AM) [divided in regions with degree of polymerization (DP) > 1500 and 150–1500] and amylopectin (EE-AP) content [arbitrary units (AU)] of control and cellulase treated (0.10 U per g dm flakes) PFs after 6 h of incubation are also listed.

PF	SP (g/g dm)	Relative EE- AM content (AU)	150 < DP ≤ 1500 (AU)	DP > 1500 (AU)	Relative EE- AP content (AU)	PV (mPas)	CPV (mPas)
1 Control	17.7 (0.2) ^b	3.9 (0.1) ^b	1.5 (0.1) ^a	2.4 (0.2) ^b	21.7 (0.7) ^b	1285 (30) ^b	900 (10) ^a
Cellulase treated	19.4 (1.0) ^a	4.7 (0.2) ^a	1.7 (0.1) ^a	3.0 (0.1) ^a	32.2 (1.2) ^a	2080 (100) ^a	925 (10) ^a
4 Control	15.9 (0.3) ^b	3.4 (0.4) ^b	2.2 (0.2) ^b	1.2 (0.1) ^a	13.4 (0.5) ^b	960 (5) ^b	880 (5) ^b
Cellulase treated	18.1 (0.5) ^a	6.2 (0.3) ^a	4.6 (0.3) ^a	1.6 (0.3) ^a	25.4 (1.1) ^a	1705 (10) ^a	985 (5) ^a
8 Control	16.9 (0.5) ^b	2.7 (0.5) ^a	1.5 (0.3) ^a	1.2 (0.3) ^a	12.6 (0.4) ^b	1185 (25) ^b	815 (5) ^a
Cellulase treated	18.1 (0.4) ^a	3.2 (0.6) ^a	1.7 (0.2) ^a	1.5 (0.3) ^a	21.6 (0.3) ^a	1495 (5) ^a	820 (5) ^a
10 Control	17.4 (0.3) ^b	3.8 (0.2) ^a	1.8 (0.1) ^a	2.0 (0.1) ^a	22.3 (0.7) ^b	690 (25) ^b	590 (5) ^a
Cellulase treated	20.0 (1.4) ^a	3.9 (0.1) ^a	1.8 (0.1) ^a	2.1 (0.2) ^a	32.6 (0.2) ^a	1005 (5) ^a	605 (5) ^a

Standard deviations are given between brackets. Mean values from the same sample in the same column differ significantly ($p < 0.05$, Tukey's test) when not sharing the same letter. Means and standard deviations of 3 analytical replicates are shown.

Fig. 4. Extractable extracellular starch (EE-S) content of untreated and ball milled potato flakes (PFs). Mean values for the same sample differ significantly ($p < 0.05$, Tukey's test) when not sharing the same lower case letter.

Potato cell walls limit the release of starch molecules from the cellular matrix since parenchyma cell walls hamper starch swelling and, hence, starch leaching.

Fig. 5A shows the HPSEC profiles of debranched EE-S extracted from untreated PFs and PFs ball milled for 60 min. In general, ball milling increased EE-AP content by about 30%. However, ball milling of PFs 1, 8 and 10 did not release AM from the cellular matrix. Only in the case of PF 4 did ball milling during 60 min lead to a higher relative EE-AM content (20.8 AU vs. 13.9 AU), which was mainly due to a higher extractability of EE-AM_{150–1500} (12.8 AU vs. 7.9 AU). Ball milling thus mainly increased the extractability of short AM molecules.

In a next step, PFs were incubated with cellulase. Although the EE-S content of the control samples increased by 15–50% merely as a result of the incubation (Fig. 6), addition of cellulase further increased the EE-S content of all PFs studied at every incubation time. After 6 h of incubation, enzymatic cell wall breakdown had significantly increased the EE-S content of PF 1, 4, 8 and 10 from 16.3 to 23.6% dm, from 13.4 to 24.8% dm, from 9.6 to 16.3% dm and from 20.5 to 26.6% dm, respectively. The HPSEC profiles (Fig. 5B) of EE-S extracted from control and cellulase treated PFs after 6 h of incubation showed that cell wall hydrolysis mainly had increased the relative EE-AP content. Cellulase

Fig. 5. High performance size exclusion chromatography (HPSEC) profiles of debranched extractable extracellular starch (EE-S) of (A) untreated (full line) and ball milled (60 min, dotted line) potato flakes (PFs) and (B) control (full line) and cellulase treated (0.10 U per g dry matter, incubation time 6 h, dotted line) PFs.

treatment resulted in significantly higher relative EE-AM contents only for PF 1 (increase from 3.9 to 4.7 AU) and PF 4 (increase from 3.4 to 6.2 AU). In the case of PF 1, enzymatic cell wall breakdown mainly increased the relative amount of EE-AM_{>1500} (3.0 AU vs. 2.4 AU) while

Fig. 6. Extractable extracellular starch (EE-S) content of control and cellulase treated (0.10 U per g dry matter, 1, 2, 4 and 6 h of incubation) potato flakes (PFs). Mean values for the same sample at different time points differ significantly ($p < 0.05$, Tukey's test) when not sharing the same upper case letter. Mean values at the same time point (with or without cellulase treatment) differ significantly ($p < 0.05$, Tukey's test) when not sharing the same lower case letter.

for PF 4, a higher relative EE-AM₁₅₀₋₁₅₀₀ content was observed (4.6 AU vs. 2.2 AU).

3.5. Pasting properties

Fig. 7 shows the RVA profiles (8.0% dm) of (A) untreated and ball milled PF suspensions and (B) PF suspensions with and without (control) addition of cellulase. The pasting properties of all 8.0% dm PF suspensions were measured in a concentration regime exceeding their C^* at 50 °C (results not shown) and thus under conditions where the viscosity development is influenced by both PF swelling and rigidity (Eerlingen et al., 1997; Steeneken, 1989). Prior ball milling of PFs gradually increased PV values (Fig. 3). Milling during 60 min resulted in significantly higher PV readings (2130 vs. 1470 mPa s, 2140 vs. 1080 mPa s, 1990 vs. 1715 mPa s and 1570 vs. 1200 mPa s for PFs 1, 4, 8 and 10, respectively). Treating PFs with cellulase increased PV values with 26% (PF 8) to 78% (PF 4) (Table 3) but did not alter PF mean particle size. This indicated that especially PF swelling properties rather than their mean particle sizes play a key role in the instant viscosity development of the PF suspensions. At the same time, both physical and enzymatic cell wall opening led to substantially larger viscosity breakdown of the PF suspensions in the RVA model. Potato starch is subject to larger viscosity breakdown than cereal starches due to its high SP and the accompanying disintegration of the granules (Gomand, Lamberts, Visser et al., 2010; Waterschoot, Gomand, Willebrords, Fierens, & Delcour, 2014). Cell wall breakdown of PFs probably allows starch granule remnants to swell to a larger extent and their disintegration is held responsible for the large viscosity breakdown of the treated PFs.

Finally, Table 2 shows that the CPVs of ball milled PFs were significantly higher than those of their untreated counterparts. For PFs 1, 8 and 10, however, the relative increase in CPV values amounted to less than 10% as a result of 60 min of ball milling while, for PF 4, a 30% increase was observed. Similar to what was the case for ball milling, only PF 4 showed a significantly higher CPV when cellulase was added to the suspension (985 vs. 880 mPa s). Gomand, Lamberts, Visser et al. (2010) reported that the AM content of various potato starches is related to the CPV of suspensions thereof when analyzed at levels exceeding C^* . The large increase in CPV values of PF 4 upon cell wall

breakdown is most likely due to pronounced increase in relative EE-AM content. Moreover, the increased level of EE-AM was mainly due to higher levels of EE-AM₁₅₀₋₁₅₀₀. These results provide further evidence that especially relatively short AM molecules contribute to the gelation of PF suspensions (see Section 3.1). Liu et al. (2017) recently showed that the fine structure of pre-gelatinized rice starch strongly impacts its pasting and gelation properties in RVA models suggesting that a decrease in AP MW during pre-gelatinization would hinder AM association during cooling and, hence, hamper gel formation. Moreover, Li, Prakash, Nicholson, Fitzgerald, and Gilbert (2016) studied the impact of AM fine structure on the textural properties of cooked rice and found a positive relationship between the amount of short AM molecules and product hardness. We here advance the current state of the art by providing direct evidence that especially short AM molecules play a major role in gel formation of pre-gelatinized starches probably because they are more mobile than larger such molecules and thus readily associate with each other upon cooling.

4. Conclusions

In the present work, the properties of PFs governing their viscosifying potential were unraveled. We showed that potato parenchyma cell walls inhibit instant swelling of the pre-gelatinized starch enclosed in the cellular matrix of PFs and that they hamper the leaching of starch from the cells directly resulting in lower PVs and CPVs in an RVA model system. Partial cell wall opening significantly increased the SP of PFs and, hence, their instant viscosity development. Higher PV values were accompanied by a substantially larger viscosity breakdown since the starch granule remnants are more susceptible to degradation upon extensive swelling. At the same time, physical and enzymatic cell wall breakdown led to a substantial release of starch (mainly AP) from the cellular matrix. However, CPV values of PF suspensions were significantly related to the amount and degree of polymerization of EE-AM. Higher levels of short EE-AM molecules positively impacted gel formation. Taken together, partial opening of potato cell walls improves the viscosity development and gel forming capacity of PFs and can expand their applicability in instant food concepts such as instant soups, sauces and fried or extruded potato-based snacks.

Fig. 7. Rapid Visco Analyzer (RVA) profiles of 8.0% dry matter (dm) suspensions of (A) untreated and ball milled potato flakes (PFs) and (B) PFs with or without (control) addition of 0.10 U cellulase per g dm flakes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.carbpol.2018.04.057>.

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