Received: 14 March 2019 | Revised: 15 May 2019 | Accepted: 3 June 2019

DOI: 10.1111/jfpe.13168

ORIGINAL ARTICLE

Journal of Food Process Engineering WILEY

Effect of high hydrostatic pressure in physicochemical properties and in vitro digestibility of cornstarch by nuclear magnetic resonance relaxometry

Ilhami Okur[1,2] | Baris Ozel[1,3] | Mecit H. Oztop[1] | Hami Alpas[1]

[1]Department of Food Engineering, Middle East Technical University, Ankara, Turkey

[2]Department of Food Engineering, Niğde Ömer Halisdemir University, Nigde, Turkey

[3]Food Engineering Department, Ahi Evran University, Kirsehir, Turkey

Correspondence
Hami Alpas, Middle East Technical University, Engineering Faculty, Food Engineering Department, Ankara, Turkey.
Email: imah@metu.edu.tr

Funding information
European Cooperation in Science and Technology, Grant/Award Number: 15209; METU-BAP, Grant/Award Number: BAP-03-14-2017-001

Abstract

Starch is the major polysaccharide consumed by human being. It is not classified as a dietary fiber as it is digestible by the enzymes present in the saliva and small intestines. However, it is possible to modify starch with thermal and nonthermal techniques. High hydrostatic pressure (HHP) is a cold pasteurization technique that has increased application in food industry with minimum effect on nutritional quality of the food products. It is hypothesized that the use of HHP could be a modification strategy for starch. In this study, effects of different HHP parameters (400 and 500 MPa) at different temperatures (20, 30, and 40°C) for 5, 15, and 30 min on in vitro digestibility and physicochemical properties of cornstarch were studied by Nuclear magnetic resonance (NMR) relaxometry. Results showed that HHP treatment increased slowly digestible starch (SDS) and rapid digestible starch (RDS) significantly with pressure and temperature ($p < .05$). In addition, it was shown that HHP treatment decreased the solubility and swelling power of the cornstarch and it is proposed that 30 min HHP treatment at 500 MPa and 40°C is the onset for cornstarch gelatinization according to NMR relaxometry results.

Practical Applications

High hydrostatic pressure (HHP) is a nonthermal processing technology that is commonly used in the food industry for extending the shelf life of food products by destroying vegetative cells, enzymes, microorganisms effectively, and it can modify the starch so the aim of this study was to investigate the effects of different HHP parameters on in vitro digestibility and physicochemical properties of cornstarch by nuclear magnetic resonance relaxometry.

1 | INTRODUCTION

Starch is a carbohydrate consisting of a large number of glucose and it is a cheap, widespread, abundantly available, pollution-free, degradable, and renewable resource. Starch can be extracted from plants such as corn, wheat, rice, and so forth. Cornstarch is a widely available ingredient in the food industry and it is used as a gelling agent, thickener, bulking, and water retention agent. According to the digestion rate, cornstarch is divided into rapidly digestible starch (RDS), slowly digestible starch (SDS), and resistant starch (RS). In the small intestine, SDS is digested completely at a lower rate than RDS so SDS maintains a sustained supply of glucose with a low glycemic index (GI). This contributes to the prevention of different hyperglycemia-related diseases (Englyst, Kingman, & Cummings, 1992). In addition to this, SDS is beneficial to maintain body weight when SDS is used as a raw material in the production of foods (Jenkins et al., 2002). As a result, food having a high percent of SDS is accepted as a functional food with a low GI (Han et al., 2006; Zhang & Hamaker, 2009).

High HHP, a nonthermal processing technology, is a cold pasteurization technique and commonly used in the food industry for extending the shelf life of food products by destroying vegetative cells, enzymes, microorganisms effectively (Alpas et al., 1999; Alpas, Kalchayanand, Bozoglu, & Ray, 2000; Alpas, Lee, Bozoglu, & Kaletunç, 2003). It can be performed between 100 and 900 MPa to sterilize packed materials in a vessel (Tian, Li, Zhao, Xu, & Jin, 2014) so HHP is an alternative method to traditional treatments in food processing (Vallons & Arendt, 2009). Recent studies have shown the effects of HHP on the physicochemical properties of starches. According to the results, HHP treatment leads to gelatinization of starch and decrease swelling power and solubility of the starch. It was observed that starch gelatinization depends on the treatment pressure, time, and temperature (Bauer & Knorr, 2005; Li et al., 2015; Liu, Wang, Cao, Fan, & Wang, 2016; Oh, Pinder, Hemar, Anema, & Wong, 2008).

Nuclear magnetic resonance (NMR) is a rapid and nondestructive technique that is generally used in food science to investigate physiological and biochemical changes in food samples so it can be used to interpret the properties of various starch systems like starch gelatinization (Kirtil & Oztop, 2016; Ritota, Gianferri, Bucci, & Brosio, 2008). ^{1}H NMR relaxometry is used to measure the spin–spin relaxation and mobility of hydrogen molecules, and it is a practical tool to analyze proton relaxation in starch gels because signals come from all protons in the sample so that distribution and mobility of protons could be well expressed and spin–spin relaxation time (T_2) measurements are used to monitor the starch gelatinization (Hansen et al., 2009; Zhu, 2017).

The objective of the study was to find the effects of different HHP parameters on in vitro digestibility and physicochemical properties of cornstarch analyzed by NMR relaxometry and to explore if it was possible to modify cornstarch by using HHP.

2 | MATERIALS AND METHODS

2.1 | Materials

Cornstarch (Kenton, Turkey) was purchased from the local market (Ankara, Turkey). Cornstarch slurries (10%, wt/vol) were prepared and equilibrated at room temperature for a day before HHP treatment.

2.2 | HHP treatment

HHP treatment was performed with 760.0118 type pressure equipment (SITEC-Sieber Engineering AG, Zurich, Switzerland). Built-in heating–cooling system (Huber Circulation Thermostat, Offenburg, Germany) was used to maintain and control the temperature, which was measured by a thermocouple. The HHP equipment includes a pressurization chamber, two end closures, a means for restraining the end closures, a hydraulic unit, a pressure pump, and a temperature control device. A mixture of water and glycol and the liquid used as a pressure-transmitting medium was heated prior to pressurization to reach the desired temperature by using an electrical heating system surrounding the pressurization chamber. Pressurization chamber is 24 mm in internal diameter, 153 mm in length, and it has 100 mL capacity. Also, the rate of pressure increase and pressure release was roughly 5–10 s for the designed system so pressurization time reported in this study excluded the pressure increase and release times. Prepared cornstarch slurries (10%, wt/vol) were pressured in 25 mL sterile polyethylene cryotubes (Biosigma Sri, CLEARLINE, CryoGen Tubes) at different pressures (400 and 500 MPa) at different temperatures (20, 30, and 40°C) for 5, 15, and 30 min. After HHP treatment, samples were lyophilized (LGJ-10, China) for 48 hr to obtain powder form.

2.3 | In vitro digestibility

In vitro digestibility of powder, cornstarch samples was performed by Li and Zhu (2018). Two hundred milligram of cornstarch sample was dissolved in 15 mL phosphate buffer (Sigma, Germany) at pH 5.2 by using seven glass balls having 10 mm diameter. Next, the mixture was equilibrated at 37°C for 5 min. After this, the mixture was hydrolyzed by using 5 mL mixed enzyme mixture. Enzyme mixture included porcine pancreatic α-amylase (Sigma, Germany), 290 U/mL; amyloglucosidase (Sigma, Germany), 15 U/mL where U denotes the amount of enzyme which liberates 1.0 mg glucose from starch in 1 min at pH 5.2 at 37°C. During the time intervals of 20 and 120 min, 0.5 mL aliquots of the hydrolyzed solution were taken. Then, they were mixed with 4 mL of absolute ethanol (Sigma, Germany) to deactivate the enzyme and were centrifuged at 385*g* (Hettich EBA 20, Germany) for 10 min. According to 3,5-dinitrosalicylic acid method (Miller, 1959), the reducing sugar content in the supernatant was determined. The percentage of the hydrolyzed sample was calculated by multiplying the reducing sugar content by a conversion factor from glucose to starch of 0.9, which considers the removal of one water molecule per glucose unit.

The percentages of RDS, SDS, and RS fractions in starch samples were calculated by using the following formulas:

$$\mathrm{RDS}\,(\%) = \frac{(G_{20} - \mathrm{FG})}{\mathrm{TS}} \times 0.9 \times 100$$

$$\mathrm{SDS}\,(\%) = \frac{(G_{120} - G_{20})}{\mathrm{TS}} \times 0.9 \times 100$$

$$\mathrm{RDS}\,(\%) = \frac{(\mathrm{TS} - \mathrm{SDS} - \mathrm{RDS})}{\mathrm{TS}} \times 0.9 \times 100$$

G_{20} and G_{120} denoted the amounts of glucose released at the time interval of 20 and 120 min hydrolysis, respectively. Furthermore, FG denoted the amount of free glucose in cornstarch and TS means total cornstarch amount.

2.4 | Solubility

The solubility of the samples was measured according to Liu et al. (2016). Solubility was measured at 60, 70, 80, and 90°C in triplicate. Two hundred milligram of cornstarch sample and 10 mL of distilled water were put into 15 mL centrifuge tubes and kept in a water bath for 30 min at solubility temperature. While samples were in a water

bath, the sample–water mixture was vortexed every 5 min. After 30 min, the mixture was centrifuged at 2408*g* for 15 min and the supernatant was removed and incubated at 110°C for 8 hr. Then, the sample was cooled at room temperature at desiccator. The solubility of the cornstarch was measured by using the following equation:

$$\text{Solubility} = \frac{\text{Weight of dried supernatant}}{\text{weight of starch}}$$

2.5 | Swelling power

The swelling power of the samples was performed according to Liu, Guo, et al. (2016). The swelling power was calculated at 60, 70, 80, and 90°C in triplicate. In brief, 200 mg cornstarch sample and 10 mL of distilled water were put into 15 mL centrifuge tubes and kept in a water bath for 30 min at the desired temperature. While samples were in a water bath, the sample–water mixture was vortexed every 5 min. After 30 min, the mixture was centrifuged at 2,408*g* for 15 min and the supernatant was removed and incubated at 110°C for 8 hr. Then, the sample was cooled to room temperature at desiccator. SP of the cornstarch was measured according to the following formula:

$$\text{Swelling Power } (\mathbf{SP}) = \frac{\text{weight of swollen granules}}{\text{weight of starch}}$$

2.6 | NMR relaxometry

Spin–spin relaxation time experiments (T_2) were carried out for the powder samples using 0.5 T NMR spectrometer operating at the Larmor frequency of 20.34 MHz, equipped with a 10-mm diameter radio frequency coil (Spin Track SB, Russia). Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence was used to take the relaxation data with 50 ms echo time, 50 echoes, 4 scans, and 3 s repetition time.

2.7 | Scanning electron microscopy

Scanning electron microscopy (SEM) was used to interpret the morphological analysis of cornstarch samples after HHP treatment. The analysis was performed with a SEM (Quanta SC7620, England). Before imaging, samples were coated with a thin layer of Au–Pd (6–11 nm; 10 mA; 40 s) at room temperature.

2.8 | Statistical analysis

The Sigma Plot software package (SigmaPlot Ver.12, Chicago, IL) was used to analyze the results. Using *p* values less than .05 was accepted as statistically significant. Three-way ANOVA was used to determine which parameters (pressure, time, and temperature) were significantly important on physicochemical properties of cornstarch. Tukey's multiple range test was implemented to evaluate significant differences among the experimental mean values ($p < .05$).

3 | RESULTS AND DISCUSSION

3.1 | Solubility and swelling power

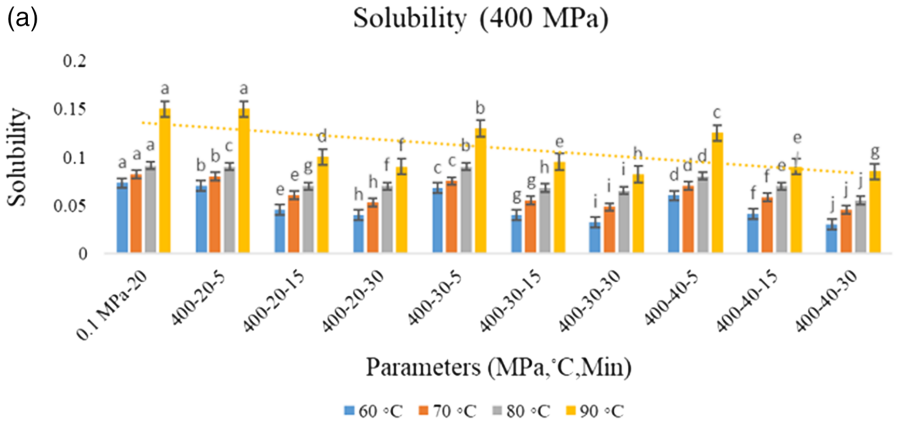
The effect of HHP on the SI and SP of cornstarch was shown in Figures 1 and 2. As seen in figures, the SI and SP of all samples decreased. In addition to this, the highest value for the SI and SP of all samples were obtained at 90°C. On the other hand, the SI and SP of the cornstarch decreased by HHP treatment and the reduction of SI and SP were related with pressure, temperature, and time parameters. Pressure, temperature, and time were found to be statistically significant at 60, 70, and 80 ($p < .05$). However, pressure, temperature, and time were not statistically significant at 90°C ($p > .05$). The previous studies in the literature also reported that the SI and SP of the starch samples decreased by HHP treatment and this was in agreement with our findings (Kim, Choi, Kim, & Baik, 2010; Li et al., 2015; Li & Zhu, 2018).

The SI and SP analyses of the starch were evidences about structural changes of the starch granules after HHP treatment (Singh & Kaur, 2004) and these analyses were affected by different factors such as amylose content, amylose–amylopectin ratio, length of branching (Hoover, 2001). During HHP treatment, rearrangement of starch molecules may have occurred due to HHP treatment. Partially or completely disintegrated starch granules limited the solubility of amylose and this inhibited the swelling of cornstarch and disintegrated the starch granules (Oh et al., 2008). Although the reduction of the SI and SP of starch occurred due to HHP treatment, more studies are needed to explain the mechanism of HHP treatment inhibiting SI and SP of starch, which is beyond the main aim of this study.

3.2 | In vitro digestibility

RS, RDS, and SDS content of cornstarch samples at different HHP treatments were shown in Figure 3. According to the results, RDS and SDS increased significantly by HHP treatment with pressure and temperature ($p < .05$). However, RS decreased significantly by HHP treatment with pressure and temperature ($p < .05$). Highest RS content was observed for native starch (62.5%). On the other hand, the highest RDS and SDS content (30 and 45%, respectively) were observed at 500 MPa–40°C–30 min.

These results demonstrated that HHP treatment could change the structure of cornstarch (Hu, Zhang, Jin, Xu, & Chen, 2017). A high enough level of pressure was reported to destroy the helical form of the amylopectin chains and to promote the distribution of water molecules and other components in waxy starch gels (Li, Bai, Mousaa, Zhang, & Shen, 2012; Tian et al., 2014). In addition to these, the formation of SDS might realize due to the transformation of RS in the granule state (Zeng, Li, Gao, Liu, & Yu, 2018). These reasons may have led to a reduction in the percentage of RS content in cornstarch and increase the percentage of SDS and RDS content as our pressure



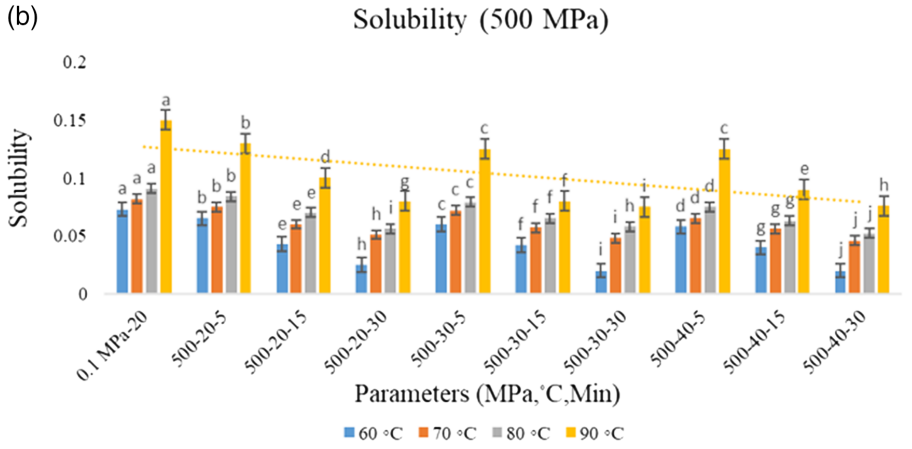
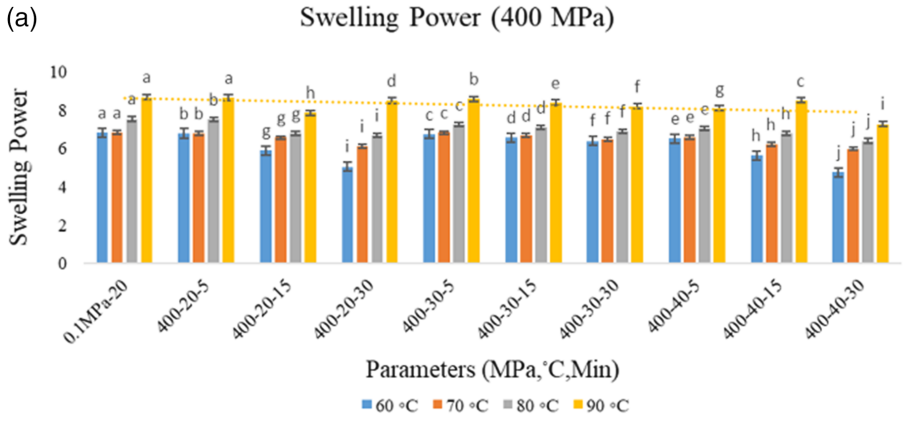


FIGURE 1 (a) The solubility (SI) of cornstarch as affected by HHP at 400 MPa. (B) The solubility (SI) of cornstarch as affected by HHP at 500 MPa



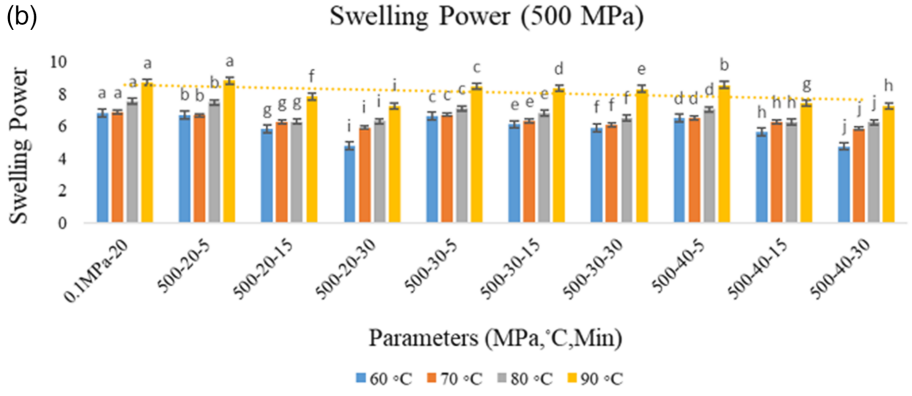


FIGURE 2 (a) The swelling power (SP) of cornstarch as affected by HHP at 400 MPa. (b) The swelling power (SP) of cornstarch as affected by HHP at 500 MPa

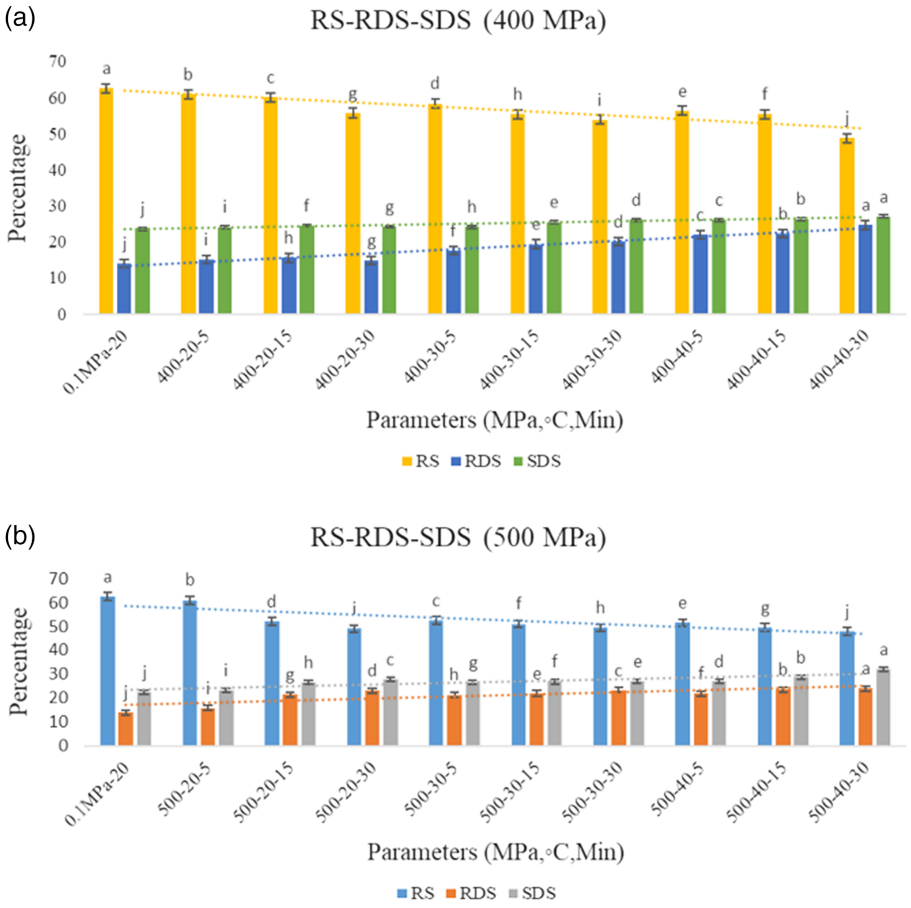


FIGURE 3 (a) The content of RDS, SDS, and RS fractions in HHP-treated cornstarch samples at 400 MPa. 0.1 MPa–20°C shows native starch. RDS, SDS, and RS show rapidly digestible starch, slowly digestible starch, and resistant starch, respectively. (b) The content of RDS, SDS, and RS fractions in HHP-treated cornstarch samples at 500 MPa

range was also within these reported limits (Hu et al., 2017; Li et al., 2012).

3.3 | Nuclear magnetic resonance relaxometry

Spin–spin relaxation time experiment (T_2) results at different HHP parameters were shown in Table 1. Pressure, temperature, and time combination was not found to be statistically significant on T_2 ($p > .05$) except for the HHP treatment of 500 MPa–40°C–30 min ($p < .05$). At this pressure–temperature–time combination, T_2 of the samples also increased significantly with respect to other HHP treated samples ($p < .05$). When the T_2 values were examined in detail, it was obvious that at 30 min treatment time, temperature increase from 30 to 40°C for either treatment pressure (400 and 500 MPa), increased the T_2 value ($p < .05$) (Figure 4a). Moreover, as shown in Figure 4a, pressure elevation from 400 to 500 MPa also resulted in T_2 increase in this case ($p < .05$). These results indicated the importance of longer HHP treatment at elevated temperatures in terms of T_2 increasing effect. Despite the T_2 increasing effect of HHP treatment on starch–water systems, several studies reported a decrease in T_2 values during heat-induced starch gelatinization without HHP treatment (Gonera & Cornillon, 2002; Ozel, Dag, Kilercioglu, Sumnu, & Oztop, 2017; Tananuwong & Reid, 2004). Reasons behind this phenomenon were mainly related to the effect of HHP on the crystalline and supramolecular structures (lamellae characteristics, fractal structures, etc.) of starch granules (Yang, Gu, et al., 2016). In addition, differences in the nature of heat and HHP induced starch gelling also contributed to this reverse T_2 correlation between conventional and HHP methods regarding starch gelatinization (Yang, Chaib, Gu, & Hemar, 2017). One of the differences was the shear forces (i.e., stirring) applied during conventional heating of a starch suspension. Stirring provoked granule disintegration, which was an absent incident in starch gelatinization by HHP (BeMiller & Huber, 2015).

Starch granules consist of amorphous and semicrystalline rings. Amorphous rings have disordered amylose and amylopectin conformations whereas semicrystalline rings have a lamellar structure with alternating crystalline and amorphous regions. The semicrystalline structure of starches plays a crucial role in starch gelatinization by HHP (Yang, Gu, et al., 2016). HHP was effective both on the lamellar and crystal structures. First, high pressure treatment of starch-water slurries could result in a transition from A-type to B-type crystalline structures (Katopo, Song, & Jane, 2002). Native cornstarch is mainly composed of A-type crystalline structure (Tananuwong & Reid, 2004). Due to its staggered lattice unit, A-type crystalline structures contain less water molecules per unit cell with respect to B-type crystallines having a more open packing helices inducing a more linear structure. B-type crystalline starches possess a larger amount of interhelical water leading to better hydrogen bonding networks. The helix structure is stabilized by a high number of associated water molecules via van der Waals forces (Yang, Gu, & Hemar, 2013). Therefore, B-type crystalline

TABLE 1 T_2 result of HHP treated cornstarch samples. 0.1 MPa–20°C shows native starch

Parameters (MPa, Temp, min)	T_2 (ms)
0.1 MPa–20	0.360 ± 0.007^{e}
400–20–5	0.206 ± 0.004^{h}
400–20–15	0.612 ± 0.011^{c}
400–20–30	0.430 ± 0.004^{d}
400–30–5	0.218 ± 0.008^{h}
400–30–15	0.218 ± 0.008^{h}
400–30–30	0.221 ± 0.003^{h}
400–40–5	0.211 ± 0.006^{h}
400–40–15	0.381 ± 0.006^{e}
400–40–30	0.294 ± 0.009^{g}
500–20–5	0.573 ± 0.011^{c}
500–20–15	0.845 ± 0.034^{b}
500–20–30	0.195 ± 0.003^{h}
500–30–5	0.307 ± 0.006^{g}
500–30–15	0.468 ± 0.005^{d}
500–30–30	0.372 ± 0.014^{e}
500–40–5	$0.351 \pm 0.015^{e,f}$
500–40–15	$0.314 \pm 0.005^{f,g}$
500–40–30	0.941 ± 0.009^{a}

Note. Values represented with different superscript letters are statistically different at $p < .05$.

starches are more resistant to pressure. Under HHP treatment, the A-type crystalline structure of cornstarch granules started to partially convert into B-type structures (Yang, Swedlund, et al., 2016). The emergence of B-type crystals favored less double helix dissociation contrary to intense double helix dissociation promoted by conventional heat induced starch gelatinization (Pei-Ling, Xiao-Song, & Qun, 2010). This distinct impact of HHP treatment on the starch crystalline structure during gelatinization led to less swelling of starch granules due to poor amylose leaching and granules remained intact (Yang et al., 2017). Restricted granule swelling was also induced by the presence of minor amounts of lipids within the starch molecules since starch gelatinization under HHP could form amylose-fatty acid complexes (Katopo et al., 2002). During HHP treatment, most of the amylose was retained within the granules so that the formation of these complexes limited the gelatinization of starch granules. These effects of HHP treatment on starch granules supported the decrease in SI and SP of our samples. HHP caused limited granule swelling thus lower SP and SI. SP and SI are enhanced by heat set gelling via granule disintegration due to the increased hydrogen bonding capability between the exposed starch amorphous regions and water, which could not be achieved by HHP, completely (Yang et al., 2017). Although swelling and solubilization properties of HHP treated starch granules depend on the type of starch, similar trends for SI and SP of different types of HHP treated starches were also observed by several studies (Guo et al., 2015; W. Li et al., 2012; Oh et al., 2008). In heat-set gelling, on the other hand, starch granules swell and disintegrate. This promotes more interaction between the starch and water molecules resulting in decreasing T_2 values (Tananuwong & Reid, 2004). However, less broken-intact HHP-treated starch granules could not interact with the continuous liquid phase intensely and the free portion of the water molecules increased the T_2 values. In our study, at 500 MPa pressure, water was forced into starch granules and increased their degree of hydration (Buckow, Jankowiak, Knorr, & Versteeg, 2009). This was mainly achieved by the effect of HHP on the lamellar and lattice structures of starch. At first, pressure induced compression decreased both the lamellar distance and lattice space but, at the onset of gelatinization, water penetrated into the lamellar blocks. After water migration, both the lamellar distance and lattice space increased (Yang et al., 2017). Diffused water was entrapped within the starch crystalline structure by high pressure and this entrapped water was another reason for the increased T_2 value of starch powders that were obtained from starch-water slurries exposed to 500 MPa–40°C–30 min HHP treatment. Therefore, it is proposed that 30 min HHP treatment at 500 MPa and 40°C is the onset for cornstarch gelatinization. Comparison of CPMG relaxation curves for native starch (Control) and 500 MPa–40°C–30 min HHP treated starch powders revealed the different transverse relaxation characteristics of the cornstarch samples in native and gelatinized states (Figure 4b). A rapid decay in signal intensity of Control samples ended up with lower final T_2 with respect to gelatinized samples by HHP treatment having a more gradual signal decay. A more detailed relaxation spectrum analysis of these two samples was also conducted by non-negative-least-squares (NNLS) analysis as depicted in Figure 4c. Each sample possessed two distinct proton populations with different peak times and peak areas representing the nature of distinct interactions taking place within the samples (Ozel, Uguz, Kilercioglu, Grunin, & Oztop, 2017). After 500 MPa–40°C–30 min HHP treatment, both the first and the second peak times of Control samples increased emphasizing the longer relaxation time. Especially the peak of HHP treated sample located at 1.7 ms contributed to the higher T_2 of these starch powders. This peak was the result of the entrapped water mainly interacting with each other within the crystalline structure of pressure-treated starch powders, which was induced by gelatinization. Shen et al. (2018), on the other hand, reported that HHP treatment on high amylose maize starch under 400 MPa did not change the fractal dimension significantly indicating that the 400 MPa and lower pressures had no significant influence on starch structure. In contrast, they reported a reduction in fractal dimension when the pressure was increased beyond 400 MPa, suggesting a minimum pressure value around 500 MPa for the beginning of starch gelatinization (Shen et al., 2018). Furthermore, complete gelatinization of starch granules under HHP treatment through strong interactions between the amylose and amylopectin chains leading to the formation of cavities and fractures on the granule surface was observed starting from 600 MPa pressure (Liu, Wang, et al., 2016; Shen et al., 2018). These findings were in agreement with our cornstarch gelatinization onset claim. The distinct increase in T_2 value for 500 MPa–40°C–30 min HHP treatment revealed that the starch

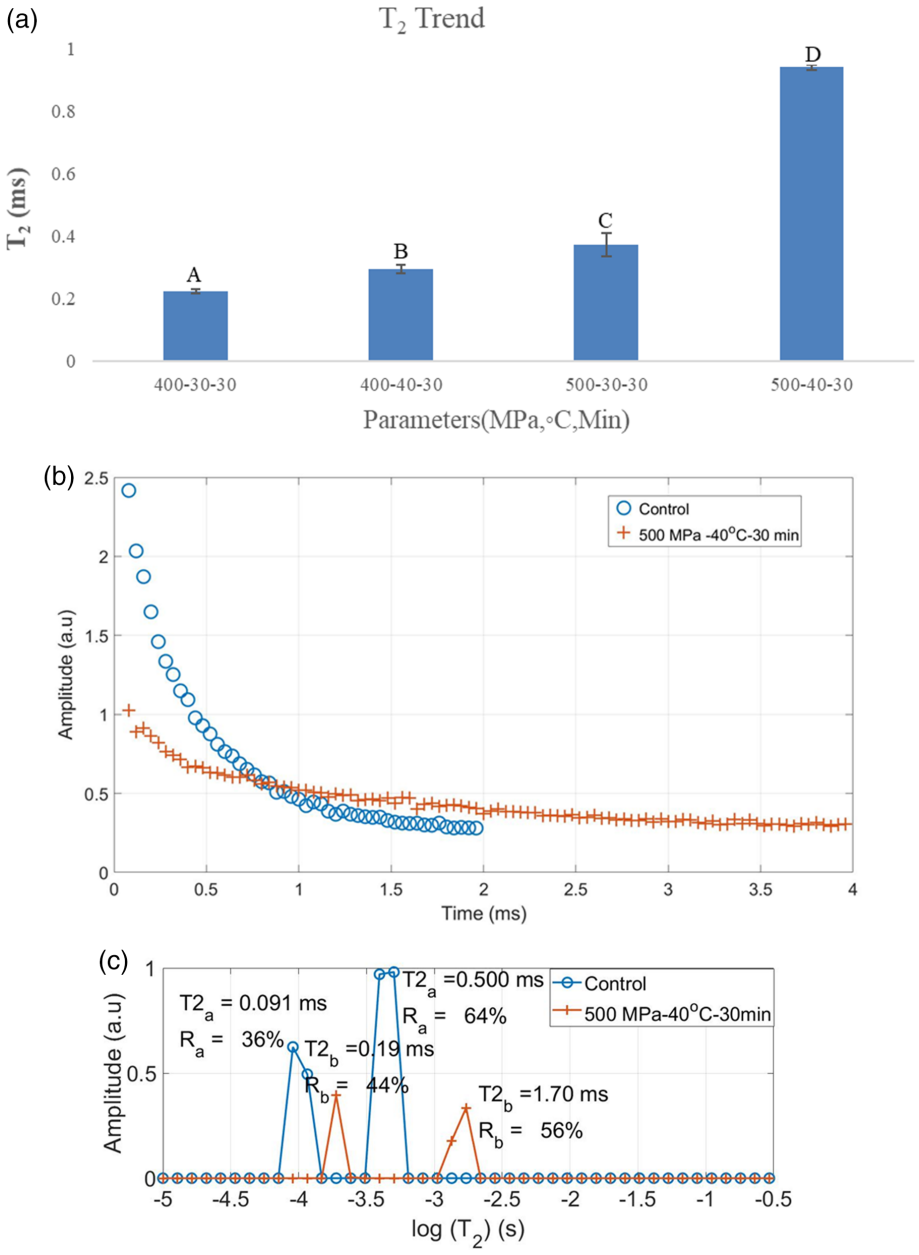


FIGURE 4 (a) T_2 trend of cornstarch samples treated at 30 min with HHP (400–500 MPa) and temperatures (30–40°C). (b) CPMG decay curves of Control (0.1 MPa–20°C) and HHP treated (500 MPa–40°C–30 min) cornstarch samples. (c) Non-negative-least-squares (NNLS) analysis of Control (0.1 MPa–20°C) and HHP-treated (500 MPa–40°C–30 min) cornstarch samples

gelatinization under HHP could be monitored by NMR relaxometry via transverse relaxation parameters.

3.4 | Morphological changes

Morphological changes of cornstarch granules were performed by SEM. Native cornstarch granules were smooth and had irregularly oval, spherical, and polygonal shapes on the surfaces (Figure 5a). Compared with native cornstarch, morphological changes started to form slowly at HHP treated samples especially at 500 MPa–40°C–30 min (Figure 5b–c) and this finding was also approved by NMR results. These samples' granules collapsed and gained an erythrocyte shape showing the typical granular structure upon pressure gelatinization (Douzals, Perrier Cornet, Gervais, & Coquille, 1998). The results showed that the effect of HHP on cornstarch morphological properties was affected by HHP treatment time. HHP treatment caused strong interactions between amylose and amylopectin chains and this was related to a compact structure with fissures, cavities, and holes on the surface (Błaszczak, Valverde, & Fornal, 2005). These observations were in good agreement with previous studies in the literature (Katopo et al., 2002; Li et al., 2012).

4 | CONCLUSION

In recent years, there has been many studies about the effects of HHP on starches. However, to the best of our knowledge, there is no report on the effect of HHP on physicochemical properties of cornstarch by NMR relaxometry. HHP treatment caused to rise in SDS and RDS content of cornstarch. On the other hand, the RS content of

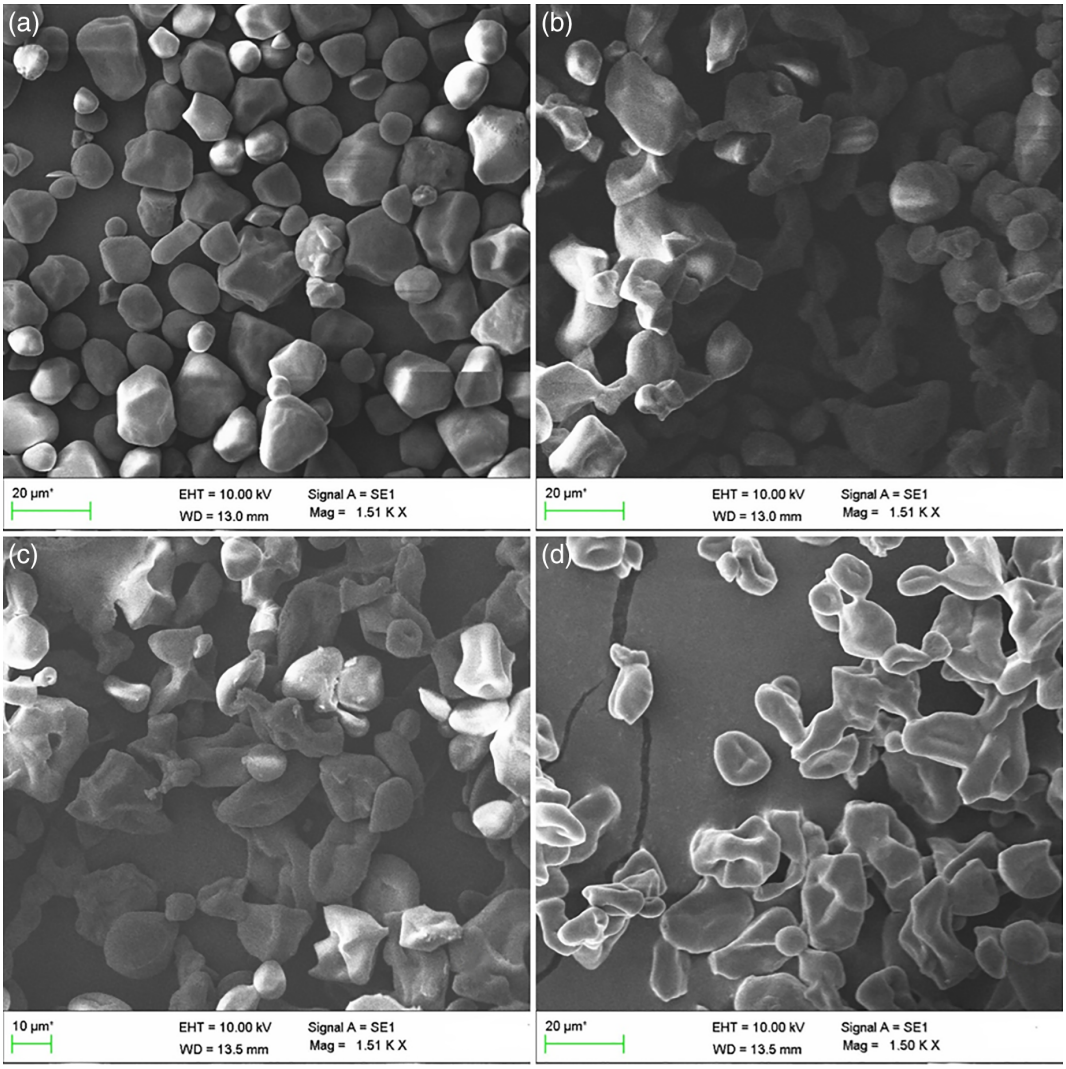


FIGURE 5 SEM images of HHP-treated cornstarch samples, Panel (a) 0.1 MPa–20°C (native starch) and Panel (b) HHP treatment (500 MPa–40°C–5 min). Panel (c) HHP treatment (500 MPa–40°C–15 min). Panel (d) HHP treatment (500 MPa–40°C–30 min)

cornstarch decreased by HHP treatment. The SI and SP of cornstarch were decreased. According to NMR results, the T_2 value was increased by HHP treatment because less broken-intact HHP-treated starch granules could not interact with the continuous liquid phase intensely and the free portion of the water molecules. In addition to these, HHP treatment affected the morphological properties of cornstarch. These results indicated that HHP treatment caused structural changes in cornstarch and this had an effect upon physicochemical properties of cornstarch.

ACKNOWLEDGMENTS

This study was funded by Middle East Technical University Research Fund Project (grant number BAP-03-14-2017-001). Also, COST Action CA 15209 European Network on Relaxometry is acknowledged as some of the findings are discussed in the action's network meetings and suggestions were taken into consideration in the final text. A part of the funding also came from Dr. Oztop's award of Science Academy's Young Scientist Awards Program (BAGEP).

ORCID

Mecit H. Oztop https://orcid.org/0000-0001-6414-8942
Hami Alpas https://orcid.org/0000-0002-7683-8796

REFERENCES

Alpas, H., Kalchayanand, N., Bozoglu, F., & Ray, B. (2000). Interactions of high hydrostatic pressure, pressurization temperature and pH on death and injury of pressure-resistant and pressure-sensitive strains of foodborne pathogens. *International Journal of Food Microbiology*, *60*(1), 33–42. https://doi.org/10.1016/S0168-1605(00)00324-X

Alpas, H., Kalchayanand, N., Bozoglu, F., Sikes, A., Dunne, C. P., & Ray, B. (1999). Variation in resistance to hydrostatic pressure among strains of food-borne pathogens. *Applied and Environmental Microbiology*, *65*(9), 4248–4251. Retrieved from. http://www.pubmedcentral.nih.gov/articlerender.fcgi?artid=99771&tool=pmcentrez&rendertype=abstract

Alpas, H., Lee, J., Bozoglu, F., & Kaletunç, G. (2003). Evaluation of high hydrostatic pressure sensitivity of *Staphylococcus aureus* and *Escherichia coli* O157:H7 by differential scanning calorimetry. *International Journal of Food Microbiology*, *87*(3), 229–237. https://doi.org/10.1016/S0168-1605(03)00066-7

Bauer, B. A., & Knorr, D. (2005). The impact of pressure, temperature and treatment time on starches: Pressure-induced starch gelatinisation as pressure time temperature indicator for high hydrostatic pressure processing. *Journal of Food Engineering*, *68*(3), 329–334. https://doi.org/10.1016/J.JFOODENG.2004.06.007

BeMiller, J. N., & Huber, K. C. (2015). Physical modification of food starch functionalities. *Annual Review of Food Science and Technology*, *6*(1), 19–69. https://doi.org/10.1146/annurev-food-022814-015552

Błaszczak, W., Valverde, S., & Fornal, J. (2005). Effect of high pressure on the structure of potato starch. *Carbohydrate Polymers*, *59*(3), 377–383. https://doi.org/10.1016/j.carbpol.2004.10.008

Buckow, R., Jankowiak, L., Knorr, D., & Versteeg, C. (2009). Pressure-temperature phase diagrams of maize starches with different amylose contents. *Journal of Agricultural and Food Chemistry*, *57*(24), 11510–11516. https://doi.org/10.1021/jf902246t

Douzals, J. P., Perrier Cornet, J. M., Gervais, P., & Coquille, J. C. (1998). High-pressure gelatinization of wheat starch and properties of pressure-induced gels. *Journal of Agricultural and Food Chemistry*, *46*(12), 4824–4829. https://doi.org/10.1021/jf971106p

Englyst, H. N., Kingman, S. M., & Cummings, J. H. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition*, *46*(Suppl. 2), S33–S50. https://doi.org/10.1111/j.1750-3841.2010.01627.x

Gonera, A., & Cornillon, P. (2002). Gelatinization of starch/gum/sugar systems. *Starch/Stärke*, *54*, 508–516.

Guo, Z., Zeng, S., Lu, X., Zhou, M., Zheng, M., & Zheng, B. (2015). Structural and physicochemical properties of lotus seed starch treated with ultra-high pressure. *Food Chemistry*, *186*, 223–230. https://doi.org/10.1016/j.foodchem.2015.03.069

Han, X. Z., Ao, Z., Janaswamy, S., Jane, J. L., Chandrasekaran, R., & Hamaker, B. R. (2006). Development of a low glycemic maize starch: Preparation and characterization. *Biomacromolecules*, *7*(4), 1162–1168. https://doi.org/10.1021/bm050991e

Hansen, M. R., Blennow, A., Farhat, I., Nørgaard, L., Pedersen, S., & Engelsen, S. B. (2009). Comparative NMR relaxometry of gels of amylomaltase-modified starch and gelatin. *Food Hydrocolloids*, *23*(8), 2038–2048. https://doi.org/10.1016/j.foodhyd.2009.05.008

Hoover, R. (2001). Composition, molecular structure, and physicochemical properties of tuber and root starches: A review. *Carbohydrate Polymers*, *45*(3), 253–267. https://doi.org/10.1016/S0144-8617(00)00260-5

Hu, X. P., Zhang, B., Jin, Z. Y., Xu, X. M., & Chen, H. Q. (2017). Effect of high hydrostatic pressure and retrogradation treatments on structural and physicochemical properties of waxy wheat starch. *Food Chemistry*, *232*, 560–565. https://doi.org/10.1016/j.foodchem.2017.04.040

Jenkins, D. J. A., Kendall, C. W. C., Augustin, L. S. A., Franceschi, S., Hamidi, M., & Marchie, A. (2002). Glycemic index : overview of implications in health and disease. *The American Journal of Clinical Nutrition*, *76*(1–4), 266–273.

Katopo, H., Song, Y., & Jane, J. L. (2002). Effect and mechanism of ultra-high hydrostatic pressure on the structure and properties of starches. *Carbohydrate Polymers*, *47*, 233–244.

Kim, H. S., Choi, H. S., Kim, B. Y., & Baik, M. Y. (2010). Characterization of acetylated corn starch prepared under ultrahigh pressure (UHP). *Journal of Agricultural and Food Chemistry*, *58*(6), 3573–3579. https://doi.org/10.1021/jf903939y

Kirtil, E., & Oztop, M. H. (2016). 1H nuclear magnetic resonance Relaxometry and magnetic resonance imaging and applications in food science and processing. *Food Engineering Reviews*, *8*(1), 1–22. https://doi.org/10.1007/s12393-015-9118-y

Li, G., & Zhu, F. (2018). Effect of high pressure on rheological and thermal properties of quinoa and maize starches. *Food Chemistry*, *241*, 380–386. https://doi.org/10.1016/j.foodchem.2017.08.088

Li, W., Bai, Y., Mousaa, S. A. S., Zhang, Q., & Shen, Q. (2012). Effect of high hydrostatic pressure on physicochemical and structural properties of Rice starch. *Food and Bioprocess Technology*, *5*(6), 2233–2241. https://doi.org/10.1007/s11947-011-0542-6

Li, W., Tian, X., Liu, L., Wang, P., Wu, G., Zheng, J., … Zhang, G. (2015). High pressure induced gelatinization of red adzuki bean starch and its effects on starch physicochemical and structural properties. *Food Hydrocolloids*, *45*, 132–139. https://doi.org/10.1016/j.foodhyd.2014.11.013

Liu, H., Guo, X., Li, Y., Li, H., Fan, H., & Wang, M. (2016). In vitro digestibility and changes in physicochemical and textural properties of tartary buckwheat starch under high hydrostatic pressure. *Journal of Food Engineering*, *189*, 64–71. https://doi.org/10.1016/j.jfoodeng.2016.05.015

Liu, H., Wang, L., Cao, R., Fan, H., & Wang, M. (2016). In vitro digestibility and changes in physicochemical and structural properties of common buckwheat starch affected by high hydrostatic pressure. *Carbohydrate Polymers*, *144*, 1–8. https://doi.org/10.1016/J.CARBPOL.2016.02.028

Miller, G. L. (1959). Use of dinitrosalicylic acid reagent for determination of reducing sugar. *Analytical Chemistry*, *31*(3), 426–428. https://doi.org/10.1021/ac60147a030

Oh, H. E., Pinder, D. N., Hemar, Y., Anema, S. G., & Wong, M. (2008). Effect of high-pressure treatment on various starch-in-water suspensions. *Food Hydrocolloids*, *22*(1), 150–155. https://doi.org/10.1016/J.FOODHYD.2007.01.028

Ozel, B., Dag, D., Kilercioglu, M., Sumnu, S. G., & Oztop, M. H. (2017). NMR relaxometry as a tool to understand the effect of microwave heating on starch-water interactions and gelatinization behavior. *LWT - Food Science and Technology*, *83*, 10–17. https://doi.org/10.1016/j.lwt.2017.04.077

Ozel, B., Uguz, S. S., Kilercioglu, M., Grunin, L., & Oztop, M. H. (2017). Effect of different polysaccharides on swelling of composite whey protein hydrogels: A low field (LF) NMR relaxometry study. *Journal of Food Process Engineering*, *40*(3), 1–9. https://doi.org/10.1111/jfpe.12465

Pei-Ling, L., Xiao-Song, H., & Qun, S. (2010). Effect of high hydrostatic pressure on starches: A review. *Starch - Stärke*, *62*(12), 615–628. https://doi.org/10.1002/star.201000001

Ritota, M., Gianferri, R., Bucci, R., & Brosio, E. (2008). Proton NMR relaxation study of swelling and gelatinisation process in rice starch–water samples. *Food Chemistry*, *110*(1), 14–22. https://doi.org/10.1016/j.foodchem.2008.01.048

Shen, X., Shang, W., Strappe, P., Chen, L., Li, X., Zhou, Z., & Blanchard, C. (2018). Manipulation of the internal structure of high amylose maize starch by high pressure treatment and its diverse influence on digestion. *Food Hydrocolloids*, *77*, 40–48. https://doi.org/10.1016/j.foodhyd.2017.09.015

Singh, N., & Kaur, L. (2004). Morphological, thermal, rheological and retrogradation properties of potato starch fractions varying in granule size. *Journal of the Science of Food and Agriculture*, *84*(10), 1241–1252. https://doi.org/10.1002/jsfa.1746

Tananuwong, K., & Reid, D. S. (2004). DSC and NMR relaxation studies of starch-water interactions during gelatinization. *Carbohydrate Polymers*, *58*(3), 345–358. https://doi.org/10.1016/j.carbpol.2004.08.003

Tian, Y., Li, D., Zhao, J., Xu, X., & Jin, Z. (2014). Effect of high hydrostatic pressure (HHP) on slowly digestible properties of rice starches. *Food Chemistry*, *152*, 225–229. https://doi.org/10.1016/J.FOODCHEM.2013.11.162

Vallons, K. J. R., & Arendt, E. K. (2009). Effects of high pressure and temperature on the structural and rheological properties of sorghum starch. *Innovative Food Science and Emerging Technologies*, *10*(4), 449–456. https://doi.org/10.1016/j.ifset.2009.06.008

Yang, Z., Chaib, S., Gu, Q., & Hemar, Y. (2017). Impact of pressure on physicochemical properties of starch dispersions. *Food Hydrocolloids*, *68*, 164–177. https://doi.org/10.1016/j.foodhyd.2016.08.032

Yang, Z., Gu, Q., & Hemar, Y. (2013). In situ study of maize starch gelatinization under ultra-high hydrostatic pressure using X-ray diffraction. *Carbohydrate Polymers*, *97*(1), 235–238. https://doi.org/10.1016/j.carbpol.2013.04.075

Yang, Z., Gu, Q., Lam, E., Tian, F., Chaieb, S., & Hemar, Y. (2016). In situ study starch gelatinization under ultra-high hydrostatic pressure using synchrotron SAXS. *Food Hydrocolloids*, *56*, 58–61. https://doi.org/10.1016/j.foodhyd.2015.12.007

Yang, Z., Swedlund, P., Hemar, Y., Mo, G., Wei, Y., Li, Z., & Wu, Z. (2016). Effect of high hydrostatic pressure on the supramolecular structure of corn starch with different amylose contents. *International Journal of Biological Macromolecules*, *85*, 604–614. https://doi.org/10.1016/j.ijbiomac.2016.01.018

Zeng, F., Li, T., Gao, Q., Liu, B., & Yu, S. (2018). Physicochemical properties and in vitro digestibility of high hydrostatic pressure treated waxy rice starch. *International Journal of Biological Macromolecules*, *120*, 1030–1038. https://doi.org/10.1016/j.ijbiomac.2018.08.121

Zhang, G., & Hamaker, B. R. (2009). Slowly digestible starch: Concept, mechanism, and proposed extended glycemic index. *Critical Reviews in Food Science and Nutrition*, *49*(10), 852–867. https://doi.org/10.1080/10408390903372466

Zhu, F. (2017). NMR spectroscopy of starch systems. *Food Hydrocolloids*, *63*, 611–624. https://doi.org/10.1016/j.foodhyd.2016.10.015

How to cite this article: Okur I, Ozel B, Oztop MH, Alpas H. Effect of high hydrostatic pressure in physicochemical properties and in vitro digestibility of cornstarch by nuclear magnetic resonance relaxometry. *J Food Process Eng*. 2019;42: e13168. https://doi.org/10.1111/jfpe.13168