Functional Properties of Acid-Thinned Potato Starch: Impact of Modification, Molecular Starch Characteristics, and Solution Preparation

Marco Ulbrich* and Eckhard Flöter

A matrix of 27 acid-thinned (AT) potato starch (PS) samples is prepared in a laboratory scale in slurry by gradation of the process parameters temperature (30, 40, and 50 °C), acid concentration (0.3, 0.6, and 0.9 M HCl) and time (4, 10, and 20 h), and is investigated in terms of functional properties (range of molar mass [M_w] between 17.7 × 10^6 and 1.95 × 10^4 g mol^-1). The solubility (S) increased basically with a higher degree of molecular degradation and disintegration temperature, and the viscosity decreased systematically with decreasing M_w and increasing disintegration temperature. The existence of a specific M_w range of the starch to achieve highest gel strength is proved. However, an impact of the molecular properties on the light transmittance (T_gel) can be excluded, since all starch gels are opaque. A correlation between the strength and the specific non-freezeable bound water content (w_nf) of the gels is found. High gel strength is accompanied by comparatively low w_nf. In particular, the viscosity (processing) and the gel strength (final product characteristic), which are important technofunctional properties for the industrial application of AT starches, are found to be directly correlated to the M_w of the starch product. Moreover, the latter is controllable by the hydrolysis process parameters.

1. Introduction

Acid-thinned (AT; tantamount to thin-boiling starch) starches have great importance for food applications, for example, in the manufacture of gelled sweets. AT products are commonly prepared by partial hydrolysis of the granular native starch using mineral acids (e.g., HCl or H_2SO_4) in aqueous suspension (slurry).[1] The preservation of the semicrystalline granular structure is mandatory. Several factors like starch source (initial inherent starch properties), hydrolysis temperature (reaction rate), molar acid concentration, and acid type (pH), respectively, and the duration of the hydrolysis (time) can control the process and accordingly determine the resulting molecular, the solution as well as the technofunctional properties of the modified starch. Since the hydrolysis occurs within the amorphous regions of the semicrystalline granule structure, the acid-induced cleavage of the starch polymers can be basically considered as effectively specific with the predominantly molecular degradation of the amylpectin (AP). However, a recent study proved the basically collaborative degradation of both starch polysaccharide fractions, the largely unbranched amyllose (AM) and the highly branched AP.[4] Anyway, quasi-specifically modified AT starches (e.g., with the desired degree of degradation; specific M_w range) may possess excellent technofunctional properties making them suitable and interesting for industrial application. Compared to the native starch, AT products normally have a significantly reduced hot paste viscosity, which is a prerequisite for the processing (e.g., pumping) of particularly concentrated dispersions on the one hand. On the other hand, a high tendency to gelation (retrogradation and crystallization) and formation of a mechanically stable gel structure is an indispensable characteristic and requirement for the purpose of application.[5] Low solution viscosity, as a consequence of the decreased average chain length of the starch polysaccharides (e.g., decreased M_w), ensures a high dosage if desired, and particularly the reduction of the hydrodynamic size of the AP enables the fast and comprehensive formation of a 3D AM network with corresponding strength development. Additional functional key aspects like elasticity, syneresis effects and the turbidity presumably bear on structural features of the biopolymer network.

A requirement for the deployment and development of the inherent starch properties is the transformation of suspended starch semicrystalline granules by heating and gelatinization (decomposing most hydrogen bonds; dissolved starch polymers; first step) to a solution or paste, respectively, followed by a partial rearrangement of starch polymers (retrogradation; preferentially AM) after cooling the dispersion (second step).[7] Hence, the paste preparation conditions impact the portion and molecular composition of the soluble polymers (continuous phase) and equipollent the swollen remnants (dispersed phase) in addition...
to the degree of modification significantly. The gradation of the pasting temperature (70, 90, and 120 °C) was reported to influence the solution state and hence the overall gel properties. Higher temperatures were found to facilitate disentanglement of the AP (non-covalent bonds) to a greater extent, allowing the separation of AM and AP, which effectuates a smoother character (high yielding, reduced strength) and higher opacity of the gels on the one hand, but allows a faster rate of rearrangements causing the AP rich (highly swollen) granule remnants to become relatively firmer after longer ageing time on the other hand. The relevance of the starch’s solution state for the functionality is conspicuous and unquestioned.

The time dependence of the retrogradation effects cause the mechanical properties of starch gels to be essentially controlled by the storage duration. Short-term changes in the starch-water system, which are mainly ascribed to the gelation of AM (irreversible; intermolecular hydrogen bonds) are related to the development of the gel network including rigidity, molecular order and crystallinity. In contrast, the long-term enhancement of the gel strength is attributed to reordering and crystallization processes mainly within the AP (reversible). A multistage process including 1) the formation of double-helices (conformational ordering) and the fast development of crystalline AM regions (AM aggregation), 2) the AP helix–helix aggregation and crystallization and phase-separation of water (syneresis) was reported elsewhere based on FT-IR technique experiments. Moreover, lowered storage temperature can increase the crystallization rate and extent (DSC experiments at 4, 21, and 30 °C, respectively), but the perfection of the crystals appears to increase at higher temperatures (narrowing of DSC endotherms), probably similar to reordering processes in terms of crystalline perfection induced by heat moisture treatment or annealing of granular starch. Increasing the degree of chain aggregation initiates progressively heterogeneous and turbid structures. Furthermore, the specific impact of different salts on the color of starch gels was proved.

For the purpose of investigating the modification process – molecular starch structure relationship, corresponding potato starch based AT samples were prepared in slurry by systematic gradation of the process parameters hydrolysis temperature (30, 40, and 50 °C), acid concentration in the aqueous phase (0.3, 0.6, and 0.9 M HCl) and hydrolysis time (4, 10, and 20 h). The denotation of the modified sample (AT) is systematically applied, according to the hydrolysis temperature (e.g., 30 °C), the adjusted acid concentration (e.g., 0.3 M) and the reaction time (e.g., 4 h) in the form of, for example, AT-30-0.3-4.

The molecular properties (\(M_w\) starch and \(M_w\) AM fraction; analysis by means of SEC-MALS-DRI) and the dry matter contents (DM) of the starch samples (acid hydrolyzed and native) were determined in a previous study by Ulbrich and Flöter and are summarized in Table 1. The \(M_w\) of the native potato starch and the corresponding AM fraction were 25.8 × 10^6 and 5.7 × 10^5 g mol\(^{-1}\), respectively.

### 2. Experimental Section

#### 2.1. Native Starch and Acid-Thinned Samples

Commercial native PS (Superior, Emsland-Stärke, Emlichheim, Germany) was used as the basis for the modification. The dry matter and the TAM content of the native starch were 81.3% w/w and 24.5 ± 1.0% (blue value method), respectively. The protein, lipids, and ash contents were ≤0.1% w/w, ≤0.1% w/w, and ≤0.5% w/w, respectively (data provided by the supplier). Deionized water was used for the experiments.

The acid modification was performed in an aqueous suspension (40% w/w) under continuous stirring (400 min\(^{-1}\)) according to the description elsewhere using HCl as acid. The reaction was stopped by addition of NaOH. Altogether, 27 AT samples were produced by systematic gradation of the process parameters hydrolysis temperature (30, 40, and 50 °C), acid concentration in the aqueous phase (0.3, 0.6, and 0.9 M HCl) and hydrolysis time (4, 10, and 20 h). The denotation of the modified sample (AT) is systematically applied, according to the hydrolysis temperature (e.g., 30 °C), the adjusted acid concentration (e.g., 0.3 M) and the reaction time (e.g., 4 h) in the form of, for example, AT-30-0.3-4.

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#### 2.2. Preparation of Concentrated Starch Pastes

Concentrated pastes of the starch samples (native and AT) were prepared based on aqueous dispersions of 7.5% w/w at three different temperatures (95, 120, and 145 °C) by means of two different methods (atmospheric pressure: water bath, pressure cooking: autoclave). Heating to 95 °C was performed using a water bath under continuous stirring (250 min\(^{-1}\)) of the slurry for 30 min in a round bottom flask. The paste preparation at 120 and 145 °C was carried out using an autoclave (Model I, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) under continuous stirring (300 min\(^{-1}\)) for 20 min. For both methodological approaches (disintegration in water bath and autoclave, respectively), the dispersion subsequently underwent a high-shear-treatment using an Ultra-Turrax T25 (IKA-Werke GmbH & Co. KG, Staufen, Germany) at 24 000 min\(^{-1}\) for 2 min at about 85 ± 5 °C. The freshly prepared aqueous starch solutions were immediately analyzed, and gels were casted, respectively. Short-term storage of the solution was performed in an oven at 85 °C until its analysis in order to prevent undesirable changes of the dispersion.

#### 2.3. Solubility and Molecular Composition of the Dispersion Phases

##### 2.3.1. Preparation and Analysis

An aliquot of the respective starch dispersion was diluted with the twofold mass of water to a concentration of 2.5% w/w. A mass of 30.0 g was subsequently centrifuged at 10 000 min\(^{-1}\) (11 180 g) for 10 min (Biofuge 28RS, Heraeus, Hanau, Germany). After the centrifugation step, the amount of supernatant was determined.
Table 1. Molecular properties and dry matter content of the starch samples.

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M&lt;sub&gt;w&lt;/sub&gt;</td>
<td>Starch</td>
<td>AM</td>
</tr>
<tr>
<td>Concentration [M]</td>
<td>Time [h]</td>
<td>[10&lt;sup&gt;6&lt;/sup&gt; g mol&lt;sup&gt;-1&lt;/sup&gt;]</td>
<td>[%]</td>
</tr>
<tr>
<td>0.3</td>
<td>4</td>
<td>17.70</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>15.10</td>
<td>2.27</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>12.80</td>
<td>1.93</td>
</tr>
<tr>
<td>0.6</td>
<td>4</td>
<td>15.50</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>7.58</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>4.46</td>
<td>0.92</td>
</tr>
<tr>
<td>0.9</td>
<td>4</td>
<td>9.02</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>6.07</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>2.67</td>
<td>0.97</td>
</tr>
</tbody>
</table>

<sup>a</sup>Hydrolysistemperature; <sup>b</sup>acid concentration (HCl; concentration in the aqueous phase of the 40% w/w slurry); <sup>c</sup>hydrolysis time.

by decanting and weighing, and an aliquot of 0.5 mL was diluted 1:10 v/v in preheated dimethyl sulfoxide (DMSO). Additionally, a part of the sediment was dispersed in DMSO and finally dissolved by stirring (400 min<sup>−1</sup>) at 80 °C (oil bath) for 20 h. Both solutions (supernatant and sediment) were characterized by means of SEC-MALS-DRI. The chromatograms were determined and M<sub>w</sub> calculated, respectively. Moreover, the polymer concentration of the supernatant sample was determined from the SEC chromatograms and, based on the amount of the supernatant, the total starch content solubilized within the supernatant phase calculated. The portion of the latter fraction related to the starch content of the initial dispersion (30.0 g of a 2.5% w/w solution) was multiplied by 100 and expressed as %. Based on the S, the SEC chromatograms corresponding to the dissolved (supernatant) and swollen (sediment) dispersion phase, respectively, were weighted according to the relative portion of the starch polymers.

### 2.3.2. Chromatographical System

The molecular characterization of the polydisperse solutions was carried out by means of SEC-MALS-DRI. The separation was executed with an SEC-3010 module (WGE Dr. Bures GmbH & Co. KG, Dallgow-Doeberitz, Germany) including degasser, pump and auto sampler connected to a MALS detector and a differential refractive index detector (DRI). The MALS detector was a Bi-Mwa (Brookhaven Instruments Corporation, Holtsville, NY, USA) fitted with a diode laser operating at λ<sub>0</sub> = 635 nm and equipped with seven detectors at angles ranging from 35 to 145°. The DRI was a SEC-3010 RI detector operating at λ = 620 nm. Three columns in a row were used: AppliChrom ABOA DMSO-Phil-P-100 (100–2500 Da), P-350 (5–1500 kDa) and P-600 (20 to >20000 kDa) (AppliChrom, Oranienburg, Germany). The samples were eluted with degassed DMSO (Emsure ACS, Merck KGaA, Darmstadt, Germany) containing 0.1 M NaNO<sub>3</sub> at a flow rate of 0.5 mL min<sup>−1</sup> and a temperature of 70 °C. During the sample run on the SEC-MALS-DRI system (single determination), the data from the MALS and DRI detectors were collected and processed using ParSEC Enhanced V5.6 1 chromatography software to give the concentration of the eluted solution and molar mass (MM) at each retention volume (M<sub>r</sub>). The basis for the molecular characterization by means of SEC-MALS-DRI has been described elsewhere.[23,24]

### 2.4. Hot Paste Viscosity

The rheological measurements were carried out using a rotational rheometer (MCR 302, Anton Paar GmbH, Graz, Austria) with a cone-plate geometry (CP50-1/TG: 50 mm and 1°, True Gap). The freshly prepared starch solutions (7.5% w/w) were filled in the measuring system, and the hot paste viscosity curves were determined in the shear rate range 0.1–125 s<sup>−1</sup> at 60 °C.

### 2.5. Light Transmittance of the Diluted Solutions and the Gels

The clarity of the freshly prepared starch solutions as well as the gels was determined as described elsewhere[5] with modifications. The starch solution (7.5% w/w) was diluted with water to a concentration of 1% w/w and filled in cuvettes (Poly(methyl methacrylate); PMMA, 4 mL, Rotilabo, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) before measurement (T<sub>solution</sub>). For the determination of the T of the gels (T<sub>gel</sub>), the freshly prepared 7.5% w/w solution was filled into the cuvettes and subsequently capped to prevent drying-out as well as shrinking and stored for 24 h at 5.5 ± 1.5 °C before being analyzed. The clarity was determined as T at λ = 650 nm using a spectrophotometer (Jenway 6505 UV/visible, Stone Staffordshire, UK) and deionized water as the reference.

### 2.6. Gel Preparation and Gel Strength

The gels were prepared on the basis of freshly prepared starch pastes and characterized according to the description elsewhere[5]...
with modifications. After casting and storage for 24 h at 5.5 ± 1.5 °C a fresh and planar surface was realized by cutting. The mechanical strength of the starch gel (diameter 30.0 mm, height 20.0 mm) was determined by compression using a texture analyzer (Test Control II, Z1.0; 1 kN, Zwick/Roell, Ulm, Germany) equipped with a cylindrical penetration probe (diameter 25.4 mm). The peak force [N] of the first penetration was taken as gel strength. Gel preparation and measurement of hardness were carried out in triple determination. The arithmetic average and the corresponding standard deviation were calculated.

2.7. Non-Freezable Bound Water in Starch Gels

The water binding of the starch gels (7.5% w/w, storage for 24 h at 5.5 ± 1.5 °C) was determined based on differential scanning calorimetry (DSC; DSC 204 F1 Phoenix fitted with an intracooler, Netzsch, Selb, Germany) freezing experiments according to the description elsewhere[25] with modifications. Within the present study, the water binding capacity (WBC) of the gels was defined as the specific non-freezable fraction (w_{nf}) of the water bound to the starch polysaccharides and expressed in g non-freezable bound water per g dry starch. The w_{nf} was calculated according w_{nf} = \Delta H_{\text{sample}} / \Delta H_{\text{bulk water}} \times w, where w is the total water content related to the starch (w = 12.33 g x g⁻¹), \Delta H_{\text{sample}} the melting enthalphy of the ice in the gel (heating run), and \Delta H_{\text{bulk water}} the melting enthalphy of bulk water. The scans were performed with a scanning rate of 10 K min⁻¹ and air as the reference. Conditions were: start at ambient temperature (20 ± 2 °C) and equilibrium to 20 °C with isotherm for 2 min, cooling to −50 °C with isotherm for 2 min and heating to 50 °C with isotherm for 2 min, followed by cooling to 20 °C. The DSC experiments were performed in duplicate, and the thermograms were evaluated by means of Netzsch Proteus-thermal analysis-Version 4.8.0 software.

2.8. Data Evaluation

The impact of the different process parameters (hydrolysis temperature, acid concentration, and hydrolysis time) as well as the disintegration temperature on several starch–water system properties was investigated based on an experimental design (N = 81) using Statgraphics Plus 5.0 software. The analysis distinguished between the composition of the starch dispersion, shear viscosity of the solution and gel characteristics. The values for the probability of error (p-value) were listed in the ANOVA table (analysis of variance; Table 2). With a p-value less than 0.05, the factor investigated had a statistically significant effect with a 95.0% level of significance (boldface type in the ANOVA table). Additionally, selected results from the statistical evaluation were summarized in mean and interaction diagrams (S, M_w of the starch dispersion phases, w_{nf}) showing the calculated means of each category and the confidence interval with a 95.0% confidence level. With no overlapping of the confidence intervals in the mean diagrams, there was a statistically significant difference in the observed categories with a 95.0% level of confidence.

3. Results and Discussion

3.1. Dispersion and Gel Properties: Statistical Evaluation (ANOVA)

Table 2 summarizes the p-values from the statistical evaluation of the data in regard to composition of the starch dispersion (solution state: carbohydrate S, quality: M_w of the starch dissolved and swollen, respectively), hot paste viscosity (viscosity at specific shear rates: 0.951, 4.265, and 85.88 s⁻¹, respectively), and gel characteristics (\(T_{\text{gel}}\), gel strength and w_{nf} of the gel structure) in dependence on the main effects (starch modification: hydrolysis temperature, acid concentration, and hydrolysis time; paste preparation: disintegration temperature) and several interaction effects. The latter were just sporadically discussed in detail within the study in the following sections.

The composition and the shear viscosity of the starch dispersion were identified to be clearly affected by the modification parameters as well as the disintegration temperature (Table 2). All main impacts were shown to be statistically significant with a 95.0% level of significance, since the p-values were lower than 0.05 (exception: effect of the disintegration temperature on the S). However, the effects on the gel characteristics were nonuniform. The \(T_{\text{gel}}\) as well as w_{nf} was not significantly impacted by the modification parameters, but the disintegration temperature depicts a highly significant impact on the gel clarity. The w_{nf} and the mechanical strength of the gel were impacted in particular by the hydrolysis temperature and the disintegration temperature (Table 2). The specificity of the influence was discussed in detail in the respective sections.

3.2. Composition of the Starch Dispersions

Figure 1 summarizes the effects of the hydrolysis temperature and the disintegration temperature on specific starch dispersion characteristics. An increasing hydrolysis temperature, which is accompanied with a higher degree of molecular degradation, increases the S (1A). However, the specific additional impact of the disintegration temperature is distinct from the interaction plot in Figure 1 B. The higher the disintegration temperature, the lower the impact of the hydrolysis temperature on the S was found. In particular, after cooking the starch in an autoclave at 145 °C, the S was not impacted by the hydrolysis temperature (is synonymous with the level of molecular degradation). A comparatively high level of molecular degradation makes the S of the polymers more or less independent of the disintegration temperature within the investigated range. This is also visualized by the chromatograms in Figure 2, which are shown exemplarily for the impact of increasing hydrolysis temperature (acid concentration: 0.6 M HCl, hydrolysis time: 10 h). The chromatogram areas relate to the carbohydrate concentration or the relative portions, respectively, in the corresponding phase of the dispersion (after centrifugation; supernatant: dissolved, sediment: highly swollen). Based on that, systematically increasing S with increasing disintegration temperature is evident in particular from Figure 2 A (AT-30-0.6-10, comparatively low level of molecular degradation [M_w = 7.58 x 10^5 g mol⁻¹, Table 1]). On the other hand, almost no differences in terms of the chromatogram area and
Table 2. Values (p-values) from statistical analysis (ANOVA) of main (hydrolysis temperature, acid concentration, hydrolysis time and disintegration temperature) and interaction effects (combinations) on the composition of the starch dispersion, shear viscosity, and gel properties (*N*= 81).

<table>
<thead>
<tr>
<th>Factors</th>
<th>Composition of the dispersion</th>
<th>Shear viscosity*</th>
<th>Gel characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Solubility a)</td>
<td><em>M</em>&lt;sub&gt;w&lt;/sub&gt; (sup) b)</td>
<td><em>M</em>&lt;sub&gt;w&lt;/sub&gt; (sed) c)</td>
</tr>
<tr>
<td>Temperature</td>
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<td>0.0000</td>
</tr>
<tr>
<td>Acid concentration</td>
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<td>0.0000</td>
<td>0.0001</td>
</tr>
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<td>Hydrolysis time</td>
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<td>0.0000</td>
<td>0.0000</td>
</tr>
<tr>
<td>Disintegration temperature</td>
<td>0.3084</td>
<td>0.0014</td>
<td>0.0089</td>
</tr>
</tbody>
</table>

Interaction

| Temperature-acid concentration   | 0.1400                       | 0.0000           | 0.0113              | 0.0427                | 0.0131                | 0.0000                |
| Temperature-hydrolysis time      | 0.2584                       | 0.0000           | 0.0712              | 0.3673                | 0.0976                | 0.0009                |
| Temperature-disintegration temp.  | 0.0406                       | 0.0069           | 0.0051              | 0.1250                | 0.0006                | 0.0000                |
| Acid concentration-hydrolysis time| 0.7898                       | 0.3214           | 0.1221              | 0.3392                | 0.2161                | 0.0377                |
| Acid concentration-disintegration temp.| 0.4729                      | 0.5200           | 0.9078              | 0.0031                | 0.1129                | 0.0009                |
| Hydrolysis time-disintegration temp.| 0.2906                      | 0.3974           | 0.2058              | 0.3045                | 0.6266                | 0.0093                |

<table>
<thead>
<tr>
<th>Gel characteristics</th>
<th>T&lt;sub&gt;solution&lt;/sub&gt; d)</th>
<th>T&lt;sub&gt;gel&lt;/sub&gt; f)</th>
<th>Gel strength</th>
<th>w_dil</th>
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</tr>
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<td>0.1942</td>
<td>0.6805</td>
</tr>
<tr>
<td>Hydrolysis time</td>
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<td>0.9486</td>
<td>0.0400</td>
<td>0.7279</td>
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<tr>
<td>Disintegration temperature</td>
<td>0.5422</td>
<td>0.0000</td>
<td>0.0014</td>
<td>0.0112</td>
</tr>
</tbody>
</table>

Interaction

| Temperature-acid concentration   | 0.0689                      | 0.1660            | 0.0000              | 0.0008                  |
| Temperature-hydrolysis time      | 0.2508                      | 0.5474            | 0.0000              | 0.6523                  |
| Temperature-disintegration temp.  | 0.6220                      | 0.6762            | 0.4358              | 0.0031                  |
| Acid concentration-hydrolysis time| 0.2173                      | 0.8841           | 0.1957              | 0.1336                  |
| Acid concentration-disintegration temp.| 0.1555                      | 0.4224           | 0.9469              | 0.0312                  |
| Hydrolysis time-disintegration temp.| 0.7706                      | 0.4987           | 0.8200              | 0.2437                  |

Shear viscosity at different shear rates (0.951, 4.265, and 8.88 s<sup>−1</sup>); relative portion of the starch dissolved; determined after separation by means of centrifugation; *M*<sub>w</sub> of the starch fraction in the supernatant; determined after separation by means of centrifugation; *M*<sub>W</sub> of the starch fraction in the sediment; determined after separation by means of centrifugation; f) light transmittance of the freshly prepared starch solution diluted with water (1.0% w/w); g) light transmittance of the gel after storage of the starch solution (7.5% w/w) at 5.5 ± 1.5 °C for 24 h.

Shape are visible from Figure 2C (AT-50-0.6-10, comparatively high degree of molecular degradation [*M*<sub>W</sub> = 0.168 × 10<sup>6</sup> g mol<sup>−1</sup>, Table 1]). Particularly in Figure 2A, B, a systematical and comprehensible change in the molecular properties due to incremental increase of the disintegration temperature is obvious. The chromatograms are shifted to a higher elution volume and the respective *M*<sub>W</sub> decreased in most cases (Figure 2). Accordingly, increasing cooking temperature was identified, effectuating a noticeable molecular degradation during paste preparation. However, within the experimental design, only the samples hydrolyzed at 30 °C showed a statistically significant decrease of the respective *M*<sub>W</sub>. Hence, the AT samples with higher initial MM (modified at 30 °C) appear to be much more sensitive against heat-induced chain cleavage during pasting compared to the AT samples with lower initial MM (hydrolyzed at 40 and 50 °C, Figure 1 C, D). The impacts “degree of molecular degradation” (AT starches) and “paste preparation” (solution state; controlled by disintegration temperature and subsequent optionally high shear treatment) of potato starches were comprehensively investigated and discussed elsewhere.[8]

### 3.3. Hot Paste Viscosity

Regarding viscosity curves, hot dispersions of native potato starch exhibit a shear-thinning behavior, which is typical.[6, 26] However, next to several other factors, the viscosity level is strongly impacted, for example, by the disintegration temperature. The viscosity decreases with assumed improved solution state 1) on the one hand and supposed molecular cleavage to a certain degree 2) on the other hand, about half a decade maximally (Figure 3A). The acid-induced molecular degradation of the starch polymers...
3.4 Gel Properties

3.4.1 Mechanical Strength of the Gels

Figure 4 displays the mechanical gel strength of all investigated starch samples dependent on their molecular properties (starch and corresponding AM fraction) and the disintegration temperature. The gel hardness is significantly impacted by two of the investigated modification parameters (hydrolysis temperature and time) and the disintegration temperature, since the p-values were lower than 0.05 (Table 2, ANOVA). This is basically reflected in Figure 4 in two ways. On the one hand, the existence of a somewhat specific range of $M_w$ of the starch (optimum) to achieve highest strength becomes clearly obvious. Highest gel strength of about 10 N was determined with AT starch samples having a $M_w$ (starch) of about 5–8 × $10^6$ g mol$^{-1}$ and a corresponding $M_w$ of the AM fraction of about 1.1–1.4 × $10^5$ g mol$^{-1}$ when disintegrated at 95 °C. On the other hand, the application of higher disintegration temperatures decreased the strength level successively to a maximum of about 8 N (120 °C) and 7 N (145 °C), respectively. Moreover, a slight shift of the optimum $M_w$ to lower values becomes apparent (Figure 4). Starch samples with significantly lower or higher $M_w$ exhibited a correspondingly reduced ability to form
mechanically stable gels. Improved gelation characteristics due to AT seem to be strongly associated with an increased tendency for retrogradation. Singh et al.\cite{28} reported increasing retrogradation of AT starches (DSC experiments) with increasing degree of modification (gradation acid concentration). However, the phenomenon was attributed preferentially to improved realignment and self-association (double-helical structures, crystallization) of 1) smaller macromolecules released by the chain cleavage within the (amorphous) AP structure and 2) the accompanying reduction of the steric hindrance. Ulbrich et al.\cite{6} identified an optimum of $M_w$ of AT corn starch (basis: native common corn starch) being within the range between 8 and $12 \times 10^6$ g mol$^{-1}$. High gel strength was ascribed mainly to intensive AM–AM interaction forming a stable 3D polymer network. Moreover, the reduction of the molecular size of the AP fraction could concurrently further facilitate the gel formation.

3.4.2. Clarity of the Starch–Water System

The freshly prepared and diluted (1% w/w) starch dispersions exhibited a high degree of T widely within the range between 80 and 100% $T_{solution}$ (Figure 5). However, none of the investigated impacts was found to be statistically significant (ANOVA, Table 2). Moreover, no distinct correlation of the gel clarity ($T_{gel}$) to the molecular properties of the starch ($M_w$ [starch]) becomes obvious. Storage of the concentrated starch system (7.5% w/w) for 24 h at 5.5 $\pm$ 1.5 °C induced and accelerated the retrogradation and effectively the gelation process. As a result, the $T_{gel}$ levelled out to values between 0 and 5%. Altogether, the appearance of the system differed strongly from clear (solution) to turbid or opaque (gel), respectively. However, since the disintegration temperature reflects a statistically significant impact (ANOVA, Table 2), the slightly higher level of $T_{gel}$ after disintegration at 95 °C compared to the disintegration by means of pressure cooking was conspicuous. Anyway, the sol-to-gel-transition of the AT samples generally equals a starch system change from largely transparent to turbid.

3.4.3. Water Binding in Starch Gels

The WBC and in particular the type of water bound in the starch gel system, respectively, was investigated by means of DSC freezing and thawing experiments. Based on the ANOVA (Table 2), the hydrolysis and the disintegration temperature were identified to be statistically significant impacts on the specific non-freezable bound water content ($w_{nf}$) in the gel. On the one hand, $w_{nf}$ increases with increasing hydrolysis temperature (Figure 6A, impact modification), that is, the $w_{nf}$ of the samples modified at 30 °C was significantly lower than that of the samples hydrolyzed at higher temperatures. On the other hand, the solution preparation at 95 °C caused a statistically significantly lower $w_{nf}$ of the gel matrix compared to the disintegration at 145 °C (Figure 6B). Both the group of gentle modified samples (mostly hydrolyzed at 30 °C) and the disintegration at lowest temperature (95 °C), respectively, ensure the optimal molecular starch characteristics and a solution state which can result in the highest mechanical strength by trend (Figure 6C). High gel strength is based on a distinct network formation. The network consists again of zones of retrograded starch polymers, which includes 1) double helix formation and 2) corresponding crystallization. These strong interchain interactions (retrogradation) are accompanied by the comprehensive formation of H-bonds. Since the latter involves an attenuated interaction of the OH groups with water, $w_{nf}$ is consequently reduced in the starch–water system. Generalized and simplified, pronounced retrogradation-induced solidification of an aqueous starch system is associated with a quasi-release of water (e.g., freezable water content, $w_{f}$) and a...
Figure 3. Viscosity curves (shear rate 0.1–125 s\(^{-1}\)) of native PS dependent on A) the disintegration temperature (95, 120, and 145 °C) and the specific viscosity (shear rate 85.88 s\(^{-1}\)) of the native PS and the AT starches in dependence on the \(M_w\) (starch) and B) the disintegration temperature.

Figure 4. Gel strength of the native PS and the AT samples dependent on the disintegration temperature (95, 120, and 145 °C) and the molecular properties (\(M_w\)) of the starch and the corresponding AM fraction.

decrease in polymer-bound water (\(w_{nf}\)), respectively. In particular, the starch gels with the highest mechanical strength (about 7–11 N) exhibit a \(w_{nf}\) below 0.8 g g\(^{-1}\) (corresponds to about 6.5% of the total water content). In contrast, the gels having lower strength (about 0.5–5.5 N) had basically higher \(w_{nf}\) with values up to about 1.8 g g\(^{-1}\) (corresponds to about 14.5% of the total water content). However, the values determined scattered in a comparatively strong manner and were actually less systematic over all, which necessitates questioning the methodical approach.
Figure 5. T (T_solution, freshly prepared, 1% w/w; T_gel, after cold storage, 7.5 w/w) of the native PS and the AT samples dependent on the disintegration temperature (95, 120, and 145 °C) and M_w (starch).

Figure 6. w_{nf} of the gels prepared with AT samples. Mean values and 95% confidence level from statistical analysis of the main effects A) hydrolysis temperature and B) disintegration temperature; experimental design, N = 81; C: w_{nf} dependent on the gel strength (disintegration temperature: 95 °C).
3.5. Gel Strength-Molecular Properties-Modification Process-Relationship

The correlation of the mechanical gel strength to the molecular properties of the AT starch ($M_w$ [starch] and $M_w$ [AM]) is shown in the diagram in Figure 4 for the different disintegration temperatures (95, 120, and 145 °C). Since highest gel strength was achieved using AT starch samples having a $M_w$ (starch) of about $5–8 \times 10^6 \text{ g mol}^{-1}$ (paste preparation at 95 °C), the correlation of the inherent molecular properties (optimum $M_w$ range) to the respective hydrolysis process parameters and their specificity, respectively, is the subject of the next step. In particular the green range in Figure 7 represents the optimum $M_w$ obtained at hydrolysis temperature 30 °C (Figure 7A) and 40 °C (Figure 7B). The acid hydrolysis of the starch polymers to the desired degree (optimum $M_w$) is controllable without steps by varying both acid concentration and hydrolysis time within the investigated parameter field according to the relationship apparent from Figures 7A,B, which is limited by the experimental design. The conditions can vary between about 0.45–0.60 m HCl at 20 h and 4–12 h at 0.9 m HCl (30 °C; Figure 7A) and between about 0.40–0.65 m HCl at 4 h and 6–12 h at 0.3 m HCl (40 °C; Figure 7B), respectively. However, the hydrolysis of the starch aiming for the desired $M_w$ was not possible at 50 °C within the investigated range of the process parameters (Figure 7C). At 50 °C the AT process provoked a very intensive and rapid molecular degradation of the starch resulting in AT samples with a $M_w$ significantly below the optimum range (Table 1).

4. Conclusions

The acid modification of granular potato starch by variation of the hydrolysis temperature (30, 40, and 50 °C), acid concentration (0.3, 0.6, and 0.9 m HCl) and hydrolysis time (4, 10, and 20 h), respectively, was evidently shown to be a suitable method to produce a matrix of AT samples differing greatly in terms of their molecular properties. The molecular state of the starch polymers as well as the disintegration conditions (95, 120, or 145 °C, respectively) finally control several characteristics of the starch dispersions like the carbohydrate S, the molecular composition of the dispersion phases and the viscosity of the hot solutions. In particular, the $M_w$ of the AT starch as well as the solution state determine the flow behavior of the aqueous starch system, which is an important feature relating to industrial processing. Highest gel strength requires a specific $M_w$ of the converted starch (range), which depends additionally on the solution state. A minimal molecular degradation of the AP fraction and a preferable intact AM fraction are beneficial. Moreover, a certain portion of highly swollen granular remnants is presumably advantageous for the mechanical strength of the gel network. Increasing gel strength is apparently based on increasing polymer-polymer-interaction, which accordingly reduces the polymer-water interaction with corresponding reduction of the tightly bound water fraction. Since the retrogradation effects last usually a long time period, the ageing process of the starch gels effectuates the occurrence of syneresis with expected increasing separation of free (freezable) water. The transition from a transparent to a turbid system due to storage (and gelation) seems to be an inherent characteristic of the AT starch and not significantly controllable by the molecular structure and the solution state, respectively. A distinct relationship between the acid modification process, the resulting molecular properties of the hydrolyzed starch, the paste preparation conditions as well as several technofunctional properties was proved. Basically two main benefits arise from the reported findings. On the one hand, desired starch properties can be produced specifically, controllable by the different hydrolysis parameters of the slurry process (starch industry). On the other hand, the availability of AT starches equipped with the inherent properties for the specific purpose (e.g., high gel strength) in combination with the appropriate process technology is advantageous for applying the starch economically, for example, for gelled sweets (sweets industry). Specifically modified starch products have a significantly increased potential to substitute, for example, gelatin or comparatively expensive pectin as gelling agent, which in perspective, contributes to increasing the number of respective vegan products.

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Conflict of Interest

The authors declare no conflict of interest.

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