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Acid hydrolysis of corn starch genotypes. II. Impact on functional properties

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ABSTRACT

The impact of the acid modification on the molecular properties of two corn starch genotypes (high amylose corn starch: HACS, amylose (AM) content about 70% w/w; waxy corn starch: WxCS, AM content < 2% w/w) was reported comprehensively in a previous study. Based on that, the data referring to the solution and the gel properties, which are important attributes for the application in e.g. gelled sweets, were presented in the present study. Polydisperse solutions were prepared by pressure cooking. The hot paste viscosity (η) of the concentrated native HACS solution was significantly higher compared to WxCS. The reduction of the weight average molar mass (M_w) due to acid-thinning reduced η by trend (WxCS). Native HACS tends to form very stable gels. However, acid-thinning reduced the stability of the gel system slightly. The non-gelling character of the WxCS wasn't changed either by the modification. Furthermore, the light transmittance differed strongly depending on the type of starch variety. Independent of the state, i.e. either the freshly prepared solution or the corresponding cold stored product, the HACS samples were generally turbid and the WxCS samples of high clarity. The specificity of the functionality in blends basically behaved according to the mixing ratio of the two genotypes. However, increasing relative portions of amylopectin (AP) reduced the ability to inter-chain associations and resulting gel hardness disproportionally on the one hand, but the light transmittance didn't increase adequately on the other hand.

1. Introduction

Starch is a versatile ingredient for food applications. In particular, for gelled sweets like jelly gums special native, acid-thinned as well as other chemically modified starch products are used as the structuring agent. For decades starch gels have been basically described as a three-dimensional (3-D) AM network embedded with highly swollen granule fragments consisting mainly of AP (Ott & Hester, 1965). On the one hand, functional key aspects e.g. mechanical strength, elasticity, syneresis and transparency bear on structural features of the biopolymer network. On the other hand, the industrial processing requires a preferably low hot paste η. Particularly aiming at the latter, partially hydrolyzed products, the so-called acid-thinned starches, are favored.

A prerequisite to forming a gel is the transformation of suspended granular starch e.g. by heating and gelatinization (decomposing of most hydrogen bonds; dissolved starch polymers; first step). Higher temperatures facilitate the disentanglement of the polymer chains in general (non-covalent bonds), but the solution state can also depend strongly on the AM content of the starch inherent by the variety (Ai & Jane, 2015). Cooling the sol (second step) enables the partial rearrangement of certain chain areas (retrogradation; preferentially of AM) (Harada & Harada, 1998). Lowered storage temperature can increase the crystallization rate and extent (DSC experiments at 4, 21 and 30 °C, respectively), but the perfection of the starch crystals appears to increase at higher temperatures (Longton & LeGrys, 1981), probably similar to reordering processes (heat moisture treatment, annealing) (Jacobs & Delcour, 1998; Tester, Debon, & Karkalas, 1998; Tester & Morrison, 1990). Anyway, the mechanical gel properties are essentially controlled by the storage conditions as well as the molecular composition of the starch sample (Keetels, van Vliet, & Walstra, 1996). Discussing genotypes differing strongly with respect to the AM-AP ratio, it is mandatory to elucidate the specific properties of the pure polysaccharide fractions. During the gelation process, the AM self-organization plays a major role (Biliaderis, 1998). The conversion to an elastic network is possibly initiated by a phase-separation (demixing; diffusion-controlled; fast process) in the homogenous sol, which yields to

Abbreviations: AM, amylose; ANOVA, analysis of variance; AP, amylopectin; DP, degree of polymerization; HACS, high amylose corn starch; M_w, weight average molar mass; PMMA, Poly(methyl methacrylate); SEC-MALS-DRI, size exclusion chromatography-multi angle laser light scattering-differential refractive index detection; TAM, total amylose content; WxCS, waxy corn starch

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polymer-rich regions interspersed with polymer-deficient regions. The process includes the cooperative molecular interaction of many AM chains (non-covalent crosslinking), the formation of double helical associations as well as interhelix aggregates (partial crystallization; B-type) and finally, a specific solidification (Biliaderis, 1998; Gidley, 1989). The properties of AM gels may depend on molecular features, the carbohydrate concentration and numerous process conditions (Clark, Gidley, Richardson, & Ross-Murphy, 1989; Morris, 1990). Compared to AM, the structuring of pure AP is much slower and needs substantially higher concentrations (Biliaderis, 1998). The network formation is closely related to the association of relatively short exterior amylopectin chains [DP ≈ 15; length of helical side regions: 5 nm (Imberty & Pérez, 1998)] and is thermoreversible below 100 °C (40–60 °C) (Ring et al., 1987).

Most industrial acid-thinned products are prepared based on a common starch (e.g. wheat, potato or corn) having AM contents between about 20 and 30% w/w. The hydrolysis is mainly targeted on molecular size reduction of the AP fraction by chain cleavage. Moreover, the hot solution viscosity is likewise reduced due to the depolymerization. However, the degradation of the AM is preferably prevented, since the linear chains are essential for the favored network formation. The required depolymerization of the branched dextrins on the one hand and the desired intact structure of the linear polymer fraction on the other hand, reflect the actual targeted character of the acid hydrolysis process. It is most likely always a compromise of both desired AP and concurrent avoided AM degradation, which is controllable at least partly by the process factors (Ulbrich & Flöter, 2019). Therefore, an optimum degree of molecular degradation seems to provide the best possible functional properties. However, this accounts most probably exclusively for regular starches, and there is lack of information on corresponding varieties. Accordingly, the present study investigates the molecular starch properties-functionality relationship of two commercial available corn starch genotypes. The process parameter-starch properties relationship of both corn starch genotypes was investigated comprehensively in a previous study (Ulbrich, Daler, & Flöter, 2019).

2. Material and methods

2.1. Starch samples

Two commercial native corn starches genotypes were used for the experiments. Both the high AM corn starch (HACS; AmyloGel 03003; country of origin: USA) and the waxy corn starch (WxCS; C*Gel 04201; country of origin: Netherlands) were provided by Cargill Deutschland GmbH (Krefeld, Germany). The dry matter contents were 88.9% w/w and 87.5% w/w, respectively. The total AM content (TAM) of the HACS was given between 65 and 75% w/w, and the TAM of the WxCS was 0% w/w (supplier information). The starches were stored in closed containers at 20 ± 2 °C.

2.2. Acid hydrolysis procedure and molecular properties

The acid modification was performed in slurry (40% w/w) under continuous stirring (400 min^{-1}) at 30 °C according to the description elsewhere (Ulbrich & Flöter, 2019) with modifications. HCl was used as acid, and the reaction was stopped by adding NaOH dropwise until the desired pH between 5.5 and 6.0 was reached. Altogether, nine acid-thinned samples of each genotype were produced by systematic gradation of the process parameters acid concentration in the aqueous phase (0.3, 0.6, and 0.9 M HCl) and hydrolysis time (4, 10, and 20 h). The samples were denoted systematically according to the starch used (e.g. HACS), the acid concentration adjusted (e.g. 0.3 M) and the reaction time (e.g. 4 h) in the form of e.g. HACS-0.3-4. The HCl (1 M: preparation of 0.3 M HCl in suspension; 2 M: preparation of 0.6 and 0.9 M in suspension, respectively) and the NaOH (1 and 2 M, respectively) solutions were supplied by Carl Roth GmbH & Co. KG, Karlsruhe, Germany. Deionized water was used for the experiments.

The starch samples were comprehensively investigated by means of SEC-MALS-DRI and SEC-cal-DRI technique, respectively. For this purpose, polydisperse starch solutions were prepared by pressure cooking (2.5% w/w, 145 °C, 20 min; laboratory-scale autoclave Model I, Carl Roth GmbH & Co. KG, Karlsruhe, Germany), subsequent high-shear-treatment (24000 min^{-1}, 2 min; Ultra-Turrax T25, IKA-Werke GmbH & Co. KG, Staufen, Germany) and dilution in DMSO to a concentration of about 2.5 mg mL^{-1} (SEC-MALS-DRI, M_w starch). Additionally, the aqueous solutions (2.5% w/w) were enzymatically debranched (pullulanase; PromozymeD2, Novozymes A/S, Bagsvaerd, Denmark) before stabilizing in DMSO. The SEC-chromatograms of the debranched starch samples were analyzed using peak separation and analysis software PeakFit® Version 4.12, and single chromatograms representing the AM fraction and the AP branch chains fraction were calculated. The M_w of the AM fraction was calculated by means of the correspondent separated chromatogram and the MM curve (fit) from the MALS-detector (SEC-MALS-DRI, M_w AM), and the M_w of the AP branch chain fraction was determined based on the relevant chromatogram and the standard calibration curve (SEC-cal-DRI, M_w AP branch chains). The weight average degree of polymerization (DP_w) was calculated from the M_w divided by 162.

The detailed molecular characterization and the description of the chromatographic system are presented in a previous study (Ulbrich et al., 2019), and the relevant molecular data regarding to the starch (M_w Starch), the corresponding AM fraction (M_w AM) and the AP branch chains fraction (M_w an DP_w, respectively, AP branch chains) summarized in Table 1.

2.3. Starch blends

On purpose of producing starch blends, mixtures of the two genotypes modified at same condition were prepared. The starch samples were mixed in the powder form based on the corresponding dry matter content according the desired ratio. Taking 70% w/w as the AM content for the HACS and 0% w/w for the respective WxCS samples, the assumed AM contents of the mixtures were 70% w/w (pure HACS), 52.5% w/w (75% HACS:25% WxCS), 35% w/w (50% HACS:50% WxCS), 17.5% w/w (25% HACS:75% WxCS) and 0% w/w (pure WxCS). The possibly changed AM-AP ratio of the samples due to modification wasn't considered.

2.4. Paste preparation and rheological investigation

Solutions of the starch samples were prepared by heating dispersions of 7.5% w/w in an autoclave (Model I, Carl Roth GmbH & Co. KG, Karlsruhe, Germany) to 145 °C under continuous stirring (300 min^{-1}) for 20 min and subsequent high-shear-treatment using an Ultra-Turrax T25 (IKA-Werke GmbH & Co. KG, Staufen, Germany) at 24000 min^{-1} for 2 min at about 85 ± 5 °C. After disintegration, the pastes were stored at 80 °C for a short period (< 15 min) in closed screw cap bottles and processed immediately.

The rheological measurements were carried out using a rotational rheometer (MCR 302, Anton Paar, Graz, Austria) with a cone-plate geometry (CP50-1/TG: 50 mm und 1°, True Gap). The freshly prepared starch solutions were filled in the measuring system. The hot paste η curves were determined in the range of shear rate ($\dot{\gamma}$) 0.1–125 s^{-1} at 60 °C. Values for the apparent shear η (η_{app}) at $\dot{\gamma} = 0.95\ s^{-1}$ and $\dot{\gamma} = 4.27\ s^{-1}$ were calculated from the data. The $\eta_{app}(\dot{\gamma} = 0.95\ s^{-1})$ was used for the statistical evaluation (ANOVA).

The viscoelastic properties were determined in the oscillation mode at a frequency of 1 Hz and a deformation of 4% within the linear viscoelastic range (LVR). The samples solutions were filled in the system and rapidly heated to 90 °C. Both the storage (G′) and the loss modulus (G″) were monitored during cooling to 5 °C at a rate of 2 K min^{-1} and