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Water mobility and textural properties of native and hydroxypropylated wheat starch gels

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Abstract

The effect of wheat starch concentration and degree of hydroxypropylation on the water dynamics and textural attributes of starch gels was studied using ^{1}H NMR and texture profile analysis. Starches were prepared with molar substitution (MS) of hydroxypropyl groups of 0.05, 0.12, and 0.18. Gels were formed from modified starches at concentrations between 25 and 40%. For all gels, two distinct water fractions were identified using distributed exponential analysis of transverse relaxation results. For the less mobile fraction, T_{2a} ranged from 2 to 6 ms, while for the more mobile state, T_{2b} ranged from 20 to 200 ms. Values of both T_{2a} and T_{2b} increased with increasing moisture content and hydroxypropyl MS. Control experiments indicated that more mobile states could be associated with both the extragranular amylose gel, as well as intragranular amylopectin-rich gel. The less mobile state was associated only with granule remnants. Gel hardness decreased significantly with increasing moisture content, and with increasing hydroxypropylation. Cohesiveness increased with degree of hydroxypropylation. Results from multi-regression analysis between hardness and NMR parameters showed that the mobility and amount of water in the less mobile state was most related to gel hardness. © 2003 Published by Elsevier Science Ltd.

Keywords: Starch; Water; Mobility; Nuclear magnetic resonance

1. Introduction

Starch is the most important of food biopolymers, and exhibits gelling properties that are used to control the texture and mechanical properties of many foods. Starch is a mixture of two polysaccharides, the linear chain amylose and the heavily branched amylopectin. Heating starch in excess of water results in starch granule melting and water imbibitions. It also causes irreversible swelling of granules to many times their original size, with the final size dependent upon the available space and the amount of amylose leaching out of the granules (Keetels, van Vliet, & Walstra, 1996).

Water is necessary to hydrate starch molecules and provides the fluid environment in which starch aggregates to form gels. Water also serves as a plasticizer, and thus influences the molecular mobility of starch molecules. Interactions of starch with water also determine how water is retained within the gel, for example, whether water is 'bound' or immobilized near the starch surface, and whether the gel network entraps it. Several researchers have studied the molecular dynamics of water in starch systems. Nuclear magnetic resonance spectroscopy (NMR) has been especially useful in this regard, as water may be studied through the use of ^{1}H, ^{2}H, and ^{17}O nuclear resonance. A wide variety of starches and physical states have been explored. In relatively low-moisture waxy corn starch powders and suspensions, Li, Dickinson, and Chinachoti (1998) measured a single relaxation component that increased with moisture content. Kou, Dickinson, and Chinachoti (2000) found two components, one associated with starch, and one with water. Richardson, Baianu, and Steinberg (1987) analyzed a single NMR relaxation component to show three mobility regions existed with respect to water activity. Le Botlan, Rugraff, Martin, and Colonna (1998) found two relaxation components in intact starch, one corresponding to bound water and one to unbound water. Tang, Godward, and Hills (2000) studied the dynamic states of water in several types of starch granules. In B-type starch, they found three transverse relaxation regimes that were assigned to water in amorphous growth rings, semi-crystalline lamella, and channels in crystalline amylopectin.

The textural and mechanical properties of starch gels depend mainly on the rheological properties of the continuous amylose phase, the volume fraction of the granules, the deformability of the granules, and the interaction between the dispersed and continuous phase (Eliasson, 1986; Ring et

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Table 1
Chemicals used to prepare control and hydroxypropylated wheat starch and the resulting MS of hydroxypropyl groups

Starch (g)	Na_2SO_4 (g)	Propylene oxide (ml)	MS[a]
200	10	0	0
200	10	8	0.05
200	10	16	0.12
200	10	25	0.18

[a] MS: molar substitution (moles of hydroxyprpopyl per anhydroglucose unit).

al., 1987). Water plays an important role in controlling these factors in starch gels and starch-based foods. Several researchers have studied the role of water, water holding capacity, and water mobility in determining the texture of starch-based foods. Keetels et al. (1996) suggested that increased moisture content caused greater deformation of swollen granules and a lower-strength amylose network, leading to decreased gel firmness. Inaba, Oshizawa, Adachi, Matsumara, and Mori (1994) investigated the textural and mechanical properties of starch gels prepared at various moisture contents. They reported that compressive force and work increased with starch concentration, while resiliency and compressibility did not depend on starch concentration. Chung and Lee (1991) demonstrated that the bound water (unfreezable water at −30 °C) of surimi gels prepared with potato starch, with and without pre-gelatinization, was highly correlated with compressive force and inversely related to expressible moisture. Ruan et al. (1997) used ^{1}H NMR spectroscopy and texture analysis to study various types of cooked rice. They found that the hardness of cooked rice was highly correlated with spin–spin relaxation constants of protons ($p < 0.01$).

Chemical modification of starch by hydroxypropylation has been used to improve its functional properties. Hydroxypropylation reduces gelatinization temperature, decreases gel firmness, and increases water-holding capacity (Hoover, Hannouz, & Sosulski, 1988; Liu, Ramsden, & Corke, 1999; Yeh & Yeh, 1993), as hydroxypropyl groups introduce steric restrictions that weaken the internal bond structure holding the granule together. Hydroxypropylation also prevents water in the starch gel from separating through syneresis, when subjected to freeze-thaw cycles (Eliasson & Kim, 1992). Seow and Thevamalar (1993) reported that the introduction of hydroxypropyl groups in starch molecules acted as an internal plasticizer and reduced the energy of gelatinization. Liu et al. (1999) reported that hydroxypropylation increased swelling power and solubility in starch pastes.

The objective of this study was to investigate the effects of hydroxypropylation and starch concentration on water mobility and textural attributes of wheat starch gels. Time domain ^{1}H NMR was used to study dynamic water properties in gels, while texture profile analysis (TPA) was used to study various textural attributes. To further investigate the contributions of different gel phases, studies were also done on isolated amylose gel and granule-rich fractions.

2. Materials and methods

2.1. Preparation of hydroxypropylated wheat starch

Hydroxypropylation of wheat starch was accomplished as described by Kim, Hermansson, and Eriksson (1992). Native wheat starch (Sigma Chemical Company, St Louis, MO) was lyophilized for 48 h, then kept over phosphorous pentoxide (Sigma Chemical Company, St Louis, MO) to ensure maximum dryness. Dry sample (200 g) was suspended in 440 ml of distilled water containing 40 g Na_2SO_4, then the pH adjusted to 11.3 with 1N NaOH. The mixture was placed in 500 ml screw cap jars and maintained at 35 °C in a Model BT-23 controlled temperature water bath equipped with a rotary shaker (American Scientific Products, Cambridge, MA). Aliquots (8, 16, or 25 ml) of propylene oxide (Acros Organics, NJ) were added by pipette to the jars. The jars were immediately capped and vigorously shaken, then returned to the water bath. The reaction proceeded for 24 h, while being shaken at 120 rpm, and was terminated by adjusting the pH to 5.5 using 1N HCl. The suspension was washed with distilled water and centrifuged several times for 15 min at 3200*g*. Control wheat starch was prepared with the same reagents and procedure, but without addition of propylene oxide. This was to ensure that any measured changes were due to hydroxypropylation and not from effects of pH change or heating. The hydroxypropyl content was determined by the method of Johnson (1969). The molar substitution (MS) was defined as moles of substituent per mole of anhydroglucose unit (Table 1).

2.2. Gel preparation

In order to prepare homogeneous gels from highly concentrated starch suspensions, a microwave heating method was used. Starch samples (0.5 g) were weighed into glass tubes (3 cm × 1 cm diameter) fitted with screw caps. Distilled water (0.75, 1.0, and 1.5 g, respectively) was added to the tube to make a suspension (40, 33, and 25% starch by weight), then vortexed for 20 s. The sealed containers were placed on a rotating turntable and heated in a microwave oven (Daewoo, KOR-630A) for 40 s at 800 W. After heating, the sample temperature was 94 ± 2 °C. Gels were formed as the samples were allowed to cool to 25 °C for 1 h. Fresh gels were immediately measured by NMR. For TPA, gels were formed in glass jars (7 cm diameter × 8 cm height). Cylindrical samples were cored from the gel (1 cm diameter × 1 cm height).

2.3. Amylose and granule remnants

In order to better understand the origin of ^{1}H NMR signals, preparations of isolated amylose and granule

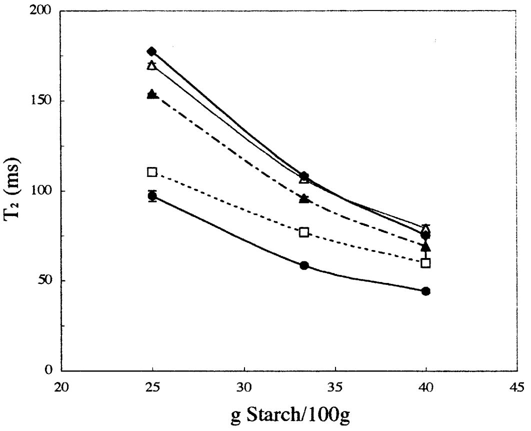

Fig. 1. Single exponential transverse relaxation times (T_2) as a function of starch gel concentration for native wheat starch (●), alkali-treated wheat starch (□), and hydroxypropylated (▲, MS 0.05; △, MS 0.12; ◆, MS 0.18) wheat starch gels.

remnants were prepared. A 7% wheat starch paste was held at 70 °C and gently stirred for 90 min. The paste was diluted with 200 ml of distilled water at 70 °C and centrifuged at 2500*g* for 15 min. The suspension was separated into two phases. The supernatant gave a blue color after staining with 0.2% iodine solution (0.2 g iodine, 2 g KI, and 100 ml distilled water) and was clear of granules, when examined by light microscopy. This was considered to be the soluble starch fraction. The precipitate consisted of concentrated gelatinized starch granules when observed at 40 ×, and gave a purple color when reacted with iodine solution. This was considered as the insoluble starch fraction. To adjust the concentration of the soluble starch solution, water was allowed to evaporate from the sample, while gently stirring at 72 °C. The moisture contents of adjusted soluble solution and insoluble starch were determined by drying in vacuo at 75 °C for 48 h. Gels were prepared from the amylose preparations and from the granule-rich sediment as described previously.

2.4. Texture profile analysis

Cylindrical gel samples (1 cm length × 1 cm diameter) were subjected to instrumental TPA. The specimens were placed between parallel plates fitted to an Instron Model 5500R Universal Testing Machine (Instron Corporation, Canton, MA). The gels were compressed twice at 1 mm/s to a distance 50% of the initial height. From the resulting force/deformation curves, the textural parameters of hardness, cohesiveness, and springiness were calculated. Hardness (N/m^2) was defined as the maximum force achieved during the first compression cycle, and cohesiveness as the ratio of the area under the first and second compression curves. Springiness was calculated as the ratio of the distance at the maximum force during first compression to the distance at the maximum force during second compression.

2.5. NMR measurements

Proton relaxation measurements were made using a MARAN 20 MHz NMR spectrometer (Resonance Instruments, Whitney, UK). The glass tubes with gel specimens were placed in 18 mm diameter NMR tubes, which were covered with parafilm. All measurements were made at 25 ± 0.1 °C. Transverse (T_2) relaxation curves were developed using the Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence: $90x - (t - 180y - \tau - \text{echo})_n$. Acquisition parameters were set to a 90° pulse of 4.1 μs, relaxation delay of 6 s, and τ of 300 μs. Relaxation curves obtained from the CPMG sequence were analyzed using a mono-exponential model:

$$S = A\,\mathrm{e}^{-t/T_2} \tag{1}$$

where T_2 describes the rate of change of the signal S, and A is a pre-exponential factor dependent upon the number of protons. Alternately, a distributed exponential software package (DXP, Resonance Instruments, Whitney, UK) was used to analyze the relaxation curves. This routine calculates a distribution of T_2 terms that best describe the data.

$$g_i = \sum_{j=1}^{m} f_j\,\mathrm{e}^{-t_i/T_{2,j}} \tag{2}$$

where g_i are the values of the exponential distribution at time t_i, f_j are the pre-exponential multipliers, and $T_{2,j}$ are the time constants. In general, the distributions assumed more than one distributed region, suggesting the existence of various regions of water with similar mobility. In this case, the number of protons in a given region was measured by the integrated signal intensity over the region of the distribution.

2.6. Statistical analysis

Five treatment groups were considered in this experiment including unmodified wheat starch, control wheat starch (subject to reaction conditions but without propylene oxide), and three levels of hydroxypropylation (MS = 0.05, 0.12, and 0.18). Gels were prepared at three levels of starch (25, 33, and 40% by weight), and all samples were prepared and analyzed in triplicate. SAS software was used for data analysis (SAS Institute, Inc., 1990). The general linear model ANOVA was utilized to test for effects of treatments. The Duncan test was conducted to differentiate the treatments. Correlation coefficients between measurements were calculated and compared. Significance of difference was defined at $p < 0.05$.

3. Results and discussion

3.1. Hydroxypropylation of wheat starch

Analysis of modified starches showed that the MS,

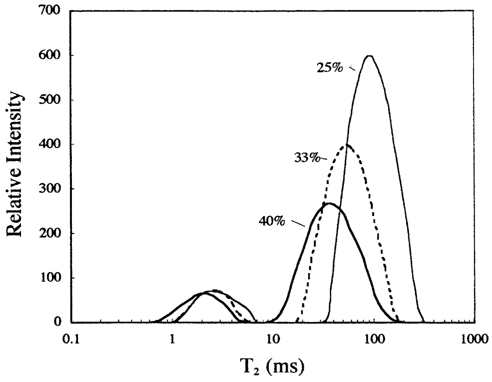

Fig. 2. T_2 distribution for unmodified wheat starch gel at 25, 33, and 40% starch concentration.

defined as the moles of hydroxypropyl per anhydroglucose unit, was 0.05, 0.12, and 0.18, respectively (Table 1).

3.2. Transverse relaxation

Relaxation time constants (T_2) of heterogeneous systems can be determined from the transverse relaxation decay curves using mono-exponential, multi-exponential, or distributed exponential fitting (Chen, Long, Ruan, & Labuza, 1997). In this study, the proton relaxation decay curves were analyzed using mono-exponential (Eq. (1)) and distributed exponential (Eq. (2)) models. Mono-exponential analysis was used to assess the effects of chemical modification and moisture content on overall water mobility. Fig. 1 shows T_2 for unmodified, alkaline-treated (control), and hydroxypropylated starch gels as a function of starch concentration. For all treatment groups, T_2 values decreased with increasing starch concentration, suggesting that on average water is less mobile in gels at higher starch concentration. More specifically, at higher starch concentration each water molecule has, on average, a shorter distance to diffuse before interacting with starch molecules. Consequently, proton decay is enhanced by decreased water mobility, proton exchange, or cross-relaxation mechanisms (Hills, Takacs, & Belton, 1990; Yakubu, Ozu, Baianu, & Orr, 1993). Hydroxypropylation had a significant effect on relaxation behavior of water protons in starch gels. In general, T_2 values increased with the level of hydroxypropylation, although differences in the 33 and 40% gels at MS 0.12 and 0.18 were not significant. In general, this would argue that the volume in which water is free to move before interacting with starch is greater in the hydroxypropylated starch gels. T_2 values for the control gel were intermediate between the unmodified and hydroxypropylated gels. This indicates that alkali treatment alone has some affect on starch apart from subsequent chemical modification. Alkali treatment has been shown to allow enhanced granule swelling and to produce changes in crystal structure in potato starch (Perara, Hoover, & Martin, 1997).

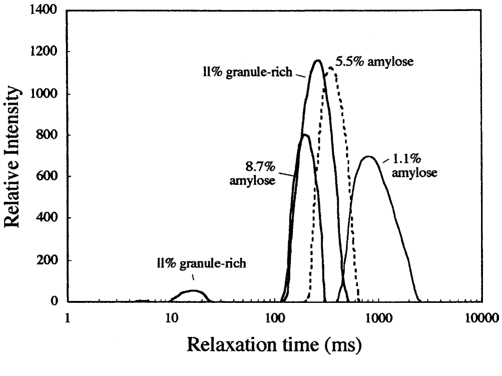

Fig. 3. T_2 distribution for gels made 1.1, 5.5, and 8.7% solubilized amylose, and from 11% granule-rich sediment.

Distributed exponential fits to the relaxation data showed two distinct regions of T_2 values, one with T_2 values between 0.8 and 7 ms, one with values between 10 and 300 ms, depending on starch concentration. Fig. 2 shows the distribution of T_2 values for unmodified wheat starch gels in the starch concentration range of 25–40%. The peak maxima of the 0.8–7 ms region is denoted by T_{2a}. Spin–spin relaxation is enhanced when, on average, water molecules have hindered rotation and proton spins can exchange energy. Thus, T_{2a} is associated with less mobile water, although contributions from chemical exchange and cross-relaxation may also be factors. The peak at longer time constants (10–300 ms) is denoted by T_{2b} and the region associated with more mobile water. The phenomenon of multi-phase behavior in water proton relaxation has been observed in other systems, such as flour dough (Leung, Magnuson, & Bruinsma, 1979), hydrated elastin (Ellis & Parker, 1976), and bread (Chen et al., 1997; Engelsen, Jensen, Pedersen, Norgaard, & Munch, 2001). In addition, to changes in time constants, the integrated signal intensity of each region increased with moisture content, again reinforcing the notion that these signals emanate from water domains.

The source of the dual peaks is explored in more detail in Fig. 3. Starch gelatinization results in solubilized starch, primarily amylose, and swollen starch granules and fragments. On cooling, solubilized amylose forms a continuous network that links swollen granules (Hermansson & Svegmark, 1996; Morris, 1990). Fig. 3 shows distributed T_2 values for isolated amylose gels, as well as those from a granule-rich sediment. The amylose gel showed a single peak, with a maximum value of T_{2b}. T_{2b} varied from 212 ms (at 8.7% amylose) to 840 ms (at 1.1% amylose). Subsequent studies (data not shown) showed that these peaks did not change during 15 days storage at 5 °C. Although the soluble starch phase was initially clear, it rapidly formed an opaque gel when cooled. This suggests that the amylose gel quickly retrograded, even before NMR measurements could be accomplished. The single peak indicates that fast-exchange conditions exist, that is, the average diffusion time from the bulk water phase to a starch surface is short compared to T_2 of bulk water. Isolated granule remnants showed two peaks, one in a region similar to

Table 2
Peak transverse relaxation times and associated water content of native, alkali-treated, and hydroxypropylated wheat starch gels

Starch	Concentration[a] (%, w/w)	Less mobile fraction		More mobile fraction	
		T_{2a} (ms)	w_a (g H_2O)	T_{2b} (ms)	w_b (g H_2O)
Native	40	2.26 ± 0.04	0.093 ± 0.001	38.83 ± 6.81	0.657 ± 0.001
	33	2.50 ± 0.10	0.107 ± 0.005	55.10 ± 0.85	0.893 ± 0.005
	25	2.64 ± 0.15	0.117 ± 0.002	96.04 ± 0.37	1.383 ± 0.002
Alkali-treated	40	2.97 ± 0.01	0.093 ± 0.004	50.33 ± 3.65	0.657 ± 0.004
	33	3.73 ± 0.17	0.105 ± 0.012	73.10 ± 1.64	0.895 ± 0.012
	25	4.28 ± 0.16	0.111 ± 0.001	103.2 ± 1.03	1.389 ± 0.001
Hydroxypropyl MS = 0.05	40	3.09 ± 0.11	0.010 ± 0.016	49.77 ± 2.83	0.650 ± 0.016
	33	4.11 ± 0.18	0.117 ± 0.002	85.57 ± 3.75	0.883 ± 0.002
	25	6.13 ± 0.02	0.122 ± 0.007	129.30 ± 0.52	1.378 ± 0.007
Hydroxypropyl MS = 0.12	40	3.66 ± 0.27	0.115 ± 0.007	72.20 ± 0.10	0.635 ± 0.007
	33	4.38 ± 0.35	0.122 ± 0.006	97.00 ± 1.03	0.878 ± 0.006
	25	6.23 ± 0.17	0.125 ± 0.000	149.00 ± 0.00	1.375 ± 0.000
Hydroxypropyl MS = 0.18	40	4.50 ± 0.15	0.121 ± 0.002	72.17 ± 0.05	0.629 ± 0.002
	33	5.72 ± 0.31	0.129 ± 0.006	101.20 ± 4.41	0.871 ± 0.006
	25	6.29 ± 0.27	0.131 ± 0.009	151.36 ± 1.74	1.369 ± 0.009

[a] Starch comcentrations of 40, 33, and 25% correspond to moisture contents of 0.75, 1.0, and 1.5 g, respectively.

amylose, and one at times between 10 and 25 ms. Both regions shift considerably during storage (data not shown), indicative of changes seen in amylopectin during retrogradation. This suggests that the T_{2b} region is associated with a fairly porous structure, perhaps an intergranular gel network. The T_{2a} region is associated with a more restricted environment of the granule remnant, and one that does not rapidly exchange water with the T_{2a} region. Ring et al. (1987) reported that leached amylose molecules had higher water mobility compared with amylopectin molecules in mixed aqueous systems of purified samples of amylose and amylopectin.

The effect of alkali treatment and hydroxypropylation on the peak relaxation times (T_{2a} and T_{2b}) in the starch gel systems is shown in Table 2. In addition, the amount of water associated with either region a (w_a) or region b (w_b) was calculated by:

$$w_a = \frac{I_a}{I_a + I_b}(\text{Total g } H_2O) \tag{3}$$

$$w_b = \frac{I_b}{I_a + I_b}(\text{Total g } H_2O) \tag{4}$$

where I_a or I_b are the total integrated signal intensity in regions a and b, respectively.

At all gel concentrations, hydroxypropylation increased the T_{2a} and I_{2a} values, as compared to equivalent gel concentrations of unmodified starch. Hydroxypropylation resulted in more water (w_a) being associated with the low-time constant region. Using light microscopy, Perara et al. (1997) showed that hydroxypropylation caused more highly deformed starch granules. Liu et al. (1999) reported that swelling was greater in starch granules after hydroxypropylation. Our results indicate that there is slightly greater moisture in the swollen granules after hydroxypropylation, and slightly less in the amylose gel network. For example, there was 12% more water in the leached granules of the 0.18 MS 40% gel (0.131 g H_2O), as compared to the granules in the unmodified gel (0.117 g H_2O). Concurrently, there was a slight decrease in moisture in the amylose network of the 0.18 MS 40% gel (1.369 g H_2O) as compared to the amylose network of the unmodified gel (1.383 g H_2O).

In general, increased moisture in the gels was associated with slightly higher T_{2a} values. Larger increases in T_{2a} were observed due to hydroxypropylation than to changes in moisture content. However, increases in T_{2a} and the distribution of T_2 values were not great, suggesting that the water in this region has greatly hindered motion.

The T_{2b} and distribution of T_2 values in the high T_2 region also increased with moisture content and with degree of hydroxypropylation. Again, the increase in T_2 with moisture content may be attributed to the fact that water molecules must diffuse a longer distance before interacting with the biopolymer interface. The increase in moisture in this region is greater than that in the low-time constant (T_{2a}) region. For example, in the unmodified starch gels w_b increased from 0.657 to 1.383 g (a 112% increase) as the starch concentration decreased from 40 to 25%. This may explain the greater increases in T_{2b} than were observed in T_{2a}. T_{2b} values also increased with the degree of hydroxypropylation. Studies indicate that the bulky hydroxypropyl group on starch is mainly distributed on amylose molecules, and that this disturbs the aggregation of solubilized amylose in a continuous phase (Steeneken, 1984).

Table 3
Textural properties of starch gels with different concentration (values in a column followed by different letters are significantly different ($p < 0.05$))

Starch	Hardness			Cohesiveness			Springiness		
	40%	33%	25%	40%	33%	25%	40%	33%	25%
Native	11.38 ± 1.90^{a}	5.53 ± 1.73^{a}	2.03 ± 0.63^{a}	0.69 ± 0.04^{a}	0.70 ± 0.07^{a}	0.85 ± 0.02^{ab}	0.81 ± 0.02^{a}	0.83 ± 0.03^{a}	0.83 ± 0.03^{a}
Alkali-treated	6.21 ± 0.98^{b}	3.11 ± 1.73^{b}	0.93 ± 0.39^{b}	0.76 ± 0.03^{a}	0.80 ± 0.08^{b}	0.88 ± 0.03^{a}	0.85 ± 0.03^{a}	0.84 ± 0.04^{a}	0.83 ± 0.05^{a}
Hydroxypropyl MS = 0.05	1.57 ± 0.98^{c}	0.44 ± 0.01^{c}	0.34 ± 0.10^{bc}	0.84 ± 0.07^{b}	0.89 ± 0.02^{b}	0.79 ± 0.01^{b}	0.81 ± 0.05^{a}	0.83 ± 0.10^{a}	0.81 ± 0.01^{a}
Hydroxypropyl MS = 0.12	1.25 ± 1.29^{c}	0.39 ± 0.06^{c}	0.21 ± 0.09^{c}	0.87 ± 0.03^{b}	0.87 ± 0.03^{b}	0.82 ± 0.06^{ab}	0.79 ± 0.02^{a}	0.79 ± 0.03^{a}	0.75 ± 0.03^{b}
Hydroxypropyl MS = 0.18	0.96 ± 0.36^{c}	0.30 ± 0.11^{c}	0.150 ± 0.02^{c}	0.89 ± 0.02^{b}	0.87 ± 0.03^{b}	0.86 ± 0.02^{b}	0.78 ± 0.09^{a}	0.77 ± 0.06^{a}	0.73 ± 0.01^{b}

3.3. Mechanical properties of gels

Selected textural attributes of unmodified, control, and hydroxypropylated starch gels in the starch concentration ranges of 25–40% are presented in Table 3. For all samples, gel hardness increased significantly with gel concentration ($p < 0.05$). In addition, gels formed from alkali-treated (NaOH and Na_2SO_4) starch were less hard than those formed from unmodified starch, and those from hydroxypropylated starch were even less hard. No significant difference in gel hardness was observed due to degree of MS. These results are consistent with those reported by Liu et al. (1999), who demonstrated that hydroxypropylation decreased gel hardness. It is known that the extent of the amylose gel network and deformability of swollen granules are the main factors contributing to gel strength (Luyten, van Vliet, & Walstra, 1992). Our results in Fig. 2 show higher T_2 values for control or modified starch gels. Distributed analysis showed that there was higher water mobility in both T_{2a} and T_{2b} fractions, and that the amount of water associated with the less mobile state was increased with hydroxypropylation (Table 2). As control experiments showed that this less mobile state was associated with granule remnants, it appears that enhanced hardness in the modified starches can be attributed to greater granule swelling.

Cohesiveness is a measure of degree of difficulty in breaking down the gel's internal structure. The effect of moisture content in starch gels varied with the type of starch. For example, cohesiveness of unmodified and control starch gels increased with increasing moisture, whereas that of hydroxypropylated starch gels decreased. In general, hydroxypropylated starch had higher cohesiveness. In hydroxypropylated starch, amylose is more easily leached from the swollen granules. Thus, it is likely that the increased cohesiveness in the hydroxypropylated starch is due to increased polymer concentration in the continuous phase.

Springiness represents the extent of recovery of gel height and sometimes is referred to as 'elasticity' (Sanderson, 1990). For unmodified and control starch gels, springiness was not significantly affected by starch concentration in the range of 25–40%. However, for highly substituted hydroxypropylated starch gels (0.12 and 0.18 MS), springiness decreased as moisture content increased. In the 25% gels, hydroxypropylated starch gels had lower springiness than unmodified or control gels.

3.4. Correlation between texture and NMR parameters

From the TPA analysis, textural parameters, such as hardness, springiness, and cohesiveness were obtained. Correlation analysis between hardness and NMR parameters, such as T_{2a}, I_{2a}, T_{2b}, and I_{2b} were performed using a multiple variable regression model. The results are presented in Table 4. The gel hardness had significant negative correlation with all parameters ($p < 0.05$). The level of correlation

Table 4
Correlation coefficient (r) between hardness and NMR parameters (T_{2a}, I_{2a}, T_{2b}, and I_{2b}) of gels

Attribute	T_{2a}	I_{2a}	T_{2b}	I_{2b}
Hardness	− 0.9061	− 0.8774	− 0.7376	− 0.5424
T_{2a}		0.88150	0.68038	0.55703
I_{2a}			0.55505	0.21985
T_{2b}				0.8421
I_{2b}				

was in order of T_{2a} ($R^2 = 0.90$) > I_{2a} ($R^2 = 0.87$) > T_{2b} ($R^2 = 0.73$) > I_{2b} ($R^2 = 0.54$). The higher correlation coefficients of T_{2a} and I_{2a} than those of T_{2b} and I_{2b} may indicate that the mobility and amount of water in the less mobile state, which may be associated with starch molecules in swollen granules, is a more dominate factor in gel hardness at high starch concentration. This interpretation is consistent with that of Evans and Lips (1992), who studied the viscoelasticity of gelatinized starch dispersions at concentrations between 5 and 25% (w/w). They proposed that the phase volume of the swollen granules and their inherent deformability were the key variables in the mechanical behaviors of concentrated gelatinized starch dispersion systems, rather than the component released from the granules.

4. Conclusion

The water mobility and textural properties of native and hydroxypropylated starch gels were investigated at different gel concentrations. Two distinct water fractions having different mobility were identified in all starch gels. Control experiments indicated that the less mobile state was associated with granule remnants, while more mobile states could be attributed to both intergranular and extragranular gel networks. Hydroxypropylation produced gels with greater water mobility in all regions. Gel hardness and springiness were significantly decreased in hydroxypropylated samples. As cohesiveness was increased in hydroxypropylated samples, this suggests enhanced deformation of starch granule remnants. Multi-regression analysis showed that the mobility and amount of water in the less mobile state is a dominant factor for hardness of gels with starch concentration in the range of 25–40%.

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