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Effects of Mineral Elements and Annealing on the Physicochemical Properties of Native Potato Starch

Johanna A. Thomann [1,2,3], Michael Polhuis [4], Alessia Lasorsa [5], Hero J. Heeres [2] and André Heeres [1,3,*]

[1] Research Centre Biobased Economy, Hanze University of Applied Sciences, Zernikeplein 11, 9747 AS Groningen, The Netherlands; j.a.thomann@pl.hanze.nl
[2] Green Chemical Reaction Engineering, Engineering and Technology Institute Groningen, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands; h.j.heeres@rug.nl
[3] Innovation Hub East Groningen, Billitonweg 1, 9640 AE Veendam, The Netherlands
[4] Royal Avebe Innovation Center, Zernikelaan 8, 9747 AA Groningen, The Netherlands
[5] Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
* Correspondence: a.heeres@pl.hanze.nl; Tel.: +31-505-952-517

Abstract: Native potato starch is an excellent carrier of minerals due to its inherent ion exchange capacity. Mineral enrichment not only changes the nutritional value but also influences starch pasting and swelling properties. Hydrothermal treatments like annealing constitute a straightforward and green way to tune functional properties. Here, novel combinations of mineral enrichment and annealing were studied. Ion exchange was readily achieved by suspending starch in a salt solution at room temperature over 3 h and confirmed by ICP-OES. Annealing at 50 °C for 24 h using demineralized water or salt solutions strongly affected pasting, thermal, and swelling properties. The obtained XRD and DSC results support a more ordered structure with relative crystallinity increasing from initially 41.7% to 44.4% and gelatinization onset temperature increasing from 60.39 to 65.94 J/g. Solid-state NMR spectroscopy revealed no detectable changes after annealing. Total digestible starch content decreased after annealing from 8.89 to 7.86 g/100 g. During both ion exchange at room temperature and annealing, monovalent cations promoted swelling and peak viscosity, and divalent cations suppressed peak viscosity through ionic crosslinking. The presented combination allows fine-tuning of pasting behavior, potentially enabling requirements of respective food applications to be met while offering an alternative to chemically modified starches.

Keywords: hydrothermal modification; starch annealing; mineral enrichment; native potato starch; food industry; nutrients

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1. Introduction

Chemically modified starches are frequently used in the food sector. However, increasingly stringent environmental regulations coupled with changes in consumer perspectives and preferences are exerting pressure on the current portfolio of chemically modified starches. As a result, starch companies are increasingly focusing on more environmentally benign approaches (e.g., enzymatic and physical) to develop sustainable products meeting the changing requirements of the food sector [1–4].

Starch is biosynthesized in various plant organelles and functions mainly as an energy reserve. Starch is naturally found in granular form and consists of two types of polysaccharides, namely amylose (AM) and amylopectin (AP). The monomeric units are D-glucose, connected through α-1,4-glycosidic bonds to form long chains. Amylopectin has a more branched structure than the mostly linear amylose through α-1,6-glycosidic bonds that introduce side chains. These α-1,6-glycosidic linkages also occur in amylose, however, but to a much smaller extent than in amylopectin. Potato amylopectin tends to be less branched and have longer chain lengths than amylopectin from other starches [5]. Besides amylose and amylopectin, other components of starch are lipids, proteins, minerals, and phosphorus [6].

Phosphorus is present either in the form of phospholipids or phosphate monoesters. The former occurs more commonly in cereal and pulse starches, whereas potato starch is known for its uniquely high phosphorus content in the form of phosphate monoesters. The concentration of phosphate groups in potato starch depends on the soil quality and growing conditions. This property of potato starch is responsible for some of its unique pasting properties [5]. For example, native potato starch (NPS) has a pronounced swelling power and peak viscosity compared to other starches due to repulsion of the negatively charged phosphate groups enabling water penetration into the granule interior, among other factors. On the other hand, its long AM and AP chains make potato starch capable of withstanding shear forces for longer than starches that, albeit having, e.g., pore channels also facilitating hydration, show early disintegration and breakdown [6]. Phosphate groups are bound to C-6 (60%) and C-3 (40%) of the glucose units of amylopectin and are mostly located on the longer chains. Typically, phosphorylated glucose units of potato amylopectin are nine glucose units away from α-1,6 branching points. The majority (74–78%) of phosphorus is present in the amorphous region of AP [5–7]. Using XRF elemental and phase contrast maps, Buléon et al. visualized that in native potato starch granules, the highest phosphorus levels are at the periphery of the granule, while low amounts are found at the hilum [7].

The negative charges on the phosphate group are balanced by cations, thereby significantly increasing the amount of minerals in potato starch compared to other starches.

The mineral composition of starch is dependent on the growing conditions of the plants and the process conditions during starch extraction (i.e., composition/hardness of process water). The main minerals found in starch are potassium, sodium, calcium, and magnesium. Despite being minor components, minerals have a pronounced impact on the properties of native potato starch (NPS). Exchange of the cations normally present in NPS for individual mono- or divalent cations changes both the physical and thermal properties of potato starch. Several studies investigated the correlations of pasting and thermal properties with the natural or altered mineral composition of potato starches [8–11]. Zhou et al. studied the influence of a variety of monovalent cations and anions on swelling and pasting behavior [11]. Other research groups have focused on the influence of divalent cations, proposing an ionic crosslinking effect between these cations and the negatively charged potato starch phosphate groups [12,13]. Besides influencing certain properties of starch, enriching potato starch with target minerals is an easy way to fortify staple foods and meet dietary requirements. This could include, for example, the prevention of magnesium deficiency for at-risk groups [14,15].

Since the properties of native starches do not always meet the requirements for food applications, chemical or physical modifications are often necessary. Taking environmental concerns and consumer preferences into account, hydrothermal modifications seem a promising way of tuning starch properties, as they require no toxic chemicals, nor do they produce problematic waste streams. Hydrothermal treatments vary in terms of employed moisture contents, temperatures, and treatment times. One example is annealing, where high moisture contents ($\geq$40%) and temperatures below the gelatinization temperature of the respective starch are used [16,17]. Annealing can change the arrangement of polysaccharide chains, thereby altering its crystallinity and, as a result, strongly influencing, among others, the pasting properties of starch [16,17]. Another interesting aspect of hydrothermal modification is its influence on starch digestibility. Higher proportions of starch that are resistant to intestinal digestion and function as probiotic fiber could be beneficial to gut health [16,18].

To the best of our knowledge, only a few studies have investigated the combination of mineral enrichment and hydrothermal modifications [19,20]. Zhang et al. studied the dual modification of potato starch using dry heat treatment and Ca enrichment to produce low-viscosity starch products [19]. In a recent study by Yang et al., a mixture of native potato starch, sodium tripolyphosphate, and sodium chloride was subjected to hydrothermal treatment to prepare gluten-free noodle formulations [20].

This study aims to demonstrate the potential for the development of healthy and environmentally benign starch-based food ingredients high in targeted essential minerals and resistant starch prepared by novel combinations of cation enrichment and hydrothermal modifications of starch. For this, regionally sourced potato starch and salts were used. The properties of the obtained starch products were then compared to native potato starch and to starches that were mineral-enriched or annealed only. Compositional changes were investigated by ICP-OES and titrations for amylose content determination. Pasting, swelling and thermal properties were studied using a rapid visco analyzer (RVA), swelling power determinations, and differential scanning calorimetry (DSC). Changes in crystallinity in native potato starch after annealing were studied by means of XRD, solid-state NMR spectroscopy, and DSC. Lastly, the proportions of the digestible and resistant starch of native potato starch before and after annealing were determined with commercial enzymatic assays.

2. Materials and Methods

2.1. Chemicals

Native and drum-dried potato starches were provided by Royal Avebe (Veendam, The Netherlands). Food-grade $MgCl_2 \cdot 6H_2O$ and technical-grade $CaCl_2$ were provided by Nedmag (Veendam, The Netherlands). KCl and NaCl (Acros Organics, Geel, Belgium) had a purity of 99+% and 99.5%, respectively. For the preparation of aqua regia, 37% hydrochloric acid (Boomlab, Meppel, The Netherlands) and 65% nitric acid (SigmaAldrich, Zwijndrecht, The Netherlands) were used. ICP standards for Mg, Ca, Na, K, and P (LabKings, Hilversum, The Netherlands) had a concentration of either 1 g/L or 10 g/L. Indium (pure metal) for the calibration of the DSC device was supplied by the manufacturer (Thermo Fisher, Hilversum, The Netherlands). All chemicals were used as received unless otherwise indicated.

2.2. Ion Exchange Procedure

The ion exchange reactions were performed as previously published by Noda et al. [9]. The concentrations of the salt solutions were 1% (*w*/*w*) for $CaCl_2$, 2% (*w*/*w*) for $MgCl_2 \cdot 6H_2O$, and 5% (*w*/*w*) for both NaCl and KCl solutions. Native potato starch was dispersed in salt solution (25% (*w*/*w*) dry starch in solution). The amount of starch was corrected for moisture, which was determined using a moisture content analyzer (Mettler Toledo HE73, Mettler Toledo, Selangor, Malaysia). The suspension was stirred for 3 h before filtering in vacuo, followed by washing with demineralized water (five times the amount of starch) and drying in a ventilation oven overnight at 35–40 °C in an air atmosphere.

2.3. Annealing Procedure

Annealing was performed in batch in double-walled reaction vessels with an overhead stirrer, connected to a water bath controlled by specialized software (Labworldsoft, Version 6). First, 200 g native potato starch (NPS) on a dry basis was dispersed in 600 g solution, which was either demineralized water or one of the salt solutions, yielding a starch concentration of 25%. The reactor was closed and heated to 50 °C for 24 h, including the heating phase (3 h) and cooling phase (3 h). Conditions (starch/water ratio and salt concentrations) were adapted from the ion exchange procedure as described above. Afterwards, the resulting starch product was filtered in vacuo and washed five times with 200 mL demineralized water. After drying in a ventilation oven overnight at 35–40 °C, the starch product was ground and stored at room temperature until analyzed.

2.4. Inductively Coupled Plasma—Optical Emission Spectroscopy (ICP-OES)

For determination of mineral contents, ca. 5 g starch (wet weight) was weighed into a porcelain cup (exact mass and moisture noted) and placed in an oven at 500–550 °C for 1 h. When ashing was incomplete, the samples were kept in the oven for another hour.

Next, the ashed samples were suspended in ca. 60–80 mL ultrapure water in dedicated digestion beakers and 12 mL of 37% hydrochloric acid and 4 mL of 65% nitric acid (aqua regia) were added. The temperature was set to 130 °C, and the digestion beakers were placed in the heating device for 30–45 min. After cooling, ultrapure water was added to yield exactly 100 mL. Syringes and syringe filters (LLG Labware-syringe filters SPHEROS, PES, 0.22 µm, diameter 25 mm, green) were used to avoid contamination with ash particles. For phosphorus determination, 1 g of starch sample was used as is (exact mass and moisture noted) and prepared in digestion beakers as already described for the ashed samples. Calibration standards containing the ions of interests and aqua regia were prepared in four different concentrations and measured with each measurement. The samples and calibrations standards were then measured by ICP-OES (Agilent Technologies 5110, Autosampler SPS4, Santa Clara, CA, USA), and the wavelengths were as follows: 317.933 nm for calcium, 766.491 nm for potassium, 588.995 nm for sodium, 383.829 nm for magnesium, and 213.618 nm for phosphorus. To establish reproducibility of cation determination (including the ashing step), native potato starch was measured five times. The reproducibility of phosphorus determination (without the ashing step) was established by measuring native potato starch in duplicate.

2.5. Amylose Content

Amylose contents were measured by iodine complex formation using the titration techniques reported by Bates et al. [21]. Native potato starch before and after annealing was measured in duplicate.

2.6. X-ray Diffraction (XRD)

The long-range order of the samples was analyzed using a Bruker Advance D8 Powder XRD with theta-theta geometry (Bruker, Billerica, MA, USA). Measurements were performed between 3 and 50° 2θ (time/step = 0.65, increment = 0.03). Relative crystallinity was determined using Spectragryph—optical spectroscopy software by performing a baseline correction (Advanced Baseline; adaptive 25% coarseness) and comparing the integrals of the original (amorphous and crystalline) and baseline-corrected (crystalline) spectrum (integration by area from 3° to 30° 2θ) [22].

$$\text{Relative crystallinity} = \text{area of crystalline peaks}/(\text{area of crystalline peaks} + \text{area of amorphous background}) \quad (1)$$

2.7. Solid-State ^{13}C CP/MAS NMR Spectroscopy (ssNMR)

Solid-state NMR experiments were carried out on a Bruker Avance Neo NMR spectrometer equipped with a standard bore 14.1 T magnet and a 3.2 mm EFree HCN CPMAS probe from Bruker Biospin. Approximately 40 mg of starch samples (with a moisture content of ca. 15% w/w) were packed in thin-wall 3.2 mm rotors and sealed with a Vespel bottom and drive cap. The 1D ^{13}C cross-polarization (CP) magic angle spinning (MAS) spectra were acquired at 15 kHz MAS and temperature set to 293 K under the following conditions: ^{1}H 90° pulse was set to 2.5 µs; CP was performed with a contact time (CT) of 1 ms using a 70%–100% ramped-amplitude shape (on ^{1}H) and a 50 kHz square pulse on ^{13}C; recycle delay was 3 s and number of scans 3 k. During acquisition, a two-pulse phase-modulated (TPPM) decoupling scheme was employed using a pulse length for the basic decoupling units of 5.8 µs at rf field strength of ca. 83 kHz [23]. Chemical shifts were referenced to aqueous 2,2-dimethyl-2-silapentane-5-sulfonic acid using the indirect method, by measuring adamantane ^{13}C signals [24]. Spectra were processed in TopSpin 4.0.7.

2.8. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) was used to measure the thermal properties of the starches. Indium standards were used for calibration. A DSC25 (Thermo Fisher with Autosampler) was used to determine the onset, peak, conclusion temperatures, and enthalpy of the endothermic event. Samples of 5 to 10 mg were prepared from starch in water suspension (20% starch on dry basis) and placed in a Tzero Pan with a syringe and sealed with Tzero Hermetic Lids using a crimper press. The sample pan was heated to 85 °C or 95 °C with a heating rate of 10 °C/min. The measurements were performed at least in duplicate. For statistical analysis, a one-way ANOVA and a Tukey HSD test was carried out with significance differences defined at $p < 0.05$.

2.9. Rapid Visco Analyzer (RVA)

An RVA4500 was used with disposable RVA cups and stirrers (Perten Instruments, Stockholm, Sweden). RVA measurements were carried out using starch on 5% dry weight based on the total mass of 28.0 g filled up with demineralized water. Measurement conditions are shown below in Table 1. Reproducibility was established by measurement of native potato starch in triplicate.

Table 1. Standard measurement profile for RVA measurements.

Time (hh:mm:ss)	Function Type	Value
00:00:00	Temp	50 °C
00:00:00	Speed	960 rpm
00:00:10	Speed	160 rpm
00:01:00	Temp	50 °C
00:04:42	Temp	95 °C
00:07:12	Temp	95 °C
00:11:00	Temp	50 °C
00:13:00	End	

2.10. Swelling Power (SWP) and Solubility

Swelling power and solubility of starch were determined at two measurement temperatures by adapting the procedure by Zhou et al. [11]. Starch suspensions (2% (w/w) on a dry basis) were heated at 70 °C or at 90 °C, respectively, for 30 min while shaking at 200 rpm, followed by rapid cooling in ice to room temperature. The suspension was then centrifuged at 3600 g for 40 min. Supernatant was separated carefully using Pasteur pipettes, and the gel-like residue was weighed. The ratio between the residue and initial amount of starch was calculated (g/g of starch on dry weight basis) as the swelling power. The supernatant was pipetted off carefully into tared test tubes, and the test tubes were placed in a vacuum oven until all liquid was evaporated. The dry residue was then weighed and used for calculation of solubility. Measurements were performed in triplicate. For statistical analysis, a one-way ANOVA and a Tukey HSD test were carried out, with significance differences defined at $p < 0.05$.

$$\text{Solubility} = (\text{sample weight (dry basis)} \times 100)/\text{sediment weight} \tag{2}$$

$$\text{Swelling power} = (\text{gel weight} \times 100)/(\text{sample weight (dry basis)} \times (100\text{-solubility}) \tag{3}$$

2.11. Resistant Starch Content

The digestibility of the starch samples was determined using a resistant starch assay kit from Megazyme following the procedure from Englyst et al. with some adaptations, as follows [25]. The calibration was performed using five concentrations of glucose standard in duplicate, and the GOPOD procedure was downscaled to use microtiter plates for incubation and measurement with spectrophotometer. The calculations of rapid digestible starch (RDS) (measured after 20 min), slowly digestible starch (SDS) (measured after 2 h), total digestible starch (TDS), and resistant starch (RS) (measured after 4 h) were changed accordingly. Furthermore, additional aliquot samples were taken at t(0) and t(end) (total digestible starch). The starch was used as is, thus in granular form (typically 10 to 110 µm for native potato starch [6]).

3. Results and Discussion

3.1. Ion Exchange and Annealing Combined with Ion Exchange

Mineral-enriched potato starch samples (Mg, Ca, Na, and K) were readily prepared by following a procedure of Noda et al. [9] that was developed for enrichment with divalent cations. All salt concentrations were chosen to provide an excess of the cation of interest during ion exchange, and a thorough washing step ensured only bound cations remained. For the divalent cations, these concentrations were 1% (*w*/*w*) for calcium chloride (c($CaCl_2$) = 0.090 mol/L) and 2% (*w*/*w*) for magnesium chloride hexahydrate (c($MgCl_2 \cdot 6\ H_2O$) = 0.098 mol/L). For monovalent cations, 5% (*w*/*w*) was chosen for both sodium (c(NaCl) = 0.901 mol/L) and potassium chloride (c(KCl) = 0.706 mol/L).

For all annealed starches, typical heating profiles and temperatures below the starch gelatinization temperature were chosen [16,26–28]. A picture of the annealing set-up is provided in the Supplementary Materials. Starch recovery was generally high due to the straightforward work-up and implies no starch dissolution taking place under the applied conditions. The success of the ion exchange procedure at room temperature and during annealing was confirmed by the analysis of its mineral composition as described in the following section.

3.2. Compositional Changes

Changes in the elemental composition of native potato starch, mineral-enriched starches, and all annealed starches were measured by ICP-OES. The phosphorus content of the untreated native potato starch was 748 ± 3 ppm, and the amylose content was 239.66 ± 0.22 mg/g (24.0%), which are typical values for native potato starch [6]. Cation enrichment of the native potato starch did not greatly affect the amount of phosphorous present (see Table 2).

Table 2. Composition of starch samples as analyzed by ICP-OES.

Sample	Ca (µmol/g)	K (µmol/g)	Mg (µmol/g)	Na (µmol/g)	P (µmol/g)
NPS	4.16 ± 0.16	17.67 ± 0.08	1.84 ± 0.03	2.55 ± 0.17	24.16 ± 0.11
NPS Mg	0.70	0.15	15.88	0.48	24.57
NPS Ca	16.99	0.03	0.29	0.48	22.41
NPS Na	0.62	0.20	0.37	30.71	24.31
NPS K	0.75	29.16	0.33	0.65	23.99
ANN NPS	4.74	14.27	1.93	3.57	23.37
ANN NPS Mg	1.32	0.38	14.94	0.43	-
ANN NPS Ca	14.37	0.36	0.21	0.35	-
ANN NPS Na	0.50	0.46	0.21	28.71	-
ANN NPS K	0.45	30.08	0.25	0.39	-

Abbreviations: Native potato starch enriched with Mg (NPS Mg); native potato starch enriched with Mg during annealing (ANN NPS Mg), etc.

Starch granules undergo a reversible swelling with increased AP–AM interactions expected when heating in water at elevated temperature below the gelatinization temperature [16,17]. The AM content remained roughly constant after annealing with 23.5% for ANN NPS. Titrations of ANN NPS Mg, ANN NPS Na, and ANN NPS K all yielded an AM content of 23.3%; and ANN NPS Ca yielded 23.2%. Decreases in AM content remained lower than 1%. In terms of mineral composition, annealing itself caused a slight decrease of K levels, which were high in NPS. The levels of Mg and Ca were relatively stable, while a slight increase in Na was observed in ANN NPS.

Ion exchange led to a concentration increase in the target metal ion and depletion of other cations. The results for starches annealed with simultaneous ion exchange correspond to those for ion exchange at room temperature. This means that ion exchange does not seem to be affected by increased temperature (room temperature to 50 °C) and longer exposure time (3 h to 24 h) (see Table 2).

For the starches enriched with monovalent cations, these levels were around 29–31 µmol/g. For the starches enriched with divalent cations, these were around 15–17 µmol/g. The results for NPS Mg (15.88 µmol/g or 386 ppm Mg) and NPS Ca (16.99 µmol/g or 681 ppm Ca) are in agreement with data published by Noda et al. in 2014 [9]. The levels of monovalent cations were therefore twice as high as levels of divalent cations, matching their valence.

A few research groups have questioned the coordination sites for multivalent cations in potato starch [12,29]. Besides the phosphate moieties, the glucose units of starch possess five potential coordination sites, namely the oxygen atoms of the three hydroxyl groups of the pyranose ring or of the glycosidic bond. One study of potato starch and its complexes with various transition metals found that Werner-type complexes are formed, in which the cations are coordinated to phosphate groups and the lone pairs of the hydroxyl groups in their vicinity. Importantly, they reported preferential coordination of cations to the phosphate monoester group of amylopectin [29]. An ionic crosslinking effect of divalent cations via adjacent phosphate monoester groups has also been suggested by different authors [5,12,30]. Herein, a divalent cation coordinates to two phosphate groups, thereby crosslinking the respective chains on which the negatively charged functional groups are located. The phosphorylated glucose units are clustered in close proximity to each other in the amorphous region of amylopectin, with exception of the hilum, and located at least nine glucose units away from branching points [6]. Due to their close proximity, ionic crosslinking between adjacent phosphate monoesters is theoretically feasible despite the overall low levels of phosphorus in potato starch.

3.3. Crystallinity

3.3.1. Long-Range Order

X-ray diffraction was used to study crystalline type and obtain an indication of changes in the long-range order of native potato starch after annealing. Characteristic peaks for B-type starch were observed at 5°, 17°, and 22–24° 2θ for both NPS and ANN NPS [31] (Figure 1). Relative crystallinity was calculated using the two-phase model, as frequently applied in the literature [32]. Native potato starch showed a relative crystallinity of 41.7%, while the ANN NPS had a slightly increased relative crystallinity of 44.4%. This is attributed to partial removal of defects through increased AP–AP and AP–AM interactions and induced entanglement of free AM molecules with outer AP chains during annealing, thereby affording more perfect crystalline structures within the starch granules [16].

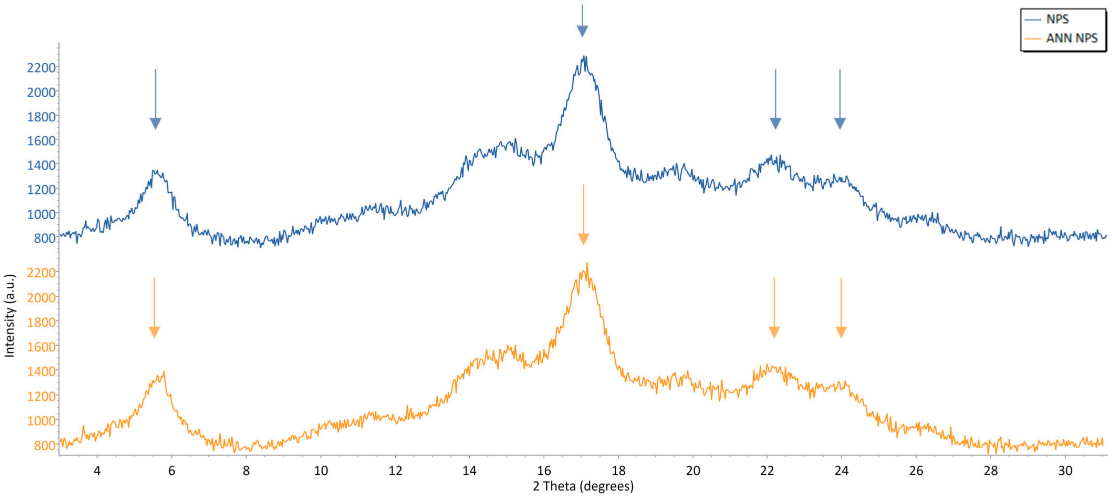


Figure 1. X-ray diffractograms of native potato starch (NPS) (above in blue) and annealed native potato starch (ANN NPS) (below in orange). The crystalline type remains B-type after modification with characteristic peaks at 5°, 17°, and 22–24° 2θ.

3.3.2. Short-Range Order

Other techniques for estimating crystallinity and particularly short-range order in starches include FT-IR and solid-state NMR spectroscopy [33–36]. Similar to the approach taken for long-range order (Section 3.3.1), native potato starch was measured before and after annealing. The corresponding 1D ^{13}C CP/MAS NMR spectra are shown in Figure 2. The respective contributions of crystalline and amorphous signals in the solid-state NMR spectra of native potato starch were reported earlier by López-Rubio et al. [37].

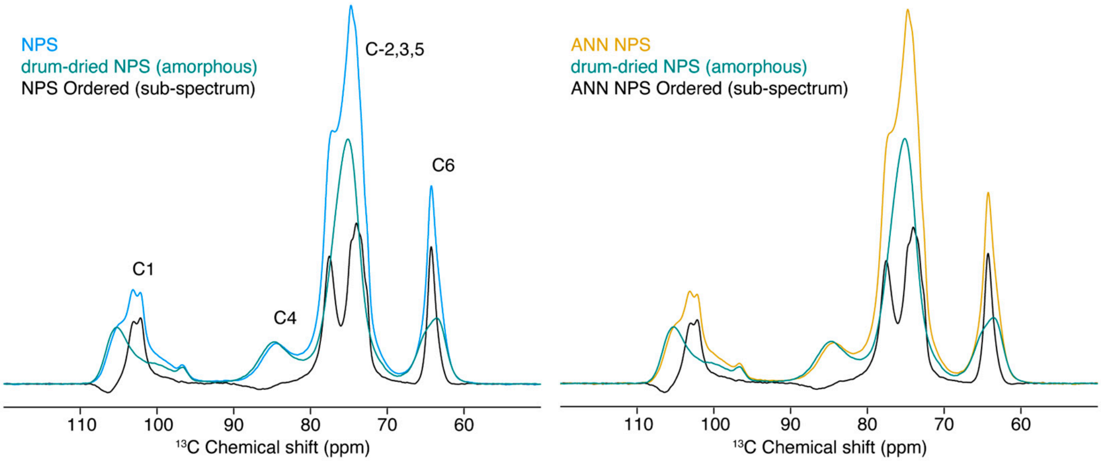


Figure 2. The 1D ^{13}C CP/MAS NMR spectra of native potato starch before (left, blue spectrum) and after annealing (right, orange spectrum). The corresponding ordered sub-spectra were derived by subtraction of the spectrum for the amorphous phase (drum-dried native potato starch) by scaling the intensity of the amorphous spectrum so that the resultant intensity was zero at around 84 ppm.

The signal around 64 ppm corresponds to C6 of the glucose units, while peaks within the 70 to 80 ppm range are associated with C2, C3, and C5. The peak attributed to amorphous C4 carbon presents around 84 ppm, and the signal at approximately 103 ppm corresponds to C1. Sub-spectra due to the ordered components were generated by scaling the intensity of the amorphous spectrum so that zero intensity was obtained at 84 ppm, as previously described [37]. In the ordered sub-spectra, no detectable differences were observed between the two samples, indicating that the short order was not altered to a detectable extent. The doublet at around 103 ppm, distinctly visible in the ordered sub-spectra, is indicative of the typical B-type crystalline polymorphic form [36,37]. This is in agreement with XRD results described in the previous Section 3.3.1.

3.4. Thermal Properties

In terms of thermal properties, mineral exchange at room temperature had a small but varying impact on the onset (T_o), peak (T_p), and conclusion (T_c) temperatures compared to native potato starch (NPS) with statistical significance indicated in Table 3. Ion exchange with Na and K resulted in slightly lowered T_o and T_p, whereas Ca and Mg had no effect. Noda et al. reported similar results for Mg- and Ca-fortified native potato starch that had a comparable phosphorous content, although slightly but significantly higher onset and peak temperature after enrichment with divalent cations were reported, whereas gelatinization enthalpies were slightly but significantly lower [9].

Table 3. Thermal properties of native potato starch before and after annealing, with or without enrichment with Na, K, Mg, or Ca. The measurement was performed at least in duplicate and results are given as mean ± standard deviation.

Sample	**T_o (°C)**	**T_p (°C)**	**T_c (°C)**	**ΔH (J/g) ***
NPS	60.39 ± 0.15 d	65.54 ± 0.18 c	70.92 ± 0.26 b	17.00 ± 0.20 b
NPS Mg	60.55 ± 0.11 d	65.33 ± 0.11 c	69.90 ± 0.21 b,c	17.75 ± 0.32 b
NPS Ca	60.70 ± 0.00 d	65.29 ± 0.11 c	71.13 ± 0.06 b	23.45 ± 0.34 a
NPS Na	60.18 ± 0.08 d,e	64.50 ± 0.23 d	69.70 ± 0.40 c	19.90 ± 1.30 a
NPS K	59.74 ± 0.24 e	64.38 ± 0.18 d	68.60 ± 0.08 d	13.30 ± 1.70 c
ANN NPS	65.94 ± 0.14 a	69.16 ± 0.20 a	73.29 ± 0.25 a	21.54 ± 0.89 a
ANN NPS Mg	65.71 ± 0.06 a,b	69.18 ± 0.08 a	73.31 ± 0.20 a	20.45 ± 1.69 a
ANN NPS Ca	65.20 ± 0.22 b,c	68.90 ± 0.34 a,b	73.38 ± 0.30 a	18.70 ± 0.20 b
ANN NPS Na	65.04 ± 0.06 c	68.41 ± 0.01 b	72.84 ± 0.04 a	20.15 ± 0.86 a
ANN NPS K	64.97 ± 0.07 c	68.32 ± 0.12 b	72.72 ± 0.12 a	19.38 ± 0.48 b

Values with the same letter in the same column are not significantly different ($p < 0.05$). * Values for ΔH are prone to larger errors due to settlement of particles in starch water suspensions during preparation of sample pans.

Annealing caused a shift of the thermal transition towards higher temperatures by around 5 °C (Figure 3). This observation hints at a higher order in the crystalline layers after annealing. This is in line with XRD results for native potato starch before and after annealing, as discussed earlier. Moreover, the endothermic peak observed in ANN NPS is less broad than the transition peak of NPS. The increased temperatures (50 °C instead of room temperature) combined with abundant water allows reversible swelling of granules, which increases the mobility of polysaccharide chains and thus facilitates the removal of defects present in the stacked amylopectin double helices. This effect on the crystalline structure during annealing is well known in the literature [16,17].

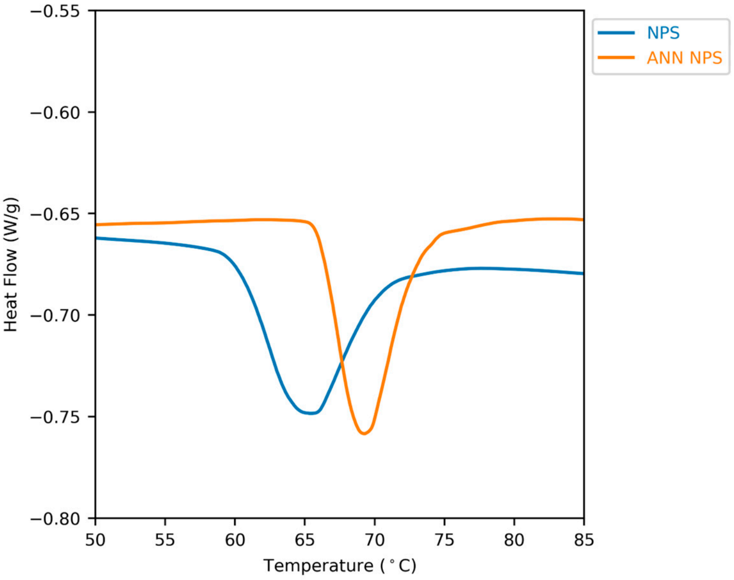


Figure 3. Thermograms of endothermic transition of native potato starch (NPS) before (blue) and after annealing (ANN NPS) (orange).

Similar to what was observed for the cation-enriched starches (NPS Mg, NPS Ca, NPS Na, and NPS K), ion exchange during annealing had only a limited impact on thermal properties. Slightly lower onset, peak, and conclusion temperatures were found for native potato starch annealed in salt solution (ANN NPS Mg, ANN NPS Ca, ANN NPS Na, and ANN NPS K) compared to native potato starch annealed in demineralized water (ANN NPS). The differences within the annealed samples do not exceed 1 °C (Table 3). The enthalpies are also slightly lower for NPS annealed in the presence of cations. Upon gelatinization, a thermal transition takes place that includes melting of the crystallites and decoiling of double helices, ultimately destroying the granular structure [38]. Both endothermic processes describe molecular changes that occur in the crystalline regions of the starch. However, as described earlier, phosphorylated glucose units of AP chains are clustered together in the amorphous regions, which is where any ionic crosslinking of divalent cations would take place. This could be an explanation for the negligible influence of mineral composition changes on thermal properties. Moreover, the coordination of cations to phosphate groups is reversible and weaker than the chemically modified, crosslinked starches, which are characterized by covalent bonds. Disruption of these relatively weak ionic crosslinks upon full gelatinization does not seem to affect the transition temperatures strongly or in an obvious way.

3.5. Pasting Properties

Pasting properties are an important first indicator for the performance of starch products in food applications. The influence of enrichment with monovalent and divalent cations on starch pasting in comparison to the native potato starch can be seen in Figure 4. Both NPS K and NPS Na display higher peak viscosity than the starting material due to replacement of Ca, while the trough and final viscosities are hardly affected. The electrostatic repulsion of phosphate groups in potato starch may be affected by its counter cations, exhibiting varying shielding effects. This could potentially influence the swelling ability of potato starch granules. On the other hand, the proposed ionic crosslinking effect induced by divalent cations, which was discussed earlier, can also be used to rationalize the pasting properties of ion-exchanged starches. No difference in pasting properties was observed between NPS Na and NPS K. Both Na and K have similar hydrated radii of 0.36 and 0.33 nm [39], respectively. This could be part of the reason for their similar impact on pasting properties if the shielding of phosphate groups is indeed the origin of the observed peak viscosity changes.

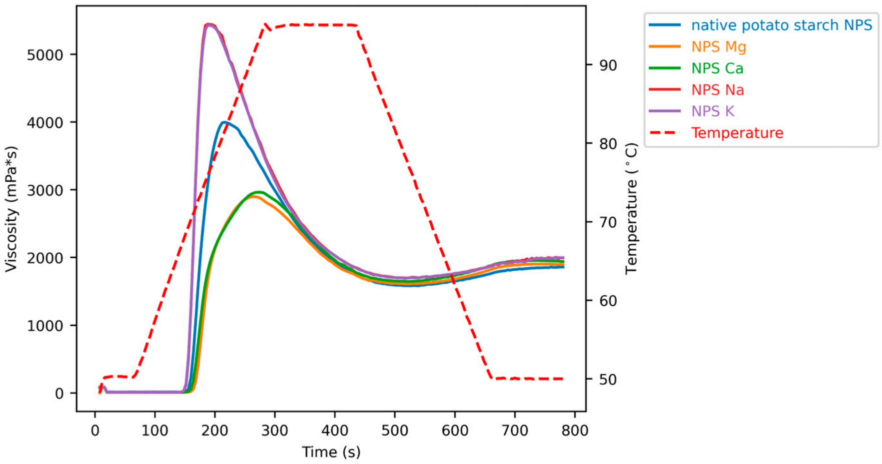


Figure 4. RVA pasting profiles for native potato starch (NPS) before and after enrichment with Na, K, Mg, or Ca.

Enrichment with divalent cations had the opposite effect on peak viscosity compared to starches enriched with monovalent cations. The swelling of granules by penetration of water into amorphous regions is inhibited by ionically crosslinked amylopectin chains. This might also impact the leaching out of free amylose located in the amorphous regions during gelatinization, also impacting viscosity development in RVA measurements. No difference was observed between Mg- and Ca-enriched potato starch, potentially due to their similar hydrated radii of 0.43 and 0.41 nm, respectively [39]. This is consistent with results using aqueous Mg and Ca chloride solutions published by Noda et al. [9]. They reported a decrease in peak viscosity and breakdown suggesting good paste stability and cited ionic crosslinking of adjacent phosphate groups through divalent cations as cause.

The lower breakdown is due to the reduced development of viscosity upon heating. At this stage of the RVA measurement, the granules have disintegrated, and the amylose has dissolved. The AP double helices in the crystalline layers are no longer stacked and start to disentangle adopting a random coil conformation, effectively distancing phosphate groups from each other. Since the phosphorylated glucose units in the amylopectin chains are no longer clustered together, the crosslinking of phosphate groups via divalent cations no longer occurs in the hot paste or during retrogradation. Hence, the trough and final viscosity remain unaffected. This is different from chemically modified, covalently crosslinked starches, where final viscosities are strongly impacted [40].

After annealing of native potato starch, the pasting properties are altered, as can be seen in Figure 5. Annealing led to a decrease of peak viscosity and an increase in both final viscosity and pasting temperature. ANN promotes the interaction of amylose and amylopectin in NPS, perfecting crystalline structures and inhibiting initial granular swelling. This leads to a decrease in peak viscosity but improves the shear stability of the starch granules, as can be seen in the lower breakdown. Higher final viscosities are observed due to the presence of more intact granule remnants [16,28].

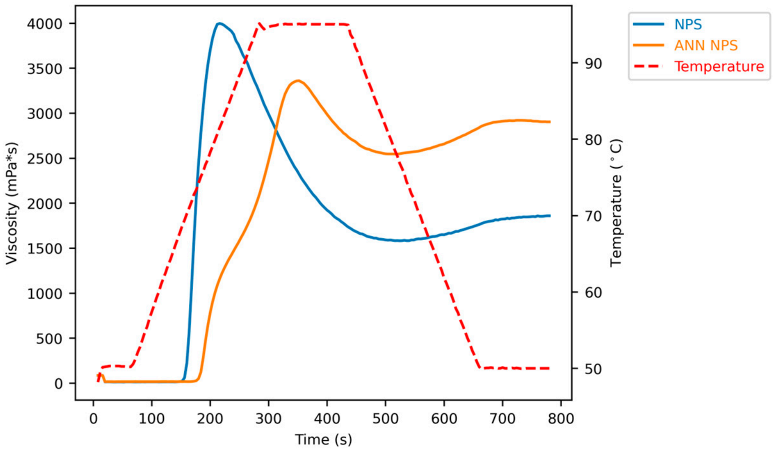
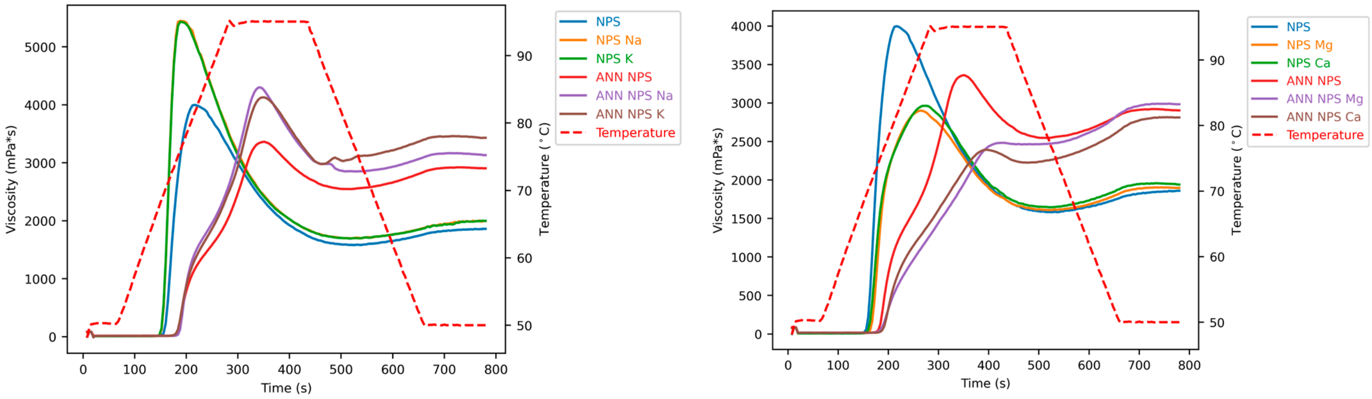


Figure 5. RVA profile of native potato starch NPS before (blue) and after annealing ANN NPS (orange) for 24 h at 50 °C.

During the granular swelling phase, a shoulder becomes visible for ANN NPS that was not observed for the native potato starch NPS. Sieved fractions of ANN NPS revealed that starch granules from different sizes were affected differently by the treatment, with smaller granules showing a more pronounced shoulder, whereas it is almost completely absent in the fraction with larger granules (Figure S3 in the Supplementary Materials).

An increase in pasting temperature from 69.5 °C before annealing to 74.4 °C after annealing indicates a more ordered and therefore reinforced granular structure. These findings are commensurate with increased relative crystallinity as indicated by XRD results and the shift of the endothermic transition towards higher temperatures in DSC measurements.

Next, the influence on pasting properties of minerals present during the annealing step was studied. Similar tendencies to those found for NPS K and NPS Na were observed in ANN NPS K and ANN NPS Na (Figure 6a). The increase in peak viscosity is slightly less pronounced, yet it is still prevalent. The increased amounts of monovalent cations and/or the absence of divalent cations promote the swelling of starch granules, allowing a higher peak viscosity development before the granule breakdown and leaching of amylose occurs. As before, the trough viscosities after granular breakdown and final viscosities after retrogradation appear to be less influenced by altered mineral composition than the peak viscosities, with only minor differences being observed in these values between samples. Similarly, the tendencies towards decreased peak viscosities (between 26–29%) and breakdown in the presence of divalent cations are the same in annealed and native potato starch (Figure 6b). The presence of divalent cations leads to a small increase in pasting temperature in all cases (Table 4), similar to the marginal effects on gelatinization temperatures in DSC studies.



(**a**) (**b**)

Figure 6. RVA profiles of mineral-enriched starch samples: (**a**) native potato starch and annealed native potato starch with and without monovalent cations; (**b**) native potato starch and annealed native potato starch with and without divalent cations.

Table 4. Pasting properties of native potato starch, mineral-enriched starches, and all annealed starches (PV, peak viscosity; TV, trough viscosity; BD, breakdown; FV, final viscosity; SB, setback; PT, pasting temperature).

Sample	PV (mPa·s)	TV (mPa·s)	BD (mPa·s)	FV (mPa·s)	SB (mPa·s)	PT (°C)
NPS	4036 ± 50	1597 ± 24	2439 ± 29	1864 ± 28	267 ± 17	69.5 ± 0.1
NPS Mg	2901	1610	1291	1897	287	71.2
NPS Ca	2963	1646	1317	1941	295	71.1
NPS Na	5446	1700	3746	1995	295	68.6
NPS K	5430	1693	3737	1997	304	68.7
ANN NPS	3361	2546	815	2904	358	74.4
ANN NPS Mg	2480	2156	324	2983	827	76.0
ANN NPS Ca	2392	2225	167	2812	587	76.0
ANN NPS Na	4298	2853	1445	3131	278	76.0
ANN NPS K	4128	2982	1146	3431	449	74.4
ANN NPS, Enriched with Mg	2355	1931	424	2355	1931	74.2

In addition, the annealing of NPS with subsequent ion exchange at room temperature shows similar results in pasting properties compared to the corresponding experiment (only tested for Mg). The presence of ions therefore does not greatly influence the annealing process of native potato starch. The RVA data for Mg-exchanged ANN NPS can be found in Table 4 and in the Supplementary Materials (Figure S4).

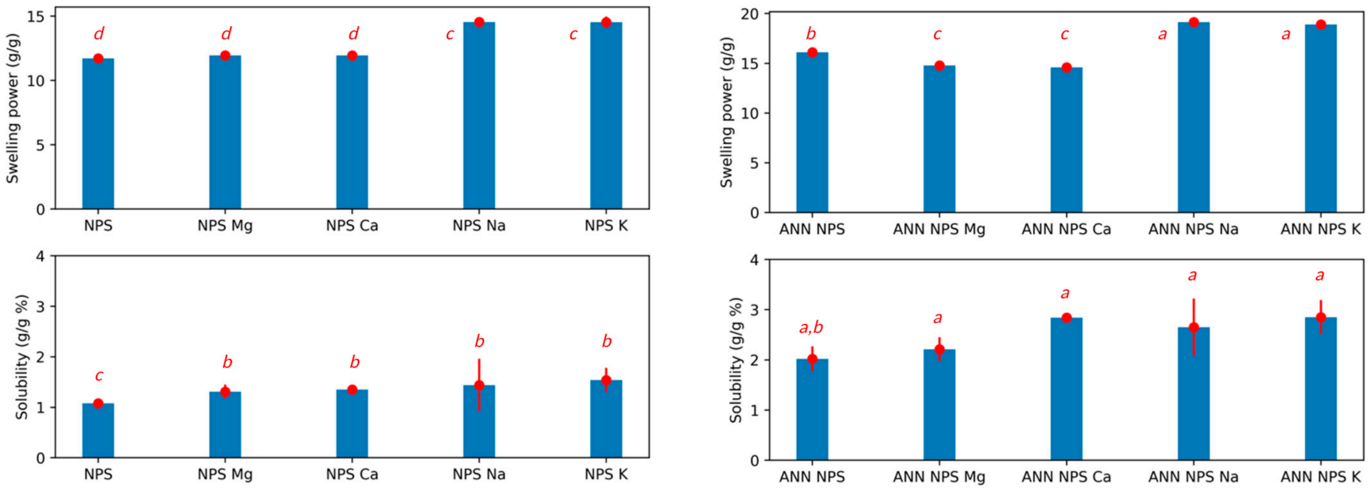
In contrast to what was observed for the thermal properties, the rheological properties were more strongly influenced by changes in mineral composition. Both DSC and RVA characterize starch gelatinization, but one is a calorimetric technique that gives insight into transitions occurring mainly in crystalline structures, and the other focuses on rheology, which is also strongly influenced by processes occurring in amorphous regions. These processes are, namely, granular swelling by penetration of water into amorphous regions and the leaching of free amylose from amorphous regions. Thus, if changes in mineral composition mostly affect swelling and amylose leaching, the influence of cations (i.e., ionic crosslinking of divalent cations) is more likely to be reflected in RVA data rather than in DSC data.

3.6. Swelling Power

The swelling behavior was tested in triplicate by swelling power (SWP) determination at two different temperatures above the gelatinization temperature of native potato starch. While the analysis has its weaknesses, as discussed in recent reviews, it was performed to complement the RVA studies [41]. Swelling power is a measurement for the swelling properties of starch that give insight into how much water is bound by the formed starch gel at applied conditions (Equation (3) in Section 2.10).

The swelling power (SWP) and solubility (SOL) results of the starch samples measured at 70 °C are shown in Figure 7 and Table 5. In the samples that were ion-exchanged at room temperature, enrichment with divalent cations hardly changed the swelling power measured at 70 °C, whereas monovalent cations caused an increase in this property. No differences between NPS Na and NPS K or NPS Mg and NPS Ca were observed. These findings overall fit the influence on pasting properties discussed in the previous section. However, the influence of divalent cations on pasting properties was more pronounced. A larger negative impact on the swelling power of divalent cations was expected than what was observed in these studies, as ionic crosslinking would hamper the hydration of amorphous regions [10]. In the presented results, divalent cations seem to influence peak viscosity development upon heating more strongly than the water-holding capacity of the formed gels in SWP measurements.

Annealing caused the SWP of native potato starch to increase from 11.71 ± 0.34 g/g to 16.10 ± 0.49 g/g when measured at 70 °C. Increased AP–AM and AP–AP interaction led to formation of a gel that was more capable at holding water and thus yielding higher readings [17]. Along the same lines, the breakdown according to RVA data is also lower in annealed starch than in native starch, pointing towards stronger gels (Table 4). The influence of ions during annealing is depicted in Figure 7b. At 70 °C, the presence of monovalent cations increased SWP, while divalent cations suppressed SWP compared to ANN NPS. There was no significant difference observed between the SWP values of ANN NPS Mg and ANN NPS Ca or ANN NPS Na and ANN NPS K, respectively. This is again similar to the small difference in pasting properties among starches enriched with cations of the same valence.



(**a**) (**b**)

Figure 7. Swelling power and solubility of annealed native potato starch without and with ion enrichment with Mg, Ca, Na, and K, measured in triplicate at 70 °C: (**a**) ion-exchanged native potato starches at room temperature including control (NPS); (**b**) annealed native potato starches with and without cation enrichment as indicated. (a, b, c, d are values for swelling power or solubility with the same letter are not significantly different).

Table 5. Swelling power (SWP) and solubility (SOL) results in triplicate at two measurement temperatures. The measurement was performed in triplicate, and results are given as mean ± standard deviation.

	Swelling Power (SWP) (g/g) Measured at		**Solubility (SOL) (g/g %) Measured at**	
Sample	**70 °C**	**90 °C**	**70 °C**	**90 °C**
NPS	11.71 ± 0.34 d	17.30 ± 0.60 c,d	1.08 ± 0.08 c	2.56 ± 0.32 a
NPS Mg	11.95 ± 0.33 d	18.20 ± 0.70 c	1.31 ± 0.14 b	2.79 ± 0.11 a
NPS Ca	11.95 ± 0.21 d	16.34 ± 0.24 d	1.35 ± 0.08 b	1.60 ± 1.60 a
NPS Na	14.54 ± 0.27 c	14.00 ± 0.60 e	1.44 ± 0.52 b	2.08 ± 0.15 a
NPS K	14.53 ± 0.43 c	15.60 ± 2.10 d	1.54 ± 0.24 b	2.12 ± 0.18 a
ANN NPS	16.10 ± 0.49 b	18.99 ± 0.30 c	2.02 ± 0.25 a,b	0.85 ± 0.13 b
ANN NPS Mg	14.78 ± 0.35 c	19.30 ± 0.21 b,c	2.21 ± 0.24 a	1.27 ± 0.24 a
ANN NPS Ca	14.58 ± 0.20 c	18.20 ± 0.07 c	2.84 ± 0.09 a	1.94 ± 0.55 a
ANN NPS Na	19.13 ± 0.10 a	23.51 ± 0.59 a	2.65 ± 0.57 a	0.88 ± 0.30 b
ANN NPS K	18.90 ± 0.07 a	21.46 ± 0.50 a,b	2.85 ± 0.34 a	1.04 ± 0.16 b

Values with the same letter in the same column are not significantly different ($p < 0.05$).

When testing the SWP of ion-exchanged NPS as measured at elevated temperatures (90 °C), the presence of Mg led to a marginal increase and Ca to a marginal decrease (Table 5). For NPS Na and NPS K, the SWP at 90 °C was lower than in NPS, NPS Mg, and NPS Ca. This contrasts the SWP results obtained at 70 °C as well as the clear increase in swelling ability through higher peak viscosity development in RVA measurements. However, the breakdown of NPS Na and NPS K in RVA studies is very high. A possible explanation is that even though more water was bound in the heating phase of the swelling power measurement, the resulting gel was less stable and therefore collapsed upon centrifugation. This was sometimes observed for waxy potato starches in swelling power determinations at higher temperatures [41].

Annealing caused the swelling power of native potato starch to increase from 17.30 ± 0.60 g/g to 18.99 ± 0.30 g/g when measured at 90 °C. This increase was also observed at 70 °C. Higher values for SWP were found for ANN NPS Na and ANN NPS K at both measurement temperatures. Potentially, the better stability of the gel formed by annealed starches allowed higher readings at 90 °C without the pronounced swelling-induced collapse of the resulting gel, as was observed for NPS Na and NPS K at 90 °C. At 90 °C, no difference was observed between ANN NPS and ANN NPS Mg, while a slightly lower SWP was found for ANN NPS Ca.

Noda et al. tested the swelling power of Ca-enriched native potato starches and found a significant reduction in swelling power compared to the control throughout the tested temperature range. They did not provide data on Mg-enriched native potato starch [10]. Overall, the trends in swelling behavior of the annealed ion exchanged starch samples are reminiscent of trends seen in ion-exchanged starch samples at room temperature (Table 5). Moreover, the swelling power results largely match the RVA results.

3.7. Digestibility of Starch in Granular Form

As hydrothermal treatments are known to potentially affect starch digestibility, this property was probed with a commercial enzyme kit in duplicate for native potato starch before and after annealing [16,25]. Starch was formally divided into fractions of rapidly digestible starch (RDS, digested after 20 min), slowly digestible starch (SDS, digested after 2 h), total digestible starch (TDS, digested after 4 h), and resistant starch (RS, not digested after 4 h) [18]. Functioning as a probiotic fiber, RS is interesting in food applications regarding gut health. Its fermentation products, namely short-chain fatty acids, are frequently connected to positive health effects [18]. The resistance to digestion can have different causes, and resistant starch is classified accordingly.

Native potato starch in untreated, granular form is typically very high in resistant starch, and the amount decreases after cooking, providing more accessible carbohydrates. Since enzymes attack the amorphous regions first followed by the crystalline regions, changes in crystallinity can impact resistant starch content. Whether annealing impacts crystallinity and digestibility depends strongly on the employed conditions. In the literature, no influence of ion exchange on RS content of native potato starch was found [9].

Table 6 shows the amount of RDS, SDS, TDS, and RS of native potato starch before and after annealing. The amount of total digestible starch decreases after annealing from initially 8.89 ± 0.10 g/100 g in NPS to 7.86 ± 0.22 g/100 g in ANN NPS, which indicates a larger fraction of indigestible starch. The value for resistant starch decreases; however, the RS content is more prone to errors due to the immediate settlement of solids in suspension, as can be seen by the high standard deviations. Higher onset temperatures and a slight increase in relative crystallinity in annealed starch also suggest that the RS content would be higher due to a more ordered starch structure being less accessible for enzymes.

Table 6. Overview of digestible starch contents after 20 min (RDS), after 120 min (SDS), and after 240 min (TDS). The amount of non-digested starch after 240 min is the resistant starch content (RS). The measurement was performed in duplicate and results are given as mean ± standard deviation.

Sample	Digestible Starch Amount (g/100 g) at T0	RDS (g/100 g) (after 20 min)	SDS (g/100 g) (after 120 min)	TDS (g/100 g) (after 240 min)	RS * (g/100 g) (after 240 min)
NPS	2.91 ± 0.12	4.26 ± 0.16	2.17 ± 0.02	8.89 ± 0.10	92.03 ± 4.46
ANN NPS	3.20 ± 0.14	4.18 ± 0.36	1.27 ± 0.64	7.86 ± 0.22	82.07 ± 9.97

* Values for RS are prone to larger errors due to settlement of particles in suspension when taking aliquots.

For a more accurate picture of digestibility properties, testing resistant starch in the final food product is advisable over testing the behavior of individual food ingredients. Moreover, in later stages of product development, more sophisticated analytical protocols need to be followed that mimic digestion in the mouth, stomach, and intestine and gut in a more realistic way [42].

4. Conclusions

The mineral enrichment of native potato starch in suspension at room temperature and during annealing experiments was carried out for native potato starch using a series of cations (Na, K, Mg, and Ca, all with chloride as counterion). The mineral exchange of NPS resulted in different pasting and swelling properties, with monovalent ions (Na and K) increasing peak viscosity (RVA, from 4000 to 5400 mPa·s), while divalent cations (Mg and Ca) diminished these parameters (RVA, from 4000 to 2950 mPa·s).

Pasting, thermal, and swelling properties were strongly influenced by the annealing procedure due to a more perfected crystalline structure of the starch granules, as indicated by XRD and DSC studies. However, solid-state NMR did not reveal a change in short-range order. Changes in properties through the annealing of native potato starch in a salt solution were compared with that of corresponding ion-exchanged starches at room temperature. Divalent cations suppressed swelling during viscosity development in RVA studies, whereas monovalent cations (or the absence of divalent cations) promoted these processes. Only a minor and varying influence of cations was observed in thermal properties.

Annealing in the presence of mono- and divalent cations allows for fine-tuning of the pasting behavior of native potato starch, thereby offering an alternative to chemically modified starches for respective food applications. Furthermore, these findings can be used for the development of healthy and environmentally benign starch-based food ingredients high in target essential minerals like magnesium and probiotics through highly resistant starch content.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/chemengineering8030060/s1. Figure S1: Typical heating profile (a) and annealing set-up (b); Figure S2: RVA profiles of ANN NPS and its sieved fractions; Figure S3: RVA profiles of ANN NPS Mg and NPS Mg in comparison with ANN NPS that was Mg-enriched as second step; Table S1: Overview of sample composition including duplicate experiments for NPS Mg, NPS Ca, and ANN NPS that was Mg-enriched as second step; Table S2: Overview of pasting properties including duplicate experiments for NPS Mg and NPS Ca and result for ANN NPS, Mg-enriched in second step (PV, peak viscosity; TV, trough viscosity; BD, breakdown; FV, final viscosity; SB, setback; PT, pasting temperature).

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