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RETROGRADATION AND GELLING BEHAVIOURS OF PARTIALLY GELATINISED POTATO STARCH AS AFFECTED BY THE DEGREE OF PRE-GELATINISATION

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Gel network structure, gelatinisation, potato starch, retrogradation, starch gelling

Abstract

This study explored the gelling and structural properties of partially gelatinised potato starch before and after reheating in response to their initial degree of starch gelatinisation (DSG). The retrogradation R and setback of starch increased from 4.18 to 17.14 and 179 to 579 mPa·s, respectively, with increasing initial DSG from 56.11% to 90.56%. The starch gel strength increased, whereas the short-range ordered structure decreased as DSG increased without reheating. After reheating, the starch gel strength with relatively low initial DSG (56.11%) was 2.4 times higher than that of native starch and 1.7 times higher than that of starch with high DSG (90.56%). The interspersed starch granules in gels without reheating affected the formation of the network. After reheating, all gel samples formed a honeycomb structure with increased porosity as DSG increased. This could be related to the different degrees of dehydration synthesis of starch with different DSGs during retrogradation.

Introduction

Potato starch production ranks third in the world after maize and wheat starch (Reyniers *et al.*, 2020). It is an essential energy source for a well-balanced diet worldwide, and it also exerts functional properties in a variety of food applications. Native potato starch has many constraints in industrial applications, including its unstable functional properties and poor resistance to temperature changes or mechanical treatment. Pre-gelatinisation is a widely used method for modifying starch. Pre-gelatinised starch is extensively applied in the food industry (e.g. noodles, bread, and cakes) because of its dispersibility in hot or cold water, high viscosity, and desirable pasting and texturising properties (Fu *et al.*, 2016; Wang *et al.*, 2019). Moreover, as a strengthening agent, pre-gelatinised starch can facilitate water absorption, leading to a stable gel formation, thus creating a protective layer around other molecules (Liu et al., 2017; Wang *et al.*, 2019).

Through pre-gelatinisation, the intra- and intermolecular hydrogen bonds between starch molecules and water were broken. The micelle structure arrangement of starch granules was also destroyed (Dos Santos *et al.*, 2020). Compared to native starch, pre-gelatinised starch has a more porous structure with less birefringence. The crystalline structure of starch was partially or completely rearranged depending on the intensity of the process (Liu *et al.*, 2017; Santos *et al.*, 2019b).

In addition to native and pre-gelatinised starch, partially gelatinised starch also has recently drawn attention. The degree of starch gelatinisation (DSG) of partially gelatinised starch significantly affects its physicochemical properties and the final quality of products containing partially gelatinised starch. To date, several studies have investigated the structural and thermal properties of partially gelatinised corn, cassava, and maize starches prepared by spray drying or mechanical activation (Huang *et al.*, 2008; Fu *et al.*, 2012; Zhang *et al.*, 2013). However, most of the previous studies focused on starch gelatinisation (Wang *et al.*, 2016) or the characterisation of the partially gelatinised starch (Yu *et al.*, 2016; Liu *et al.*, 2020). Since heating is normally required in food processing, it is also important to investigate the retrogradation and gelling behaviours of partially gelatinised starch with different DSG during the reheating process.

Starch retrogradation is an inevitable property of gelatinised starch, in which starch molecules aggregate from a disordered state to a more ordered or apparent microcrystalline structure (Li *et al.*, 2016). Storage of starch gels at 4 °C induces high levels of recrystallisation (Denchai *et al.*, 2019; Jiang *et al.*, 2020). Starch has also been shown to age faster at 4 °C than at 25 °C, and storage temperature negatively correlates with starch retrogradation (Jiang *et al.*, 2020). The gelatinisation of starch granules strongly influences its gelling properties (Albano *et al.*, 2014; Malumba *et al.*, 2018). A higher gelatinisation temperature leads to an increase in the retrogradation of pre-gelatinised rice starch (Denchai *et al.*, 2019). To our knowledge, to date, the pasting and retrogradation properties of partially gelatinised potato starch and the resulting gel strength and structural properties before and after reheating in response to their initial DSG are still largely unknown.

This study aims to investigate the effect of DSG on the gelling properties of potato starch before and after reheating treatment. To this end, the pasting and retrogradation of potato starch with different DSG were analysed, as well as the strength, microstructure, and short-range molecular structure of potato starch gels before and after reheating. We expected our findings to provide essential guidance for partially gelatinised potato starch processing and its widespread application as an ingredient in food manufacture.

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Materials and methods

RAW MATERIALS

Potato starch containing 89.32% starch, 0.27% protein, and 0.42% ash based on dry matters of samples was purchased from Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Potato starch was freeze-dried for around 48 h using a vacuum freeze dryer (GenesisTM SQ, Virtis, Warminster, PA, USA), and the resulting moisture content was 2.89%. The sample was used on a dry basis for further analysis. Moisture content was determined by drying samples to a constant weight in an oven at 105 °C (AOAC 925.09). Crude protein was determined using the Kjeldahl method, with total nitrogen content being converted to protein content using a conversion factor of 6.25 (AOAC 979.09). Ash content was determined by dry mineralisation of samples in a muffle oven at 550 °C for 8 h (AOAC 923.03). Starch content was determined using a Total Starch Assay Kit (K-TSTA; Megazyme, Ireland).

SAMPLE PREPARATION

PREPARATION OF STARCH SAMPLES WITH DIFFERENT DSG

Partially gelatinised potato starch samples were obtained by controlled gelatinisation, as previously reported (Xu *et al.*, 2021). In brief, native potato starch (NPS) dispersion (10%, w/w; pH: 6.78) was thoroughly stirred at 300 rpm and heated at 60 ± 1 °C for 1, 3, 6, 9, and 18 min separately using a thermostatic water bath. The temperature was chosen based on the results of the pre-experiments and the onset gelatinisation temperature of NPS. The selected heating temperature provides starch samples with different DSG in a convenient heating time. Starch samples with higher DSG are difficult to obtain when treated with lower temperature in a relatively short period, while starch gelatinised too quickly when treated with higher temperature. After heating, samples were quickly moved into ice water, cooled to 25 °C, then freeze-dried for around 48 h using a vacuum freeze dryer (GenesisTM SQ, Virtis, Warminster, PA, USA) and ground into powders. The DSG was determined using a differential scanning calorimeter (DSC 8000, PerkinElmer, Waltham, MA, USA). The environmental temperature for DSC is 25 °C. The DSC analyser was equipped with a cooling accessory, and the analysis was performed with dry nitrogen purge flow. Starch samples (3 mg) were weighed into aluminium pans with 10 µL of distilled water, and the pans were hermetically sealed. A sealed empty aluminium pan was used as a reference. After equilibrating at room temperature for 2 h, samples were heated from 20 °C to 100 °C at a rate of 5 °C min^{-1}. The endothermic enthalpy (ΔH) was obtained from the DSC software. The DSG was determined using Equation (1) given as follows:

$$DSG\ (\%) = (1 - \Delta H_{sample}/\Delta H_{native}) \times 100\% \qquad (1)$$

where ΔH_{native} and ΔH_{sample} are the enthalpy change due to gelatinisation of native and modified starches, respectively. The DSG of the partially gelatinised potato starch samples was 56.11% (MPS1), 72.55% (MPS2), 75.63% (MPS3), 84.06% (MPS4), and 90.56% (MPS5).

PREPARATION OF STARCH GELS WITHOUT REHEATING

Partially gelatinised starch dispersions cooled to 25 °C (as described in Section 2.2.1) were directly poured into weighing bottles (40 mm in diameter and 25 mm in depth). All bottles were then sealed with plastic wrap to prevent moisture loss and stored at 4°C for 24 h to induce high levels of recrystallisation (Cui *et al.*, 2014).

PREPARATION OF STARCH GELS WITH REHEATING

Partially gelatinised starch dispersions cooled to 25 °C (as described in Section 2.2.1) were reheated at 95 °C for 20 min in a water bath with manual stirring, then poured into weighing bottles, and stored at 4 °C for 24 h.

X-RAY DIFFRACTION (XRD)

The X-ray diffraction analysis of partially gelatinised potato starch samples was performed using a diffractometer (D8 Advance, Bruker, Germany) operating at 40 kV and 30 mA. The samples were scanned from 2° to 40° (2θ, the angle of diffraction) at a rate of 2° min^{-1} at 25 °C.

DSC RETROGRADATION MEASUREMENT

The retrogradation of starch samples was determined using the same DSC equipment and same analysis conditions as described in Section 2.2.1. Samples after DSC thermal scanning were taken out of the equipment and stored in a refrigerator at 4 °C for 14 days before analysis (Santos *et al.*, 2019a). The onset temperature (T_0), peak temperature (T_p), conclusion temperature (T_c), and endothermic enthalpy (ΔH) were calculated automatically. The percentage of retrogradation (R%) was calculated using Equation (2) (White *et al.*, 1989; Jaspreet & Narpinder, 2001):

$$\text{R (\%)} = \Delta H_{ret}/\Delta H_{gel} \times 100 \qquad (2)$$

where ΔH_{ret} and ΔH_{gel} are the enthalpy change of retrogradation and gelatinisation, respectively.

PASTING PROPERTIES

Starch powder samples (1.25 g each) were suspended in 25 mL of water to analyse the pasting properties of starch using an RVA (Perten Instruments, Australia) following the previously described methods (Witczak *et al.*, 2014). Samples were mixed at 50 °C for 10 s at 960 rpm and then kept at a constant rotating speed (160 rpm), and fixed heating and cooling processes were adopted for measurement. The heating temperature was maintained at 50 °C for 1 min, and then the temperature was increased to 95 °C at 12 °C min^{-1}. The temperature was maintained at 95 °C for another 2.5 min^{-1}, then cooled to 50 °C at the same rate (12 °C min^{-1}), and held at that temperature for 3 min. The peak viscosity, trough viscosity, final viscosity, peak time, breakdown, setback, and pasting temperature were recorded during the heating and cooling processes (Al-Ansi *et al.*, 2021).

GEL STRENGTH MEASUREMENT

Gel strength was measured by a Texture Analyser (CT3, Brookfield, USA) according to the previously described methods with small modifications (Cui *et al.*, 2014). Analyses were performed using a return-to-start model with a cylindrical probe (TA5, 12.7 mm in diameter). The tests were programmed to move downward with a compression ratio of 50% of the original sample height at 1.5 mm s^{-1}. The test speed was set to 1.0 mm s^{-1} after contacting the sample with a trigger force of 2 g, and the post-test speed was set to 1.0 mm s^{-1}. The maximum force (N) required to compress the sample was used as an indicator of the strength of the gel structure (Fonseca-Florido *et al.*, 2019). Each measurement was taken six times.

SCANNING ELECTRON MICROSCOPY (SEM)

The gel microstructure was observed using a field-emission environmental SEM (SU8010, Hitachi, Japan) with a 10 KV acceleration voltage according to the previously described method (Jiang *et al.*, 2020). The gel samples aged 24 h at 4 °C were lyophilised and affixed to double-sided adhesive tape mounted on an aluminium stub. After being sprayed with gold, SEM was used to observe and photograph the samples at 200 × magnification.

FOURIER TRANSFORM INFRARED (FTIR) SPECTROSCOPY

The gel samples were lyophilised and ground into powders; the short-range molecular order was determined using an FTIR spectrometer (Tensor 27, BrukerOptics, Germany). FTIR spectra were recorded from 4000 to 600 cm^{-1} at a resolution of 4 cm^{-1} from 64 scans taken using an attenuated total reflectance (ATR) accessory. All spectra were automatically baseline-corrected using OMNIC 8.2 software and deconvoluted from 1200 to 800 cm^{-1} with a half bandwidth of 19 cm^{-1} and an enhancement factor of 1.9. Intensity measurements were performed on the deconvoluted spectra by recording the peak height of the absorbance bands from the baseline. The absorbance ratio at 1047/1022 cm^{-1} and 1022/ 995 cm^{-1} was used to estimate the short-range ordered structure of starch (Wang *et al.*, 2017a, 2017b).

STATISTICAL ANALYSIS

Reported data are the average of triplicate observations expressed as the mean ± standard deviation. ANOVA followed by Tukey's test at the 0.05 significance level was used to evaluate the differences among sample means. ANOVA was conducted using SPSS 18.0 (SPSS Inc., Chicago, IL, USA). All graphs were generated using Excel and Origin 9 (OriginLab, Northampton, Massachusetts, USA).

Results and discussion

RETROGRADATION PROPERTIES OF STARCH SAMPLES WITH DIFFERENT DSG

The obtained retrogradation parameters from the DSC thermograms, T_0, T_p, T_c, ΔH_{ret}, and R, are shown in **Table 1**. Results showed that T_0 did not significantly differ between NPS and partially gelatinised starches. In contrast, the T_p, T_c, and ΔH_{ret} of partially gelatinised starch samples were significantly higher than those of NPS. No significant differences in T_p, T_c, and ΔH_{ret} were observed between partially gelatinised potato starch samples with different DSG. The T_c and ΔH_{ret} of MPS2 were the highest among partially gelatinised starch samples, caused by the experimental error according to the significant difference analysis. The ΔH_{ret} of partially gelatinised potato starch is larger than its ΔH_{gel}. This is because the crystalline regions of partially gelatinised starch were partially destroyed due to preheating. It requires less energy for full gelatinisation and thus showed less ΔH_{gel} (Xu *et al.*, 2021), while in the retrogradation measurement, the ΔH_{ret} of samples represents the reorganised crystalline structure of the gelatinised starch formed from preheating and the DSC measurement. Similar melting characteristics for the retrograded starches were previously reported (Chung *et al.*, 2006; Fonseca-Florido *et al.*, 2019). As described, ΔH_{ret} is associated with the formation of double helices of the amylopectin due to the recrystallisation during storage. Moreover, the heterogeneity in the crystalline structure, including its different sizes, stability, and the perfection of the crystals formed during retrogradation, may also influence its retrogradation properties (Fonseca-Florido *et al.*, 2019).

Table 1

DSC retrogradation parameters of potato starch samples prepared from native and partially gelatinised starch with different DSG

Starch	T_0 (°C)	T_p (°C)	T_c (°C)	ΔH_{ret} (J/g)	R (×0.01, %)
NPS	44.24 ± 1.17^{a}	58.57 ± 0.54^{b}	75.08 ± 1.80^{b}	5.54 ± 0.59^{c}	0.43 ± 0.05^{e}
MPS1	42.57 ± 0.98^{a}	60.45 ± 0.40^{a}	81.05 ± 0.21^{ab}	23.37 ± 1.28^{ab}	4.18 ± 0.08^{d}
MPS2	42.63 ± 0.55^{a}	61.61 ± 0.26^{a}	86.40 ± 6.46^{a}	25.28 ± 1.81^{a}	7.23 ± 0.19^{c}
MPS3	42.64 ± 0.18^{a}	61.21 ± 0.89^{a}	81.99 ± 2.13^{ab}	21.78 ± 2.86^{ab}	7.04 ± 1.21^{c}
MPS4	42.92 ± 0.85^{a}	60.87 ± 0.55^{a}	81.25 ± 2.45^{ab}	19.96 ± 1.69^{b}	9.83 ± 0.92^{b}
MPS5	43.34 ± 0.90^{a}	60.71 ± 0.71^{a}	85.19 ± 1.12^{a}	20.64 ± 2.06^{ab}	17.14 ± 1.35^{a}

Data are means ± SD. $^{a, b, c, d, e}$ represent the significant difference of starch samples with different DSG in column ($P < 0.05$)

The R (×0.01, %) values of partially gelatinised potato starch samples ranged from 4.18 to 17.14, significantly higher than that of NPS (0.43). Moreover, the R value of partially gelatinised potato starch increased with increasing DSG, indicating that starch samples showed a higher degree of retrogradation in the reheating process with a higher initial DSG. The results from X-ray diffraction of partially gelatinised potato starch showed that NPS had a typical B-type XRD pattern, and fewer crystalline peaks can be observed in partially gelatinised potato starches as DSG increased (supplementary **Figure S1**). The results indicated that the relative crystallinity of partially gelatinised potato starch decreased significantly as DSG increased. As previously reported, the remaining crystals in partially gelatinised starch could decrease the macromolecular mobility of starch molecules and therefore impede retrogradation to a certain extent (Fu *et al.*, 2018).

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PASTING PROPERTIES OF STARCH SAMPLES WITH DIFFERENT DSG

The pasting profiles of starch samples are shown in **Fig. 1**. The magnified changes in the viscosity curves at the first stage (**Fig. 1**b) showed that the viscosities of partially gelatinised starch samples increased significantly, while the viscosity of NPS remained constant at low temperatures. Partially gelatinised starch with higher DSG showed a more rapid increase in viscosity. This could be because the starch granules in partially gelatinised samples absorb water more easily and swell more quickly than native starch at low temperatures (Liu *et al.*, 2017). Starch sample viscosities increased abruptly as the temperature further increased. During this process, water initially penetrates the amorphous zone of the starch granules and initiates irreversible swelling; microcrystals melt, and starch molecules spread out from the granules (Huang *et al.*, 2016). After the maximum viscosity was reached, the curves started to decrease due to the breakdown of starch granules when maximum swelling was attained, and the crystalline zones became disorganised and disrupted. As the temperature decreased further, the viscosity curves increased ascribed to the retrogradation of gelatinised starch. The viscosity curves of NPS and partially gelatinised samples showed obvious differences, especially in the retrogradation process.

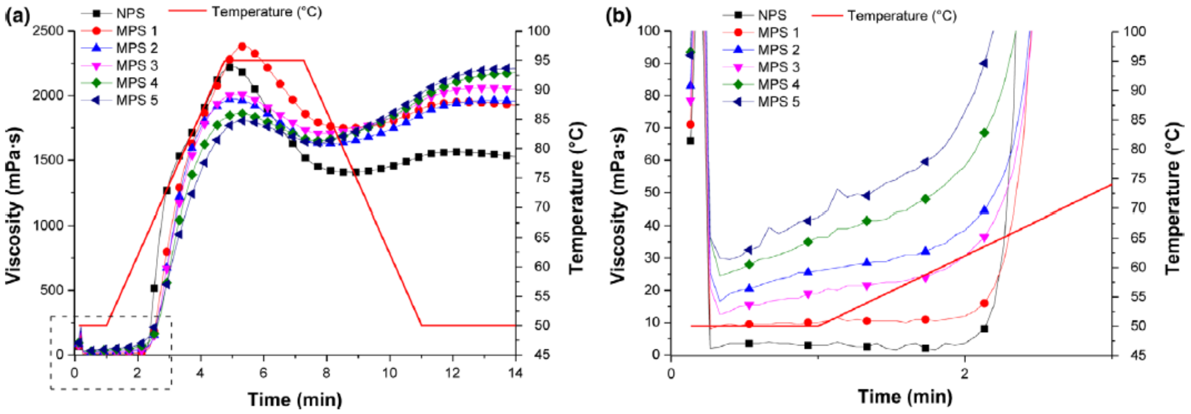


Figure 1 The RVA curves of native and partially gelatinised potato starch with different DSG

Table 2

RVA parameters of native and partially gelatinised potato starch samples with different DSG

Starch	Peak viscosity (mPa·s)	Trough viscosity (mPa·s)	Breakdown (mPa·s)	Final viscosity (mPa·s)	Setback (mPa·s)	Peak time (min)	Pasting temp (°C)
NPS	2223.50 ± 13.44^{b}	1405.50 ± 33.23^{c}	818.00 ± 19.80^{a}	1529.50 ± 20.51^{d}	124.00 ± 12.73^{e}	5.00 ± 0.10^{b}	66.20 ± 0.00^{a}
MPS1	2380.50 ± 24.75^{a}	1747.50 ± 53.03^{a}	633.00 ± 28.28^{b}	1927.00 ± 55.15^{c}	179.50 ± 2.12^{d}	5.40 ± 0.10^{a}	67.00 ± 0.00^{a}
MPS2	1975.00 ± 39.60^{c}	1627.50 ± 40.31^{b}	347.50 ± 0.71^{c}	1957.00 ± 5.66^{c}	329.50 ± 34.65^{c}	5.07 ± 0.09^{b}	67.08 ± 0.04^{a}
MPS3	2012.00 ± 84.85^{c}	1707.00 ± 42.43^{ab}	305.00 ± 42.43^{c}	2052.00 ± 16.97^{b}	345.00 ± 25.46^{c}	5.14 ± 0.09^{ab}	67.80 ± 1.20^{a}
MPS4	1861.50 ± 7.78^{d}	1650.00 ± 11.31^{b}	211.50 ± 19.09^{d}	2175.50 ± 0.71^{a}	525.50 ± 10.61^{b}	5.23 ± 0.14^{ab}	67.88 ± 1.17^{a}
MPS5	1804.00 ± 15.56^{d}	1631.50 ± 2.12^{b}	172.50 ± 13.44^{d}	2211.00 ± 0.00^{a}	579.50 ± 2.12^{a}	5.40 ± 0.10^{a}	66.15 ± 0.14^{a}

Data are means ± SD. $^{a, b, c, d, e}$ represent the significant difference of starch samples with different DSG in column ($P < 0.05$).

Table 2 shows that the peak, final, and breakdown viscosities and the pasting temperature of NPS were 2223, 1529, and 818 mPa·s and 66 °C, respectively. These results are very close to previously reported findings (Witczak *et al.*, 2014). **Table 2** also clearly shows that the peak viscosities of starch samples decreased as the DSG increased. The trough viscosity of NPS was lower than that of partially gelatinised samples. Sample breakdown decreased significantly as DSG increased; in contrast, final viscosity and setback increased as DSG increased. The peak time of NPS was lower than that of partially gelatinised starch samples. There were no significant differences in the pasting temperature of different starch samples. Peak viscosity represents the equilibrium point between the swelling and disruption of starch granules (Liu *et al.*, 2017). Since less residual granular starch existed in samples with a higher DSG, these samples swelled less in the reheating process and thus explain the decreasing peak viscosity with an increasing DSG. The breakdown is normally used to characterise the stability of starch pastes; thus, partially gelatinised starch samples with a higher DSG are more susceptible to disintegration during heating (Yang *et al.*, 2016). The short-term retrogradation was mainly attributed to amylose retrogradation and can be determined by the setback value from the RVA measurement (Denchai *et al.*, 2019). The increased final viscosity and setback indicate the larger degree of recrystallisation and the higher degree of starch dehydration synthesis in the retrogradation process as DSG increases (Bucsella *et al.*, 2016; Denchai *et al.*, 2019).

GEL STRENGTH OF STARCH SAMPLES WITH AND WITHOUT REHEATING

A dense, three-dimensional gel network can be formed by starch molecules after gelatinisation and retrogradation (Jiang *et al.*, 2020). The gel strength of potato starch samples with and without reheating is presented in **Fig. 2**. The gel strength of starch samples without reheating increased significantly as DSG increased. Starch granules in samples with shorter preheating times were not fully gelatinised, and the network was not completely formed. After extensive preheating, samples formed fine, dense, uniform gel networks; this could explain the increase in gel strength as DSG increased. After reheating, the gel strength of partially gelatinised potato starch (ranging from 1.35 to 2.27 N) was significantly higher than that of NPS (0.95 N). Similarly, a previous study reported that thermally modified starch could form stronger gels than unmodified starch after using a rheometer to determine the mechanical spectra (Gryszkin *et al.*, 2014). Moreover, the gel strength of partially gelatinised starch samples decreased as the DSG increased, indicating that partially gelatinised potato starch with a lower DSG could form stronger gels after full gelatinisation. The differences in the retrogradation of starch samples could be one of the reasons for differences in the strength of the analysed gels (Gryszkin *et al.*, 2014). The increased dehydration synthesis of samples with a higher initial DSG after full gelatinisation could increase the amount of free water in starch gels and therefore caused a decrease in gel strength as DSG increased.

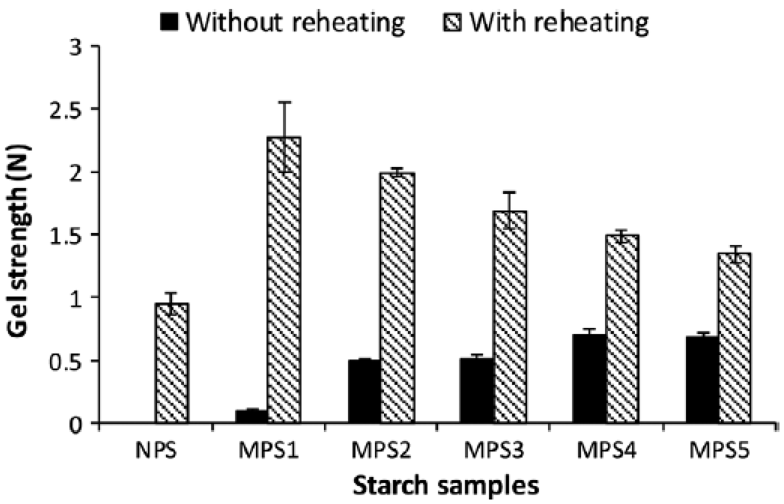


Figure 2 Gel strength (N) of potato starch prepared from native and partially gelatinised starch with different DSG without and with reheating

MORPHOLOGICAL PROPERTIES OF GEL SAMPLES

The microstructure of potato starch gels without reheating is presented in **Fig. 3** (upper case: B-F). The micrograph of NPS (**Fig. 3**a) is not shown since native starch cannot form gel without heating. Varying amounts of complete potato starch granules could be observed in the starch gel networks without reheating, and these starch granules retained their original oval or elliptical shapes. As the DSG increased, starch granules were gradually gelatinised, and residual starch granules were largely not observed. These gelatinised potato starches formed a gel network structure after retrogradation, and the interspersed complete starch granules affected the formation of the network. This explained the increased gel strength of samples with a higher DSG.

The microstructures of potato starch gel samples subjected to reheating showed no residual starch granules in the gels because all of the starch granules were fully gelatinised (**Fig. 3**, lower case: a-f). All gel samples formed a honeycomb structure, but their porosities differed. This structure is formed by the formation of a three-dimensional network with branches and edges from starch molecules after gelatinisation and ageing (Jiang *et al.*, 2020). The holes in the NPS gel were larger than those in the partially gelatinised starch gel samples. The uneven dispersion of NPS solution during the gelatinisation process may have caused its loose gel structure. The gel network structure of samples preheated for a relatively shorter time period was more compact with small holes. The gel network showed larger holes as the DSG increased, and the gel structure gradually became looser. This result was consistent with the gel strength measurement, in which the compact gel structure with small holes showed larger gel strength and vice versa. The increased dehydration synthesis of samples with a higher initial DSG after full gelatinisation could increase the number and size of ice crystals in starch gels. This may explain its loose honeycomb-like gel structure with larger pores as the DSG increased after freeze-drying.

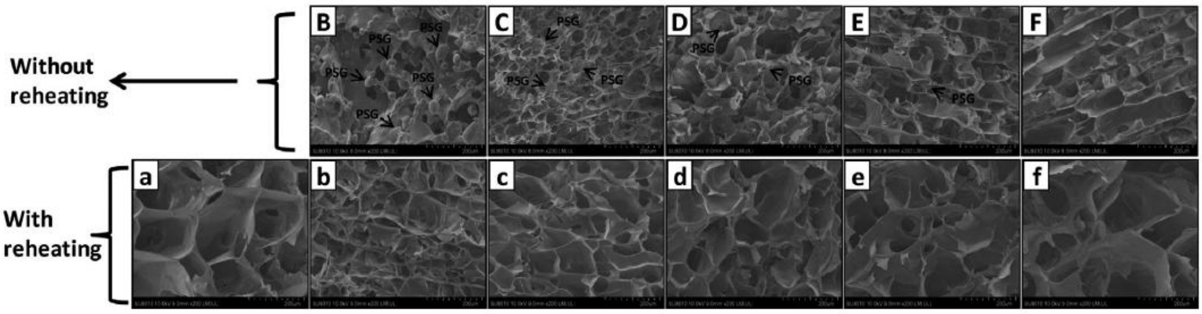


Figure 3 Scanning electron micrographs of potato starch gels prepared from native and partially gelatinised starch with different DSG (a: NPS; B and b: MPS1; C and c: MPS2; D and d: MPS3; E and e: MPS4; F and f: MPS5) without (upper case: B-F) and with (lower case: a-f) reheating

SHORT-RANGE ORDERED MOLECULAR STRUCTURE OF GEL SAMPLES

The deconvoluted FTIR spectra of potato starch gels with and without reheating are presented in **Fig. 4**. Bands at 1047 and 1022 cm^{-1} are associated with the ordered and amorphous structures of starch, respectively. The band at 995 cm^{-1} is mainly caused by the bending vibration of C-OH, corresponding to the hydrogen bond structure formed between the hydroxyl groups of starch macromolecules. The ratios of absorbance at 1047/1022 cm^{-1} and 1022/995 cm^{-1} are used to quantify the degree of short-range order in starch samples (Zeng *et al.*, 2015). The calculated ratios of absorbance of potato starch gels at 1047/1022 cm^{-1} and 1022/995 cm^{-1} are shown in **Table 3**. The 1047/ 1022 cm^{-1} ratio of starch gels without reheating significantly decreased, while the 1022/995 cm^{-1} ratio increased as DSG increased. This indicates the increased amorphous structure of starch gel samples with longer preheating times than the ordered structure. More hydroxyl groups were exposed to starch samples after extensive preheating (Zhang *et al.*, 2018). Thus, a higher DSG led to the loss of the short-range ordered structure of partially gelatinised starch gels. This result is consistent with the SEM observation since fewer residual potato starch granules existed after extensive preheating. The 1047/1022 cm^{-1} of reheated potato starch gels decreased first and then kept constant as DSG increased, and 1022/995 cm^{-1} ratios of reheated starch gels did not significantly differ. Therefore, the short-range order structures did not differ significantly between reheated gel samples.

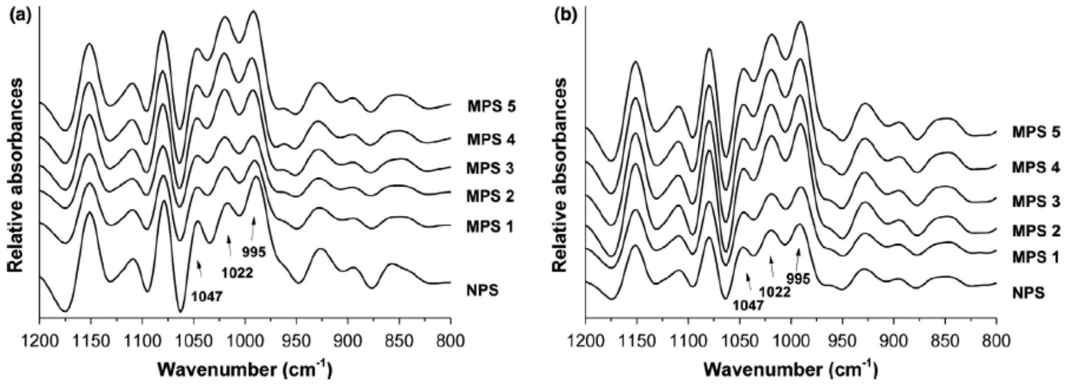
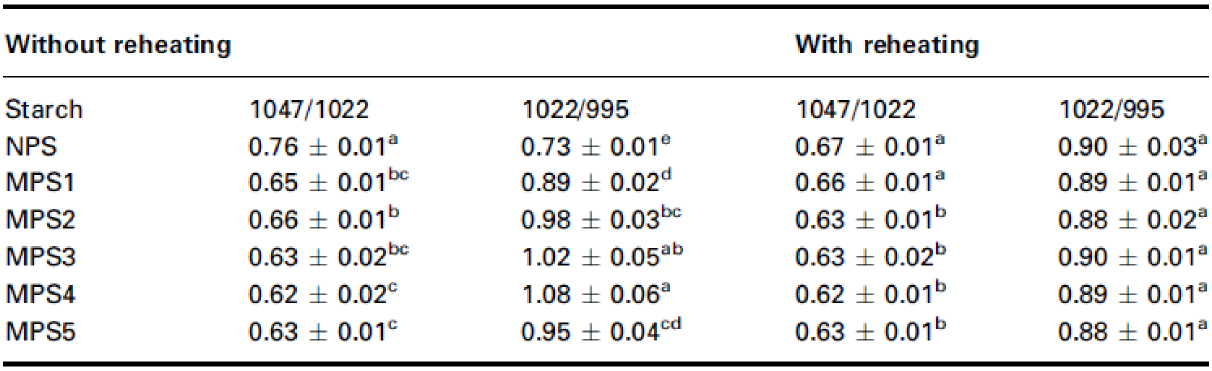


Figure 4 FTIR spectra of potato starch gels prepared from native and partially gelatinised starch with different DSG without (a) and with

reheating (b)

Table 3

Ratios of absorbance at 1047/1022cm-1 and 1022/995-1 of potato starch gels prepared from native and partially gelatinised starch with different DSG without and with reheating



Without reheating			With reheating	
Starch	1047/1022	1022/995	1047/1022	1022/995
NPS	0.76 ± 0.01^{a}	0.73 ± 0.01^{e}	0.67 ± 0.01^{a}	0.90 ± 0.03^{a}
MPS1	0.65 ± 0.01^{bc}	0.89 ± 0.02^{d}	0.66 ± 0.01^{a}	0.89 ± 0.01^{a}
MPS2	0.66 ± 0.01^{b}	0.98 ± 0.03^{bc}	0.63 ± 0.01^{b}	0.88 ± 0.02^{a}
MPS3	0.63 ± 0.02^{bc}	1.02 ± 0.05^{ab}	0.63 ± 0.02^{b}	0.90 ± 0.01^{a}
MPS4	0.62 ± 0.02^{c}	1.08 ± 0.06^{a}	0.62 ± 0.01^{b}	0.89 ± 0.01^{a}
MPS5	0.63 ± 0.01^{c}	0.95 ± 0.04^{cd}	0.63 ± 0.01^{b}	0.88 ± 0.01^{a}

Data are means ± SD. $^{a, b, c, d, e}$ represent the significant difference of starch samples with different DSG in column ($P < 0.05$).

HEAT MAP ANALYSIS

In order to visually demonstrate the changes in the physicochemical and structural properties of potato starch with different DSG, a heat map was generated, as shown in **Fig. 5**. The colours in the heat map represent the corresponding characteristics of each starch sample, and the values increased from red (minimum value) to green (maximum value). Results showed that NPS possessed the largest number of red parts of its R and setback values, while the starch sample with the DSG of 90.56% possessed the largest number of green parts. The result indicated that potato starch with larger initial DSG showed larger retrogradation than starch with lower initial DSG. The peak viscosity and breakdown decreased as DSG increased while final viscosity increased. In addition, the gel strength of starch without reheating increased as DSG increased. However, after reheating, starch samples with DSG of 56.11% showed the highest gel strength than NPS and starch samples with higher DSG. The short-range ordered structure of starch samples without reheating decreased as DSG increased since 1047/1022 decreased from green to red and 1022/995 increased from red to green.

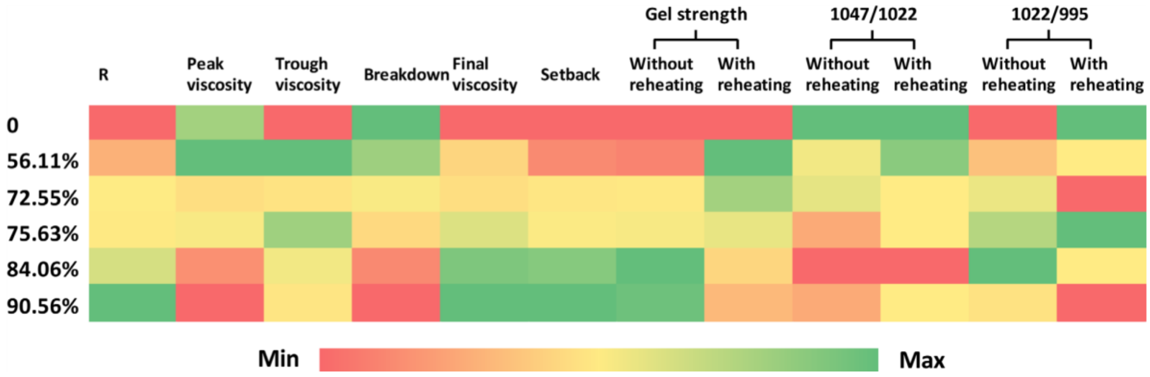


Figure 5 Heat map representation of the physicochemical and structural properties of partially gelatinised potato starch with different DSG

Conclusions

The initial DSG of partially gelatinised potato starch significantly affected its retrogradation, pasting, and structural properties. Potato starch with a larger initial DSG showed higher degrees of retrogradation after reheating. The gel strength of potato starch gels increased significantly as the DSG increased without reheating but decreased after reheating. The interspersed starch granules in starch gels without reheating affected the network formation, while all gel samples formed a honeycomb structure with increased porosity as DSG increased after reheating. The changes in the gel network structure after reheating could be related to the different degrees of dehydration synthesis in partially gelatinised potato starch samples. In conclusion, partially gelatinised potato starch with DSG equal to or greater than 56.11% has better dispersibility and stability in cold water than native starch. Moreover, partially gelatinised potato starch with moderate DSG can form starch gels with higher strength than native and fully gelatinised starch after reheating and thus has great application potential in food processing. Further studies on the application of partially gelatinised with different DSG are required in more complex food matrices.

Supplementary Material

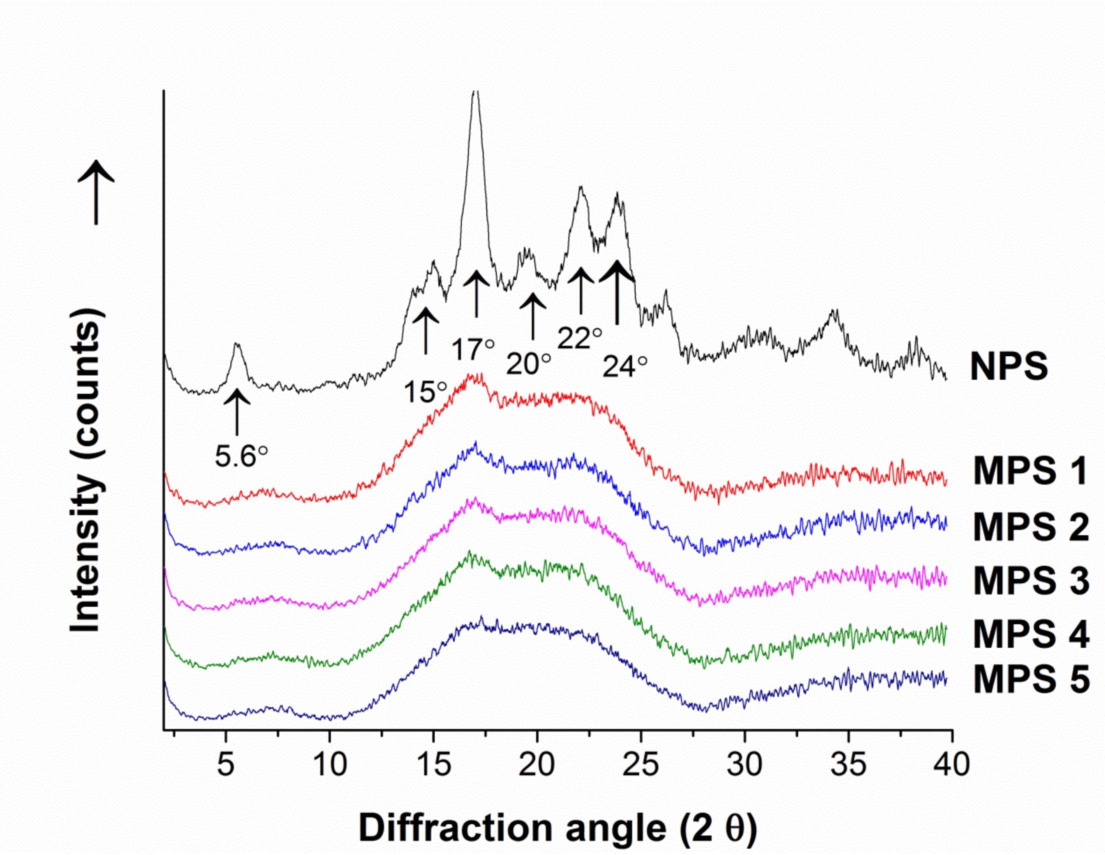


Figure S1. X-ray diffraction (XRD) patterns of native and partially gelatinized potato starch with different DSG.

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Author Contribution

Fen Xu: Formal analysis (lead); Investigation (lead); Writing-original draft (lead). **Wei Liu**: Formal analysis (equal); Investigation (equal). **Liang Zhang**: Conceptualization (equal); Methodology (equal). **Sabine Danthine**: Conceptualization (equal). **Qiannan Liu**: Formal analysis (equal); Investigation (equal). **Feng Wang**: Supervision (equal); Writing-review & editing (equal). **Hong Zhang**: Writing-review & editing (equal). **Honghai Hu**: Funding acquisition (lead); Project administration (equal); Writing-review & editing (equal). **Christophe Blecker**: Project administration (equal); Supervision (lead).

Ethical guidelines

Ethics approval was not required for this research.

Conflicts of interest

The authors declare that they do not have any conflict of interest.

Peer review

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Data availability statement

Data are available on request from the authors.

References

Al-Ansi, W., Mahdi, A.A., Al-Maqtari, Q.A. *et al.* (2021). Characterization of molecular, physicochemical, and morphological properties of starch isolated from germinated highland barley. *Food Bioscience*, 42, 101052.

Albano, K.M., Franco, C.M.L. & Telis, V.R.N. (2014). Rheological behavior of Peruvian carrot starch gels as affected by temperature and concentration. *Food Hydrocolloids*, 40, 30–43.

Bucsella, B., Takacs, A., Vizer, V., Schwendener, U. & Tomoskozi, S. (2016). Comparison of the effects of different heat treatment processes on rheological properties of cake and bread wheat flours. *Food Chemistry*, 190, 990–996.

Chung, H. J., Lim, H.S. & Lim, S. T. (2006). Effect of partial gelatinization and retrogradation on the enzymatic digestion of waxy rice starch. *Journal of Cereal Science*, 43, 353–359.

Cui, M., Fang, L., Zhou, H. & Yang, H. (2014). Effects of amino acids on the physiochemical properties of potato starch. *Food Chemistry*, 151, 162–167.

Denchai, N., Suwannaporn, P., Lin, J., Soontaranon, S., Kiatponglarp, W. & Huang, T.C. (2019). Retrogradation and digestibility of rice starch gels: The joint effect of degree of gelatinization and storage. *Journal of Food Science*, 84, 1400–1410.

This study reported that retrogradation of rice starch is found to be more prominent at higher gelatinization temperature. The result is consistent with our study and confirmed our conclusion that higher DSG leads to an increase in the retrogradation of partially gelatinized starch.

Dos Santos, T.P.R., Franco, C.M.L. & Leonel, M. (2020). Gelatinized sweet potato starches obtained at different preheating temperatures in a spray dryer. *International Journal of Biological Macromolecules*, 149, 1339–1346.

Fonseca-Florido, H.A., Méndez-Montealvo, G., Velázquez de la Cruz, G. *et al.* (2019). Physicochemical characteristics of stored gels from starch blends. *LWT - Food Science and Technology*, 114, 108408.

Fu, Z., Che, L., Li, D., Wang, L. & Adhikari, B. (2016). Effect of partially gelatinized corn starch on the rheological properties of wheat dough. *LWT - Food Science and Technology*, 66, 324–331.

Fu, Z., Wang, L., Li, D. & Adhikari, B. (2012). Effects of partial gelatinization on structure and thermal properties of corn starch after spray drying. *Carbohydrate Polymers*, 88, 1319–1325.

Fu, Z., Wu, M., Zhang, H. & Wang, J. (2018). Retrogradation of partially gelatinised potato starch prepared by ball milling. *International Journal of Food Science & Technology*, 53, 1065–1071.

Gryszkin, A., Zięba, T., Kapelko, M. & Buczek, A. (2014). Effect of thermal modifications of potato starch on its selected properties. *Food Hydrocolloids*, 40, 122–127.

Huang, T., Zhou, D., Jin, Z., Xu, X. & Chen, H. (2016). Effect of repeated heat-moisture treatments on digestibility, physicochemical and structural properties of sweet potato starch. *Food Hydrocolloids*, 54, 202–210.

Huang, Z., Xie, X., Chen, Y., Lu, J. & Tong, Z. (2008). Ball-milling treatment effect on physicochemical properties and features for cassava and maize starches. *Comptes Rendus Chimie*, 11, 73–79.

Singh, J. & Singh, N. (2001). Studies on the morphological, thermal and rheological properties of starch separated from some Indian potato cultivars. *Food Chemistry*, 75, 67–77.

Jiang, J., Zeng, J., Gao, H. *et al.* (2020). Effect of low temperature on the aging characteristics of a potato starch gel. *International Journal of Biological Macromolecules*, 150, 519–527.

This study characterized the process of starch gel formation. A dense, three-dimensional gel network with branches and edges can be formed by starch molecules after gelatinization and retrogradation. This provides information for the explanation of structure changes of potato starch gels in our study.

Li, W., Tian, X., Wang, P. *et al.* (2016). Recrystallization characteristics of high hydrostatic pressure gelatinized normal and waxy corn starch. *International Journal of Biological Macromolecules*, 83, 171–177.

Liu, Y., Chao, C., Yu, J., Wang, S., Wang, S. & Copeland, L. (2020). New insights into starch gelatinization by high pressure: Comparison with heat-gelatinization. *Food Chemistry*, 318, 126493.

Liu, Y., Chen, J., Luo, S. et al. (2017). Physicochemical and structural properties of pregelatinized starch prepared by improved extrusion cooking technology. *Carbohydrate Polymers*, 175, 265–272.

This study indicated that the starch granules in pre-gelatinized samples absorb water more easily and swell more quickly than native starch at low temperature. This could explain the increased viscosity as DSG increased at the first stage of RVA test in our study.

Malumba, P., Doran, L., Danthine, S., Blecker, C. & Béra, F. (2018). The effect of heating rates on functional properties of wheat and potato starch-water systems. *LWT - Food Science and Technology*, 88, 196–202.

Reyniers, S., Ooms, N., Gomand, S.V. & Delcour, J.A. (2020). What makes starch from potato (Solanum tuberosum L.) tubers unique: A review. *Comprehensive Reviews Food Science and Food Safety*, 19, 2588–2612.

Santos, T. P. R. D., Franco, C. M. L., Mischan, M. M. & Leonel, M. (2019). Improvement in spray-drying technology for preparation of pregelatinized cassava starch. Food Science and Technology, 39(4), 939–946.

Santos, T. P. R. D., Franco, C. M. L., Mischan, M. M., Fernandes, D. D. S., Bem, M. S. D. & Leonel, M. (2019a). Production of partially gelatinized cassava starch: Effects of preheating temperature and starch concentration on physicochemical characteristics during the spray-drying process. *Australian Journal of Crop Science*, 13, 1486–1494.

Wang, H., Xiao, N., Wang, X., Zhao, X. & Zhang, H. (2019). Effect of pregelatinized starch on the characteristics, microstructures, and quality attributes of glutinous rice flour and dumplings. *Food Chemistry*, 283, 248–256.

Wang, J., Zhu, H., Li, S., Wang, S., Wang, S. & Copeland, L. (2017a). Insights into structure and function of high pressuremodified starches with different crystalline polymorphs. *International Journal of Biological Macromolecules*, 102, 414–424.

This study provides the methods of starch characterization, for example the calculation of short-range ordered structure of starch. We referred to their methods in our experiments.

Wang, S., Li, P., Yu, J., Guo, P. & Wang, S. (2017b). Multi-scale structures and functional properties of starches from Indica hybrid, Japonica and waxy rice. *International Journal of Biological Macromolecules*, 102, 136–143.

Wang, S., Zhang, X., Wang, S. & Copeland, L. (2016). Changes of multi-scale structure during mimicked DSC heating reveal the nature of starch gelatinization. *Scientific Reports*, 6, 28271.

White, P.J., Abbas, R. & Johnson, L.A. (1989). Freeze-thaw stability and refrigerated-storage retrogradation of starches. *Starch - Stärke*, 41, 176–180.

Witczak, T., Witczak, M. & Ziobro, R. (2014). Effect of inulin and pectin on rheological and thermal properties of potato starch paste and gel. *Journal of Food Engineering*, 124, 72–79.

Xu, F., Zhang, L., Liu, W. *et al.* (2021). Physicochemical and structural characterization of potato starch with different degrees of gelatinization. *Foods*, 10, 1104.

Yang, L., Zhou, Y., Wu, Y. *et al.* (2016). Preparation and physicochemical properties of three types of modified glutinous rice starches. *Carbohydrate Polymers*, 137, 305–313.

Yu, S. X., Mu, T.H., Zhang, M. & Zhao, Z. K. (2016). Effects of inorganic salts on the structural and physicochemical properties of high-hydrostatic-pressure-gelatinized sweet potato starch. *Starch - Stärke*, 68, 980–988.

Zeng, F., Ma, F., Kong, F., Gao, Q. & Yu, S. (2015). Physicochemical properties and digestibility of hydrothermally treated waxy rice starch. *Food Chemistry*, 172, 92–98.

Zhang, L., Zhao, Y., Hu, W. *et al.* (2018). Multi-scale structures of cassava and potato starch fractions varying in granule size. *Carbohydrate Polymers*, 200, 400–407.

Zhang, Y., Huang, Z., Yang, C. *et al.* (2013). Material properties of partially pregelatinized cassava starch prepared by mechanical activation. *Starch - Stärke*, 65, 461–468.