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Ultra high pressure (UHP)-assisted hydroxypropylation of corn starch

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ABSTRACT

Reactivity and property of corn starches hydroxypropylated under ultra high pressure were investigated as a function of either pressure levels or pressure holding times. Corn starch was derivatized with propylene oxide (PO) either at 0.1–400 MPa for 15 min or at 400 MPa for 5–25 min, and assessed with respect to molar substitution (MS), X-ray diffraction pattern, solubility, swelling power, gelatinization, and pasting behavior. While an increase in pressure level enhanced MS values of UHP-assisted PO starch derivatives, starch reactivity was less influenced by pressure holding time. UHP-assisted PO reaction reduced reaction time to the greatest extents compared to long reaction time in conventional PO reaction. UHP-assisted PO starch derivatives revealed similar solubilities/swelling powers, and gelatinization properties, regardless of pressure levels. Higher gelatinization temperature was observed for UHP-assisted PO starch derivatives and their respective controls relative to native starch, implying that UHP-assisted reaction might involve starch annealing.

1. Introduction

Starch consisting of both linear and highly branched polymers of α-D-glucose (amylose and amylopectin, respectively) is present in a granular form within higher plants (Jane, 1995). It has been extensively used as textural stabilizer and/or physical property regulator for food and non-food industrial applications, due to its relative low cost, worldwide abundance, and renewable nature (Jane, 1995; Lawal, 2009; Singh, Kaur, & McCarthy, 2007). However, utilization of granular starch in its native form is limited, due to its undesirable defects such as poor solubility, low heat and shear resistance, uncontrolled paste consistency, high tendency toward retrogradation and gelling, and low freeze–thaw stability of pastes (BeMiller, 1997; Lawal, 2009; Singh et al., 2007). To overcome these shortcomings, modification of starch is widely used to improve and enhance its inherent properties in accordance with the intended purposes (BeMiller, 1997; Singh et al., 2007). Starch modification is generally realized via derivatization (e.g., etherification, esterification and cross-linking), partial decomposition (e.g., acid or enzymatic hydrolysis and oxidation), and physical treatment (e.g., annealing and heat-moisture treatment) (BeMiller, 1997; Jane, 1995; Singh et al., 2007). Within the chemically modified starches for food industrial applications, hydroxypropylation is the most common way of preparing starch ether by reacting starch granules with propylene oxide (PO) (Liu, Ramsden, & Corke, 1999). Incorporation of hydrophilic, bulky hydroxypropyl groups into starch chains weakens the internal bonds among starch molecules and in turn impacts granule stability, altering starch granule properties and functionalities (Gunaratne and Corke, 2007; Lawal, 2009). Hydroxypropylated starch derivatives retarded retrogradation, decreased gelatinization temperature, enhanced granule swelling, increased peak viscosity and paste clarity, and improved freeze–thaw stability (BeMiller, 1997; Chuenkamol, Puttanlek, Rungsardthong, & Uttapap, 2007; Gunaratne and Corke, 2007; Lawal, 2009; Liu et al., 1999; Singh et al., 2007; Wootton and Manatsathit, 1983). However, the diverse demands for textural and physical properties inherent to complex food systems exceed the beneficial effects of hydroxypropylation on native (unmodified) starch granule properties/functionalities (under the current regulatory practice). Thus, it is needed to expand properties and functionalities of hydroxypropylated starches.

Great attention to ultra high pressure (UHP), or high hydrostatic pressure (HHP), technology has been paid for physical modification of starch (Stute, Klingler, Boguslawski, Eshtiaghi, & Knorr, 1996), though annealing and/or heat-moisture treatment are conventionally devoted to alteration of granule structures via starch molecule interaction and starch crystallite disruption/reorientation within the amorphous and crystalline regions, respectively (Gunaratne and Corke, 2007; Jayakody and Hoover, 2008). UHP treatment of the starch–water suspension hydrates starch granules, leading to the granule swelling and crystalline region distortion within granules, and thus, the crystalline regions become more accessible to water (Buckow, Heinz, & Knorr, 2007; Douzals, Marechal, Coquille, & Gervais, 1996; Douzals, Perrier-Cornet, Gervais, & Coquille, 1998;

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Oh, Pinder, Hemar, Anema, & Wong, 2008). Finally, starch granules are non-thermally gelatinized over a critical pressure level which varied depending on botanical sources and crystal packing arrangements within starch granules (Blaszczak, Fornal, Valverde, & Garrido, 2005; Buckow et al., 2007; Oh et al., 2008; Stolt, Oinonen, & Autio, 2001). Further, UHP-treated starches that are little or partially gelatinized still preserve their granular structures (Blaszczak et al., 2005; Stolt et al., 2001; Stute et al., 1996), and inhibit leaching of starch molecules (including amylose) from granules and granule swelling capacity (Douzals et al., 1998; Katopo, Song, & Jane, 2002; Stolt et al., 2001; Stute et al., 1996). Moreover, treatment of starch granule with UHP has been reported to convert its crystallite patterns from A-type to B-type (Hibi, Matsumoto, & Hagiwara, 1993; Katopo et al., 2002). These noted characteristics of UHP-treated starch granules are anticipated to impact reactivities and physical properties of chemically modified starch granules. However, little information is available for association of starch chemical modification with the UHP technique to develop modified starch products with novel properties for food and non-food industrial applications. To date, there have been several attempts to apply UHP to modification of native starch granules via partial hydrolysis with acids (e.g., hydrochloric acid, sulfuric acid, oxalic acid) (Choi, Lee, Ahn, Kim, & Baik, 2009; Lee et al., 2006) and derivatization with phosphorus oxychloride (Hwang, Kim, & Baik, 2009) and acetic anhydride (Choi, Kim, Park, Kim, & Baik, 2009). UHP is thought to promote acid-hydrolysis and chemical derivatization of native starch in the non-thermal state. However, the fast-reacting nature of phosphorus oxychloride and acetic anhydrous overshadows UHP effects on cross-linking and acetylation reactions. Thus, this study investigated impact of UHP (as function of pressure level and pressure holding time) on reactivity of corn starch granules in substitution reaction with PO (a slow-reacting reagent). Furthermore, the UHP-assisted PO starch derivatives were characterized with respect to starch solubility, swelling power, gelatinization, and pasting properties in order to aid an understanding of UHP effects on starch hydroxypropylation.

2. Materials and methods

2.1. Materials

Normal corn starch, possessing 26.5% (dry starch weight basis or s.b.) amylose and 10.5% (dry weight basis or d.b.) moisture contents, was kindly donated from Daesang Co. (Ichon, Korea), and used for this study without further purification. PO and sodium sulfate (anhydrous) were purchased from Sigma Chemical Co. (St. Louis, MO, USA). All other chemical reagents used in this study were analytical grade.

2.2. Conventional starch derivatization with propylene oxide

Conventional derivatization of normal corn starch with PO was conducted according to the method of Wootton and Manatsathit (1983). Native starch (20 g, d.b.) was combined with 80 ml of double distilled water (DDW) containing anhydrous sodium sulfate (8%, s.b.) under rapid stirring using a magnetic stir bar. The pH of the starch slurry was elevated to 11.5 using 1 M NaOH, followed by addition of PO (12%, s.b.) in a dropwise fashion with vigorous stirring. The reaction vessel was sealed tightly with a rubber stopper, after which it was incubated for 20 h in a water bath at 45 °C under continuous stirring using immersing magnetic stirrer (PL-S300R, Poong Lim Co., Seoul, Korea). At the conclusion of reaction, the resultant reaction mixture was neutralized to pH 5.5 with 1 M HCl, and centrifuged at 1500 × *g* for 20 min. The recovered starch pellet was washed three times with double distilled water (DDW), and dried at 40 °C for 24 h. The dried starch pellets were ground using a mortar and pestle, and passed through an 80-mesh sieve (pore size: 180 μm) for further analysis. The conventional PO starch derivative was used as a reaction control.

2.3. Ultra high pressure (UHP)-assisted starch derivatization with propylene oxide

For UHP-assisted PO derivatization, the reaction mixture was same to that prepared for conventional PO derivatization (Section 2.2). After completion of PO addition, the reaction mixture (approximately 100 g) was immediately transferred into a retortable pouch and hermetically sealed using a heat sealer (the minimal headspace in the sealed pouch was maintained). It was pressurized in an UHP unit (2 L capacity, Autoclave Engineers, Erie, PA, USA) at rate of 20 MPa/s using DDW as a pressure medium. The temperature of the UHP unit increased from 25 to 27 °C by pressurization up to 400 MPa, and returned to 25 °C in a few seconds. The UHP unit was maintained at 25 °C during pressure holding time (up to 25 min). The UHP treatments were conducted either at different pressure levels (0.1, 100, 200, 300, and 400 MPa) for 15 min or at 400 MPa for different pressure holding periods (5, 15, and 25 min) to investigate effects of UHP treatment parameters on derivatization of normal corn starch with PO. Reaction system parameters for all PO starch derivatives are depicted in Table 1. Moreover, to determine influence of UHP on solubility/swelling, gelatinization, and pasting properties of the UHP-assisted PO starch derivatives, the UHP controls were prepared via subjection of the reaction mixture in the absence of PO to UHP treatment for 15 min at 100, 200, 300, and 400 MPa (designated as UHP2C, UHP3C, UHP4C, and UHP5C, respectively). After pressurization for predetermined periods, the resultant reaction mixtures were subjected to the post-reaction procedures (i.e., neutralization, recovery, washing, drying, grinding, and sieving) as previously described for conventional PO starch derivative (Section 2.2).

2.4. Determination of molar substitution (MS)

Both conventional and UHP-assisted PO starch derivatives were assayed for hydroxypropyl group contents via a spectrophotometric method of Johnson (1969) to determine molar substitution (MS) levels. Starch samples (0.1 g, d.b.) were weighed into a 100-ml volumetric flask, followed by addition of 0.5 M sulfuric acid (25 ml). The flasks were heated in a boiling water bath until starch suspension became a clear solution. The resultant starch solutions were cooled in an ice bath and diluted to 100 ml with DDW. The aliquots (1 ml) of the diluted solutions were transferred into the 25-ml graduated test tubes (with a glass stopper) in the ice bath, after which concentrated sulfuric acid (8 ml) was added dropwise to the tubes and mixed well. The tubes were heated for 3 min in the boiling water bath, and then immediately chilled in the ice bath. Ninhydrin reagent (3% ninhydrin in 5% $Na_2S_2O_5$; 0.6 ml) was added and mixed well. The tubes were incubated at 25 °C for 100 min, after which the purplish solutions were diluted to 25 ml with concentrated sulfuric acid and mixed well by inverting the tubes 10 times. It was transferred to 1-cm cells, and after 5 min, the absorbance was measured at 590 nm. Native starch was used as reference. A calibration curve was also prepared with aliquots (1 ml) of aqueous standard solutions, containing 10, 20, 30, 40 and 50 mg of propylene glycol per unit volume (ml). Measured propylene glycol was converted to hydroxypropyl group equivalent by applying the factor of 0.7763. MS values were calculated as the ratio of moles of hydroxypropyl groups to those of starch within the modified starches.

2.5. Starch analysis

For native (unmodified) and all PO starch derivatives (including UHP control), X-ray diffraction (XRD) patterns were obtained using

Table 1
Reaction system parameters and mean[a] molar substitution (MS) values for hydroxypropylated corn starches.

Sample	Reagent (%, s.b.[b])	pH	Na_2SO_4 (%, s.b.[b])	Temperature (°C)	Pressure (MPa)	Time (min)	MS[c]
Reaction control[d]	12.0	11.5	8.0	45	0.1	1200[e]	0.112 ± 0.001^{A}
UHP1[f]	12.0	11.5	8.0	25	0.1	15[g]	0.018 ± 0.001^{F}
UHP2[f]	12.0	11.5	8.0	25	100	15[g]	0.040 ± 0.001^{E}
UHP3[f]	12.0	11.5	8.0	25	200	15[g]	0.041 ± 0.001^{E}
UHP4[f]	12.0	11.5	8.0	25	300	15[g]	0.064 ± 0.008^{D}
UHP5[f]	12.0	11.5	8.0	25	400	15[g]	0.090 ± 0.001^{B}
UHP6[f]	12.0	11.5	8.0	25	400	5[g]	0.075 ± 0.001^{C}
UHP7[f]	12.0	11.5	8.0	25	400	25[g]	0.087 ± 0.001^{B}

[a] Mean value of three replicate reactions; MS values sharing the same uppercase letter within a column are not significantly different ($p < 0.05$).
[b] Dry starch weight basis.
[c] Defined as the ratio of moles of hydroxypropyl groups to those of starch within hydroxypropylated corn starch granules.
[d] Conventional aqueous reaction.
[e] Incubation time.
[f] Reactions under ultra high pressure environment.
[g] Pressure holding times.

an X-ray diffractometer (M18XHF-SRA, Mac Science Co., Yokohama, Japan) at scanning angle 2θ from 5 to 35° (Lee et al., 2006). Solubility and swelling power were determined at 90 °C using a scheme outlined by Choi, Kim, et al. (2009). Gelatinization temperatures (e.g., onset, peak, completion) and enthalpy were analyzed using a differential scanning calorimeter (DSC-650, Sinco Co., Seoul, Korea) (Choi, Kim, et al., 2009). Pasting viscosity profiles and characteristics were investigated using the Rapid Visco Analyzer (RVA) (Newport Scientific, NSW, Australia) according to standard method 1 (STD1) instructed by a supplier.

2.6. *Statistical analysis*

The conventional and UHP-assisted PO reactions (including UHP control) were replicated three times for each treatment combination of pressure levels and holding periods. MS values, and all measured starch characteristics and properties were determined at least twice for each experimental replicate. Also, experimental data were analyzed using Analysis of Variance (ANOVA), and expressed as mean values ± standard deviations. A Duncan's multiple range test was conducted to assess significant differences among experimental mean values ($\alpha < 0.05$). All statistical computations and analyses were conducted using SAS version 8.02 for Windows (SAS Institute, Inc., Cary, NC).

3. Results and discussion

3.1. *Effect of pressure level on reaction of normal corn starch with propylene oxide*

Our previous studies accomplished successful derivatization of normal corn starch with either phosphorus oxychloride (Hwang et al., 2009) or acetic anhydride (Choi, Kim, et al., 2009) under UHP. However, utilization of the fast-reacting reagents in both previous studies may make it difficult to verify impacts of UHP treatment on reactivity of starch granules in chemical derivatization and physicochemical property of modified starch derivatives. To avoid interference of highly reactive reagent in UHP effects on starch chemical derivatization, normal corn starch was derivatized with PO at different pressure level/pressure holding time combinations so as to provide definite evidence that UHP facilitates chemical derivatization of starch. Conventional PO reaction was also conducted as a reaction control to verify the validity and efficiency of UHP-assisted PO reaction. The MS value of the reaction control was 0.112 (Table 1), comparable to that of the hydroxypropylated normal corn starch prepared by Wootton and Manatsathit (1983) whose reaction conditions were very similar to those used in this study.

Reactivities of starch to PO increased, along with increasing pressure levels from 0.1 to 400 MPa (Table 1), consistent with trends observed by others (Choi, Kim, et al., 2009; Choi, Lee, et al., 2009). Choi, Lee, et al. (2009) exhibited that acid-hydrolysis of starch under UHP was enhanced, as pressure levels increased from 150 to 600 MPa. Choi, Kim, et al. (2009) revealed that an increase in pressure levels (up to 400 MPa) increased degree of substitution values of the UHP-assisted acetylated starch derivatives. Thus, the observed results in this study may be explained as described by Choi, Kim, et al. (2009) that the elevation of pressure levels increasingly enhanced hydration and swelling of starch granules in an aqueous reaction mixture, facilitating infiltration of reagent and/or alkali into interior of granules; further, improved accessibility of reagent into starch molecules and/or internal matrix led to greater reactivity of starch granule.

Relative to the MS value of the reaction control, furthermore, all the UHP-assisted PO starch derivatives exhibited lower MS values over applied pressure levels (Table 1). While the maximum MS value (UHP5, reacted at 400 MPa) of the UHP-assisted PO starch derivatives was reached only 80.3% of the MS value of the reaction control, UHP-assisted PO reaction was achieved within reaction time of 15 min, equivalent to an approximately 0.2% level of reaction time (1200 min) in conventional PO reaction (Table 1). The similar phenomenon was also observed between UHP-assisted and conventional acetylation reactions (Choi, Kim, et al., 2009), though reduction in reaction time by UHP treatment was much less (≈25%) than in this study (≈99%). Moreover, conventional derivatization of starch with PO is commonly known to require long reaction times (24–72 h depending on starch sources) in which PO is allowed to diffuse into granule matrix prior to its reaction with starch molecules (Han and BeMiller, 2005; Huber and BeMiller, 2001). Consequently, the pronounced findings (the increased starch reactivities along with increasing pressure levels and the shortened reaction time) in this study strongly supported the suggestion of Choi, Kim, et al. (2009) in UHP-assisted acetylation reaction, and provided obvious evidence that UHP accelerated chemical derivatization of starch. Nevertheless, further research to investigate starch granule reactivities at UHP levels over 400 MPa will be needed to elucidate and clarify interrelation between starch granule reactivity and UHP in chemical modification reaction.

3.2. *Effect of pressure holding time on reaction of normal corn starch with propylene oxide*

In native starch (e.g., corn, wheat, potato, tapioca)-water suspension, extended pressure holding time (up to 1 h) at a given pressure level have been reported to enhance irreversible swelling (i.e., gelatinization) of starch granules (which is anticipated to

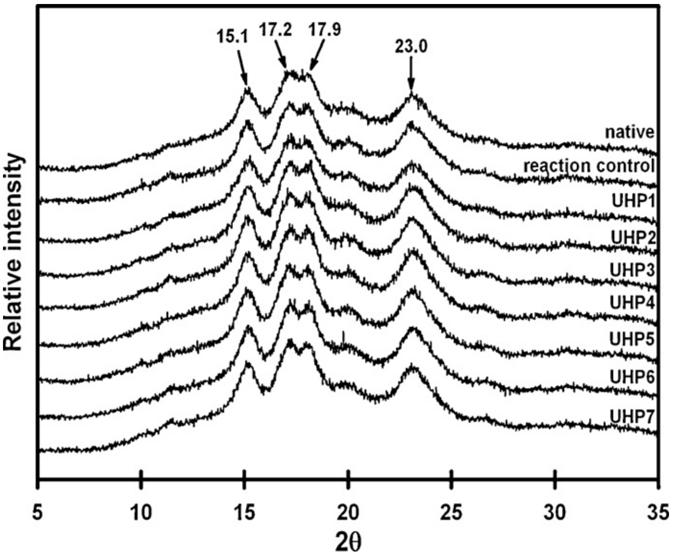

Fig. 1. X-ray diffractograms of native (unmodified) and hydroxypropylated starch derivatives.

impact starch granule reactivity) (Buckow et al., 2007; Kawai, Fukami, & Yamamoto, 2007). Thus, to determine whether pressure holding time (reaction time) is a critical factor in the UHP-assisted starch chemical derivatization, reaction of normal corn starch with PO was conducted at 400 MPa for 5, 15, or 25 min, corresponding to UHP6, UHP5, and UHP7, respectively (Table 1). While an increase in MS values was observed along with increasing reaction time from 5 to 15 min, further extension of reaction time up to 25 min exhibited very similar MS value to that of UHP5 (reacted for 15 min at 400 MPa) (Table 1). The results appeared to exhibit that starch granule reactivity in UHP-assisted PO reaction was much less influenced by pressure holding time compared to pressure level. It might be proposed that reaction equilibrium is achieved between alkoxide ions on starch molecules and PO at a given pressure level within 15 min. On the other hand, very similar trends in starch solubility/swelling power, gelatinization, and pasting properties were observed over pressure holding times (5, 15, and 25 min) for the UHP-assisted PO starch derivatives (UHP5-UHP7). Thus, effects of pressure holding time on properties of modified starch were no longer depicted and explained in this study.

3.3. *X-ray diffraction*

The X-ray diffraction patterns of native and hydroxypropylated starches were investigated to assess influence of UHP-assisted PO reaction on crystalline structure in starch granules (Fig. 1). Native starch revealed four major peaks at 15.1°, 17.2°, 17.9°, and 23.0° of 2θ, representing an A-type crystal packing arrangement of cereal starches. For the reaction control and UHP-assisted PO starch derivatives (UHP1–UHP7), noticeable shifts or changes in X-ray diffraction patterns were not identified. Moreover, significant variations in X-ray signal intensity were not observed among native and hydroxypropylated starches. As commonly reported by others (Chuenkamol et al., 2007; Lawal, 2009), the X-ray diffraction patterns and intensities did not differ for native and hydroxypropylated (up to MS value = 0.16) starches. In UHP-assisted cross-linking and acetylation reactions (Choi, Kim, et al., 2009; Hwang et al., 2009), there were no differences in X-ray diffraction patterns and relative crystallinities between native and UHP-assisted modified starches. Consequently, the results in this study appeared to exhibit that both conventional and UHP-assisted PO reactions did not impact crystalline structures within starch granules, further implying that reaction may occur mainly at amorphous regions within granules.

Table 2
Mean[a] values for solubility and swelling power of native starch,[b] UHP control,[c] and hydroxypropylated corn starches.

Starch samples	Solubility (%)	Swelling power (g/g)
Native[b]	14.9 ± 0.1^{G}	16.5 ± 0.0^{F}
Hydroxypropylation		
Reaction control[d]	39.2 ± 1.0^{A}	31.7 ± 0.2^{A}
UHP1[e]	24.7 ± 0.8^{B}	19.5 ± 0.1^{D}
UHP2[e]	21.1 ± 0.4^{CD}	23.9 ± 0.2^{B}
UHP3[e]	21.6 ± 0.2^{C}	22.7 ± 0.6^{C}
UHP4[e]	19.8 ± 1.1^{DE}	22.0 ± 0.8^{C}
UHP5[e]	19.5 ± 1.3^{DE}	22.3 ± 0.1^{C}
UHP control[c]		
UHP2C	15.8 ± 0.4^{F}	17.7 ± 0.1^{E}
UHP3C	15.3 ± 0.0^{F}	17.9 ± 0.0^{E}
UHP4C	15.7 ± 0.1^{F}	18.0 ± 0.2^{E}
UHP5C	15.4 ± 0.2^{F}	17.3 ± 0.1^{EF}

[a] Mean value of three replicate reactions; values sharing the same uppercase letter within a column are not significantly different ($p < 0.05$).

[b] Unmodified corn starch.

[c] Subjected to the same UHP-assisted PO reaction in the absence of PO at 100, 200, 300, and 400 MPa (designated as UHP2C, UHP3C, UHP4C, and UHP5C, respectively), corresponding to their respective hydroxypropylated starches (UHP2, UHP3, UHP4, and UHP5, respectively).

[d] Subjected to conventional PO reaction (20 h incubation at 45 °C).

[e] Subjected to UHP-assisted PO reaction at the pressure range of 0.1–400 MPa (Table 1).

3.4. *Starch solubility and swelling power*

Solubility and swelling capacity of native starch, reaction control (generated from conventional PO reaction), UHP-assisted PO starch derivatives (UHP1–UHP5), and UHP controls (UHP2C–UHP5C; subjected to identical UHP-assisted PO reaction at the pressure range of 100–400 MPa without PO addition) were determined at 90 °C, and are shown in Table 2. All PO starch derivatives (reaction control and UHP1–UHP5) exhibited greater solubilities and swelling powers than native starch (Table 2). It is commonly known that incorporation of bulky, hydrophilic hydroxypropyl groups into starch molecules within granules prevents inter-chain association among starch molecules, leading to destabilization of starch granule structures. The loosened granules facilitate hydration, and thus, enhance granule swelling, which further results in an increase in leaching of hydroxypropylated starch molecules from swollen granules (Gunaratne and Corke, 2007; Lawal, 2009; Liu et al., 1999; Singh et al., 2007). Within hydroxypropylated starch derivatives, the UHP-assisted PO starch derivatives (UHP1–UHP5) exhibited lower starch solubility and swelling power than the reaction control (Table 2). These results were due to differences in MS values between the reaction control and the UHP-assisted PO starch derivatives (Table 1). Increased MS values of hydroxypropylated starch derivatives were correlated to their enhanced solubility and swelling power (Gunaratne and Corke, 2007; Lawal, 2009; Liu et al., 1999).

Aside from effects of differential MS values, lower starch solubility and swelling power for the UHP-assisted PO starch derivatives (UHP2–UHP5, except for UHP1 which is similar to the reaction control prepared via conventional reaction for 15 min at 25 °C) relative to the reaction control might be attributable to improved crystallite perfection. During UHP-assisted PO reaction, amylopectin double helices in the lamellar clusters of the crystalline regions might experience transition of nematic to smectic arrangement as achieved via starch annealing. The smectic structure of starch crystallites via annealing inhibit further hydration of crystalline regions (following hydration of amorphous regions) by restricting accessibility of water molecules into amylopectin clusters; consequently, annealed (relative to native) starches exhibited reduced swelling capacity of starch granules, resulting in decreased leaching of starch molecules from granules (Jayakody and Hoover, 2008). For this study, differences in starch solubility and swelling power between native starch and UHP controls (UHP2C–UHP5C) (Table 2) were much smaller (approximately 85% less) than those reported in the literature (Gunaratne and Corke, 2007). This finding may suggest the presence of potential interactions among starch molecules, amylopectin clusters, and/or crystals within granules (i.e., starch annealing) even in the high alkaline reaction condition, facilitated by UHP treatment. Moreover, Biliaderis (1992) postulated that hydroxypropylation reaction appeared to occur predominantly at amorphous regions and/or outer surfaces of amylopectin clusters and/or crystallites, which propose that hydroxypropylation might not interfere with starch annealing. Kweon, Slade, and Levine (2008) reported that annealing occurred within native dent and waxy corn starch granules through transition of amylopectin melting observed by DSC. Overall, for this study, it might be inferred that both starch chemical derivatization and annealing simultaneously occur within granules during UHP-assisted PO reaction.

Within the UHP-assisted PO starch derivatives (UHP2–UHP5), similar starch solubility and swelling power (though subtle variation in swelling powers were observed between UHP2 and UHP3) were observed regardless of pressure level (Table 2), despite the common pattern that MS values of the hydroxypropylated starches were positively correlated with their solubility and swelling capacity (Chuenkamol et al., 2007; Jyothi, Moorthy, & Rajasekharan, 2007; Lawal, 2009; Liu et al., 1999). While their solubility and swelling power were higher compared to those of the UHP controls (UHP2C–UHP5C), similar patterns were obtained over pressure levels for the UHP-assisted PO starch derivatives and their respective UHP controls (Table 2). This finding might be because UHP-assisted PO reaction annealed starch to similar extents when relatively mild UHP treatments (up to 400 MPa) were applied. Furthermore, it might propose that the properties of the UHP-assisted PO starch derivatives were more likely determined by UHP treatment which starch granules were subjected to during UHP-assisted reaction than their derivatization degrees; chemical derivatization only boosted the magnitude of their properties up. However, further investigation is needed to verify interrelation between UHP-assisted derivatization reaction and starch annealing.

3.5. *Starch gelatinization*

Gelatinization properties of native, reaction control, and UHP-assisted PO starch derivatives (UHP1–UHP5) and corresponding UHP controls (UHP2C–UHP5C) were investigated using DSC, and are shown in Table 3. Native starch exhibited higher gelatinization onset and peak temperatures and enthalpy than the reaction control (subjected to conventional PO reaction), though gelatinization completion temperature did not statistically differ for native starch and reaction control (Table 3). These results were in partial agreement with those of others (Chuenkamol et al., 2007; Jyothi et al., 2007; Lawal, 2009; Liu et al., 1999), who reported higher gelatinization temperature and enthalpy for native starch relative to hydroxypropylated starches. In general, destabilized starch granules via introduction of bulky hydroxypropyl groups onto starch molecules require less energy to gelatinize, resulting in reduced gelatinization temperature and enthalpy (Chuenkamol et al., 2007; Jyothi et al., 2007; Liu et al., 1999).

For the UHP-assisted PO starch derivatives (UHP2–UHP5, except for UHP1), similar gelatinization temperatures and enthalpies were observed over pressure levels (Table 3), even though an increase in pressure level resulted in elevation of MS values (Table 1). The increased MS values in hydroxypropylated starches commonly reduced their gelatinization temperatures and enthalpies (Chuenkamol et al., 2007; Lawal, 2009; Liu et al., 1999). Nevertheless, the consistency in gelatinization properties observed among the UHP-assisted PO starch derivatives may be due to starch annealing during UHP-assisted PO reaction as suggested in the previous section of starch solubility and swelling power (Table 2). The noted suggestion was further supported by the fact that the UHP-assisted PO starch derivatives (UHP2–UHP5) possessed higher gelatinization onset and peak temperatures compared to native starch (Table 3). Furthermore, UHP controls (UHP2C–UHP5C), which exhibited higher gelatinization onset, peak, and completion temperatures (Table 3) than native starch, revealed similar trends in gelatinization temperatures observed for annealed starches (Jayakody and Hoover, 2008). Consequently, the findings in this study provided probable evidence that UHP-assisted PO reaction annealed starch, while individual starch molecules in amorphous regions reacted with propylene oxide.

Table 3
Mean[a] values for gelatinization properties of native[b] and hydroxypropylated corn starches.

Starch samples	T_o[c]	T_p[c]	T_c[c]	ΔH[c]
Native[b]	64.5 ± 0.5^{B}	70.7 ± 0.1^{DC}	87.5 ± 0.6^{A}	7.6 ± 0.2^{A}
Hydroxypropylation				
Reaction control[d]	63.2 ± 0.2^{C}	68.9 ± 0.2^{E}	89.0 ± 1.5^{A}	5.6 ± 0.2^{D}
UHP1[e]	64.9 ± 0.2^{AB}	70.3 ± 0.3^{D}	87.4 ± 0.6^{A}	5.5 ± 0.7^{BCD}
UHP2[e]	65.5 ± 0.3^{A}	71.4 ± 0.3^{A}	88.3 ± 0.3^{A}	5.8 ± 0.2^{D}
UHP3[e]	65.8 ± 0.5^{A}	71.4 ± 0.3^{A}	87.9 ± 0.2^{A}	5.7 ± 0.0^{D}
UHP4[e]	65.7 ± 0.1^{A}	71.2 ± 0.3^{AB}	87.1 ± 0.9^{A}	5.8 ± 0.2^{D}
UHP5[e]	65.4 ± 0.1^{AB}	71.3 ± 0.2^{AB}	87.7 ± 0.7^{A}	5.7 ± 0.0^{D}
UHP control[f]				
UHP2C	65.2 ± 0.5^{AB}	71.3 ± 0.3^{A}	87.9 ± 3.9^{A}	6.9 ± 0.0^{B}
UHP3C	65.1 ± 0.5^{AB}	71.3 ± 0.1^{A}	89.3 ± 0.6^{A}	6.8 ± 0.3^{BC}
UHP4C	65.1 ± 0.8^{AB}	71.2 ± 0.3^{AB}	89.0 ± 0.9^{A}	6.1 ± 0.7^{CD}
UHP5C	65.1 ± 0.6^{AB}	71.1 ± 0.3^{ABC}	88.0 ± 0.1^{A}	6.0 ± 0.1^{CD}

[a] Mean value of three replicate reactions; values sharing the same uppercase letter within a column are not significantly different ($p < 0.05$).

[b] Unmodified corn starch.

[c] Referred to as gelatinization onset, peak, and completion temperatures (°C) and gelatinization enthalpy (J/g), respectively.

[d] Subjected to conventional PO reaction (20 h incubation at 45 °C).

[e] Subjected to UHP-assisted PO reaction for 15 min at the pressure range of 0.1–400 MPa (Table 1).

[f] Subjected to the same UHP-assisted PO reaction in the absence of PO at 100, 200, 300, and 400 MPa (designated as UHP2C, UHP3C, UHP4C, and UHP5C, respectively), corresponding to their respective hydroxypropylated starches (UHP2, UHP3, UHP4, and UHP5, respectively).

3.6. *Pasting behavior*

Starch pasting properties were assessed for native starch, reaction control, and the UHP-assisted PO starch derivatives and their respective UHP controls, and are shown in Fig. 2 and Table 4. According to commonly observed pasting properties of hydroxypropylated starches (Chuenkamol et al., 2007; Gunaratne and Corke, 2007; Jyothi et al., 2007; Lawal, 2009; Liu et al., 1999), the enhanced hydration and swelling of starch granules via starch hydroxypropylation result in rapid viscosity development and the increased peak viscosity (corresponding to the increase in breakdown viscosity) of the starch paste. Also, bulky substituent restricts inter-chain association, leading to reduced final viscosity (associated with decreased setback viscosity). Further, the noted phenomena are correlated to degree of derivatization of the hydroxypropylated starches in positive and negative fashions for peak and final viscosities, respectively. Relative to native starch, the reaction control and UHP1 (similar to the hydroxypropylated starch conventionally reacted for 15 min at 25 °C) exhibited general patterns in pasting properties (Fig. 2 and Table 4).

Table 4

Mean[a] values for pasting behavior characteristics of native[b] and hydroxypropylated corn starches.

Starch samples	T_p[c]	Viscosity (RVU)				
		Peak	Trough	Final	Breakdown	Setback
Native[b]	75.2 ± 0.4^{A}	262.3 ± 2.1^{E}	180.7 ± 4.0^{A}	274.0 ± 4.0^{CD}	81.7 ± 5.7^{G}	93.3 ± 7.8^{D}
Hydroxypropylation						
Reaction control[d]	71.4 ± 0.2^{D}	271.0 ± 2.0^{CD}	114.7 ± 2.3^{H}	268.0 ± 6.1^{DEF}	156.3 ± 1.2^{A}	153.3 ± 7.6^{A}
UHP1[e]	76.6 ± 0.1^{A}	278.3 ± 2.9^{B}	164.7 ± 2.3^{CD}	294.3 ± 3.1^{A}	113.7 ± 0.6^{DE}	129.7 ± 1.2^{B}
UHP2[e]	74.4 ± 0.2^{B}	296.0 ± 5.0^{A}	154.0 ± 3.6^{EF}	286.7 ± 4.7^{B}	142.0 ± 5.3^{B}	132.7 ± 2.5^{B}
UHP3[e]	74.2 ± 0.3^{B}	255.7 ± 1.5^{F}	144.7 ± 3.2^{G}	260.3 ± 3.1^{FG}	111.0 ± 2.0^{E}	115.7 ± 5.7^{C}
UHP4[e]	74.3 ± 0.2^{B}	253.0 ± 3.0^{F}	148.3 ± 2.9^{FG}	262.0 ± 5.6^{EFG}	104.7 ± 1.5^{F}	113.7 ± 3.1^{C}
UHP5[e]	73.3 ± 0.6^{C}	275.7 ± 4.0^{BC}	156.7 ± 4.0^{E}	277.7 ± 2.1^{C}	119.0 ± 0.0^{CD}	121.0 ± 2.6^{C}
UHP control[f]						
UHP2C	75.2 ± 0.3^{A}	262.3 ± 1.5^{E}	181.0 ± 2.0^{A}	279.3 ± 3.5^{C}	81.3 ± 2.1^{G}	98.3 ± 1.5^{D}
UHP3C	75.2 ± 0.2^{A}	246.3 ± 2.5^{G}	170.7 ± 2.1^{BC}	262.7 ± 4.7^{EFG}	75.7 ± 1.5^{H}	92.0 ± 2.6^{DE}
UHP4C	75.5 ± 0.2^{A}	246.0 ± 5.3^{G}	172.7 ± 8.3^{B}	257.7 ± 2.9^{G}	73.3 ± 4.2^{H}	85.0 ± 5.6^{E}
UHP5C	75.3 ± 0.1^{A}	228.7 ± 3.8^{H}	160.7 ± 3.8^{DE}	236.3 ± 6.1^{H}	68.0 ± 1.0^{I}	75.7 ± 3.2^{F}

[a] Mean value of three replicate reactions; values sharing the same uppercase letter within a column are not significantly different ($p < 0.05$).

[b] Unmodified corn starch.

[c] Pasting temperature (°C) defined as temperature when starch pasting viscosity increased.

[d] Subjected to conventional PO reaction (20 h incubation at 45 °C).

[e] Subjected to UHP-assisted PO reaction for 15 min at the pressure range of 0.1–400 MPa (Table 1).

[f] Subjected to the same UHP-assisted PO reaction in the absence of PO at 100, 200, 300, and 400 MPa (designated as UHP2C, UHP3C, UHP4C, and UHP5C, respectively), corresponding to their respective hydroxypropylated starches (UHP2, UHP3, UHP4, and UHP5, respectively).

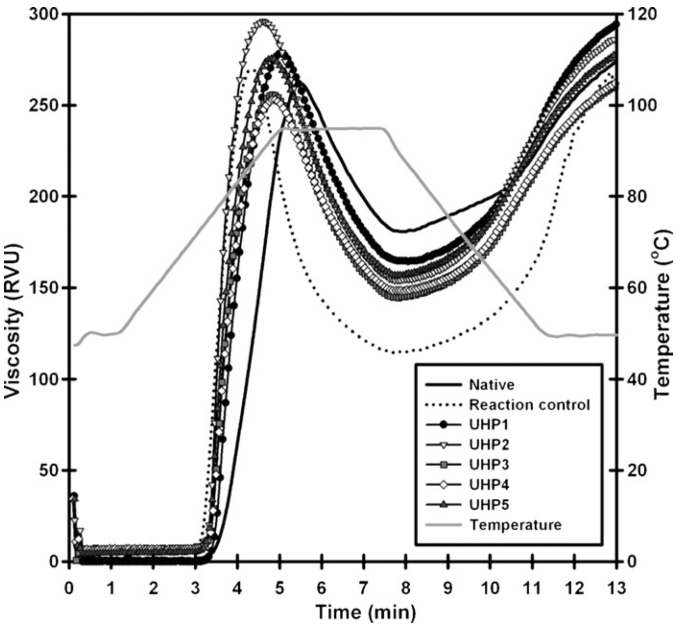

Fig. 2. Pasting viscosity profiles of corn starches reacted with propylene oxide for 15 min under differing pressure levels ranging from 0.1 to 400 MPa (from UHP1 to UHP5).

For UHP-assisted PO reaction, the UHP controls (UHP2C–UHP5C) revealed decreasing patterns in pasting characteristics, along with increasing pressure levels, though no apparent differences were acquired either between native starch and UHP2 or between UHP3 and UHP4 (Table 4). Nevertheless, the UHP-assisted PO starch derivatives (UHP2–UHP5) did not exhibit consistent viscosity profiles and characteristics of the starch pastes despite which MS values increased with applied pressure levels (Fig. 2 and Table 4). Though the common trends mentioned in the previous paragraph did not provide reasonable explanation for differences in pasting properties among the UHP-assisted PO starch derivatives, a possible explanation might be heterogeneity in granular reaction patterns within the UHP-assisted PO starch derivatives which resulted from short reaction time (up to 25 min), compared to long reaction periods in derivatization of starch with propylene oxide.

4. Conclusions

This study investigated reactivity and property of the hydroxypropylated starches prepared via UHP-assisted reaction. It was demonstrated that hydroxypropylation reaction of starch can be accelerated by UHP treatment, though UHP-assisted (relative to conventional) reaction generates lower reaction efficiency. The pressure level was a critical factor to enhance starch granule reactivity in UHP-assisted PO reaction, while effects of pressure holding time (up to 25 min) on starch granule reactivity were not likely of practical importance. Thus, lower reaction efficiency in UHP-assisted reaction would be improved by increasing pressure level over 400 MPa (maximum pressure level used in this study). Further, UHP-assisted PO reaction may involve starch annealing (though further research would be required) while derivatization occurred at amorphous regions within starch granules. Moreover, physical and thermal properties of the UHP-assisted PO starch derivatives, generated in this study, appeared to be more influenced by UHP treatment relative to their derivatization degrees. Overall, connection of hydroxypropylation reaction with UHP may further enhance physical and textural properties of the hydroxypropylated starches under strict regulatory practice, which would expand its applications in food and non-food systems.

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References

BeMiller, J. N. (1997). Starch modification: Challenges and prospects. *Starch/Stärke*, *49*, 127–131.

Biliaderis, C. G. (1992). Physical characteristics, enzymatic digestibility, and structure of chemically modified smooth pea and waxy maize starches. *Journal of Agricultural and Food Chemistry*, *30*, 925–930.

Blaszczak, W, Fornal, J., Valverde, S., & Garrido, L. (2005). Pressure-induced changes in the structure of corn starches with different amylose content. *Carbohydrate Polymers*, *61*, 132–140.

Buckow, R., Heinz, V., & Knorr, D. (2007). High pressure phase transition kinetics of maize starch. *Journal of Food Engineering*, *81*, 469–475.

Choi, H.-S., Kim, H.-S., Park, C.-S., Kim, B.-Y., & Baik, M.-Y. (2009). Ultra high pressure (UHP)-assisted acetylation of corn starch. *Carbohydrate Polymers*, *78*, 862–868.

Choi, H.-W., Lee, J.-H., Ahn, S.-C., Kim, B.-Y., & Baik, M.-Y. (2009). Effects of ultra high pressure, pressure time and HCl concentration on non-thermal starch hydrolysis using ultra high pressure. *Starch/Stärke*, *61*, 334–343.

Chuenkamol, B., Puttanlek, C., Rungsardthong, V., & Uttapap, D. (2007). Characterization of low-substituted hydroxypropylated canna starch. *Food Hydrocolloids*, *21*, 1123–1132.

Douzals, J. P., Marechal, P. A., Coquille, J. C., & Gervais, P. (1996). Microscopic study of starch gelatinization under high hydrostatic pressure. *Journal of Agricultural and Food Chemistry*, *44*, 1403–1408.

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*, 4824–4829.

Gunaratne, A., & Corke, H. (2007). Effect of hydroxypropylation and alkaline treatment in hydroxypropylation on some structural and physicochemical properties of heat-moisture treated wheat, potato and waxy maize starches. *Carbohydrate Polymers*, *68*, 305–313.

Han, J.-A., & BeMiller, J. N. (2005). Rate of hydroxypropylation of starches as a function of reaction time. *Starch/Stärke*, *57*, 395–404.

Hibi, Y., Matsumoto, T., & Hagiwara, S. (1993). Effect of high pressure on the crystalline structure of various starch granules. *Cereal Chemistry*, *70*, 671–676.

Huber, K. C., & BeMiller, J. N. (2001). Location of sites of reaction within starch granules. *Cereal Chemistry*, *78*, 173–180.

Hwang, D.-K., Kim, B.-Y., & Baik, M.-Y. (2009). Physicochemical properties of non-thermally cross-linked corn starch with phosphorous oxychloride using ultra high pressure (UHP). *Starch/Stärke*, *61*, 438–447.

Jane, J. (1995). Starch properties, modifications, and applications. *Journal of Macromolecular Science—Pure and Applied Chemistry*, *A32*, 751–757.

Jayakody, L., & Hoover, R. (2008). Effect of annealing on the molecular structure and physicochemical properties of starches from different botanical origins—A review. *Carbohydrate Polymers*, *74*, 691–703.

Johnson, D. P. (1969). Spectrophotometric determination of the hydroxypropyl group in starch ethers. *Analytical Chemistry*, *41*, 859–860.

Jyothi, A. N., Moorthy, S. N., & Rajasekharan, K. N. (2007). Studies on the synthesis and properties of hydroxypropyl derivatives of cassava (Manihot esculenta Crantz) starch. *Journal of the Science of Food and Agriculture*, *87*, 1964–1972.

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

Kawai, K., Fukami, K., & Yamamoto, K. (2007). Effects of treatment pressure, holding time, and starch content on gelatinization and retrogradation properties of potato starch–water mixtures treated with high hydrostatic pressure. *Carbohydrate Polymers*, *69*, 590–596.

Kweon, M., Slade, L., & Levine, H. (2008). Role of glassy and crystalline transitions in the responses of corn starches to heat and high pressure treatments: Prediction of solute-induced barostability from solute-induced thermostability. *Carbohydrate Polymers*, *72*, 293–299.

Lawal, O. S. (2009). Starch hydroxypropylation: Physicochemical properties and enzymatic digestibility of native and hydroxypropylated finger millet (Eleusine coracana) starch. *Food Hydrocolloids*, *23*, 415–425.

Lee, J.-H., Choi, H.-W., Kim, B.-Y., Chung, M.-S., Kim, D.-S., Choi, S.-W., et al. (2006). Nonthermal starch hydrolysis using ultra high pressure. I. Effects of acids and starch concentrations. *LWT-Food Science and Technology*, *39*, 1125–1132.

Liu, H., Ramsden, L., & Corke, H. (1999). Physical properties and enzymatic digestibility of hydroxypropylated ae, wx, and normal maize starch. *Carbohydrate Polymers*, *40*, 175–182.

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*, 150–155.

Singh, J., Kaur, L., & McCarthy, O. J. (2007). Factors influencing the physic-chemical, morphological, thermal and rheological properties of some chemically modified starches for food applications—A review. *Food Hydrocolloids*, *21*, 1–22.

Stolt, M., Oinonen, S., & Autio, K. (2001). Effect of high pressure on the physical properties of barley starch. *Innovative Food Science and Emerging Technologies*, *1*, 167–175.

Stute, R., Klingler, R. W., Boguslawski, S., Eshtiaghi, M. N., & Knorr, D. (1996). Effects of high pressures treatment on starches. *Starch/Stärke*, *48*, 399–408.

Wootton, M., & Manatsathit, A. (1983). The influence of molar substitution on the water binding capacity of hydroxypropyl maize starches. *Starch/Stärke*, *35*, 92–94.