Utilization of Hydroxypropylated Waxy Rice and Corn Starches in Korean Waxy Rice Cake to Retard Retrogradation

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ABSTRACT

A traditional waxy rice gel cake in Korea, *Injulmi*, was prepared with hydroxypropylated waxy rice and corn starches (molar substitutions 0.13 and 0.11, respectively), and the textural and retrogradation characteristics of the cake were compared with a conventional cake made of waxy rice flour. In the pasting viscogram, hydroxypropylated starches exhibited reduced pasting temperatures, but increased peak viscosities compared with the unmodified starches. Under differential scanning calorimetry, the T_g' and ice melting enthalpy of the starch gel cakes were reduced by hydroxypropylation, which indicated that the modified starches had higher water-holding capacity than the unmodified starches. The degree of retrogradation, as measured by the hardness of the gel cake and the melting enthalpy, was significantly reduced by hydroxypropylation and hydroxypropylated waxy rice starch was more effective in retarding the retrogradation than hydroxypropylated waxy corn starch

Starch is often modified to change or improve its cooking characteristics, gelling tendency, flow behavior, freeze-thaw stability, and for other reasons (BeMiller 1997). Structural derivatizations by substituting the hydroxyl groups of anhydroglucose units include esterification (acetylation, phosphorylation, octenylsuccinylation, and phosphate ester cross-linking), and etherification (hydroxyethylation and hydroxypropylation) (Gray and BeMiller 2003). Of these possibilities, hydroxypropylation has been most widely used for food starches because it raises the paste viscosity and the cold stability of starch and improves paste and gel texture (Wootton and Manatsathit 1984; Butler and Christianson 1986; Hoover et al 1988). The hydroxypropyl groups enhance the hydrophilic nature of the starch and weaken the internal bonds that hold the granules, thus facilitating starch gelatinization and improving the stability of the starch paste or gel (Butler and Christianson 1986; Yeh and Yeh 1993). These effects have been ascribed to the steric effects imposed by the bulky hydroxypropyl groups, which prevent the starch chain alignment.

It was also reported that, when starch in granule form is hydroxypropylated, amylose is modified to a greater extent than amylopectin, presumably because amylose was located in more accessible amorphous regions (Perera et al 1997; Kavitha and BeMiller 1998). Steeneken (1984) reported that the bulky hydroxypropyl groups were mainly substituted on amylose molecules, thus disturbing the aggregation of solubilized amylose in the continuous starch paste phase. However, in amylopectin, the substitution occurred heterogeneously (Hood and Mercier 1978; Kavitha and BeMiller 1998; Van der Burgt et al 1998; Richardson et al 2001). Each cluster in amylopectin contains a highly branched region that is amorphous, which may be the most accessible region for the modifying regents (Manners 1989). According to Kavitha and BeMiller (1998), when the molar substitution of amylopectin was ≈0.1, more than half of the amylopectin was modified close to branch points.

One of the popular traditional foods in Korea, *Injulmi*, is commercially produced from waxy rice flour by steam-cooking into a chewy gel-type cake. However, it readily hardens during ambient storage due to the amylopectin retrogradation. The addition of enzymes or emulsifiers has been used to retard this retrogradation, but the use of modified starch has been rarely examined. To improve the storage stability of waxy rice gel cakes, the present study used hydroxypropylated waxy rice and waxy corn starches as whole replacements for waxy rice flour, and the texture and retrogradation characteristics of the cakes were examined during cold storage.

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MATERIALS AND METHODS

Waxy corn starch was provided by Samyang Genex (Seoul, Korea). Waxy rice flour (Japonica-type, NongMin, Korea) was purchased from a local grocery in Seoul, Korea. Waxy rice starch was isolated from the waxy rice flour using 0.2% NaOH (Lim et al 1999).

Hydroxypropylation

Waxy rice or corn starch (330 g, db) was dispersed in distilled water (500 mL) containing sodium sulfate (43 g). The dispersion was adjusted to pH 11.2 by adding 2*M* NaOH with continuous stirring with a magnetic bar. The reaction flask was sealed with a septum; propylene oxide (25 mL) was injected using a syringe; and then the flask was placed in a water bath at 49°C and magnetic-stirred for 24 hr. The slurry obtained was neutralized with dilute hydrochloric acid (1*M*) and filtered, the hydroxypropylated starch was washed with water (500 mL) three times and then with 50% acetone, and air-dried (25°C) overnight.

NMR Measurements of Molar Substitution

The modified starch (35 mg) was dispersed in deuterium oxide (D_2O, 5 mL) in a centrifuge tube and heated in a boiling water bath for 5 min. The starch solution was cooled to room temperature, α-amylase from *Bacillus* species (EC 3.2.1.1, product No. A-6814, Sigma Aldrich, St. Louis, MO) (1.0 unit) was added, and the mixture was incubated for 48 hr at room temperature. The digest was subsequently freeze-dried and redissolved in 1 mL of D_2O for H^1 NMR (INOVA 300 MHz, Varian, Palo Alto, CA). The molar mass substitution was calculated as MS = $(a/3)/[(b - a)/7]$, where a is the proton peak area for hydroxypropyl methyl groups at 1.2 ppm, and b is the area for anhydroglucose ring protons (3.0–4.3 ppm) (Stapley and BeMiller 2003).

Pasting Viscosity

The pasting viscosity of starch was measured using a Rapid Visco Analyser (model 3-D, Newport Scientific, Australia). Starch dispersion (7%, db) was pasted by heating from 50 to 95°C at a heating rate of 6°C/min, held at 95°C for 5 min, and then cooled to 50°C at 6°C/min.

Cake Preparation for Texture Analysis

The starch (50 g, db) and NaCl (1% of starch, w/w) were mixed with an equal amount of water into a dough, which was then steam-cooked in a cooking machine (SPM-MP1, Sanyo, Japan). The dough was steamed in the machine for 10 min and punched to make a homogeneous gel.

The starch gel was wrapped with polypropylene film to prevent moisture loss, and then stored in zipper bags at 4°C for seven days. The gel was cut into square pieces (2 × 2 cm, 1 cm thick), and then the texture (hardness, adhesiveness, cohesiveness, and springiness) of the gels samples was measured using a texture analyzer (TA-X2, Surrey, UK). A cylinder probe (13 mm in diameter) was used for the compression analysis at a test speed of 1 mm/sec and a strain of 20%. The moisture content of the starch gels (42.4 ± 2.0%), as determined by weight loss after drying (145°C, 5 hr), was not significantly different among the starch samples.

Differential Scanning Calorimetry (DSC)

As soon as the starch gel had been prepared by the cooking machine, a small sample (12–15 mg) was transferred into an aluminum DSC pan. It was hermetically sealed and stored in a cold chamber (4°C) for up to seven days. The thermal transition characteristics of the starch gel (glass transition temperature, and ice melting and recrystallization characteristics) were measured using a differential scanning calorimeter (DSC 6100, Seiko Instruments, Japan) after one, three, five, and seven days of storage. The DSC sample was rapidly cooled to –40°C at 20°C/min and then analyzed during heating to 120°C at a rate of 5°C/min. An empty pan was used as a reference.

RESULTS AND DISCUSSION

Molar Substitution

Figure 1 shows the ^{1}H NMR spectrum of hydroxypropylated waxy rice starch (HPWRS), in which the ratios of protons in hydroxypropyl groups and those in anhydroglucose units were determined for the molar substitution (MS) calculation. The MS values of the hydroxypropyl groups in the modified waxy rice (HPWRS) and waxy corn (HPWCS) starches were 0.13 (±0.01) and 0.11 (±0.01), respectively. Although the reaction conditions (reaction temperature and time, amount of propylene oxide, salt concentration, etc.) were identical for both starches, the MS value was slightly higher for waxy rice starch (HPWRS). Wootton et al (1985) proposed that hydroxypropylation is related to the granular arrangement and proportions of amylose and amylopectin in addition to the reaction conditions. Propylene oxide reacts slowly with starch so that penetration of reagent into granules is faster than reaction, and therefore, the reaction occurs more uniformly than other starch modification reactions (Huber and BeMiller 2001). However, the availability of individual starch molecules to a chemical reagent (propylene oxide) is influenced by granule microstructure including channels, and thus the patterns and locations of chemical reactions within granules may differ for starches from different origins (Huber and BeMiller 1997, 2000).

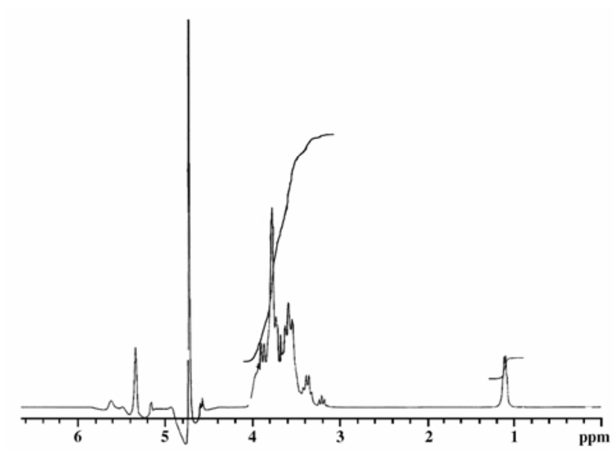

Fig. 1. ^{1}H NMR spectrum of hydroxypropylated waxy rice starch.

Pasting Viscosity

Table I shows the pasting temperature and viscosity data of waxy rice flour, and native and hydroxypropylated waxy starches. The higher pasting temperature and substantially lower peak viscosity of waxy rice flour (WRF) versus waxy rice starch (WRS), indicate that the nonstarch residues, mainly protein, hinder pasting and subsequent viscosity development in water.

Hydroxypropylation significantly reduced the pasting temperature (60.3 and 55.7°C, respectively) for waxy rice starch (HPWRS) and waxy corn starch (HPWCS). The peak viscosity of hydroxypropylated starches was higher (1,563 and 1,993 cP for HPWRS and HPWCS, respectively) than that of their native counterparts (1,338 and 1,895 cP for WRS and WCS, respectively). The hydrophilic nature of the hydroxypropyl groups facilitates water penetration into starch granules and weakens the granular structure (Seow and Thevamalar 1993). Liu et al (1999), Shi and BeMiller (2000), and Pal et al (2002) reported that hydroxypropylated corn starch showed increased shear breakdown because the susceptibility of swollen starch granules to prolonged stirring was increased by the modification. However, in the present study, the breakdown of the modified starches during the holding period at 95°C was less than that of native starch (Table I). The reason is unclear, but we presume that the absence of amylose in the waxy starches tested might have produced different shear-thinning results.

Waxy corn starches, either native or hydroxypropylated (WCS and HPWCS), showed much greater peak viscosity and breakdown than the waxy rice starches (WRS and HPWRS). This may have been due to differences in granule size and morphology. Peak viscosity resulted mainly from the granule swelling and because waxy rice starch consists of smaller granules (2≈5 μm) than waxy corn (15 μm) (Acquarone and Rao 2003); the granular swelling of the small rice starches might not be as effective at increasing peak viscosity as the swelling of waxy corn starch granules. However, breakdown was much lower for the waxy rice starches, either native or modified. This also demonstrated that the small rice starches are less disrupted than the large corn starches when swollen.

Hydroxypropylation of normal starches usually reduces starch chain association and thus reduces setback (Liu et al 1999; Pal et al 2002). However, for the waxy starches tested, hydroxypropylation somewhat increased setback. Because the setback of a normal starch mainly arises from the rapid association between amylose chains released in the paste (Miles et al 1985), the setback of waxy starch paste arises solely from amylopectin chain association, which is much slower than those between amylose chains. The hydroxypropylation of waxy starch occurs mainly in the vicinity of branching points (Kavitha and BeMiller 1998). But the increased setback shown by the hydroxypropylated starches suggests that the substitutions near branchings facilitate the association between linear amylopectin chains during cooling of

TABLE I
Pasting Viscosity of Waxy Rice Flour (WRF), Native and Hydroxypropylated Waxy Rice (WRS and HPWRS), and Waxy Corn Starches (WCS and HPWCS)

Samples	Pasting Temp. (°C)	Viscosity (cP)			
		Peak	Breakdown	Setback	Final
WRF	67.8	323	163	124	287
WRS	66.4	1,338	785	236	789
HPWRS	60.3	1,563	517	533	1,579
WCS	69.6	1,895	1,239	85	741
HPWCS	55.7	1,993	1,159	521	1,355

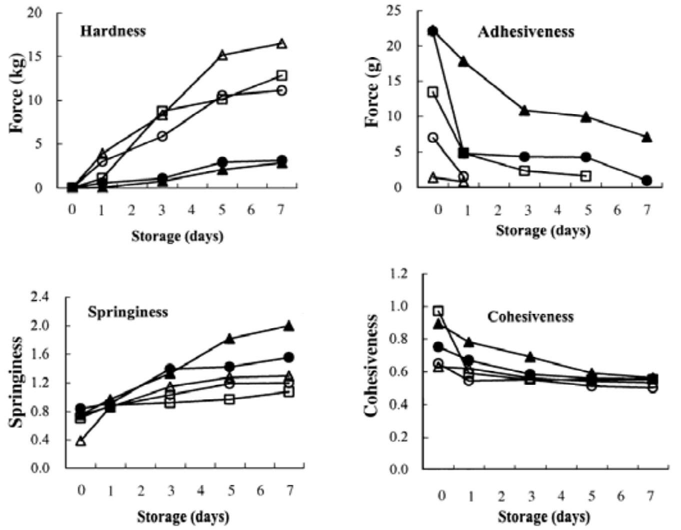

Fig. 2. Textural characteristics of gels of waxy rice flour (WRF), native, and hydroxypropylated waxy rice (WRS and HPWRS), and waxy corn starches (WCS and HPWCS) (□ WRF; △ WRS; ▲ HPWRS; ○ WCS; ● HPWCS).

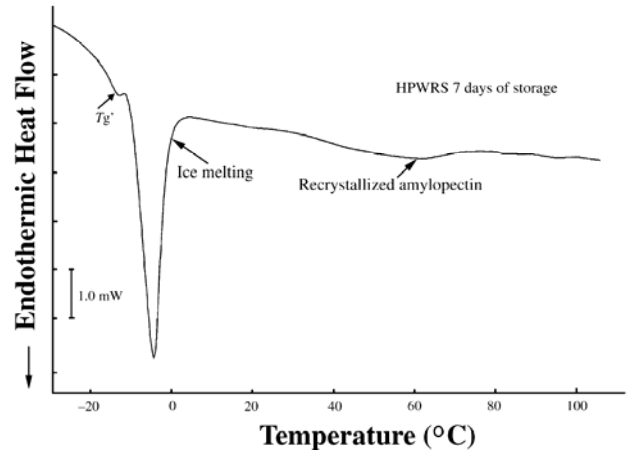

Fig. 3. DSC thermogram of hydroxypropylated waxy rice starch gel stored for 7 days at 4°C.

the paste. It is hypothesized that the bulky hydroxypropyl groups occupy more space at the branching regions so that there is more of a chance for linear chain fractions to associate for the viscosity increase.

The final viscosities of the hydroxypropylated starches (1,579 cP for HPWRS and 1,355 cP for HPWCS) were much higher than those of native starches (789 cP for WRS and 741 cP for WCS) because of their higher peak viscosity and setback but lower breakdown. Comparing the two starch types, the waxy rice starches showed higher final viscosity values, mainly because of lower degrees of breakdown (Table I).

Textural Properties of Starch Gel Cake

Figure 2 shows the textural characteristics of the starch gel cakes after different periods of storage. The fresh starch gels (0 day) were very soft and showed almost no differences in hardness between native and modified starches. However, after one week of storage, the gels became hard and this hardness change differed among the samples. The native waxy rice starch gel (WRS) was harder than the waxy corn starch gel (WCS), but the waxy rice flour (WRF) formed a relatively softer and more adhesive gel than the waxy rice starch gel (WRS), suggesting that nonstarch components (protein and lipids) in WRF influenced the gel texture.

The gels of hydroxypropylated starches remained softer than those of native starches during cold storage. This result was consistent with the report by Liu et al (1999) and shows that hydroxypropyl groups inhibited the starch chain association. Thus, the hardening of waxy rice gel cake can be effectively retarded by using hydroxypropylated starches.

Usually, decreased adhesiveness is one of the distinctive features of starch gel during the storage-induced retrogradation. In the gel of normal starch containing both amylose and amylopectin, it is mainly attributed to the association of free amylose chains leached from starch granules (Karim et al 2000). Although the starches tested in this study were waxy types, the stickiness of all waxy starch gels reduced on storage. However, the hydroxypropylated starch gels remained stickier than those of the native starches, at the beginning and during storage periods. Comparing the two hydroxypropylated starches, HPWRS showed significantly higher adhesiveness than HPWCS. This stickiness might be related to water-retention on the gel surface, as the modified starch gels are presumed to retain more water on the surface than the native starch gels.

Hydroxypropylation increased the springiness and cohesiveness of waxy starch gels. Springiness represents the extent of recovery from gel surface deformation and is often referred to as elasticity (Sanderson 1990). Cohesiveness is a measure of the difficulty of breaking the internal structure of a gel. As storage days increased, the cohesiveness values of all starch gels decreased. Compared with native counterparts, hydroxypropylated starches showed higher gel cohesiveness. We hypothesize that the higher cohesiveness was caused by the bulky hydrophilic hydroxyl groups that stabilized the gel matrix by interacting with starch chains and water. The gel texture of the hydroxypropylated starches, which was softer and more elastic, might be favored for gel cakes.

Thermal Properties of Starch Gels

If a starch gel containing sufficient moisture is rapidly frozen, ice crystallization causes solid concentration in unfrozen liquid phase (Blond and Simatos 1998). Franks et al (1979) initially referred to the glass transition temperature of the freeze-concentrated liquid phase as T_g'. This parameter indicates that the threshold of instability in solute/water systems, and is an important parameter with respect to the quality and stability of frozen food systems (Roos et al 1996). It has also been reported that T_g' is independent of the initial water content (Slade and Levin 1991; Roos et al 1996).

Figure 3 shows the DSC thermogram of the hydroxypropylated waxy rice starch gel stored for seven days. Table II shows the thermal characteristics of the waxy starch or flour gels after different periods of storage. The waxy rice flour (WRF) had T_g' values slightly lower than those of unmodified waxy rice starch (WRS), suggesting that residual impurity affected the glass transition, but the difference between the T_g' of the two native starches (WRS and WCS) was insignificant. The hydroxypropylated starches (HPWRS and HPWCS) had T_g' values of –12.8 to –14.9°C, which were significantly lower than those of the native starches (–8.1 to –7.4°C). The low T_g' values of the hydroxypropylated starch gels were due to higher levels of unfrozen water. No change in T_g' was observed during storage, but the melting enthalpy of ice, which represented the amount of freezable water, was reduced as storage time increased. Ablett et al (1993) and Chung et al (2002) reported that, when starch was recrystallized, some water molecules were incorporated into the crystalline lattices, and that this reduced the amount of freezable water in the matrix. It was also reported that the reduced freezable water content by recrystallization caused a T_g' increase in rice and wheat starches (Vodovotz and Chinachoti 1998; Chung et al 2002). However, it is not clear why no change in T_g' was observed in this experiment. One possible cause may be the absence of amylose in the waxy starches tested.

TABLE II
Thermal Characteristics of Gels of Waxy Rice Flour (WRF), Native and Hydroxypropylated Waxy Rice (WRS and HPWRS), and Waxy Corn Starches (WCS and HPWCS)

Samples	Days of Storage	T_g'	Ice Melting Temperature (°C)	Ice Melting Enthalpy (ΔH)	Retrogradation Enthalpy (ΔH)
WRF	1	–8.2 ± 0.5	–0.8 ± 0.2	163.0 ± 3.1	2.5 ± 0.7
	3	–8.3 ± 1.2	–1.0 ± 0.3	161.6 ± 8.4	6.3 ± 0.3
	5	–8.5 ± 0.7	–1.3 ± 0.2	148.3 ± 5.4	8.2 ± 0.4
	7	–8.2 ± 0.9	–1.1 ± 0.1	141.5 ± 4.8	8.5 ± 0.1
WRS	1	–7.7 ± 0.1	–1.0 ± 0.3	151.4 ± 1.4	5.8 ± 0.8
	3	–7.9 ± 0.2	–1.3 ± 0.1	147.5 ± 5.0	6.7 ± 0.1
	5	–8.1 ± 1.3	–1.1 ± 0.2	129.1 ± 7.2	9.2 ± 0.7
	7	–8.0 ± 0.7	–1.1 ± 0.9	123.9 ± 3.4	9.8 ± 1.2
HPWRS	1	–14.1 ± 0.7	–4.1 ± 0.5	144.6 ± 5.1	1.2 ± 0.4
	3	–14.4 ± 0.2	–3.9 ± 1.1	145.4 ± 7.4	2.5 ± 0.8
	5	–15.2 ± 0.1	–4.3 ± 1.4	120.3 ± 2.5	3.2 ± 0.4
	7	–14.9 ± 1.2	–2.3 ± 0.3	118.1 ± 4.6	3.9 ± 0.5
WCS	1	–7.4 ± 0.1	–0.2 ± 0.1	236.2 ± 7.8	4.9 ± 1.1
	3	–7.8 ± 0.1	–0.1 ± 0.3	239.0 ± 2.1	5.6 ± 1.1
	5	–7.8 ± 0.5	–0.7 ± 0.2	242.1 ± 7.2	8.3 ± 1.0
	7	–7.5 ± 0.9	–0.7 ± 0.8	211.0 ± 2.3	8.6 ± 0.8
HPWCS	1	–12.8 ± 0.1	–2.7 ± 0.3	160.4 ± 7.6	2.8 ± 0.2
	3	–12.2 ± 0.3	–2.7 ± 0.4	158.9 ± 4.6	4.1 ± 0.2
	5	–12.4 ± 0.2	–2.0 ± 0.2	150.7 ± 3.6	5.9 ± 0.7
	7	–12.9 ± 0.7	–3.2 ± 0.6	120.7 ± 2.7	6.6 ± 0.7

The ice melting enthalpy of WCS was substantially larger than that of WRS. As discussed in the pasting viscosity results, this indicates that the two starches have different degrees of water-retention capacity in the granules. A similar trend was observed when both modified starches were compared.

During retrogradation, amylopectin crystallization occurs by association between the outermost short branches (Ring et al 1987), and thus the retrogradation of waxy starch gel measured by the amylopectin recrystallization, was positively affected by the lengths of the branches and mole fractions of the B and A chains (Shi and Seib 1992). On comparing the retrogradation enthalpy (amylopectin recrystallization) of the two native starch (WRS and WCS) gels, WRS showed a higher enthalpy value than WCS. Molecular size of amylopectin and the length and proportion of B≥2 chains were critical for determining the retrogradation rate. The B≥2 chains in waxy rice amylopectin were longer (79.4), and their portion was greater (20.6%) than those in waxy corn amylopectin (76.2 and 20.2%, respectively). In addition, the molecular size of waxy rice amylopectin was greater than that of waxy corn amylopectin (344.4×10^6 vs. 277.4×10^6 g/mol). Thus, waxy rice starch retrogrades faster than waxy corn starch, and this is due to structural differences in the amylopectin components.

Hydroxypropylation reduced the endotherm for amylopectin recrystallization because the hydroxypropyl groups hindered formation of double helices by preventing the outer branch alignment of amylopectin. Although the hydroxypropylated groups are mainly located near the branching linkages (Kavitha and BeMiller 1998), they still appeared effective at inhibiting the associations between side chains during the cold storage. This trend was opposite to the setback increase in the fresh paste (Table I).

CONCLUSIONS

To retain softness and to retard the starch retrogradation of *Injulmi* (Korean waxy rice gel cake) during storage, hydroxypropylated waxy rice and hydroxypropylated waxy corn starch could be effectively used to replace waxy rice flour. The retarded retrogradation due to hydroxypropylation was readily revealed by following amylopectin recrystallization by DSC or texture changes by using a texture analyzer. Under identical reaction conditions, however, hydroxypropylation occurred more in waxy rice starch than in waxy corn starch, and thus hydroxypropylated waxy rice starch appeared more effective at retarding retrogradation than hydroxypropylated waxy corn starch.

LITERATURE CITED

Ablett, S., Darke, A. H., Izzard, M. J., and Lillford, P. J. 1993. Studies of the glass transition in malto-oligomers. Pages 189-206 in: The Glassy State in Foods. J. M. V. Blanshard and P. J. Lillford, eds. Nottingham University Press: Leicestershire, UK.

Acquarone, V. M., and Rao, M. A. 2003. Influence of sucrose on the rheology and granule size of cross-linked waxy maize starch dispersions heated at two temperatures. Carbohydr. Polym. 51:451-458.

BeMiller, J. N. 1997. Starch modification: Challenges and prospects. Starch 49:127-131.

Blond, G., and Simatos, D. 1998. Optimized thermal treatments to obtain reproducible DSC thermograms with sucrose + dextran frozen solution. Food Hydrocolloids 12:133-139.

Butler, L. E., and Christianson, D. D. 1986. Buffalo ground root starch. IV. Properties of hydroxypropyl derivatives. Starch 38:156-159.

Chung, H.-J., Lee, E.-J., and Lim, S.-T. 2002. Comparison in glass transition and enthalpy relaxation between native and gelatinized rice starches. Carbohydr. Polym. 48:287-298.

Franks, F., Asquith, M. H., Hammond, C. C., Skaer, H. B., and Echlin, P. 1979. Polymeric cryoprotectants in the preservation of biological ultrastructure. I. Low temperature states of aqueous solutions of hydrophilic polymers. J. Microscopy (Oxford) 110:223-228.

Gray, J., and BeMiller, J. N. 2003. Investigations of the nature and occurrence of starch granule channels and their influence on granular reactions. PhD thesis. Purdue University: West Lafayette, IN.

Hoover, R., Hannouz, D., and Sosluski, F. W. 1988. Effect of hydroxypropylation on thermal properties, starch digestibility and freeze-thaw stability of field pea (*Pisum sativum* cv. Trapper) starch. Starch 40:383-387.

Huber, K. C., and BeMiller, J. N. 1997. Visualization of channels and cavities of corn and sorghum starch granules. Cereal Chem. 74:537-541.

Huber, K. C., and BeMiller, J. N. 2000. Channels of maize and sorghum starch granules. Carbohydr. Polym. 41:269-276.

Huber, K. C., and BeMiller, J. N. 2001. Location of sites of reaction within starch granules. Cereal Chem. 78:173-180.

Karim, A. A., Norziah, M. H., and Seow, C. C. 2000. Methods for the study of starch retrogradation. Food Chem. 71:9-36.

Kavitha, R., and BeMiller, J. N. 1998. Characterization of hydroxypropylated potato starch. Carbohydr. Polym. 37:115-121.

Lim, S. T., Lee, J. H., Shin, D. H., and Lim, H. S. 1999. Comparison of protein extraction solution for rice starch isolation and effects of residual protein content on starch pasting properties. Starch 51:120-125.

Liu, H., Ramsden, L., and Corke, H. 1999. Physical properties and enzymatic digestibility of hdroxypropylated *ae*, *wx*, and normal maize starch. Carbohydr. Polym. 40:175-182.

Manners, D. J. 1989. Recent developments in our understanding of amylopectin structure. Carbohydr. Polym. 11:87-112.
Miles, M. J., Morris, V. J., Orford, P. D., and Ring, S. G. 1985. The roles of amylase and amylopectin in the gelation and retrogradation of starch. Carbohydr. Res. 135:271-278.
Pal, J., Singhal, R. S., and Kulkarni, P. R. 2002. Physicochemical properties of hydroxypropyl derivative from corn and amaranth starch. Carbohydr. Polym. 48:49-53.
Perera, C., Hoover, R., and Martin, A. M. 1997. The effect of hydroxypropylation on the structure and physicochemical properties of native, defatted and heat-moisture treated potato starches. Food Res. Int. 30:235-247.
Richardson, S., Cohen, A., and Gorton, L. 2001. High-performance anion-exchange chromatography-electrospray mass spectrometry for the substituent distribution in hydroxypropylated potato amylopectin starch. J. Chromatogr. A. 917:111-121.
Ring, S. G., Collona, P., Panson, K. J., Kalicheversky, M. T., Miles, M. J., Morris, V. J., and Oxford, P. D. 1987. The gelation and crystallization of amylopectin. Carbohydr. Res. 162:277-293.
Roos, Y. H., Karel, M., and Kokini, J. L. 1996. Glass transitions in low moisture and frozen foods: Effects on shelf life and quality. Food Technol. 50:95-108.
Sanderson, G. R. 1990. Gellan gum. Pages 201-232 in: Food Gels. P. Harris, ed. Elsevier: New York.
Seow, C. C., and Thevamalar, K. 1993. Internal plasticization of granular rice starch by hydroxypropylation: Effects on phase transitions associated with gelatinization. Starch 45:85-88.
Shi, X., and BeMiller, J. N. 2000. Effect of sulfate and citrate salts on derivatization of amylose and amylopectin during hydroxypropylation of corn starch. Carbohydr. Polym. 43:333-336.
Shi, Y.-C., and Seib, P. A. 1992. The structure of four waxy starches related to gelatinization and retrogradation. Carbohydr. Res. 227:131-145.
Slade, L., and Levine, H. 1991. Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. Critical Rev. Food Sci. Nutr. 30:115-360.
Stapley, J. A., and BeMiller J. N. 2003. Hydroxypropylated starch: Granule subpopulation reactivity. Cereal Chem. 80:550-552.
Steeneken, T. J. 1984. Reactivity of amylose and amylopectin in potato starch. Starch 36:13-18.
Van der Burgt, Y. E. M., Bergsma, J., Bleeker, I. P., Mijland, P. J. H. C., Van der Kerkvan Hoof, A., Kamerling, J. P., and Vliegenthart, J. F. G. 1998. Distribution of methyl substituents over branched and linear regions in methylated starches. Carbohydr. Res. 312:201-208.
Vodovotz, Y., and Chinachoti, P. 1998. Glassy-rubbery transition and recrystallization during aging of wheat starch gels. J. Agric. Food Chem. 46:446-453.
Wootton, M., and Manatsathit, A. 1984. The influence of molar substitution on the gelatinization of hydroxypropyl maize starches. Starch 36:207-208.
Wootton, M., Kesavamoorthy, S., and Azemi, B. M. 1985. Analysis of hydroxypropyl starch hydrolysates by high performance liquid chromatography. Starch 37:276-279.
Yeh, A.-I., and Yeh, S.-L. 1993. Some characteristics of hydroxypropylated and cross-linked rice starch. Cereal Chem. 70:596-601.

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