

Supporting Information

Dibasic Magnesium Hypochlorite as an Oxidant to Tune Pasting Properties of Potato Starch in One Step

J. O. P. Broekman ¹, Brian W. Dijkhuis ¹, Johanna A. Thomann ^{1,2,3}, André Heeres ^{2,3}, Hero J. Heeres ¹ and Peter J. Deuss ^{1,*}

¹ Green Chemical Reaction Engineering, Engineering and Technology institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

² Hanze University of Applied Sciences, Zernikeplein 11, 9747 AS Groningen, The Netherlands

³ Innovation Hub Oost Groningen, Billitonweg 1, 9640 AE Veendam, The Netherlands

* Correspondence: p.j.deuss@rug.nl Tel.: +31-503634918

Additional experimental

Procedure for the oxidation of starch by NaOCl

This is a general procedure for the oxidation of starch. For detailed reaction conditions (amounts of oxidant/pH/temperature) and results, see the main text and supporting information (Tables S1—S4). The procedures were adopted from patented procedures and used in our previous manuscript. The sample oxidised by NaOCl with 8.5 mol% NaOCl was the same sample as used in that manuscript (Tables S1—S4, entry 2) [1].

Native potato starch (39 g dry basis, 0.241 mol) was added to deionized water (~55 g) while it was being stirred vigorously with an overhead stirrer to obtain a 39 wt% suspension (dry basis) and brought to pH 8.2 by the addition of a 1.1 M NaOH solution. The suspension was heated to 35 °C and kept at this temperature using a Julabo 4 thermostat bath (Figure S2). Next, an NaOCl solution (15 % active chlorine) was added over 10 min (8.08 mL total) for a total of 3.7 wt% (active Cl to dry weight starch). During addition, the pH was kept at 8.2 by the addition of dilute sulfuric acid. After the addition and for an additional 2h reaction time, temperature and pH were monitored by a WTW InoLab pH 7310 pH meter with a WTW Sentix 81 Precision pH electrode with a temperature sensor. The pH was kept constant at 8.2 by an Arduino Uno with an Atlas Scientific EZO circuit and an Atlas Scientific pH electrode. These controlled a Watson Marlow 101 dosing pump, supplying 1.1 M NaOH. After 2h, the consumption of all NaOCl was verified by a test strip, after which the pH was increased to 10.5 for 1h. Afterwards, the suspension was acidified to pH 5 using conc. H₂SO₄, followed by filtration over a Büchner funnel and washing using 1 L deionized water. The starch residue was dried overnight in a fume hood under air. The gravimetrically determined product yield was corrected for the moisture content to determine the starch losses and final recovered solid starch yield (97 %). The moisture content was determined using a Kern moisture analyser DBS 60-3.

Determination of the degree of oxidation

The carboxyl content of oxidised starches was determined titrimetrically. Dried starch (2.5 g, wet weight) was suspended in 50 mL of 0.1 M HCl with stirring for 30 min at room temperature. The product was filtered, washed with deionized water (1 L), and dissolved in 200 mL of boiling water. The starch solution was cooled to 40—50 °C and titrated with 0.1 M NaOH using phenolphthalein as an indicator. The degree of carboxyl substitution was expressed as the amount of mol of carboxyl group per mol of glucose units calculated using Eq. S1:

$$DS_{COOH} = \frac{162 * (V_{sample} - V_{blank}) * M_{NaOH}}{1000 * m_{sample}} \quad (\text{Eq. S1})$$

With 162 the M_w of a glucose unit, V_{blank} and V_{sample} the volume of NaOH solution for the blank and sample respectively (mL), M_{NaOH} the molarity of the NaOH solution (mol/L), and m_{sample} the weight of the sample (g, dry basis).

Determination of the pasting properties

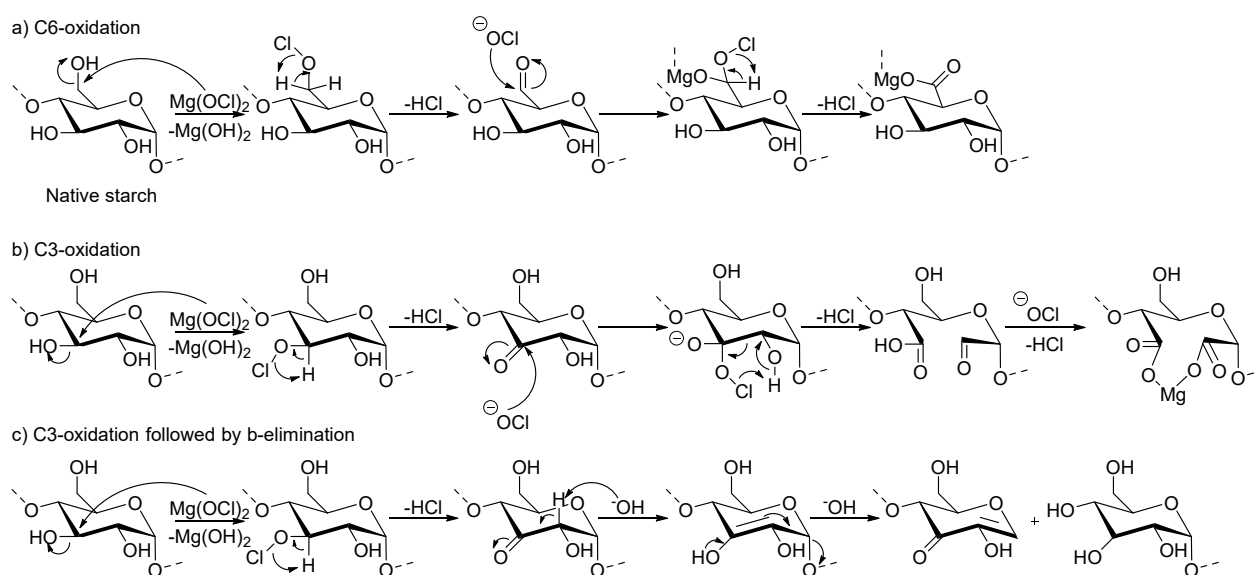
The pasting properties of the oxidised starches were determined using a Rapid Visco Analyser (RVA) from Newport Scientific. An RVA sample was prepared by mixing 8.4 g of oxidised starch (dry basis) with deionised water to a total weight of 28 g, affording a final starch concentration of 30 wt%. During analysis, the sample was spun and heated from 50 °C to 95 °C in 3.7 min, followed by a hold stage at 95 °C for 2.5 min, cooling to 50 °C in 3.7 min, and a final hold stage at 50 °C for 2 min. From the resulting RVA pasting curves, the following parameters were obtained and noted down: peak viscosity (maximum viscosity in the curve), hold viscosity (lowest viscosity after cooling), breakdown (peak – hold viscosities), final viscosity (viscosity at the end of the measurement) and setback (final – hold viscosities).

Starch structure characterization

High-performance size-exclusion chromatography (HPSEC) was performed on an Agilent Technologies 1200 Series instrument using 2 PSS Suprema columns in series (100, 1000 Å, 300 x 8 mm, 10 µm), PSS WinGPC UniChrom software and a RID detector. Calibration was performed using pullulan standards and ethylene glycol as internal standard. The eluent was 50 mM NaNO₃ in water with a flow rate of 1 mL/min, a column temperature of 40 °C and an injection volume of 10 µL. Sample preparation was performed by suspending 60–70 mg of sample (oxidised starch) in ~20 mL solvent which was subsequently heated in pressure vials for 60 min at 130 °C, followed by filtration over 0.2 µm filters.

SEM analysis

Scanning electron microscope (SEM) images were acquired on a Fei NovaNanoSEM 650 using a CBS detector and an accelerating voltage of 10 kV. Samples were loaded onto a sample holder and then sputter-coated with a layer of gold (~20 nm) prior to analysis.



Scheme S1. Likely mechanism for the oxidation of starch by dibasic magnesium hypochlorite (DMH) under reaction conditions. Oxidation shown at the a) C6-position of a glucose unit, b) C2-, and C3-position of a glucose unit, and c) C3-position, followed by β -elimination and resulting cleavage of the glycosidic bond at the C1-position. Keto-enol transformations of the formed aldehyde at C2- or C3-positions can occur as well. Scission of glycosidic bonds at the C4- or C6- (for amylopectin) are not shown, but follow similar mechanisms.

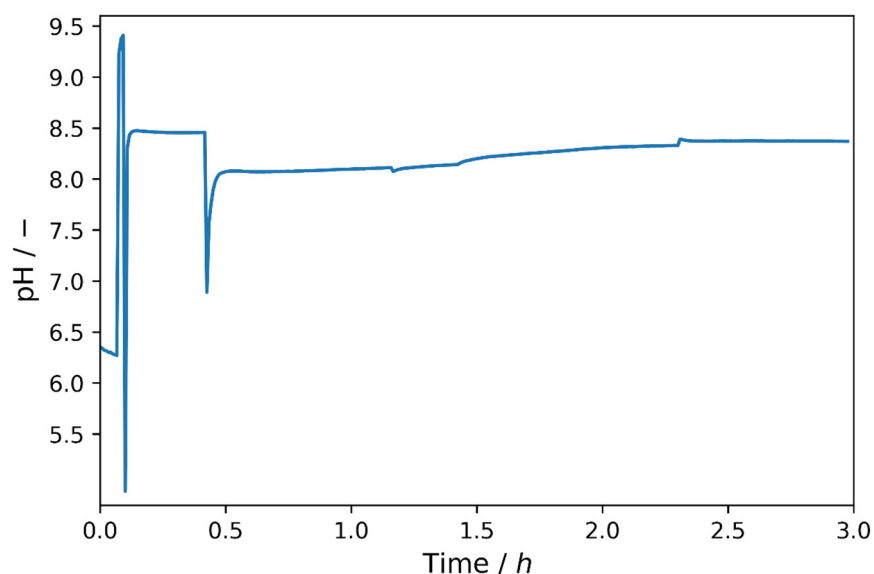


Figure S1. pH followed over the time of the reaction of starch with DMH, without keeping the pH constant using a pH-stat. The pH stays relatively stable due to the equilibrium of acid groups formed and the solubilisation of DMH. Acid was added in two batches, as seen from the two dips in pH at 5 and 30 min.

Table S1. Results of the oxidation of potato starch by NaOCl and DMH at various conditions.

Entry	Oxidant (mol%)	pH	T (°C)	Reaction time (h) ^a	DS _{COOH} (mol/mol)	Starch Recovery Yield (%)	Average M _w (kDa)
1	Native potato starch (-)	-	-	-	0.004	-	-
2	NaOCl (8.5)	8.2	35	3.5	0.029	97	104.1
3	NaOCl (5.5)	8.2	35	3	0.022	97	356.4
4	Entry 3—Mg exchanged	-	-	3	"	98	"
5	DMH (4.2)	8.2	35	8	0.020	97	174.7
6	DMH (4.2)	8.2	45	6.5	0.018	96	337.6
7	Entry 6—Na exchanged	-	-	3	-	97	"
8	DMH (8.5)	8.2	45	7.1	0.033	78	111.8
9	DMH (4.2)—No base post-treatment	8.1	45	2.5	0.022	97	272.7
10	DMH (4.2)—No pH stat, no base post-treatment	8 – 8.4 ^d	45	3	0.019	96	279.3
11	NaOCl (5.5)—Mg(OH) ₂ added (8.5)	8.2	45	4	0.022	96	268.5
12	DMH (4.2)	7	45	2.2	0.018	92	110.1
13	DMH (4.2)	9	45	>7 ^b	0.005	99	707.9 ^c
14	Ca(OCl) ₂	8.2	35	3.1	0.027	98	288.2

^aTotal reaction time from the start of hypochlorite addition until no more active -OCl was detected, including base post-treatment

^bStill active chlorine present when reaction was stopped which was destroyed with sodium thiosulfate prior to acid work-up.

^cHPSEC sample difficult to filter, the starch forms a paste making the result of the analysis unreliable

^d2 batches of concentrated HCl were added for a total of 3.09 g HCl (36 %, 31 mmol)

Table S2. Degree of oxidation (DS_{COOH}) and mineral content of NPS and starches oxidized by NaOCl and DMH, as determined by titration and ICP analysis.

Entry	Oxidant (mol%)	pH	T (°C)	DS _{COOH} (mol/mol) ^d	Ca (ppm)	K (ppm)	Mg (ppm)	Na (ppm)	Mg/COOH (mol/mol)
1	Native potato starch (-) ^a	-	-	0.004	155 ± 0.2	701 ± 1.3	43 ± 0.0	85 ± 0.8	0.07
2	NaOCl (8.5)	8.2	35	0.029	82 ± 0.0	119 ± 0.9	11 ± 0.1	3896 ± 16	0.003 ^b
3	NaOCl (5.5)	8.2	35	0.022	83 ± 0.2	111 ± 0.3	17 ± 0.3	3287 ± 10	0.005 ^b
4	Entry 3—Mg exchanged	-	-	“	19 ± 0.3	12 ± 1.2	873 ± 0.2	69 ± 0.9	0.26
5	DMH (4.2)	8.2	35	0.020	124 ± 0.5	19 ± 0.5	1732 ± 4.4	354 ± 0.6	0.57
6	DMH (4.2)	8.2	45	0.018	113 ± 0.0	11 ± 0.5	1597 ± 2.3	308 ± 0.8	0.61
7	Entry 6—Na exchanged	-	-	“	23 ± 0.0	7 ± 0.7	65 ± 0.3	2804 ± 4.3	0.02 ^b
8	DMH (8.5)	8.2	45	0.033	82 ± 0.0	16 ± 0.7	2406 ± 0.2	681 ± 1.2	0.49
9	DMH (4.2)—No base post-treatment	8.1	45	0.022	n.d.	n.d.	n.d.	n.d.	n.d.
10	DMH (4.2)—No pH stat, no base post-treatment	8 – 8.4	45	0.019	180	3	2279	50	0.80
11	NaOCl (5.5)—Mg(OH) ₂ added (8.5)	8.2	45	0.022	69 ± 0.0	48 ± 0.4	862 ± 1.1	1352 ± 2.4	0.26
12	DMH (4.2)	7	45	0.018	99 ± 0.0	13 ± 0.7	1444 ± 0.7	277 ± 0.4	0.53
13	DMH (4.2)	9	45	0.005	63 ± 0.0	n.d.	1529 ± 2.6	28 ± 0.9	1.96
14	Ca(OCl) ₂	8.2	35	0.027	3369 ± 1.2	60 ± 0.7	21 ± 0.2	578 ± 2.3	0.005 ^c

n.d.=Not determined

^aPhosphorus content of 823 ppm, assumed to not change for oxidised starches.

^bNa/COOH of entries 2, 3, 7, 15: 0.9, 1.0 and 1.1, respectively.

^cCa/COOH is 0.51.

^dAverage error determined to be <0.001 mol/mol

Table S3. Gelatinisation properties of starches oxidised by DMH and NaOCl as determined by DSC. T_o = Gelatinisation onset temperature; T_p = Gelatinisation peak temperature; T_E = Gelatinisation end temperature; ΔH = Gelatinisation enthalpy.

Entry	Oxidant (mol%)	pH	T (°C)	T_o (°C)	T_p (°C)	T_E (°C)	ΔH (J/g)
1	Native potato starch (-)	-	-	61.3	65.2	71.5	18.6
2	NaOCl (8.5)	8.2	35	55.8	60.4	66.7	15.8
3	NaOCl (5.5)	8.2	35	59.9	63.1	69.0	20.8
4	Entry 3—Mg exchanged	-	-	63.0	66.9	73.8	20.3
5	DMH (4.2)	8.2	35	62.5 \pm 0.06	66.2 \pm 0.1	72.6 \pm 0.7	19.3 \pm 2.3
6	DMH (4.2)	8.2	45	64.5	68.0	74.6	19.9
7	Entry 6—Na exchanged	-	-	60.6	65.0	73.4	20.4
8	DMH (8.5)	8.2	45	61.7	66.4	74.1	17.6
9	DMH (4.2)—No base post-treatment	8.1	45	63.0	66.6	72.2	17.2
10	DMH (4.2)—No pH stat, no base post-treatment	8 – 8.4	45	65.2	68.2	73.7	22.4
11	NaOCl (5.5)—Mg(OH) ₂ added (8.5)	8.2	45	63.1	66.9	74.6	18.2
12	DMH (4.2)	7	45	65.0	69.1	76.4	21.1
13	DMH (4.2)	9	45	65.8	68.6	74.1	23.9
14	Ca(OCl) ₂	8.2	35	60.5	64.6	70.6	16.8

Table S4. Pasting properties of starches oxidised by NaOCl and DMH as determined by RVA.

Entry	Oxidant (mol%)	pH	T (°C)	Peak viscosity (mPa·s)	Hold viscosity (mPa·s)	Breakdown (mPa·s)	Final viscosity (mPa·s)	Setback (mPa·s)
1	Native potato starch (-)	-	-	_a	_a	_a	_a	_a
2	NaOCl (8.5)	8.2	35	5595	158	5437	539	381
3	NaOCl (5.5)	8.2	35	7129	490	6639	2503	2013
4	Entry 3— Mg exchanged	-	-	9771	558	9213	2774	2216
5	DMH (4.2)	8.2	35	4507	366	4141	2332	1966
6	DMH (4.2)	8.2	45	7109	748	6361	5495	4747
7	Entry 6—Na exchanged	-	-	8401	725	7676	5925	5200
8	DMH (8.5)	8.2	45	1210	84	1126	262	178
9	DMH (4.2)—No base post-treatment	8.1	45	16200	1227	14973	7870	6643
10	DMH (4.2)—No pH stat, no base post-treatment	8 – 8.4	45	5278	438	4840	2796	2358
11	NaOCl (5.5)—Mg(OH) ₂ added (8.5)	8.2	45	6981	577	6404	2711	2134
12	DMH (4.2)	7	45	1285	113	1172	1014	901
13	DMH (4.2)	9	45	_a	_a	_a	_a	_a
14	Ca(OCl) ₂ (4.2)	8.2	35	4336	293	4043	992	699

^aViscosity too high for measurement to be completed at a concentration of 30 wt% (a thick gel is formed during the RVA measurement within 3 min).

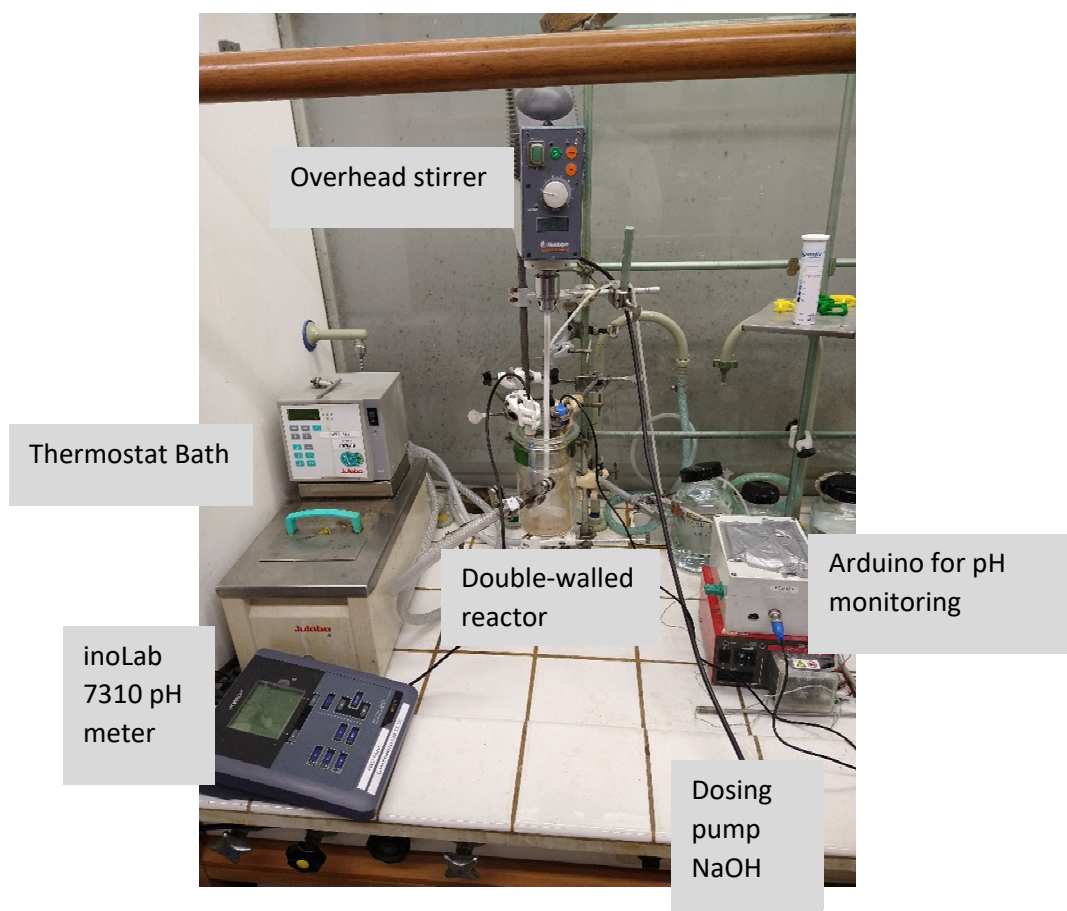


Figure S2. Reactor setup used for oxidation of starch with dibasic magnesium hypochlorite (DMH). For details on the used equipment see experimental.

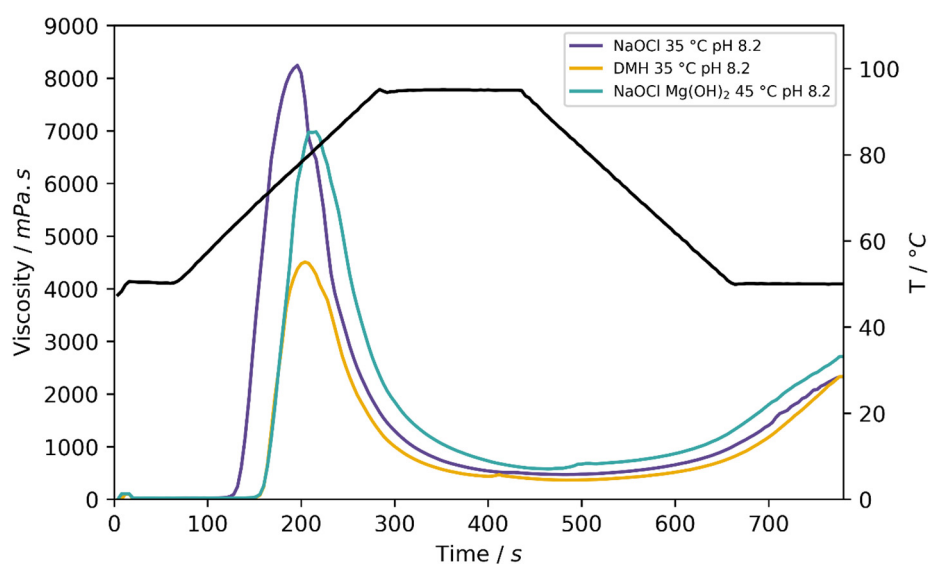


Figure S3. RVA pasting curves (30 wt% in water) of starches oxidized by NaOCl or DMH at pH 8.2 using 5.5 mol% (purple, blue) or 8.5 mol% OCl (yellow).

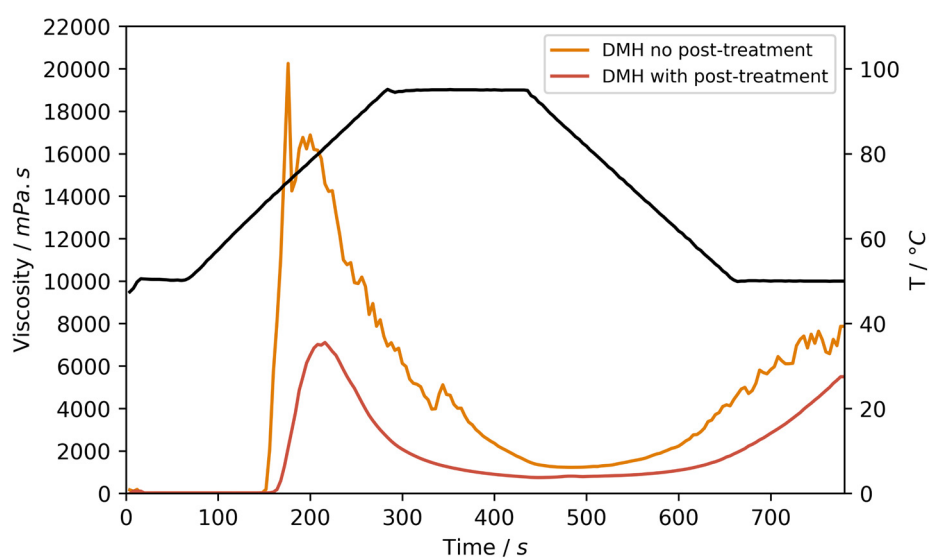


Figure S4. RVA pasting curves (30 wt% in water) of starches oxidized by DMH at 45 °C using 8.5 mol% OCl at pH 8.1 (no post-treatment) and pH 8.2 (with post-treatment).

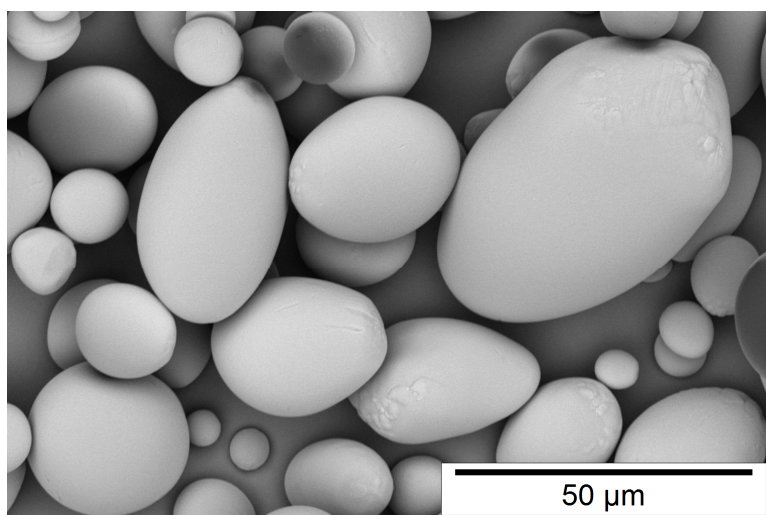


Figure S5. Scanning electron microscope (SEM) image of native potato starch.

References

1. Broekman, J.O.P.; Genuino, H.C.; Heeres, H.J.; Brinksma, J.; Wielema, T.; Deuss, P.J. Benign Catalytic Oxidation of Potato Starch Using a Homogeneous Binuclear Manganese Catalyst and Hydrogen Peroxide. *Catal. Sci. Technol.* **2023**, *13*, 1233–1243, doi:10.1039/D2CY01629J.