

Effect of Minor Addition of Xanthan on Cross-Linking of Rice Starches by Dry Heating with Phosphate Salts

Hyun-Jung Chung,¹ Deulre Min,² Jong-Yea Kim,³ Seung-Taik Lim³

¹Agriculture and Agri-Food Canada, Guelph N1G5C9, Canada

²LG Electronics, Digital Appliance Company, Changwon, Gyeongnam 641-711, Korea

³School of Life Sciences and Biotechnology, Korea University, Seoul 136-701, Korea

Received 4 September 2006; accepted 2 January 2007

DOI 10.1002/app.26237

Published online 26 April 2007 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Effects of xanthan on the crosslinking of normal and waxy rice starches using a mixture of phosphate salts (sodium trimetaphosphate and sodium tripolyphosphate, 99 : 1, dry solid basis) were investigated. The starch (158.4 g, dry solids) was dispersed in an aqueous solution containing xanthan and phosphate salts (1.6 and 0.6 g in 280 mL water, respectively), and the slurry was dried overnight at 45°C until the moisture content was less than 10%. The dry cake was then ground into powders and heated for 2 h at 130°C in a convection oven. The pasting viscosity, paste clarity, melting and *in vitro* digestion behaviors of the starches with modifying agents (xanthan and phosphate salts) were investigated. The heat treated starches displayed enhanced shear stability and reduced breakdown, as evidences of crosslinking. Xanthan (1.0% based on starch solids) enhanced the crosslinking effects in the viscosity profile. Waxy rice starch evidenced more profound viscosity changes than did normal rice

starch, indicating it was more susceptible to the heat treatment. The waxy rice starch heated with the mixture of phosphate salts and xanthan exhibited a continuous increase in pasting viscosity without any breakdown. Under a DSC analysis, melting enthalpy decreased but melting temperature increased somewhat as results of the heat treatment with xanthan. In an *in vitro* digestion analysis, the starches treated with xanthan exhibited decreases in the maximum digestion level, and increases in the resistant starch (RS) content. Dry heating, however, increased the digestion rate and glycemic index (GI) regardless of the presence of phosphate salts or xanthan indicating that the starches were thermally degraded. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2280–2286, 2007

Key words: dry heating; rice starch; xanthan; digestibility; crosslinking

INTRODUCTION

Heating changes the granule and molecular structure of starch, and the changes depend on the presence of moisture. In the presence of limited amount of moisture, heating at a temperature without starch gelatinization is commercially practiced to modify the physical properties of starch.¹ The level of modification in physical properties is dependent on heating conditions and starch sources.² Heating of starch under dry conditions (<10% moisture) is also applied for a variety of purposes, including vaporizing off-flavors or volatiles, imparting of a smoky taste, or dextrinizing.^{3,4} Dry heating, at a temperature range from 120 to 200°C, has been reported to remove woody flavors occurring in waxy maize starch, and also to modify the texture of its paste.³ More recently, Chiu et al.^{5,6} systemically introduced a dry heating process for formulating physically

modified starches. They determined that heating a starch or flour to 120–180°C generated characteristics of higher degree in paste viscosity and reduced breakdown. Based on overall properties, the thermally treated starches have been considered to be functionally equivalent to chemically crosslinked starches.

The addition of reactive compounds to starches tends to induce chemical reactions during dry heating. Starch citrates have been generated via the dry heating of a mixture of starch and citrate, thereby introducing chemical linkages between hydroxyl groups in starch and carboxylic acids in citrate.⁷ Ionic gums have also been employed in a dry heat treatment to improve the physical properties of starch.⁸ Among a variety of the gums tested, xanthan was found to render the most significant changes in the paste viscosity of waxy maize starch than did sodium alginate or sodium carboxymethylcellulose. When heated with xanthan in a mild alkalinity (pH 8.0), the starch paste became more viscous although the reactions between starch and gum molecules appeared more profound under an acidic condition (pH 6.0).⁹ The heat-induced reaction with xanthan

Correspondence to: S.-T. Lim (limst@korea.ac.kr).
Contract grant sponsor: Korea University.

also increased paste consistency and shear stability of the starch, in a similar manner observed in the chemical crosslinking.

Phosphate salts, including mono-, di-, and triphosphate salts, have been reported to form ester linkages with starch by dry heating.¹⁰ The phosphorylated starches are classified into two groups based on the ester linkages: monostarch phosphates and distarch phosphates (crosslinked starches). The ratio of both starch esters can be altered in accordance with the type of salts employed, and reaction conditions including pH and temperature.¹⁰ Under alkaline conditions, phosphate salts tend to generate distarch esters (crosslinked starches), and the starches produced in this way are commercially utilized as ingredients in a variety of foods. With safety concerns, however, consumers tend to favor minimal or no usage of chemical agents in the modification of food starches. Because xanthan provides similar crosslinking effects via dry heat treatment as do the phosphate salts, it can substitute the phosphate salts.⁸ Moreover, it has been recognized as a soluble dietary fiber, which can exert positive health effects.

In this study, xanthan was added in the mixtures of rice starches (waxy and normal) and phosphate salts, and its effects on the crosslinking of the starch induced by dry heating were examined. In addition to the changes in pasting properties, *in vitro* digestibility of the heat treated starches was also investigated.

EXPERIMENTAL

Materials

The normal and waxy rice starches were isolated from the rice flours (Japonica types) purchased from a local grocery (Seoul, Korea), using a dilute NaOH solution.¹¹ Xanthan gum (Keltrol) was acquired from the CP Kelco Corp. (Chicago, IL). Sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) were purchased from Sigma and Aldrich Chemical Company (St. Louis, MO).

Sample preparation

Xanthan gum (1.6 g) was dispersed in distilled water (280 mL) with vigorous stirring, and then the starch (normal or waxy rice, 158.4 g, dry basis) was dispersed in the gum solution.⁸ A mixture of sodium trimetaphosphate (STMP) and sodium tripolyphosphate (STPP) (99/1, total 0.6 g, dry basis) was added to this dispersion (0.4% based on the total solids), and the pH of the dispersion was adjusted to 8.0 by adding 0.1M Na₂CO₃ solution, after the salts were completely dissolved. The dispersion was then stirred magnetically for 1 h at room temperature,

and then the entire dispersion was dried at 45°C for 24 h in a convection oven. The dried starch cake (<10% moisture content) was grounded to a powder, and then heated in an electric convection oven for 2 h at 130°C. For comparison, the starch-phosphate mixture not containing xanthan was also treated under identical conditions.

Paste viscosity

The pasting viscosity of the crosslinked starches (7.0%, w/w) was measured in a neutral buffer solution (0.1M sodium phosphate, pH 7.0) using a Rapid Visco-Analyser (RVA-4, Newport Scientific Instruments, Australia). The standard procedure (No. 1) was followed (starting and ending 50°C, 3 min of holding at 95°C, and 160 rpm of speed).

Light transmittance of paste

Aqueous dispersions of the starches (1%, w/w) in sealed bottles were heated for 30 min in a boiling water bath, with occasional stirring. The starch solutions were cooled by standing for 1 h at room temperature, and then the light transmittance of the solutions was measured at a wavelength of 650 nm.

Differential scanning calorimetry

The melting behavior was measured by using a differential scanning calorimeter (Seiko Instruments, DSC 6100, Chiba, Japan). The mixtures of starch and distilled water (1 : 2, weight ratio) in sealed aluminum pans were heated from 20 to 140°C at a rate of 5°C/min for the DSC measurements.

Starch digestion

The digestion profile of the starches was evaluated according to the method of Englyst et al.¹² with minor modifications.¹³ Aliquots of guar gum solution (10 mL, 5 g/L in 0.05M HCl) and sodium acetate solution (5 mL, 0.5M) were added to starch samples (500 mg in 10 mL of distilled water) in test tubes. Seven glass balls (10 mm diameter) and 10 mL of the enzyme solution containing porcine pancreatic α -amylase (No. 7545, Sigma-Aldrich, St. Louis, MO) and amyloglucosidase (No. 9913, Sigma-Aldrich) were then added to each tube. The starch dispersions containing enzymes were incubated in a water bath (37°C) with an agitation (170 rpm), and aliquots (0.5 mL) were occasionally taken and mixed with 4 mL of 80% ethanol. The glucose content in the mixtures was measured using glucose oxidase and peroxidase assay kits (No. GAGO-20, Sigma-Aldrich). On the basis of the digestion rate, the different portions of starch were calculated: rapidly

digested starch (RDS), slowly digested starch (SDS), and resistant starch (RS).¹²

An equation established by Goni et al.¹⁴ was used to describe the kinetics of starch hydrolysis:

$$C = C_{\infty}(1 - e^{-kt}) \quad (1)$$

where C , C_{∞} , and k were the concentration at time t , the equilibrium concentration and the kinetic constant, respectively. Using hydrolysis curves (0–180 min), the hydrolysis index (HI) was calculated as the relative percentage of total glucose released from the samples in comparison to that from white bread. The glycemic indices of the samples were estimated according to the equation of Goni et al.¹⁴

$$GI = 39.71 + 0.549 HI \quad (2)$$

RESULTS AND DISCUSSION

Pasting viscosity

The viscograms of the heat treated normal and waxy rice starches are shown in Figure 1. The two starches, which differed in amylose content, showed different heating effects on the viscosity profile. The waxy rice starch (WR) displayed more significant changes than did the normal starch (NR).

Dispersing the starches in the phosphate salt solution, a process precedent to the dry heating, changed the viscosity of starch pastes. The phosphate salts decreased the viscosity of normal rice starch (NRP versus NR). Waxy rice starch, however, showed opposite trends, by increasing the peak viscosity and setback (WRP versus WR). Phosphate salts may react with starch even in the aqueous mixture.¹⁰ Diester formation between starch chains (crosslinking) was more favored than monoester formation under alkaline conditions. At pH 8.0 used in this case, therefore, starch diesters might be formed in the aqueous dispersion, although the reaction occurred in minor degrees. The different viscosity results between the two starches may indicate that the starches react differently. The diester formation reaction in the aqueous mixture is allowed only to amylopectin chains in the waxy starch, whereas it may occur in both amylopectin and amylose chains for the normal starch. It is also expected that amylose and amylopectin result in different viscosity changes by the diester formation.

The presence of xanthan in the aqueous dispersion of starch in the phosphate salt solution affected the viscosity profile of the unheated starches (NRPX and WRPX). In both starches, xanthan reduced peak viscosity and breakdown, and this effect was greater for waxy rice starch (WRPX in Fig. 1). It was

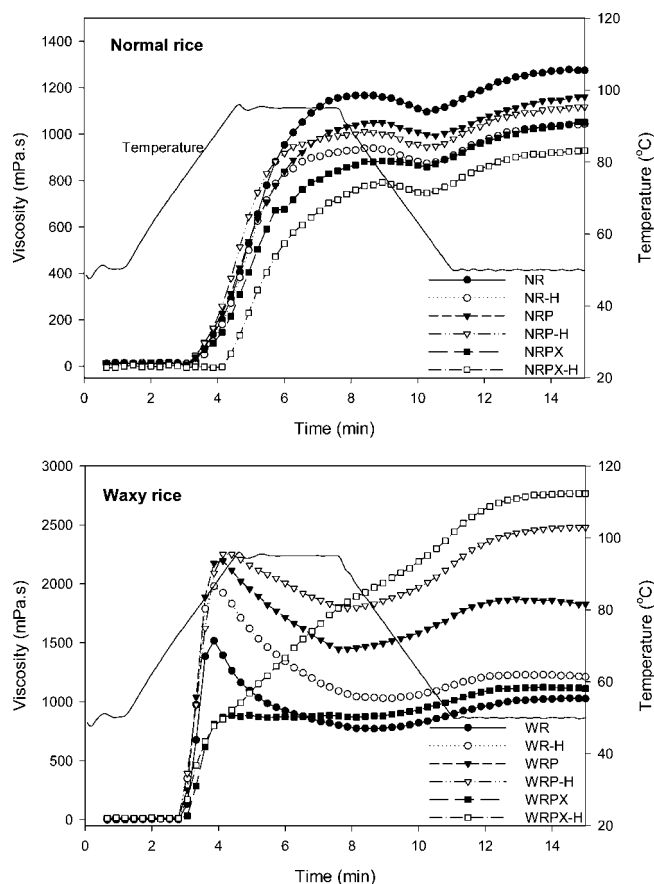


Figure 1 Pasting viscograms of the dry heated normal and waxy rice starches with phosphate salts and xanthan.

reported that xanthan itself, without forming chemical linkages, could restrict starch swelling and increase shear stability.^{15,16} These changes may be the result from either the immobilization of water molecules by xanthan or the interactions between starch and xanthan.¹⁷

Dry heating itself, without ingredients (phosphate salts or xanthan), changed the pasting viscosity of the starches. However, the viscosity changes were not identical for both starches. Normal rice starch showed a decrease in paste viscosity by the heat treatment, whereas waxy rice starch did an increase. Dry heating may have induced the disruption of hydrogen bonds between starch chains in granules, and the excessive heat could have cleaved the glycosidic linkages. The disruption of hydrogen bonds facilitates the swelling of starch granules, whereas the cleavage of glycosidic linkages induces viscosity decrease. Viscosity increase has been reported when waxy maize starch was heated under alkaline conditions.⁹ On the basis of the viscosity changes by the heat treatment (Fig. 1), it was hypothesized that the thermal cleavages in the glycosidic linkages of starch chains occurred when the normal rice starch was heat-treated (NR and NR-H), whereas the disruption

of hydrogen bonds between starch chains occurred during the heating of waxy rice starch (WR and WR-H). However, to confirm the starch chain cleavage, chemical analyses is needed.

When the dry starches were heated in the presence of the alkaline phosphate, crosslinking of starch by diester linkages of phosphates became prevalent, as proved by the viscosity profiles (Fig. 1). The heating effects on viscogram appeared somewhat different between the two starches tested as shown with the unheated starches. The waxy rice starch displayed more changes in the viscograms than did normal starch. Compared with the unheated waxy starch sample (WRP), the heated starch samples (WRP-H) displayed increased peak viscosity but reduced breakdown. When xanthan was added in the dry heat treatment, the crosslinking effects evidenced in the pasting viscosity profiles were substantially enhanced (NRPX-H and WRPX-H). The heat treated waxy rice starch, in the presence of the phosphate salts and xanthan, exhibited a continuous increase in the paste viscosity with no breakdown, during the pasting and cooling processes. The steep increase in the viscosity resulted in the highest final viscosity among the starches tested. Lim et al.⁸ claimed that ester formation might occur when mixtures of starch and ionic gum were heated in dry states. Chemical linkages between starch and xanthan would also be formed through the phosphate esters.

Any structural changes resulting from the dry heat treatment were expected to localize primarily in the amorphous regions in starch, because the reaction depended strictly on the physical contact in dry states. As the phosphate salts and xanthan were impregnated within the starch granules in the aqueous dispersion, these reagents were probably distributed mainly in the amorphous regions. More changes in the pasting viscosity for the waxy rice starch indicate that the amorphous regions in the waxy starch are more readily exposed to the gum, compared with those in the normal starch. In the granules of waxy starches, α -1, 6 branches of amylopectin exist mainly in amorphous regions,¹⁸ whereas, in normal starch, amylose chains were reported to localize in the amorphous regions.¹⁹ The side chains in amylopectin chains impart in crystalline helices and thus an amylopectin chain is likely to dispose throughout both crystalline and amorphous regions (branches mainly) in starch granules. Amylose chains, however, are readily leached from the granules by swelling in the early stage of pasting. Therefore, the crosslinkages between the amylopectin chains may affect the overall pasting behavior of starch granules. However, the crosslinkages between amylose chains localized in the amorphous regions may provide much less effects on the pasting behav-

ior of starch granules. Therefore, even if similar degrees of the reactions possibly occurred during the thermal treatment, waxy starches rendered more susceptible results in pasting behavior than did normal starches.

Paste clarity

Figure 2 shows the light transmittance of the solutions (1% starch solids) of the heat treated normal and waxy rice starches. By simply dispersing the starches in the phosphate salt solution (NRP and WRP), the starch solutions became more opaque (decreased light transmittance), which was an evidence of the formation of crosslinkages. When xanthan was added to the aqueous starch-phosphate mixtures (NRPX and WRPX), however, the light transmittance was increased. This result might indicate that the added xanthan did not behave as a crosslinking agent, although it seemed to act like a crosslinking the starches under the pasting viscosity profiles (Fig. 1). However, xanthan might form grafts on starch chains by the phosphate ester linkages,

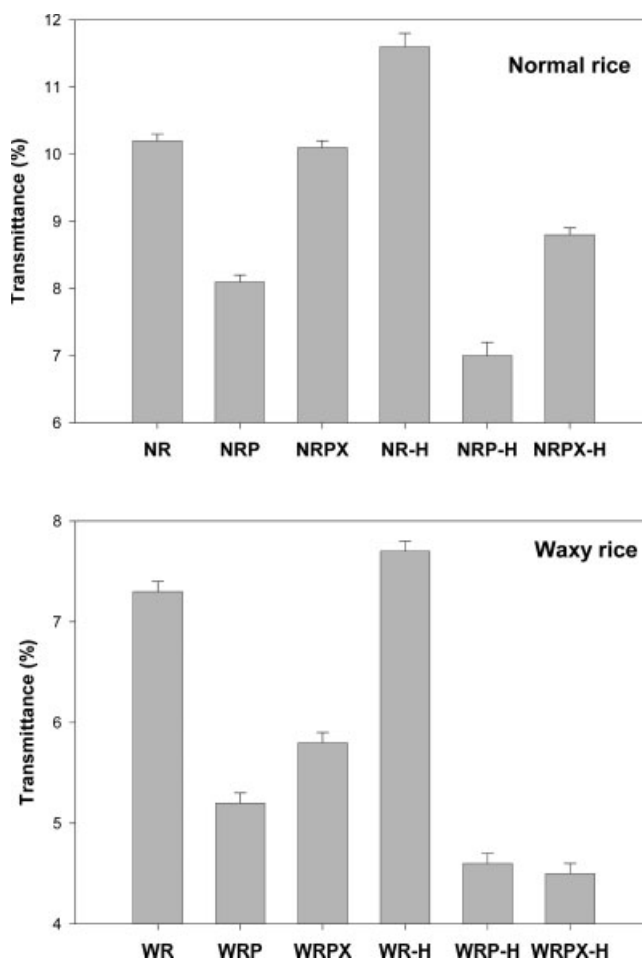


Figure 2 Light transmittance of the dry heated normal and waxy rice starches with phosphate salts and xanthan.

which could increase the paste clarity due to the increased hydrophilic nature by xanthan. Under the experimental conditions, however, the graft formation would be rare. The increased paste clarity induced by xanthan addition, more likely be caused by the simple interactions between xanthan and starch.

The paste clarity (light transmittance) of the normal and waxy rice starches was clearly increased by the simple heating (NR-H, and WR-H). It was suggested that the increase in light transmittance of starch pastes by dry heating was due to the disintegration of starch granules or the degradation of starch chains.⁸ As shown in the viscograms (Fig. 1), also in the paste clarity data (Fig. 2), waxy starch was more susceptible to the dry heat treatment than was normal starch. When the starches were heated in the presence of the phosphate salts (NRP-H and WRP-H), the starches formed the pastes with increased opaqueness due to the heat-induced cross-linkage formation. By adding xanthan to the starch-phosphate mixtures, the heating further reduced the light transmittance (NRPX-H, and WRPX-H). This change was more significant for the waxy starch (WRPX-H), which agreed with the viscosity data, thereby indicating that xanthan effect was more significant with the waxy starch than with the normal starch.

Melting behavior

Crystal melting behaviors of the dry heated normal and waxy rice starches are shown in Table I. The unheated dry mixture of starch-phosphate-xanthan showed increases in melting temperature and decreases in melting range for both starches (NRP or WRP). These changes might prove that the mild crosslinking occurred during the aqueous mixing.^{20–22} The phosphate salts did not react with starch or xanthan might also influence the melting behavior of the starch. Adding xanthan to the starch-phosphate mixtures (NRPX and WRPX), prior to the heat treatment, resulted in slight increases in melting temperature, but induced significant reductions in melting enthalpy. As Chaisawang and Suphantharika²³ reported, it was supposed that the increase in melting temperature was attributed to the immobilization of some water molecules by xanthan. The decreased enthalpy might indicate that starch crystals underwent incomplete melting. However, under the current experimental conditions with sufficient water for starch melting (67%), the water immobilization was not significant to induce the incomplete melting. The enthalpy decrease might be attributed more likely to the interactions between starch molecules and xanthan.

The dry heating of the starch-phosphate mixture in the presence of xanthan resulted in the reductions

TABLE I
Crystal Melting Behavior of Dry-Heated Normal and Waxy Rice Starches with Xanthan and Phosphate Salts

Samples	T_o (°C)	T_p (°C)	T_c (°C)	ΔH ($\times 10^3$, J/Kg)
NR	57.1 \pm 0.2	64.3 \pm 0.1	73.6 \pm 0.1	15.5 \pm 0.3
NRP	59.4 \pm 0.2	67.4 \pm 0.4	75.5 \pm 0.3	14.2 \pm 0.3
NRPX	59.7 \pm 0.2	67.5 \pm 0.1	75.7 \pm 0.4	12.7 \pm 0.2
NR-H	54.5 \pm 0.1	62.5 \pm 0.2	72.5 \pm 0.1	14.8 \pm 0.3
NRP-H	57.8 \pm 0.0	64.6 \pm 0.1	74.0 \pm 0.1	12.6 \pm 0.4
NRPX-H	57.9 \pm 0.4	64.8 \pm 0.3	73.9 \pm 0.5	11.3 \pm 0.1
WR	56.1 \pm 0.3	63.5 \pm 0.3	73.7 \pm 0.1	15.3 \pm 0.0
WRP	58.0 \pm 0.1	65.5 \pm 0.3	74.4 \pm 0.2	14.8 \pm 0.4
WRPX	58.3 \pm 0.3	66.0 \pm 0.1	74.7 \pm 0.1	12.9 \pm 0.2
WR-H	54.5 \pm 0.0	61.8 \pm 0.0	71.5 \pm 0.3	14.4 \pm 0.3
WRP-H	55.9 \pm 0.1	64.5 \pm 0.1	72.6 \pm 0.1	14.3 \pm 0.4
WRPX-H	56.6 \pm 0.2	65.4 \pm 0.1	72.9 \pm 0.3	12.5 \pm 0.0

T_o , onset temperature; T_p , peak temperature; T_c , conclusion temperature; ΔH , melting enthalpy; NR, normal rice starch; WR, waxy rice starch; P-phosphate salt; X, xanthan; H, dry-heated.

both in melting temperature and in enthalpy (NRPX versus NRPX-H and WRPX versus WRPX-H in Table I). As reported by Lim et al.,⁹ these changes indicate that thermal degradations in the granular and/or molecular structure of starch occurred during the dry heat treatment.

In vitro digestion

From the digestion analyses, the normal rice starch samples, either native or treated, could be hydrolyzed to lesser degrees (C_∞ 72–87% in Table II) than the waxy rice starch samples (C_∞ 83–94%). The kinetic constant (k), which indicated the hydrolysis rate in the initial stage of digestion, was lower for the normal rice starch samples (0.044–0.094) than that for the waxy rice starch samples (0.052–0.097), except the starch samples treated with the phosphate-xanthan mixture (NRPX and WRPX). These differences indicated that the normal rice starch samples were digested more slowly and at lesser degrees than were the waxy rice starch samples. In native starches, it has been already reported that the presence of amylose hindered the digestibility of the starch.^{24–25} However, the kinetic constant for NRPX (0.077) was slightly higher than that for WRPX (0.074). The presences of phosphate salts and xanthan, and the mild crosslinking occurred during mixing might eliminate the effects from the structural differences between normal and waxy starches on their digestion rates.

The kinetic constant (k) was increased by the presences of phosphate salts and xanthan, whereas the maximum hydrolysis level (C_∞) was decreased (Table II). The decreases in C_∞ by phosphate salts were \sim 6% for the normal rice starch (NRP versus

TABLE II
Enzyme Hydrolysis Parameters of Dry-Heated Normal and Waxy Rice Starches with Xanthan and Phosphate Salts

Samples	C_{∞} (%) ^a	k^a	RDS (%)	SDS (%)	RS (%)	HI	GI ^b
NR	82.5 ± 1.3	0.044 ± 0.002	47.5 ± 0.7	33.7 ± 1.8	17.8 ± 1.1	76.6 ± 0.6	81.8 ± 0.3
NRP	76.5 ± 1.7	0.059 ± 0.000	52.3 ± 1.4	23.0 ± 0.3	23.3 ± 1.7	73.7 ± 1.7	80.2 ± 0.9
NRPX	72.6 ± 0.6	0.077 ± 0.003	55.7 ± 0.5	15.1 ± 1.1	26.8 ± 0.6	71.7 ± 0.4	79.1 ± 0.2
NR-H	86.9 ± 2.6	0.060 ± 0.002	60.0 ± 0.9	26.0 ± 1.6	13.0 ± 2.5	83.9 ± 2.3	85.8 ± 1.2
NRP-H	83.7 ± 1.0	0.074 ± 0.002	63.9 ± 1.7	18.6 ± 0.7	16.1 ± 1.0	82.9 ± 1.2	85.0 ± 0.7
NRPX-H	82.7 ± 0.5	0.094 ± 0.002	68.5 ± 0.8	12.2 ± 0.3	16.9 ± 0.5	82.5 ± 0.6	84.9 ± 0.3
WR	89.8 ± 0.8	0.052 ± 0.003	57.5 ± 1.2	31.3 ± 1.9	10.3 ± 0.7	85.3 ± 0.2	86.6 ± 0.1
WRP	85.6 ± 0.5	0.071 ± 0.001	63.8 ± 0.2	20.6 ± 0.3	14.3 ± 0.5	83.9 ± 0.5	85.8 ± 0.3
WRPX	82.5 ± 0.3	0.074 ± 0.002	62.2 ± 0.9	18.4 ± 0.6	17.1 ± 0.3	81.2 ± 0.4	84.3 ± 0.2
WR-H	93.8 ± 0.2	0.072 ± 0.001	70.0 ± 0.0	21.9 ± 0.4	7.2 ± 0.2	92.1 ± 0.3	90.3 ± 0.2
WRP-H	92.2 ± 0.2	0.083 ± 0.000	73.9 ± 0.1	17.1 ± 0.1	7.7 ± 0.2	91.6 ± 0.1	90.0 ± 0.1
WRPX-H	89.1 ± 0.8	0.097 ± 0.001	74.6 ± 1.0	12.5 ± 0.2	10.6 ± 0.7	89.4 ± 0.8	88.8 ± 0.5

C_{∞} , equilibrium hydrolysis; k , kinetic constant; RS, resistant starch; RDS, rapidly digested starch; SDS, slowly digested starch; HI, hydrolysis index; GI, glycemic index; NR, normal rice starch; WR, waxy rice starch; P-phosphate salt; X, xanthan; H, dry-heated.

^a C_{∞} and k were determined by eq. (1).

^b GI was calculated from the eq. (2).

NR), and 4% for the waxy rice starch (WRP versus WR). The addition of xanthan to the starch-phosphate mixtures induced further decreases in C_{∞} : 4% for the normal rice starch (NRPX versus NRP) and 3% for the waxy rice starch (WRPX versus WRP).

The heat treated starch samples showed the C_{∞} and k values higher than those of the unheated samples, by 4–10% and 0.01–0.02, respectively, (Table II). Disruption of the inherent starch granule structure might induce the increase in the susceptibility to enzymatic digestion.^{13,26} The data revealed that the effect of thermal degradation on the digestion was more significant than that of the heat-induced reactions by the phosphate salts and xanthan.

From the hydrolysis patterns measured in the *in vitro* digestion test, three starch fractions of different digestion rates were quantified.¹² Normal rice starch samples, either in its native state or after the treatments, contained lower amounts of rapidly digestible starch (RDS) but higher amounts of resistant starch (RS) than was detected in the waxy rice starch samples (Table II). By simply blending the starches in the phosphate salt solution (NRP and WRP), both RDS and RS contents were increased, whereas the SDS content decreased significantly by more than 10% (NR versus NRP and WR versus WRP). This result was consistent with those found in the kinetic parameters (k and C_{∞}). The mild phosphorylation of starch in the aqueous mixture made the starch granules more readily digested during the early stage, but the maximally digested starch content was reduced in the late stage of digestion. The crosslinking by diester formation made the starch more enzyme-resistant, resulting in the increases in RS content. However, the phosphate groups made the starch more hydrophilic, possibly raising the early swelling ability of starch granules for more enzymes

to interact with the starch chains. More study is needed to confirm this.

When xanthan and phosphate salts were added simultaneously to the starch, the SDS value decreased significantly, but the RS value became highest among those of the starch samples tested (NRPX versus NRP, and WRPX versus WRP in Table II). The xanthan is indigestible by the digestive enzymes used, and thus theoretically increases the RS content and decrease the C_{∞} value. However, the RS increases (7–9%) and the C_{∞} decreases (3–4%) were much greater than the actual amount of xanthan added (1.0% based on the total solid weight). It could prove the presence of additional effects of xanthan, from the simple interaction or complex formation with starch chains. Christianson¹⁷ reported that xanthan could bind the soluble amylose chains, thereby inhibiting the starch hydrolysis by β -amylase.

As compared with the unheated samples, the dry heat treated samples, however, showed increased RDS, but decreased SDS and RS contents. As shown by the previous viscosity (pasting temperature decrease) and DSC melting results (melting temperature and enthalpy decreases), the structural disintegration induced by the thermal treatment might increase the digestibility of starch. The hydrolysis indices (HI) and the glycemic indices (GI) are shown in Table II. The HI, calculated by the hydrolysis curve, ranged between 71.7 (NRPX) and 83.9 (NR-H) in normal rice starch samples, and 81.2 (WRPX) and 92.1 (WR-H) in waxy rice starch samples. The GI, which was estimated from the HI, ranged between 79.1 (NRPX) and 85.8 (NR-H) in the normal rice starch samples, and 85.8 (WRPX) and 90.3 (WR-H) in the waxy rice starch samples. Regardless of the dry heat treatment, both starches displayed slightly reduced values in GI by the presence of xanthan.

However, the dry heating itself increased the GI value for all starch samples.

CONCLUSIONS

The minor addition of xanthan provided additional effects on the crosslinking of rice starches with phosphate salts by dry heating in an alkaline condition (pH 8.0). The gum exerted enhanced crosslinking effects by increasing the resistance to shear thinning during pasting. Therefore, by a minor addition of xanthan, the use of the phosphate salts could be reduced. Additionally, the addition of xanthan in the starch-phosphate mixture, with no heating, rendered an additional effect nutritionally favored by increasing the amount of resistant starch (RS). The subsequent dry heating, however, increased the digestion rate and glycemic index, possibly as results of thermal degradation. Waxy rice starch appeared to be more susceptible to the heating than did the normal starch.

References

- Hoover, R.; Manuel, H. *Food Res Int* 1996, 29, 731.
- Donovan, J. W.; Lorenz, K.; Kulp, K. *Cereal Chem* 1983, 60, 381.
- Seidel, W. C.; Stahl, H. D.; Orozovich, G. E. U.S. Pat. 4,303,451 (1981).
- Ohira, T.; Miyano, R.; Yoshida, R. U.S. Pat. 4,303,452 (1981).
- Chiu, C. W.; Schiermeyer, E.; Thomas, D. J.; Shah, M. B. U.S. Pat. 5,725,676 (1998).
- Chiu, C. W.; Schiermeyer, E.; Thomas, D. J.; Shah, M. B.; Hanchett, D. J.; Jeffcoat, R. U.S. Pat. 5,932,017 (1999).
- Wing, R. E. *Starch/Stärke* 1996, 48, 275.
- Lim, S. T.; Han, J. A.; Lim, H. S.; BeMiller, J. N. *Cereal Chem* 2002, 79, 601.
- Lim, H. S.; BeMiller, J. N.; Lim, S. T. *Cereal Chem* 2003, 80, 198.
- Lim, S.; Seib, P. A. *Cereal Chem* 1993, 70, 137.
- Lim, S. T.; Lee, J. H.; Shin, D. H.; Lim, H. S. *Starch/Stärke* 1999, 51, 120.
- Englyst, H. N.; Kingman, S. M.; Cummings, J. H. *Eur J Clin Nutr* 1992, 46, S33.
- Chung, H. J.; Lim, H. S.; Lim, S. T. *J Cereal Sci* 2006, 43, 353.
- Goni, I.; Garcia-Alonso, A.; Saura-Calixto, F. *Nutr Res* 1997, 17, 427.
- Lee, M. H.; Baek, M. H.; Cha, D. S.; Park, H. J.; Lim, S. T. *Food Hydrocolloids* 2002, 16, 345.
- Christianson, D. D.; Hodge, J. E.; Osborne, D.; Detroy, R. W. *Cereal Chem* 1981, 58, 513.
- Christianson, D. D. In *Food Carbohydrates*; Lineback, D. R., Inglett, G. E., Eds.; Avi Press: Westport, 1982; p 399.
- Biliaderis, C. G. *J Agric Food Chem* 1982, 30, 925.
- French, D. In *Starch: Chemistry and Technology*; Whistler, R. L.; BeMiller, J. N.; Paschall, E. F., Eds.; Academic Press: Orlando, 1984; p 183.
- Woo, K. S. Ph.D. Thesis, Kansas State University, 1999.
- Chung, H. J.; Woo, K. S.; Lim, S. T. *Carbohydr Polym* 2004, 55, 9.
- Chatakanonda, P.; Varavinit, S.; Chinachoti, P. *Cereal Chem* 2000, 77, 315.
- Chaisawang, M.; Supphantharika, M. *Carbohydr Polym* 2005, 61, 288.
- Fuwa, H.; Nakajima, M.; Hamada, A.; Glover, D. A. *Cereal Chem* 1977, 54, 230.
- Noda, T.; Kimura, T.; Otani, M.; Ideta, O.; Shimada, T.; Saito, A.; Suda, I. *Carbohydr Polym* 2002, 49, 253.
- Granfeldt, Y.; Eliasson, A. C.; Björck, I. *J Nutr* 2000, 130, 2207.