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Physicochemical properties of potato and cassava starches and their mutants in relation to their structural properties

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ABSTRACT

Physicochemical properties [swelling power (SP), pasting behaviour and retrogradation] of five wild type (wt), five amylose free (amf), four high-amylose (ha) potato starches (ps) and one wt and amf cassava starch (cs) were investigated. While swelling of wtps occurred in two phases, amfps showed a very fast swelling and no gel of swollen granules was observed at higher temperatures (>90 °C). Haps underwent only restricted swelling. SP of cassava starches were lower than those of potato starches. Wtps leached mainly amylose (AM) during heating at low temperatures. Molecules of higher molecular weight (MW) leached out at higher temperatures. Longer amylopectin (AP) chains [degree of polymerisation (DP) > 18] inhibited swelling while short chains (DP < 14) favoured swelling. Starch pasting behaviour of 5.0 and 8.0% starch suspensions was studied using Rapid Visco Analyser (RVA). For 5.0% suspensions, increased levels of high-MW AP and decreased levels of AM molecules led to higher peak viscosity. Longer AP chains (DP > 18) depressed peak viscosity, while short chains (DP < 14) increased peak viscosity for both concentrations. At 8.0%, peak viscosity increased with starch granule size. After 1 day of storage of gelatinised starch suspensions, wtps and especially amfps showed only limited AP retrogradation. In contrast, the high enthalpies of retrograded AP (ΔH_{retro}) and peak and conclusion temperatures of retrogradation ($T_{p,retro}$ and $T_{c,retro}$) of haps suggested partial cocrystallisation between AM and AP. Chains with DP 18–25 seemed to be more liable to AP retrogradation. Wtcs and amfcs did not retrograde at room temperature.

1. Introduction

Starches with a broad range of functionalities are in great demand. Knowledge of the relation between starch structure and its physicochemical properties is necessary from industrial point of view as it provides the opportunity to further define starch functional properties and end-uses. In this way, starches could be obtained tailored to a specific end-use.

Swelling power (SP) are indicative of the water uptake by starch during heating at different temperatures. Starch swelling is viewed as a property of amylopectin (AP). In the process, amylose (AM) acts as a dilutent (Svegmark & Hermansson, 1993; Tester & Morrison, 1990a). At low temperatures, mainly AM leaching (L) occurs, while molecules of higher molecular weight (MW) leach at increasing heating temperature (Eliasson & Gudmundsson, 1996; Tester & Morrison, 1990a). The **close packing concentration** (C^*) is the concentration where the swollen granules fill up the available space in the starch suspension. It is crucial in explaining starch behaviour in rheological measurements. The **Rapid Visco Analyser** (RVA) can be used to study swelling and disruption of starch granules during heating under shear (Batey, 2007). Shape and size of the granules, AM content, molecular size of AM and AP, chain length distribution and, in the case of potato starches, phosphate ester groups determine the starch viscosity behaviour (Eliasson & Gudmundsson, 1996; Jane & Chen, 1992). After heating and cooling of a starch suspension, a starch gel is formed which is believed to consist of

Abbreviations: AM, amylose; amfps, amylose free potato starches; amfcs, amylose free cassava starch; AP, amylopectin; CH, carbohydrates; C^*, close packing concentration; $T_{c,retro}$, conclusion temperature of retrogradation; DP, degree of polymerisation; d, diameter; DSC, differential scanning calorimetry; dm, dry matter; T_g, glass transition temperature; glc-6-P, glucose-6-phosphate ester groups; GBSS, granule bound starch synthase; haps, high-amylose potato starches; HPAEC, high performance anion exchange chromatography; L, leaching; T_m, melting temperature; MW, molecular weight; T_o, onset temperature of gelatinisation; $T_{o,retro}$, onset temperature of retrogradation; $T_{p,retro}$, peak temperature of retrogradation; RVA, Rapid Visco Analyser; ΔH_{retro}, enthalpy of retrograded amylopectin; SEC, size exclusion chromatography; SP, swelling power; T_{PV}, temperature at peak viscosity; wtps, wild type potato starches; wtcs, wild type cassava starch.

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a continuous network of AM with embedded starch granule remnants (Miles, Morris, Orford, & Ring, 1985). Beside AM network formation on a short term (few hours or days), cooling and storage of a starch paste is followed by AP retrogradation on a long term (few weeks) (Miles et al., 1985). Amylose crystallites have a melting temperature of *ca*. 150 °C (Eerlingen & Delcour, 1995). During storage of starch containing products, AP **retrogradation** has a marked influence on texture. Retrograded AP shows a characteristic melting temperature (T_m) around 55–60 °C. The storage temperature has an obvious impact on AP retrogradation: retrogradation occurs only between T_g (glass transition temperature) and T_m. In this temperature range, lower temperatures promote crystal nucleation while higher temperatures support crystal propagation. Beside storage temperature, water availability is another important parameter affecting AP retrogradation (Slade & Levine, 1987).

Potato starches are characterised by a more rapid and unrestricted swelling in one stage until 90 °C, already at lower temperatures (<60 °C) than are starches of many other botanical origins. This has been attributed to weak uniform bonds in the granule (Leach, McCowen, & Schoch, 1959). The presence of phosphate ester groups on potato AP results in relatively high SP (repulsion between phosphate groups) (Galliard & Bowler, 1987). The level of soluble carbohydrates (CH) at a certain degree of swelling is lower for potato starch than for other starches (Leach et al., 1959). Potato starch gels are clear and have a more bland taste than gels of cereal starches (Swinkels, 1985). AM free potato starches (amfps) have a lower viscosity and a higher gel clarity than wild type potato starches (wtps) (Visser, Suurs, Steeneken, & Jacobsen, 1997). Potato AP tends to retrograde more than cereal AP (Fredriksson, Silverio, Andersson, Eliasson, & Aman, 1998).

Although different research groups investigated the physicochemical properties of potato and cassava starches, they have, to the best of our knowledge, never been related to structural features for such a broad range of well characterised potato and cassava starches. The objective of the present study was to relate structural characteristics (Gomand et al., in press) to their swelling behaviour, and pasting and retrogradation characteristics.

2. Materials and methods

2.1. Materials

Five wtps (wtps1–wtps5), five amfps (amfps1–amfps5), four high-AM potato starches (haps1–haps4), one wild type cassava starch (wtcs) and one AM free cassava starch (amfcs) were investigated. Their origin and the corresponding enzyme suppression were described earlier (Gomand et al., in press). Wtps3 and amfps3 are a mix of starches of different cultivars. All amfps and amfcs (Raemakers et al., 2005) samples were the result of (partial) RNA inhibition of granule bound starch synthase (GBSS), except for amfps3 which arose from point mutation of GBSS by X-ray irradiation (Visser, Suurs, Bruinenberg, Bleeker, & Jacobsen, 1997). Haps samples were the result of (partial) RNA inhibition of starch branching enzymes A and B. The structures and gelatinisation properties of the different starches were described earlier (Gomand et al., in press). Table 1 provides an overview of these starch properties.

All reagents, chemicals and enzymes used were of at least analytical grade and obtained from Sigma–Aldrich (Bornem, Belgium) unless indicated otherwise.

2.2. Swelling power

SP was determined according to Eerlingen, Jacobs, Block, and Delcour (1997) with slight modifications. Starches suspended in deionized water (0.25%, w/v) in air-tight tubes with screw caps (98 × 12 mm), were heated for 15 min at different temperatures in a water bath (50, 55, 60, 65, 70, 80, 90 and 100 °C) or an oil bath (110 °C) with intermittent shaking. Following cooling for 5 min, starch suspensions were centrifuged at 4000 g for 30 min. Supernatants were discarded and the sediments were weighed. To determine AML and CHL, the levels of AM and CH of the supernatants were measured as described by Chrastil (1987) and Dubois, Gilles, Hamilton, Rebers, and Smith (1956), respectively. C^* (%) and SP (g/g) were calculated as follows:

$$C^* = \frac{\text{dry matter starch weight} \times 100}{\text{sediment weight}}$$

Table 1
Overview of the structural parameters: amylose (AM) content (%), glucose-6-phosphate (glc-6-P) content (nmol/mg), relative level of granules with diameter (d) < 20 µm, with d between 20 µm and 40 µm and with *d* > 60 µm, relative levels of chains with DP 80–150 (%), DP 25–80 (%), DP 18–25 (%), DP 10–14 (%) and DP 6–9 (%), relative levels of amylopectin of high-molecular weight (region I), low-molecular weight (region II) and amylose amylopectin (region III) of wild type (wt), amylose free (amf) and high-amylose (ha) potato (p) and cassava (c) starches (s). These data are accepted for publication in Food Hydrocolloids (Gomand et al., in press).

Sample	AM content (%)	glc-6-Pcontent (nmol/mg)	$d < 20$ µm (%)[a]	d:20–40 µm (%)[a]	$d > 60$ µm (%)[a]	DP 80–150 (%)	DP 25–80 (%)	DP 18–25 (%)	DP 10–14 (%)	DP 6–9 (%)	Region I (%)	Region II (%)	Region III (%)
Wtps1	18.9 (0.6)	16.9 (0.8)	6.3	25.6	25.4	0.9 (0.1)	8.6 (0.4)	25.2 (0.3)	36.0 (0.3)	13.7 (0.5)	42.1 (1.2)	33.4 (0.0)	24.5 (1.3)
Wtps2	22.4 (0.3)	9.2 (0.8)	6.9	23.1	30.4	1.1 (0.2)	10.7 (0.3)	26.3 (0.4)	34.7 (0.5)	12.3 (0.5)	41.1 (3.1)	28.7 (2.7)	30.2 (0.8)
Wtps3	20.3 (0.2)	9.8 (0.5)	8.2	33.1	17.8	1.0 (0.1)	9.8 (0.6)	26.1 (0.1)	33.1 (0.0)	13.2 (0.1)	48.6 (2.4)	25.8 (0.8)	25.5 (3.3)
Wtps4	20.7 (0.3)	20.4 (0.6)	6.2	18.6	38.3	0.9 (0.5)	9.0 (0.5)	26.6 (0.0)	36.1 (0.3)	11.7 (0.1)	46.1 (2.5)	24.7 (1.5)	29.2 (1.1)
Wtps5	19.9 (0.9)	12.8 (1.1)	8.5	27.9	22.8	0.8 (0.3)	9.9 (0.6)	26.9 (0.0)	34.4 (0.2)	11.9 (0.3)	40.4 (1.1)	30.3 (2.5)	29.3 (1.6)
Amfps1	3.9 (0.1)	21.4 (1.1)	10.1	33.5	18.8	1.2 (0.1)	10.5 (0.7)	25.8 (0.4)	34.4 (0.3)	13.0 (0.4)	50.2 (3.5)	37.0 (3.4)	12.9 (1.5)
Amfps2	3.6 (0.0)	10.6 (1.0)	11.3	28.2	25.9	1.5 (0.4)	11.9 (1.0)	26.1 (0.3)	34.0 (0.6)	12.2 (0.3)	42.4 (1.8)	41.4 (0.8)	16.2 (1.0)
Amfps3	4.2 (0.2)	8.6 (0.6)	8.1	33.0	15.2	2.9 (0.1)	11.1 (0.4)	26.8 (0.2)	33.3 (0.2)	11.5 (0.0)	22.2 (0.5)	50.5 (2.4)	27.3 (1.9)
Amfps4	7.5 (0.2)	14.4 (1.0)	10.0	32.3	16.6	1.9 (0.3)	10.3 (0.3)	26.0 (0.0)	34.6 (0.1)	11.9 (0.0)	58.7 (1.9)	31.6 (1.2)	9.7 (1.7)
Amfps5	3.9 (0.1)	11.6 (0.8)	5.9	23.8	27.8	0.9 (0.2)	10.4 (0.3)	26.1 (0.1)	34.6 (0.3)	11.9 (0.3)	57.5 (1.2)	29.2 (1.1)	13.4 (0.9)
Haps1	27.4 (0.5)	64.3 (2.6)	19.4	44.2	8.0	1.9 (0.2)	13.7 (1.6)	32.0 (0.3)	27.8 (0.5)	7.6 (0.7)	30.2 (2.9)	31.1 (2.1)	39.0 (1.6)
Haps2	33.1 (1.6)	73.3 (1.2)	15.8	38.4	13.2	2.7 (0.1)	13.4 (0.7)	34.6 (1.0)	24.5 (0.9)	7.0 (0.8)	10.2 (1.5)	30.3 (4.3)	59.5 (5.7)
Haps3	37.3 (1.3)	69.5 (0.8)	18.1	41.0	11.1	3.5 (0.1)	13.0 (0.3)	33.2 (0.1)	25.1 (0.9)	8.1 (0.1)	18.7 (1.4)	29.2 (0.5)	52.1 (1.4)
Haps4	78.4 (0.9)	50.0 (1.8)	22.0	50.7	3.5	14.7 (0.1)	20.1 (0.9)	33.5 (0.9)	17.9 (0.3)	10.2 (0.1)	1.6 (0.2)	10.8 (0.6)	87.6 (0.8)
Wtcs	18.4 (0.1)	0.0 (0.0)	81.1	18.3	0.0	0.5 (0.1)	8.6 (0.2)	21.4 (0.0)	39.0 (0.2)	16.8 (02)	43.8 (1.5)	28.7 (1.3)	27.6 (1.7)
Amfcs	6.0 (0.1)	0.0 (0.0)	84.2	15.3	0.0	0.7 (0.0)	9.8 (0.0)	22.1 (0.0)	38.2 (0.3)	16.0 (0.3)	52.9 (2.1)	33.3 (0.9)	13.8 (1.6)

[a] Differences between two measurements were less than 5.0%.