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RESEARCH ARTICLE

Freeze-thaw Stability, Glass Transition, and Retrogradation of High Hydrostatic Pressure-assisted Hydroxypropylated Corn Starch

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Abstract Effects of high hydrostatic pressure (HHP) and the propylene oxide (PO) concentration on the freeze-thaw stability, glass transition temperature (*Tg*'), and retrogradation degree of HHP-assisted hydroxypropylated corn starch were investigated. HHP-assisted hydroxypropylated corn starches were prepared using propylene oxide (4, 8, and 12%, v/w) at 25ºC for 15 min under HHP (100, 200, 300, and 400 MPa). The freeze-thaw stability, *Tg*', ice melting enthalpy (H_i), and retrogradation degree of HHP-assisted hydroxypropylated corn starches showed patterns different from native corn starch. In general, higher pressures and PO levels lowered *Tg*' and H_i values, and the retrogradation degree. The highest freeze-thaw stability was observed in HHP-assisted hydroxypropylated corn starch prepared using 12% PO at 400 MPa for 15 min. Retrogradation kinetics of hydroxypropylated corn starch gels observed from the glass transition temperature, ice melting enthalpy, and retrogradation degree revealed that recrystallization occurred with instantaneous nucleation, followed by rod-like growth of crystals.

Keywords: high hydrostatic pressure, hydroxypropylated corn starch, freeze-thaw stability, glass transition, retrogradation

Introduction

Starch is a major carbohydrate reserve in plants. Corn, wheat, potato, tapioca, and rice all contain large reserves of starch. Native starch is a good texture stabilizer and regulator in food systems (1), but the variety of applications in foods is limited due to low shear resistance, thermal decomposition, and a tendency towards retrogradation. Chemical modifications of starch bring about structural alterations and produce new functional groups that are suitable for industrial uses (2). Reactions of starch with the etherifying reagent propylene oxide (PO) introduce hydroxypropyl groups into the starch polymeric chain (3). Hydroxypropyl groups are hydrophilic and weaken internal bonding that holds granules together, resulting in slow retrogradation (4,5).

High hydrostatic pressure (HHP) affects the chemical reactivity of modified starch. HHP causes reversible hydration of the amorphous phase, followed by irreversible distortion of the crystalline region, which leads to destruction of the granular structure of starch. Refined high amylose maize treated at 650 MPa showed a small reduction in the size of the crystalline region, and some granules appeared to contain a cavity inside (6). In addition to hydroxypropylation (7), other chemical modifications have been performed via partial hydrolysis using acids (8.9), derivatization using phosphorus oxychloride (10) and acetic anhydride (11), and dual modification (12).

Many researches have focused on the physicochemical properties of HHP-assisted modified starch, but little information is available regarding HHP-assisted hydroxypropylated starch. Therefore, the objective of this study was to investigate the freeze-thaw stability, glass transition, and retrogradation of HHP-assisted hydroxypropylated corn starch.

Materials and Methods

Materials Corn starch (9.5% moisture content on a wet basis) was provided by Daesang Co. (Incheon, Korea).

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Propylene oxide (PO), anhydrous sodium sulfate (Na_2SO_4), and hydrochloric acid were purchased from Sigma Chemical Co. (St Louis, MO, USA).

Preparation of HHP-assisted hydroxypropylated corn starch An HHP-assisted hydroxypropylation reaction was conducted using PO following the method of Kim *et al.* (7). Native starch (20 g) was mixed with 80 mL of water containing 8% Na_2SO_4. The pH of the resulting starch slurry was elevated to 11.5 using 1 M NaOH, followed by addition of PO (4, 8, and 12%) with vigorous stirring, after which the reaction mixture (100 g) was sealed into a retort pouch and placed into an HHP unit (Autoclave Engineers, Erie, PA, USA) at 25ºC with a pressure increase rate of 20 MPa/s. HHP treatment was conducted at pressure levels from 100-400 MPa for 15 min.

After the HHP-assisted hydroxypropylation reaction, reaction mixtures were neutralized to pH 5.5 using 1 M HCl, and centrifuged at 1,500×*g* for 20 min. Recovered starch pellets were washed 3× and dried at 40ºC for 24 h, then ground and passed through an 80 mesh sieve (pore size=180 μm) for subsequent analysis.

Freeze-thaw stability The freeze-thaw stability of gelatinized starch was measured following the method of Kaur *et al.* (13). Twenty g of a starch slurry (10%, w/w) was placed into a 50 mL falcon tube and heated at 95ºC for 30 min, then cooled to room temperature. Resulting gelatinized slurries were subjected to freeze-thaw cycles performed at -20ºC for 20 h and at 30ºC for 4 h, respectively, for a total of 5 freeze-thaw cycles for each slurry sample. The amount of water separated after each freeze-thaw cycle was measured and the extent of syneresis was calculated as the percentage of separated water divided by the total slurry sample weight after the freeze-thaw cycle.

Thermal analysis Retrogradation of conventionally and HHP-assisted hydroxypropylated corn starch gels was analyzed using a 650 differential scanning calorimeter (DSC) (Sinco Co., Seoul, Korea) according to the method of Lawal (14). Approximately 10 mg of a corn starch slurry (60%, w/w) was put into an aluminum DSC pan and hermetically sealed. The slurry sample was heated from 25 to 130ºC at a heating rate of 5ºC/min with an empty pan used as a reference. Subsequently, the gelatinized slurry sample was stored at 4ºC up to 14 days to allow retrogradation. After storage, slurry samples were cooled to −50ºC at 40ºC/min, then reheated to 100ºC at a heating rate of 5ºC/min for estimation of the glass transition temperature (Tg'), and the ice melting transition and amylopectin melting transitions. The Tg' ice melting enthalpy (H_i) and the amylopectin melting enthalpy (H_s) values of corn starch gels were determined using DSC thermograms based on the first derivative curve of heat flow. The degree of retrogradation (Re) was calculated as the percentage of amylopectin melting enthalpy at time t (H_t) divided by the amylopectin melting enthalpy at gelatinization (H_0).

Analysis of the retrogradation rate and kinetic behavior The retrogradation rate and kinetic behavior were analyzed using the Avrami equations following the method of Colwell *et al.* (15).

$$\theta = (E_L - E_t)/(E_L - E_0) = \mathrm{Exp}(-kt^n)$$
$$\log\,[-\ln(E_L - E_t)/(E_L - E_t)\,] = \log k + n \log t$$

where θ is the non-crystallized fraction at time t, E_0 is the degree of retrogradation at time 0, E_t is the degree of retrogradation at time t, E_L is the maximum degree of retrogradation, k is the rate constant (time^{-1}), and n is the Avrami exponent.

Statistics All experiments were performed in triplicate and the statistical package SPSS, Version 11.0 (SPSS Inc., Chicago, IL, USA) was used for analysis of data. Results were expressed as a mean±standard deviation (SD). A one-way analysis of variance (ANOVA) followed by Duncan's Multiple Comparison Test were performed at $p<0.05$.

Result and Discussion

Freeze-thaw stability Syneresis of native and HHP-assisted hydroxypropylated corn starches are shown in Fig. 1. Effects of the HHP level on freeze-thaw stability of HHP-assisted hydroxypropylated corn starches are shown in Fig. 1A. Syneresis increased with an increasing number of freeze-thaw cycle for all slurry samples. The degree of syneresis of native corn starches increased from 4.4 to 15.8% during 5 freeze-thaw cycles. The higher degree of syneresis in native starch indicated that the retrograded starch network was easily disrupted by ice crystals formed during freezing. Thermal fluctuations and phase changes of water during cold storage cause deterioration in the gel matrix of starch (16), and this re-organization of starch molecules may result in release of water (syneresis). This poor freeze-thaw stability of native corn starch indicated extensive retrogradation during the freeze-thaw cycle. Substitution of PO; however, improved the water holding capacity of starch gels by decreasing the extent of retrogradation. The hydroxypropyl groups in starch can attenuate the steric effect imposed by bulky hydroxyl groups that prevent proper alignment of starch chains for maximum retrogradation (5).

The degrees of syneresis of HHP-assisted hydroxypropylated corn starches prepared at 100 and 200 MPa with 12% PO showed similar patterns and were both lower

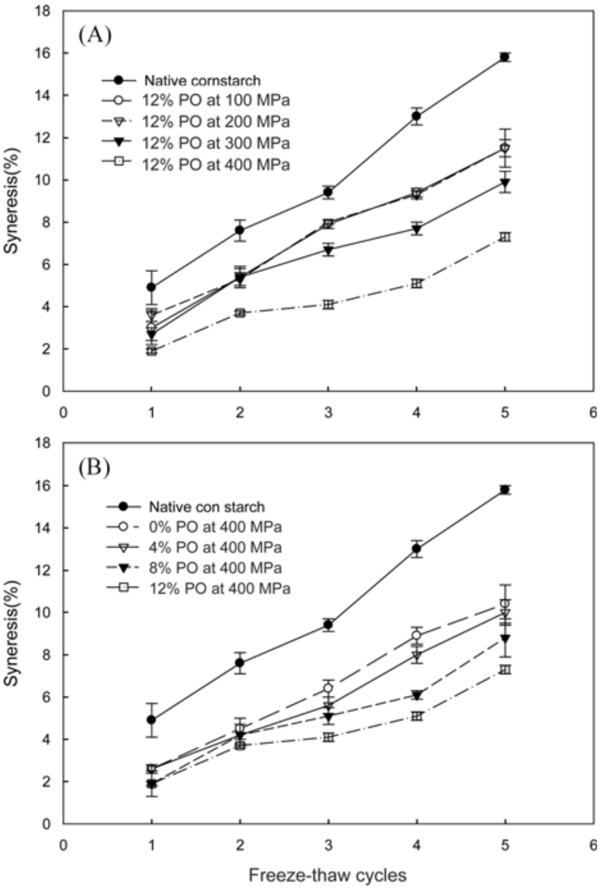

Fig. 1. Effects of the high hydrostatic pressure level (A) and the propylene oxide concentration (B) on the freeze-thaw stability of HHP-assisted hydroxypropylated corn starches.

values than for native starch for all freeze-thaw cycles, indicating relatively stable freeze-thaw behavior. Moreover, the degree of syneresis of HHP-assisted hydroxypropylated corn starch decreased with an increasing HHP level. Thus, HHP treatment and hydroxyprolyalation exhibited a synergistic effect on freeze-thaw stability.

Effects of the propylene oxide concentration on freeze-thaw stability of HHP-assisted hydroxypropylated corn starches are shown in Fig. 1B. HHP-assisted hydroxypropylated corn starch at a constant pressure showed a gradual increase in the freeze-thaw stability with an increasing PO concentration during 5 freeze-thaw cycles. Overall, HHP-assisted hydroxypropylated corn starch prepared at 400 MPa with 12% PO showed the highest freeze-thaw stability among slurry samples. The freeze-thaw stability of hydroxypropylated starch derivatives was reportedly increased with increasing molar substitution (MS) values (17). HHP-assisted hydroxypropylation of starch introduced hydroxypropyl groups into the starch molecule. Thus, the higher the hydroxypropyl content (based on the MS value), the lower the degree of syneresis and the higher the freeze-thaw stability of starch (18).

Glass transition temperature (*Tg′*) Effects of a high hydrostatic pressure level on the glass transition temperature (*Tg′*) of HHP-assisted hydroxypropylated corn starches are shown in Fig. 2A. *Tg′* values of all starches increased during storage at 4ºC and ranged between −9.5 and −7.9ºC. Retrogradation or recrystallization may decrease the amount of effective plasticizing water in starch during storage, resulting in an increase in the *Tg′* value. *Tg*′ values of all slurry samples, except a slurry prepared at 400 MPa with 12% PO, were not significantly (p>0.05) different. A slurry prepared at 400 MPa with 12% PO showed a lower *Tg*′ value than all other slurry samples over the storage time. It has been reported that hydroxypropylated starch exhibited more syneresis than unmodified starch (19). Also, hydroxypropylation reduced the retrogradation of starch by decreasing chain aggregation (20). On the other hand, HHP-assisted hydroxypropylated starch was not gelatinized under 400 MPa, resulting in no significant change in DSC thermal properties, compared with native starch (7). In freeze-thaw stability, HHP-assisted hydroxypropylated corn starches showed less syneresis and less retrogradation, resulting in lower *Tg*′ values than for native corn starch.

Effects of the PO concentration on *Tg′* values of HHP-assisted hydroxypropylated corn starches are shown in Fig. 2B. A slurry prepared at 400 MPa with 12% PO showed a lower *Tg*′ value than other slurry samples over the storage time, except for 12% PO (Fig. 2B). During hydroxypropylation, native starch is etherified to a low degree of substitution with hydroxypropyl ($-OCH_2CH_2CH_3$) groups via replacement of some hydroxyl groups. Wootton and Manatsathit (21) reported that increased molar substitution of hydroxypropylated corn starch decreased the water binding capacity and the gelatinization enthalpy value. Choi *et al.* (11) showed that the degree of substitution of HHP-assisted acetylated starch derivatives increased with an increase in pressure levels up to 400 MPa. Therefore, elevation of pressure levels enhanced hydration of starch granules, leading to greater reactivity of starch granules, resulting in lower *Tg′* values than for native starch.

Ice melting enthalpy (ΔH_i) Effects of high hydrostatic pressures on ice melting enthalpy (ΔH_i) values of HHP-assisted hydroxypropylated corn starches during storage are shown in Fig. 3A. Although the HHP level influenced the H_i values of HHP-assisted hydroxypropylated corn starches, there was no consistent tendency. At the same time, the propylene oxide concentration also affected H_i values of HHP-assisted hydroxypropylated corn starches without any trend (Fig. 3B). It has been reported that hydroxypropylated corn starch derivatives enhanced granule swelling, decreased the gelatinization temperature, and improved the freeze-thaw stability, but hindered interactions between starch chains and water molecules due to a high

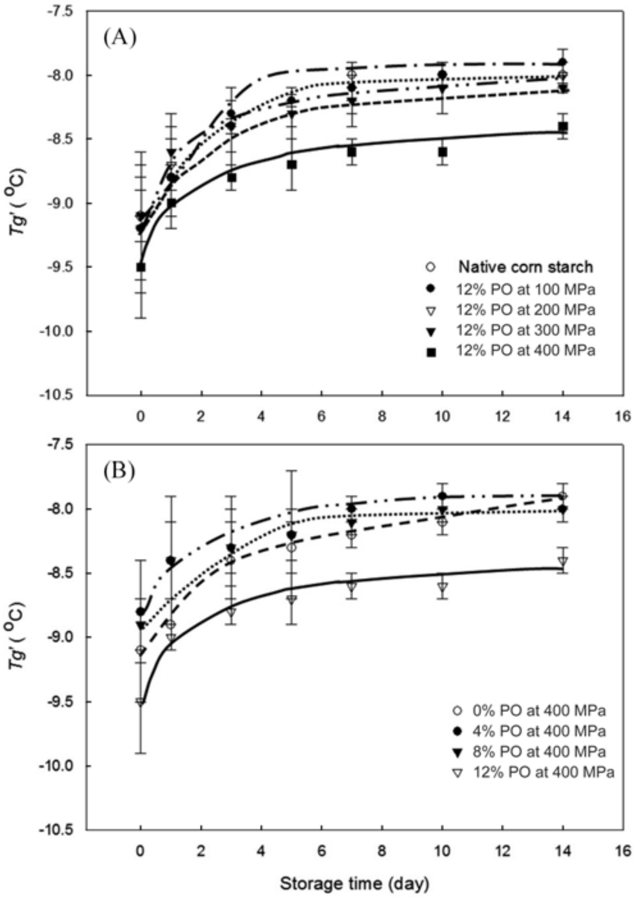

Fig. 2. Effects of the high hydrostatic pressure level (A) and the propylene oxide concentration (B) on the glass transition temperature (T*g*') of HHP-assisted hydroxypropylated corn starches.

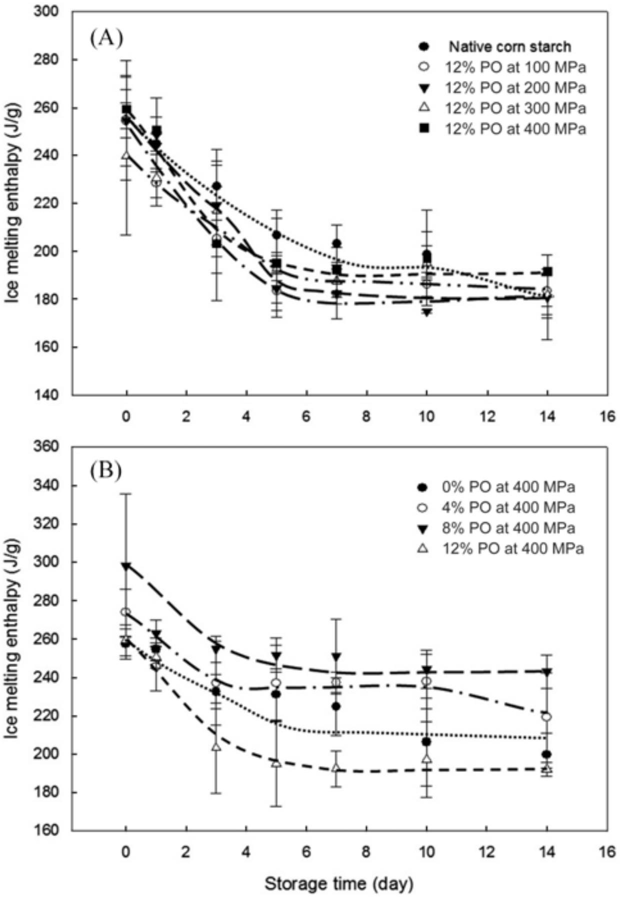

Fig. 3. Effects of the high hydrostatic pressure level (A) and the propylene oxide concentration (B) on the ice melting enthalpy (H_i) of HHP-assisted hydroxypropylated corn starches.

degree of molar substitution. Therefore, more water molecules were freezable, resulting in an increase in the ice melting enthalpy (17,18). However, in this study, hydroxypropylated corn starch did not show an increase in H_i values, perhaps due to fewer substitution reactions in HHP-assisted hydroxypropylation. HHP-assisted hydroxypropylated corn starch has been reported to exhibit a lower degree of substitution than conventionally hydroxypropylated corn starch (7).

On the other hand, H_i values of all slurry samples gradually decreased with storage time for 5 days of storage, then remained constant thereafter (Fig. 3), indicating that starch recrystallization gradually increased during 5 days of storage during which water incorporated into the crystalline matrix during recrystallization resulted in a decrease in the amount of freezable water in the starch gel system. Generally, the ice melting enthalpy reflects the amount of freezable water in a starch gel system. As less water is incorporated into the starch recrystallization matrix due to a reduced level of recrystallization in the starch gel system, more water becomes freezable.

Amylopectin melting enthalpy (ΔH_s) Effects of the HHP level and PO concentration on retrogradation of HHP-assisted corn starch are shown in Fig. 4. When starch gels are heated in a differential scanning calorimeter, new endothermic transitions, which do not appear in freshly gelatinized starch, occur and transitions are generally attributable to melting of recrystallized amylopectin. The enthalpy change involving retrogradation is generally considered to correspond to an order-disorder transition of crystallites. The retrogradation enthalpy value increased with the storage time for all slurry samples (Fig. 4). Retrogradation of hydroxypropylated corn starch molecules was less ordered in stored starch gels than in the native form (Fig. 4).

All HHP-assisted hydroxypropylated corn starch slurries showed lower retrogradation values than native corn starch (Fig. 4A). Retrogradation of HHP-assisted hydroxypropylated corn starch gradually decreased with an increasing HHP level, indicating that the HHP level influenced retrogradation of hydroxypropylated corn starch at the same PO concentration.

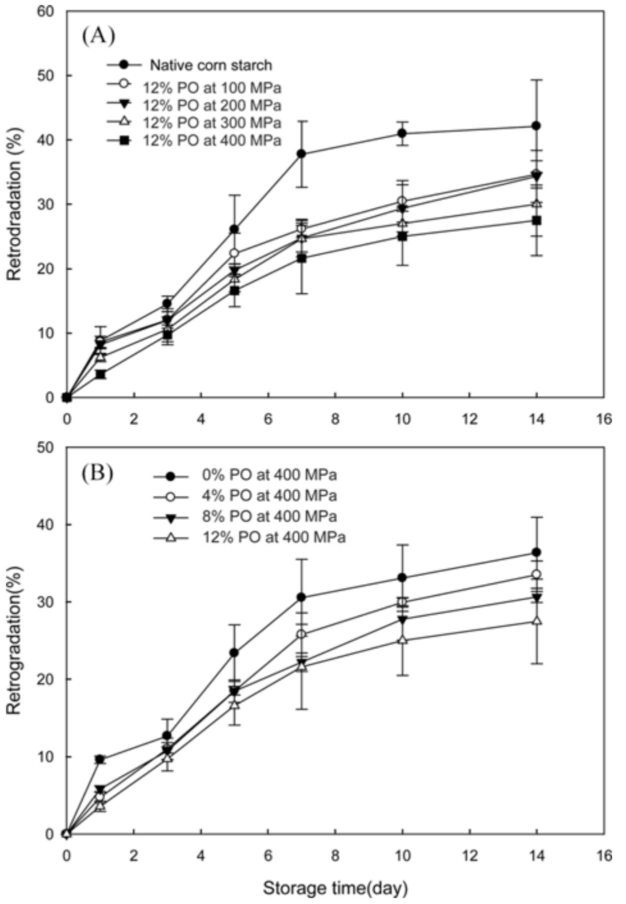

Fig. 4. Effects of the high hydrostatic pressure level (A) and the propylene oxide concentration (B) on retrogradation of HHP-assisted hydroxypropylated corn starches.

The PO concentration also influenced retrogradation of HHP-assisted hydroxypropylated corn starch at the same pressure level (Fig. 4B). As the PO concentration increased, the degree of retrogradation in HHP-assisted hydroxypropylated corn starch gradually decreased.

Generally, hydroxypropylation of starch reduces amylopectin retrogradation based on inhibition of interchain associations. Hydroxypropyl groups replaced by amylose and amylopectin chains decreased the extent of reassociation and retrogradation. Disruption and reorientation of amylopectin during HHP treatment facilitates more reaction reagent access to the amorphous and crystalline regions, causing greater modification of amylopectin. More derivatized amylopectin can reduce the interchain associations of amylopectin to a greater extent than for native corn starch, thus decreasing the degree of amylopectin retrogradation (22).

Retrogradation kinetics Changes in the glass transition temperature (*Tg*'), the ice melting enthalpy (ΔH_i), and the degree of retrogradation of hydroxypropylated corn starch during storage at 4°C were analyzed using the Avrami equations (Table 1 and 2). The Avrami exponent (*n*) in the Avrami equations describes the crystallization pattern and takes a value of 1-4 in accordance with the nucleation, propagation, and maturation modes of crystals (23,24). Avrami exponent values (*n*) of the measured glass transition temperature (*Tg*'), ice melting enthalpy (ΔH_i), and degree of retrogradation, and *n* values of all slurry samples were close to 1.0 (Table 1), indicating that retrogradation of hydroxypropylated corn starch gels during storage at a constant temperature experienced instantaneous nucleation, followed by rod-like growth of crystals (23).

Time constants (*k*) of the glass transition temperature (*Tg*'), the ice melting enthalpy (ΔH_i), and the degree of retrogradation were obtained from the Avrami equations. Values ranged from 0.17 to 1.11 (Table 2). Corn starch hydroxypropylated at 400 MPa with 4% PO showed the lowest rate constant (*Tg*') value of 0.17, indicating a slow change in the glass transition temperature during storage. On the other hand, the highest rate constant (ΔH_i) value of 1.11 was observed for corn starch hydroxypropylated at 400 MPa with 4% PO. Moreover, the lowest rate constant value of 0.23 was observed for the degree of retrogradation. Native corn starch showed the highest degree of retrogradation (Fig. 4A).

Table 1. Avrami exponents (*n*) from the glass transition temperature (*Tg*'), ice melting enthalpy (ΔH_i), and degree of retrogradation of HHP-assisted hydroxypropylated corn starches

Pressure (MPa)	Propylene oxide concentration (%)	Avrami exponents (*n*)					
		Tg'	R^2	H_i	R^2	Re*[1)]	R^2
Native corn		1.04	1.00	1.54	0.96	0.86	0.90
100	12	1.06	0.98	1.29	0.91	0.88	0.80
200	12	0.75	0.99	2.22	0.97	0.79	0.87
300	12	0.61	0.99	1.43	0.92	0.90	0.92
400	12	0.61	0.99	1.99	0.97	1.26	0.98
400	0	1.39	0.98	1.96	0.92	0.75	0.79
400	4	0.41	0.95	0.90	0.96	1.09	0.98
400	8	0.44	0.93	0.71	0.96	1.03	0.92

[1)] Re*=degree of retrogradation; $H_t/H_0\times 100$

Table 2. Rate constants (*k*) from the glass transition temperature (*Tg*'), ice melting enthalpy (ΔH_i), and degree of retrogradation of HHP-assisted hydroxypropylated corn starches

Pressure (MPa)	Propylene oxide concentration (%)	*Tg*'			ΔH_i			Re*[1)]		
		k	1/*k* (day)	R^2	*k*	1/*k* (day)	R^2	*k*	1/*k* (day)	R^2
Native corn		0.35	2.86	1.00	0.63	1.59	0.90	0.23	4.35	0.92
100	12	0.49	2.04	0.97	0.93	1.08	0.88	0.38	2.63	0.85
200	12	0.40	2.50	0.99	0.86	1.16	0.87	0.30	3.33	0.90
300	12	0.35	2.86	1.00	0.52	1.92	0.88	0.27	3.70	0.93
400	12	0.35	2.86	1.00	0.76	1.32	0.99	0.32	3.13	0.96
400	0	0.49	2.04	0.97	0.38	2.63	0.85	0.27	3.70	0.85
400	4	0.17	5.88	0.99	1.11	0.90	0.92	0.26	3.85	0.96
400	8	0.28	3.57	0.98	0.79	1.27	0.97	0.37	2.70	0.92

[1)] Re*=degree of retrogradation; $H_t/H_0 \times 100$

The degree of retrogradation and the retrogradation rate of starch do not have to be positively correlated or to be consistent. The degree of retrogradation and the retrogradation rate of starch are greatly affected by multiple factors, such as starch origin and the degree and method of modification. It has been reported that *Tg*', ΔH_i, and ΔH_s values are closely related to retrogradation of starch (24); however, each physicochemical property expresses different characteristics in different domains, resulting in non-consistent results.

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