Available online at www.sciencedirect.com

Carbohydrate Polymers 67 (2007) 366–374

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

# Preparation and physical characteristics of slowly digesting modified food starches

Jung-Ah Han, James N. BeMiller *

*Whistler Center for Carbohydrate Research, Department of Food Science, 745 Agriculture Mall Drive, Purdue University, West Lafayette, IN 47907-2009, USA*

Received 12 April 2006; received in revised form 31 May 2006; accepted 1 June 2006
Available online 25 July 2006

**Abstract**

Starches were chemically modified with the goal of making modified food starch products with high contents of slowly digestible starch (SDS). Digestibility and physical properties of the products were measured. For waxy corn starch, combinations of crosslinking (CL) followed by stabilization via hydroxypropylation (HP) or acetylation (AC) produced more SDS than did crosslinking alone; CL-HP produced the highest content of slowly digestible starch (SDS, ~21%), while CL-AC produced the highest content of resistant starch (RS, ~24%). CL-HP (prepared without salt in the reaction mixture) and hydroxypropylation (with NaCl in the reaction mixture) followed by crosslinking (HP-CL) had similar SDS contents, but HP-CL had a higher RS content, indicating that the presence of salt as well as the order of modification could affect digestibility of the modified starch. Esterification with 2-octen-1-ylsuccinic anhydride (OSA) was the most effective of the modifications used for increasing both SDS and RS. Dry heating (130 °C) of OSA waxy corn starch increased the SDS content and decreased RS content. OSA starches had lower pasting temperatures and higher peak viscosities than their native counterparts. Dry heating of OSA starches resulted in even lower pasting temperatures. Peak viscosities were higher for heated OSA waxy corn and tapioca starches, but lower for heated OSA normal corn and potato starches as compared to unheated octenylsuccinylated starches. To, Tp, and gelatinization enthalpy (ΔH) decreased in the order native waxy corn starch > OSA waxy corn starch > heated OSA waxy corn starch. Using the combination of esterification with OSA followed by dry heating the following amounts of SDS were produced: from waxy corn starch, 47%; from normal corn starch, 38%; from tapioca starch, 46%; from potato starch, 33%.

*Keywords:* Slowly digesting starch; Modified food starch

## 1. Introduction

Starch products vary in digestibility. The rate and extent of digestion is reflected in the magnitude and duration of the glycemic response (Englyst & Hudson, 1996). Most starch products contain a portion that digests rapidly (rapidly digesting starch, RDS), a portion that digests slowly (slowly digesting starch, SDS), and a portion that is resistant to digestion in the time frame of the test (resistant starch, RS). There are four distinct types of RS (Englyst, Kingman, & Cummings, 1992).

The nutritional quality of a food is related to its glycemic index (GI) (Wolever, 2003). GI is most appropriately used to compare foods within a category of foods. Differences in glycemic and insulinemic responses to dietary starch are directly related to the rate of starch digestion (O'Dea, Snow, & Nestel, 1981). Starchy foods (bread, potato, most rice, and most breakfast cereals) tend to have a high GI. A product with a low GI is preferable, not only in individuals with diabetes, but also in healthy individuals (Björck & Asp, 1994). A product that provides the nutritional benefits of starch (a supply of glucose), but that does not produce the postprandial hyperglycemic and hyperinsulinemic spikes associated with the RDS of starchy foods is most desirable. Individuals with type II diabetes may

---

* Corresponding author. Tel.: +1 765 494 5684; fax: +1 765 494 7953.
*E-mail address:* bemiller@purdue.edu (J.N. BeMiller).

doi:10.1016/j.carbpol.2006.06.011

especially benefit form a foodstuff that contains high levels SDS because it does not produce hyperglycemia followed by hypoglycemia. In addition, SDS may prolong satiety and could be incorporated into foodstuffs marketed for weight-loss programs. Finally, SDS may be beneficial in products that are utilized by athletes, as SDS would provide a longer, more consistent source of systemic glucose (Wolf, Bauer, & Fahey, 1999). Although not all low-GI foods are rich in SDS, most SDS-rich foods have a low GI. So, foods containing high levels of SDS that result in a diet with a low GI are of real public health value. For these reasons, several approaches have been used to try to make SDS: chemical modification (Wolf et al., 1999), use of a debranching enzyme (Berry, 1986; Guraya, James, & Champagne, 2001; Shin et al., 2004; Shin, Kim, Ha, Lee, & Moon, 2005), physical modification [autoclaving (Shin, Woo, & Seib, 2003), micro-wave heating (Anderson & Guraya, 2004), hydrothermal treatment (Shin et al., 2004)], and a combination of enzymic and physical modifications (Han et al., 2006). Although there are reports that modifications such as hydroxypropylation, 1-octenylsuccinylation, and combinations of crosslinking and substitution reduce the extent of enzyme-catalyzed hydrolysis (digestibility or biodegradability) (Björck, Gunnarsson, & Østergård, 1989; Hoover & Sosulski, 1986; Janzen, 1969; Li, Wen, & Chen, 2002a; Li, Chen, Wen, & Li, 2002b; Wolf et al., 1999; Wolf et al., 2001; Wootton & Chaudhry, 1979; Xie & Liu, 2004), the amounts of RDS, SDS, and RS in the products were not determined. The primary objective of this study was to compare digestibility of several chemically modified starches. A secondary objective was to establish an optimum condition for production of the highest SDS content while maintaining functionality in order to provide a food product ingredient that will provide product quality while being nutritionally superior because of its slow release of glucose.

## 2. Materials and methods

### 2.1. Materials

Normal corn, waxy corn, potato, and tapioca starches were commercially prepared products. Propylene oxide, succinic anhydride, 2-oceten-1-ylsuccinic anhydride, phosphoryl chloride, invertase (Sigma I-4504), pancreatine (Sigma P-7545), and amyloglucosidase (Sigma A-7255) were purchased from Sigma–Aldrich Chemical Co. (Milwaukee, WI).

### 2.2. Modification of starch

#### 2.2.1. Crosslinking

Starch (20 g, db) was dispersed in water (40 mL) with stirring. The pH of the slurry (at 20 °C) was adjusted to 11.8 with 1 M NaOH. Phosphoryl chloride (0.33 mL of a solution of 3 mL $POCl_3$/100 mL dioxane; 4.935% w/v) was added dropwise to the starch slurry with vigorous stirring. During the reaction, the pH was maintained at 11.8 by use of an auto-titrator. After 1 h of reaction, the reaction mixture was neutralized to pH 7.0 with 1 M HCl. The modified starch was collected by centrifugation, washed three times with water and once with acetone, and air-dried. The procedure described is for making crosslinked starch with 0.08% $POCl_3$ per unit weight of starch (db) (0.086 moles $POCl_3$/mole of glucosyl unit). Products with 1.5 and 2.0 times that much $POCl_3$ were also made.

#### 2.2.2. Hydroxypropylation

Starch (20 g, db) was dispersed in water (50 mL) with stirring. Sodium chloride was added to provide concentrations of 0.471 or 0.629 m when hydroxypropylation preceded crosslinking (Table 1). The pH of the slurry (at ~20 °C) was adjusted to 11.2 with 1 M NaOH. The reaction vessel was sealed tightly with a septum. Propylene oxide (2.5 mL [2.1 g], 10% of the weight of starch) was added via a syringe. The flask was placed in a 49 °C water bath and stirred using a submergible magnetic stir plate for 24 h. After that, the starch slurry was neutralized to pH 7 with 1 M HCl. The modified starch was collected by centrifugation, washed three times with water and once with acetone, and air-dried. This product was made with 0.29 moles of reagent/mole of glucosyl unit.

#### 2.2.3. Acetylation

Starch (20 g, db) was dispersed in water (50 mL) with stirring. The pH of the slurry (at ~20 °C) was adjusted to 8.0–8.4 with 1 M NaOH. Acetic anhydride (1.7 mL [1.8 g], 9.0% of the weight of starch) was added dropwise. During the reaction, the pH was maintained at 8.0–8.4 by use of an auto-titrator. After 10 min of reaction, the slurry was neutralized to pH 7 with 1 M HCl. The modified starch was collected by centrifugation, washed three times with water and

Table 1
Digestibility of chemically modified waxy corn starch

| Sample[a] | RDS (% ±SD) | Digestibility at 120 min (% ±SD) | SDS (% ±SD) | RS (% ±SD) | Total digestibility (% ±SD) |
|---|---|---|---|---|---|
| Unmodified | 87.8 ± 3.8 | 100.0 ± 2.4 | 12.2 ± 2.4 | 0.0 ± 1.7 | 100.0 ± 1.1 |
| CL (without salt) | 67.3 ± 2.7 | 87.2 ± 3.6 | 19.9 ± 2.1 | 12.9 ± 1. 5 | 87.2 ± 0.6 |
| CL (0.05%)-without salt – AC (8.5%)[b] | 62.9 ± 1.6 | 75.8 ± 2.8 | 12.9 ± 2.3 | 24.2 ± 2. 1 | 75.8 ± 0.4 |
| CL (0.05%)-without salt – HP (12.3%)[b] | 65.2 ± 2.3 | 86.1 ± 5.1 | 20.9 ± 4.7 | 13.9 ± 5.2 | 86.1 ± 1.6 |
| HP with NaCl (0.629 m) – CL (0.08%)[b] | 53.8 ± 1.9 | 74.4 ± 2.9 | 20.6 ± 2.7 | 25.6 ± 2.3 | 74.4 ± 0.8 |
| HP with NaCl (0.471 m) – CL (0.08%)[b] | 55.4 ± 2.5 | 76.6 ± 3.5 | 21.2 ± 3.2 | 23.4 ± 5.3 | 76.6 ± 1.5 |

[a] *Abbreviations:* CL, crosslinked with $POCl_3$; ACE, acetylated; HP, hydroxypropylated; SD, standard deviation.

[b] Crosslinking and substitution reactions were done in the order given.

once with acetone, and air-dried. This product was made with 0.14 moles of reagent/mole of glucosyl unit.

### *2.2.4. Esterification with octenylsuccinic anhydride*

Starch (20 g, db) was dispersed in water (45 mL) with stirring. The pH of the slurry (at ~20 °C) was adjusted to 8.5 ~ 9.0 with 1 M NaOH. 2-Octen-1-ylsuccinic anhydride (0.60 g [0.6 mL], 3.0% of the weight of starch) was added, and agitation was continued at room temperature (~20 °C) while maintaining the pH at 8.5. After 6 h, starch slurry was neutralized to pH 7.0 with 1 M HCl. The modified starch was collected by centrifugation, washed three times with water and once with acetone, and air-dried. This product was made with 0.023 moles of reagent/mole of glucosyl unit.

### *2.2.5. Esterification with succinic anhydride*

The procedure described above was used with use of 0.80 g (4.0% of the weight of starch) of succinic anhydride. This starch was made with 0.065 moles of reagent/mole of glucosyl unit.

### *2.2.6. Heat treatment*

Air-dried octenylsuccinylated starch (10 g) was spread in a glass Petri dish and heated at the selected temperature (120, 130, or 140 °C) for 2, 3, 4, or 5 h.

### *2.2.7. Pasting characteristics*

The pasting characteristics of the modified starches were determined with a Rapid Visco-Analyser (Model 4, Newport Scientific, Warriewood, Australia) using standard profile 1. Modified starch (2.1 g, db) and distilled water (27.9 g) (sample + water = 30 g) were added to the aluminum sample container. A 13-min analysis was used: equilibration to 50 °C for 1 min, heating to 95 °C in 222 s, holding at 95 °C for 150 s, cooling to 50 °C in 228 s, holding at 50 °C for 120 s.

### *2.2.8. Digestibility*

Starch samples (550–600 mg) and water (10 mL) were added to 50-mL polypropylene centrifuge tubes. The tubes were capped, and the contents were mixed by vortexing for 5 min. The tubes were then heated in a boiling-water bath as follows: 10 min heating, vortexing, and heating again for 9 min. After heating, 15 glass beads (0.5-mm diam) (for mechanical disruption of the physical structure of the sample), guar gum (50 mg, for keeping the sample in suspension and preventing excess disruption of the sample by the glass beads), and pH 5.2 sodium acetate buffer (10 mL) were added to each tube. The tubes were incubated 30 min at room temperature. The Englyst method (Englyst, Englyst, Hudson, Cole, & Cummings, 1999) was used to determine digestibility. Three separate tubes were prepared; duplicate aliquots were taken from each of the three.

### *2.2.9. Differential scanning calorimetry (DSC)*

For DSC analysis, a Perkin-Elmer DSC 7 analyzer with a thermal analysis data station (Perkin-Elmer Corp., Norwalk, CT) was used. The samples were prepared with a water to starch ratio of 4:1 and held for at least 2 h before analysis. The samples were heated from 20 to 140 °C at a rate of 10 °C/min. Thermal transitions for gelatinization were characterized by To (onset temperature), Tp (peak temperature), Tc (conclusion temperature), and ΔH (enthalpy of gelatinization).

## 3. Results and discussion

### *3.1. Dual modification (crosslinking and stabilization)*

The higher the amylose content of the starch, the slower the digestion (Goddard, Young, & Marcus, 1984; Granfeldt, Drews, & Björck, 1995), so cooked waxy starches are more rapidly digested than are cooked normal starches (van Amelsvoort & Weststrate, 1992). For this reason and because waxy maize starch is usually the preferred form of corn starch for generating modified food starch, waxy corn starch was the primary starch used in this work, the goal of which was to increase SDS content. The optimum condition found for waxy corn starch was then applied to other starches. Chemical modifications were done at or close to the maximum levels allowed for making modified food starch; the extent of hydroxypropylation used was the maximum allowable amount for products that are both crosslinked and hydroxypropylated.

Table 1 gives the digestion characteristics of chemically modified waxy corn starch. Unmodified waxy corn starch (cooked for 20 min in excess water) was fully digested (88% RDS, 12% SDS, 0% RS content). After crosslinking with $POCl_3$ (0.16% w/w), total digestibility decreased from 100% to 87%; SDS and RS contents increased from 12% to 20% and from 0% to 13%, respectively. The effect of stabilization [acetic anhydride (9.0% w/w) and propylene oxide (10% w/w)] in combination with crosslinking was determined. Woo and Seib (2002) found that a series of wheat starch crosslinked with sodium trimetaphosphate/sodium tripolyphosphate (0.13–0.38% P) contained 13–17% SDS after gelatinization.

Crosslinking followed by hydroxypropylation (CL-HP) produced a modified starch with higher SDS (21%) and lower RS (14%) contents, as compared to a product made by crosslinking followed by acetylation (CL-AC) (SDS 13%, RS 24%, respectively). As a result, the total digestibility of CL-AC was less than that of CL-HP, but there was a greater amount of SDS present in the CL-HP product. According to Wootton and Chaudhry (1979), hydroxypropylated wheat starch had a reduced rate of production of reducing power at all incubation times with α-amylase as compared to acetylated wheat starch, a result that was attributed to the hydroxypropyl groups being more bulky. The difference between our finding and that of Wooton & Chaudhry could be due to use of waxy corn starch as compared to wheat starch. There was little difference in the SDS contents of HP-CL (hydroxypropylation followed by crosslinking) and CL-HP, both being ~21%. However, HP-CL had a much lower RDS content and a much higher RS content (average 55% and 24.5%, respectively) than did CL-HP (65% and 14%, respectively). It is speculated that hydroxypropylation resulted in greater swelling of the granules and resulted in more effective crosslinking (Yeh & Yeh, 1993). However, Wang and Wang (2000) reported that CL (0.07%)-HP (8%) waxy corn starch (with crosslinking done in the presence of $Na_2SO_4$) underwent attack by enzymes and chemicals to a lesser extent than did HP-CL waxy corn starch. The difference in results between that reported by Wang and Wang (2000) and ours might be due to sample preparation for digestibility studies, different modification reagent concentrations, and differences in the type and amount of swelling-inhibiting salt used (Villwock & BeMiller, 2005). However, together, these results indicate that digestibility of modified food starches can be altered by changes in modification conditions.

For HP-CL starches, there was not much difference between the preparations made with different salt concentrations; HP made in the presence of a higher concentration of NaCl (0.629 m) followed by crosslinking had a little lower SDS content and a higher RS content as compared with that prepared in the presence of a lower concentration of NaCl (0.471 m). In separate experiments, among waxy corn starch products crosslinked with three different reagent concentrations (0.08, 0.12, and 0.16w% of phosphoryl chloride), starch crosslinked with 0.08% $POCl_3$ contained the most SDS. A concentration of $POCl_3$ greater than 0.08% could inhibit granule swelling to the point of inhibiting enzyme-catalyzed hydrolysis, resulting in an increased RS and a decreased SDS and total digestibility.

### 3.2. Esterification with OSA and heat treatment

Octenylsuccinylation was already known to reduce the enzyme-catalyzed degradation of starch (Viswanathan, 1999; Wolf et al., 2001) and to slow the glycemic response (Wolf et al., 2001). The resulting product, so-called OSA starch, is categorized as RS4. A characteristic of OSA starch is an increased production of breath hydrogen, which results from modified starch not digested by intestinal amylases undergoing at least partial anaerobic fermentation by colonic hydrogen-producing bacteria (Cummings, Beatty, Kingman, Bingham, & Englyst, 1996; Englyst et al., 1992). If part of an OSA starch preparation is resistant starch, the available energy from carbohydrate in the product is reduced (Heacock, Hertzler, & Wolf, 2004). In our tests, OSA starches had a high percentage of RS (waxy corn, 22%; normal corn, 29%; potato, 33%; and tapioca, 28%). However, the OSA starches also had a high content of SDS (from 25% [normal corn] to 36% [waxy corn]) (Tables 2 and 3). Therefore, OSA starches can be a good source of SDS. The combination of crosslinking with $POCl_3$ and OSA esterification decreased SDS content as compared to crosslinking alone or octenylsuccinylation alone.

Heat treatment of starches impregnated with an anionic gum resulted in changes in granule behavior, presumably as a result of crosslinking or mono-esterification (Lim, Han, Lim, & BeMiller, 2002). Therefore, it was hypothesized that heat treatment of a product esterified by OSA could result in esterification with the carboxyl group of the octenylsuccinate half-ester group resulting in crosslinking and reduced digestibility. OSA waxy corn starch showed much lower RDS (42%) as compared to native waxy corn starch (88%). With heat treatment, the extent of digestion at 120 min increased, resulting in increased SDS (Table 2). For determining an optimum temperature, three different heating temperatures (110, 120, and 130 °C) were used. As heating temperature increased from 110 to 130 °C (same 4-h period), the RDS portion decreased from 52% to 48% and the SDS portion increased from 38% to 47%. As a consequence, RS content decreased from 9.5% to 5.6%. Among the temperatures used, 130 °C was found to result in the greatest increase in SDS content. To determine the optimum heating period, digestibility was measured at three different times (3, 4, and 5 h) at 130 °C. The highest SDS

Table 2
Digestibility of modified waxy corn starch

| Treatment | RDS (% ±SD) | Digestibility at 120 min (% ± SD) | SDS (% ±SD) | RS (% ±SD) |
|---|---|---|---|---|
| Unmodified | 87.8 ± 3.8 | 100.0 ± 2.4 | 12.2 ± 2.4 | 0 ± 1.8 |
| OSA[a] (3%) | 42.3 ± 3.0 | 77.9 ± 0.3 | 35.6 ± 2.3 | 22.1 ± 0.9 |
| OSA (3%) – Heat 4 h at 110 °C | 52.3 ± 3.4 | 90.5 ± 2.9 | 38.2 ± 2.1 | 9.5 ± 0.8 |
| OSA (3%) – Heat 4 h at 120 °C | 51.6 ± 3.2 | 92.1 ± 4.5 | 40.5 ± 5.2 | 7.9 ± 4.2 |
| OSA (3%) – Heat 3 h at 130 °C | 48.0 ± 3.2 | 89.6 ± 4.1 | 41.6 ± 4.3 | 10.4 ± 3.4 |
| OSA (3%) – Heat 4 h at 130 °C | 47.7 ± 2.2 | 94.4 ± 4.3 | 46.7 ± 3.8 | 5.6 ± 3.9 |
| OSA (3%) – Heat 5 h at 130 °C | 52.2 ± 1.7 | 88.7 ± 3.8 | 36.5 ± 2.8 | 11.3 ± 3.3 |
| SA (4%) – Heat 4 h at 110 °C | 58.9 ± 2.6 | 92.1 ± 2.3 | 33.2 ± 3.2 | 7.9 ± 2.8 |
| SA (4%) – Heat 4 h at 120 °C | 50.3 ± 1.3 | 80.1 ± 0.4 | 29.8 ± 1.7 | 19.9 ± 0.4 |
| SA (4%) – Heat 4 h at 130 °C | 52.5 ± 4.5 | 75.0 ± 2.3 | 22.5 ± 2.5 | 25.0 ± 1.7 |
| HP (10%)[b]-OSA (3%) – Heat 4 h at 130 °C | 36.6 ± 2.7 | 59.3 ± 4.8 | 22.7 ± 3.4 | 40.7 ± 4.2 |
| CL (0.08%)-OSA (3%)[c] | 75.3 ± 0.5 | 94.1 ± 0.2 | 18.8 ± 0.8 | 5.9 ± 0.3 |
| OSA (3%)-CL(0.16%)[c] | 66.8 ± 0.8 | 98.9 ± 1.5 | 32.1 ± 0.2 | 1.1 ± 2.3 |

[a] Reaction with OSA (octenylsuccinic anhydride) was performed without salt.

[b] Hydroxypropylation was performed in the presence of 0.527 m $Na_2SO_4$.

[c] Rections were done in the order given.

Table 3
Digestibility of modified normal, tapioca and potato starch

| Starch | Treatment | RDS (% ±SD) | Digestibility at 120 min (% ±SD) | SDS (% ±SD) | RS (% ±SD) |
|---|---|---|---|---|---|
| Normal corn | Unmodified | 85.1 ± 3.6 | 98.9 ± 1.6 | 13.8 ± 3.8 | 1.1 ± 1.6 |
| | OSA (3%) | 46.1 ± 3.1 | 71.5 ± 1.3 | 25.4 ± 2.7 | 28.6 ± 1.3 |
| | OSA (3%) – Heat 5 h at 130 °C | 57.7 ± 4.0 | 96.0 ± 2.8 | 38.3 ± 2.1 | 4.0 ± 3.8 |
| Tapioca | Unmodified | 82.3 ± 2.4 | 99.9 ± 2.3 | 17.6 ± 3.3 | 0.1 ± 2.2 |
| | OSA (3%) | 40.7 ± 2.6 | 72.2 ± 1.1 | 31.5 ± 2.0 | 27.8 ± 3.4 |
| | OSA (3%) – Heat 4 h at 130 °C | 40.0 ± 2.6 | 86.1 ± 2.8 | 46.1 ± 4.7 | 13.9 ± 2.8 |
| Potato | Unmodified | 78.3 ± 3.4 | 96.1 ± 2.9 | 17.8 ± 4.2 | 3.9 ± 2.7 |
| | OSA (3%) | 40.3 ± 1.9 | 67.2 ± 4.1 | 26.9 ± 1.3 | 32.8 ± 3.9 |
| | OSA (3%) – Heat 5 h at 130 °C | 43.7 ± 2.6 | 76.5 ± 1.4 | 32.8 ± 1.9 | 23.5 ± 2.8 |

Table 4
Thermal characteristics native, OSA, and OSA + heat treated waxy corn starch[a]

| Starch | $T_o$ | $T_p$ | $T_c$ | ΔH (J/g) |
|---|---|---|---|---|
| Unmodified | 69.3 ± 0.4 | 74.9 ± 0.1 | 87.9 ± 0.3 | 19.2 ± 2.5 |
| OSA (3%) | 67.5 ± 0.1 | 72.8 ± 0.4 | 82.3 ± 0.8 | 15.4 ± 1.3 |
| OSA (3%) – Heat 4 h at 130 °C | 65.5 ± 0.3 | 69.9 ± 1.1 | 78.6 ± 0.1 | 12.9 ± 2.2 |
| SA (4%) | 61.7 ± 0.6 | 68.8 ± 0.2 | 81.9 ± 3.5 | 11.2 ± 1.0 |
| SA (4%) – Heat 4 h at 130 °C | 56.8 ± 1.1 | 62.6 ± 0.7 | 73.6 ± 1.4 | 8.3 ± 0.3 |

[a] All values ± SD.

content (46.7%) was obtained after 4 h heating. When a 5-h heating period was used, a color change (from white to light brown) was detected, indicating thermal degradation, and the RS content increased. The tendency that, as heating time increased, digestibility at 120 min increased and RS content decreased (except 5 h at 130 °C) might indicate a change of internal structure effected by heating. So, to examine any change of internal structure in modified starch, native, OSA, and heated OSA waxy corn starches were examined by DSC; the results are given in Table 4. The effect of octenylsuccinylation on native waxy corn starch was to shift the endotherm to a lower temperature and reduce ΔH from 19.2 to 15.4 J/g. Bao, Xing, Phillips, and Corke (2003) reported that internal bonds of starch granules are weakened by incorporation of the hydrophobic alkenyl group, allowing the starch to swell at a lower temperature. Dry-heated (130 °C, 4 h) OSA waxy corn starch had lower values of To, Tp, Tc, and ΔH as compared to unheated OSA starch (Fig. 2). According to Bryce and Greenwood (1963), heating might effect cleavage of some glycosidic bonds; it might also induce molecular rearrangements of the type that occur during dextrinization. The decrease of ΔH found for heated OSA starch can be explained as resulting from such transglycosylation reactions resulting in less crystallinity. Greater swelling and solubility would result in greater digestibility.

Starch esterification with succinic anhydride (SA) produced an opposite result, viz, as heating temperature increased from 110 to 130 °C, SDS decreased (from 33% to 2.5%), and RS increased significantly (from 7.9% to 25%) (Table 2). This difference might be the result of the two reagents (OSA and SA) being used at equal weight amounts rather than equal molar amounts, i.e., from SA producing a greater DS than OSA when applied at equal weight amounts.

The heat-treated HP-OSA (hydroxypropylation → octenylsuccinylation) sample was expected to show less digestibility than heated OSA starch, because hydroxypropylated waxy corn starch granules would swell more readily, resulting in the OSA reagent entering the granule more readily and more evenly. As expected, heat-treated HP-OSA starch had a decreased RDS content as compared to heated OSA waxy corn starch (37% vs 47%). However, contrary to heated OSA waxy corn starch, the digestion at 120 min (59.3%) of heated HP-OSA waxy corn starch also decreased. As a result of prevention of digestion, the RS content increased dramatically (to 41%). The RS contents of commercial RS products are reported to be 42% for Novelose (trademark of National Starch and Chemical Co.) 240 and 30% for Novelose 330 (National Starch and Chemical Co.); therefore heated HP-OSA starch could also be a useful source of RS, but a RS with functionality.

Based on the encouraging results with waxy corn starch, normal corn, potato, and tapioca starches were reacted with OSA and heated at 130 °C, and the digestibility of the products determined (Table 3). For normal corn starch, after OSA treatment, SDS content about doubled (from 14% to 25%) and the RS content increased from 1.1% to 29%. Heating 5 h at 130 °C created a much higher SDS content (38%) and decreased the RS content (4.0%).

Native tapioca starch was completely digested at 120 min heating (RDS, 82%; SDS, 18%). After octenylsuccinylation, both RDS and percentage digestion at 120 min decreased and SDS increased (from 18% to 31.5%). With heating, the SDS content increased from 31.5 % to 46% and RS decreased from 28% to 14%.

Native potato starch contained 78% RDS and 18% SDS. Octenylsuccinylation decreased RDS and percent digestion at 120 min and increased SDS (27%) and RS (33%). With dry heating (5 h at 130 °C), SDS increased to 33% and RS decreased slightly to 23.5%.

### 3.3. Pasting characteristics of native and OSA starches

An objective of this research was to produce a slowly digesting starch product with at least some of the functional characteristics of a modified food starch. When compared with unmodified (native) starch, incorporation (3% dry starch basis) of a bulky OSA group changed the overall pasting characteristics of the starch, viz decreased pasting temperature and increased peak viscosity (Table 5). For example, OSA waxy corn starch, as compared to the native unmodified starch had a decreased pasting temperature (69.4 vs 73.5 °C) and an increased peak viscosity from (6719 vs 2479 cP). Octenylsuccinylation of normal corn, potato, and tapioca starches decreased pasting temperatures (from 86.4 to 71.9 °C, from 67.1 to 63.8 °C, and from 69.5 to 66.3 °C, respectively) and increased peak viscosities (from 1233 to 3130, from 5669 to 6093, and from 2199 to 5260 cP, respectively), as compared to their native counterparts. These results are an indication that incorporation of the octenylsuccinate group creates disorder in granule structure, allowing granules to begin to swell at lower temperatures and swell to a greater degree as compared to native starch. Trubiano (1986) reported that starch alkenylsuccinylated starches produce higher viscosities in aqueous suspension, have lower gelatinization temperatures, and have a reduced tendency to retrograde, ie, are stabilized. Shih and Daigle (2003) concluded that the OSA group disturbed the orderly structure of the starch, decreasing thermotransition resistance. In this work, with the exception of potato starch, OSA starch pastes exhibited greater breakdown than did pastes of their native counterparts.

### 3.4. Effect of heat treatment on pasting characteristics and digestibility of OSA starches

With dry heat treatment (130 °C for 3 h), OSA waxy corn starch show significantly different pasting characteristics from those of non-heat-treated OSA starches: a decreased pasting temperature (Δ°C 4.8) and increased peak viscosity (ΔcP, 1993), breakdown (ΔcP 740) and final viscosity (ΔcP 2797). These results indicate that heat-treated OSA waxy corn starch hydrated, swelled, and disintegrated more readily than did non-heat-treated OSA waxy corn starch. However, the overall viscogram pattern was not changed significantly (Fig. 1). As heating time increased from 3 to 5 h, peak and final viscosities decreased slightly (from 8712 to 7998 cP and from 7651 to 7152 cP, respectively). The overall pasting profiles could be interpreted as indicating a low degree of crosslinking.

Heat treatment of OSA normal corn starch also changed its pasting profile. A 3-h heat treatment at 130 °C increased both peak viscosity and breakdown (ΔcP 774 and 1539, respectively) and decreased pasting temperature (Δ°C 2.4), setback (ΔcP 1131), and final viscosity (ΔcP 1896). As heating time increased from 3 to 5 h, all values decreased. Again, the overall profiles are consistent with a low degree of crosslinking.

As opposed to OSA normal and waxy corn starches, OSA potato and tapioca starches, which are B-type starches, showed lower peak viscosities after dry heating. Sekine, Otobe, Sugiyama, and Kawamura (2000) found that heating of B-type starches produced greater changes in thermal and rheological properties than did heating of A-type starches. Lim et al. (2002) also reported that heat-treated B-type

Table 5
Pasting characteristics native and OSA starches

| Starch | Treatment[a] | Pasting temperature (°C) | Peak viscosity (cP) | Breakdown | Final viscosity (cP) | Setback |
|---|---|---|---|---|---|---|
| Waxy corn | Unmodified | 73.5 | 2479 | 1086 | 1648 | 255 |
| | OSA (3%) | 69.4 | 6719 | 2236 | 4854 | 371 |
| | OSA-H3 | 64.6 | 8712 | 2976 | 7651 | 1915 |
| | OSA-H4 | 68.5 | 8865 | 3078 | 7423 | 1636 |
| | OSA-H5 | 68.6 | 7998 | 2671 | 7152 | 1825 |
| Normal corn | Unmodified | 86.4 | 1233 | 196 | 1242 | 205 |
| | OSA (3%) | 71.9 | 3130 | 216 | 5308 | 2394 |
| | OSA-H3 | 69.5 | 3904 | 1755 | 3412 | 1263 |
| | OSA-H4 | 69.4 | 3638 | 1569 | 2880 | 811 |
| | OSA-H5 | 70.3 | 3339 | 1260 | 2509 | 430 |
| Potato | Unmodified | 67.1 | 5669 | 3060 | 3260 | 651 |
| | OSA (3%) | 63.8 | 6093 | 1638 | 4931 | 476 |
| | OSA-H3 | 61.4 | 6702 | 2717 | 7350 | 3365 |
| | OSA-H4 | 61.4 | 6343 | 2615 | 6449 | 2721 |
| | OSA-H5 | 62.2 | 5618 | 2359 | 5041 | 1782 |
| Tapioca | Unmodified | 69.5 | 2199 | 936 | 1998 | 735 |
| | OSA (3%) | 66.3 | 5260 | 936 | 4791 | 467 |
| | OSA-H3 | 64.6 | 4401 | 1246 | 5037 | 1882 |
| | OSA-H4 | 65.3 | 4165 | 1313 | 4123 | 1271 |
| | OSA-H5 | 65.4 | 3736 | 1080 | 3558 | 902 |

[a] H3, H4, H5 refer to 3, 4, and 5 h of heating at 130 °C.

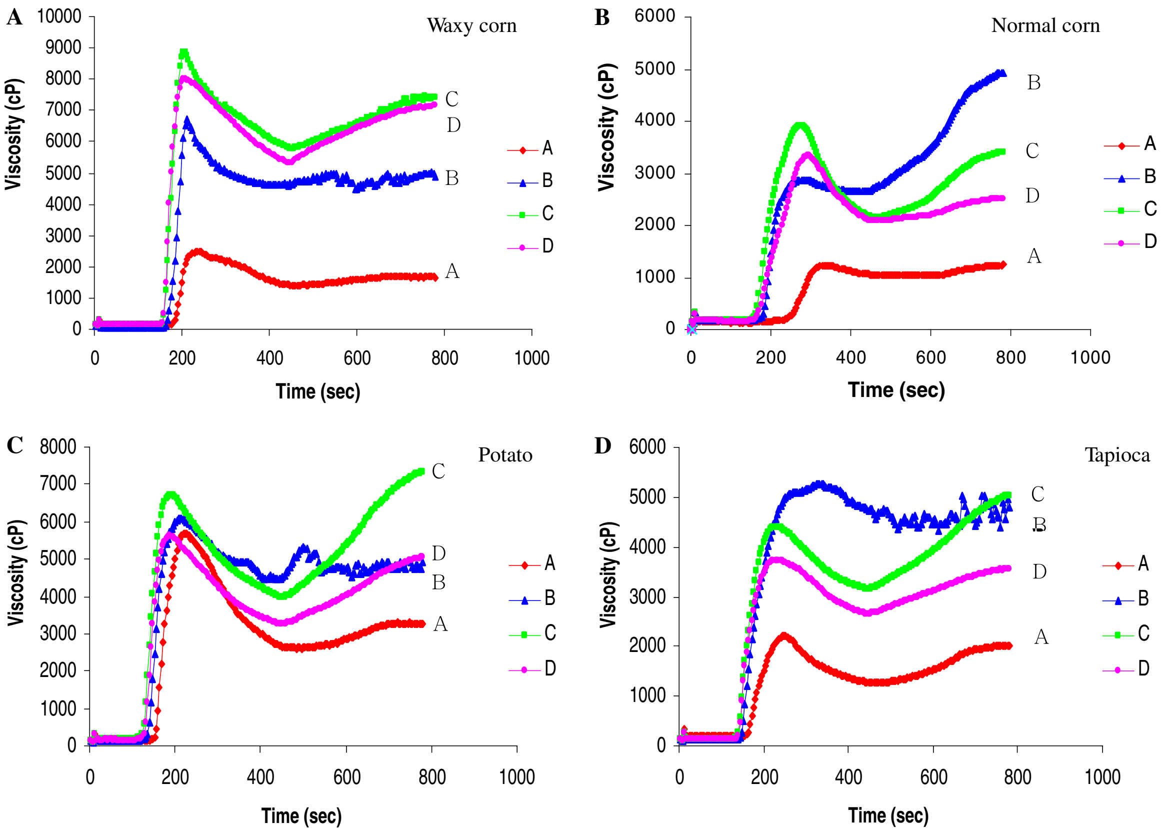

Fig. 1. Pasting characteristics of OSA starches after oven heating at 130 °C for 3, 5 h: (A) unmodified starch; (B) OSA treated starch; (C) OSA-H130, 3 h; (D) OSA-H130, 5 h.

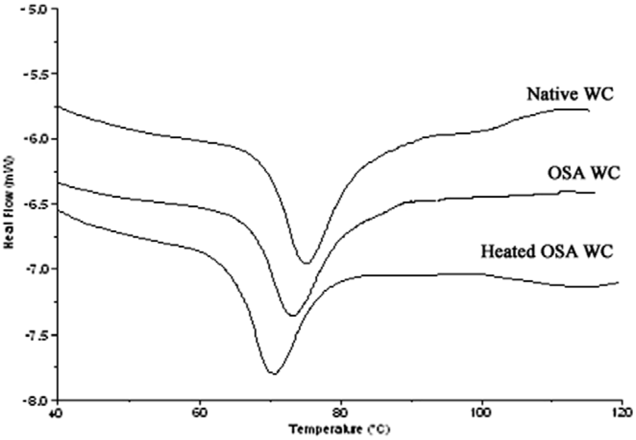

Fig. 2. DSC thermogram of waxy corn, OSA waxy corn, and heated (130 °C, 4 h) OSA waxy corn starch.

starches gelatinized at a lower temperature with less enthalpy, indicating a reduced thermostability of starch granules. When OSA potato starch was heated 3 h at 130 °C, all paste parameters increased: peak viscosity (ΔcP 609), breakdown (ΔcP 1079), setback (ΔcP 2889), final viscosity (ΔcP 2419); the pasting temperature decreased slightly. As heating time increased from 3 to 5 h, all values decreased; peak viscosity (from 6702 to 5618 cP), breakdown (from 2717 to 2359 cP), setback (from 3365 to 1782 cP), and final viscosity (from 7350 to 5041 cP); pasting temperature increased slightly (from 61.4 to 62.2 °C). The changes in native potato starch itself brought about by dry heat treatment were hypothesized to result from reaction of the native monostarch phosphate groups to form diester crosslinks (Lim et al., 2002). Once again, the overall profiles are consistent with a low degree of crosslinking, with perhaps the product produced by heating for 5 h showing somewhat greater crosslinking than that resulting from heating for 3 h. Heating of OSA tapioca starch produced the greatest inhibition of peak viscosity, with 5-h heating producing a product with a lower peak viscosity than that obtained from the product made via a 3-h heating, again an indication that some crosslinking may have occurred.

Overall, dry heating (130 °C for 3 h) increased the paste viscosity of OSA normal corn, waxy corn, and potato starches, but decreased that of OSA tapioca starch. Increasing the peak viscosity and decreasing pasting temperature suggests that the granule structure might be loosened and that the granules at least behaved as if they were slightly crosslinked. The loosening of granule structure resulted in more readily hydrated, more swollen granules, and the more swollen granules resulted in greater total percent of digestibility (Table 2). Increasing the heating time resulted in a reduced peak viscosity, indicating restricted granular swelling. Although there were no distinct differences in the RVA profiles of starches dry heated for 4 vs 5 h, the SDS content increased with an increase in heating time from 3 to

4 h, then decreased with 5 h heating (Tables 2 and 4). Transglycosylation and/or changes in granule structure as a result of heating may be the cause. A key result from this work is that heat treatment of all four OSA starches increased the SDS content (in OSA waxy maize starch to as much as 47%) and decreased the RS content (to 5.6% in the same OSA waxy maize starch product) (Tables 2 and 3), both traits being desirable from a nutritional point of view, while maintaining functionality (Fig. 1).

## 4. Conclusions

Of the several chemical modifications, including cross-linking and stabilization reactions, performed on the four starches, the one resulting in the highest percentage of SDS (viz, esterification with OSA) was chosen for dry-heat treatment. Dry-heat (130 °C) treatment changed both the physical properties as well as digestion characteristics of OSA starches: higher peak viscosity (except tapioca starch), lower pasting temperature, and higher final viscosity (except normal corn starch), increased contents of SDS. Dry-heat treatment decreased To, Tp, Tc, and ΔH in the order unmodified waxy corn > OSA-waxy corn > heated OSA-waxy corn, indicating that a weakened internal bonding was produced in the same order. The highest SDS content was obtained after heating OSA-starch at 130 °C for 4 h (waxy corn and tapioca) and 5 h (normal corn and potato starch).

It is reported that data from the in vitro hydrolysis of starch are useful in predicting glycemic responses in vivo (O'Dea et al., 1981; Seal et al., 2003). The technology revealed here produces functional modified food starches with a much higher percentage of in vitro-determined SDS. Because of the variables involved and discrepancies with previous reports, this report is not likely to be the final word on the preparation of functional modified food starches with a high content of SDS. From this work, however, it can be hypothesized that the key to producing a functional modified food starch with appreciable SDS content is some restriction of digestion resulting from introduction of crosslinks and/or bulky derivatizing groups while at the same time allowing granules to swell, ie, to open up. It can also be hypothesized that this ideal is obtainable.

## References

Anderson, A.K., & Guraya, H. (2004). Microwave heat applications to produce slowly-digestible starches. Abstr. Papers, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

Bao, J., Xing, J., Phillips, D. L., & Corke, H. (2003). Physical properties of octenyl succinic anhydride modified rice, wheat, and potato starches. *Journal of Agricultural and Food Chemistry, 51*, 2283–2287.

Berry, C. S. (1986). Resistant starch: formation and measurement of starch that survives exhaustive digestion with amylolytic enzymes during the determination of dietary fiber. *Journal of Cereal Science, 4*, 301–314.

Björck, I., & Asp, N. G. (1994). Controlling the nutritional properties of starch in foods – a challenge to the food industry. *Trends in Food Science and Technology, 5*, 213–218.

Björck, I., Gunnarsson, A., & Østergård, K. (1989). A study of native and chemically modified potato starch. Part II: digestibility in the rat intestinal tract. *Starch/Stärke, 41*, 128–134.

Bryce, D. J., & Greenwood, C. T. (1963). Thermal degradation of starch. *Stärke, 15*, 166–170.

Cummings, J. H., Beatty, E. R., Kingman, S. M., Bingham, S. A., & Englyst, H. N. (1996). Digestion and physiological properties of resistant starch in the human large bowel. *British Journal of Nutrition, 75*, 733–747.

Englyst, H. N., Kingman, S. M., & Cummings, H. J. (1992). Classification and measurement of nutritionally important starch fractions. *European Journal of Clinical Nutrition, 46*, S33–S50.

Englyst, H. N., & Hudson, G. J. (1996). The classification and measurement of dietary carbohydrates. *Food Chemistry, 57*, 15–21.

Englyst, K. N., Englyst, H. N., Hudson, G. J., Cole, T. J., & Cummings, J. H. (1999). Rapidly available glucose in foods: an in vitro measurement that reflects the glycemic response. *American Journal of Clinical Nutrition, 69*, 448–454.

Goddard, M. S., Young, G., & Marcus, R. (1984). The effect of amylose content on insulin and glucose responses to ingested rice. *American Journal of Clinical Nutrition, 39*, 388–392.

Granfeldt, Y., Drews, A., & Björck, I. (1995). Arepas made from high amylose corn flour produce favorably low glucose and insulin responses in healthy humans. *Journal of Nutrition, 125*, 459–465.

Guraya, H. S., James, C., & Champagne, E. T. (2001). Effect of enzyme concentration and storage temperature on the formation of slowly digestible starch from cooked debranched rice starch. *Starch/Stärke, 53*, 131–139.

Han, X.-Z., Ao, Z., Janaswamy, S., Jane, J.-L., Chandrasekaran, R., & Hamaker, B. R. (2006). Development of a low glycemic maize starch: preparation and characterization. *Biomacromolecules, 7*, 1162–1168.

Heacock, P. M., Hertzler, S. R., & Wolf, B. (2004). The glycemic, insulinemic, and breath hydrogen responses in humans to a food starch esterified by 1-octenyl succinic anhydride. *Nutrition Research, 24*, 581–692.

Hoover, R., & Sosulski, F. (1986). Effect of cross-linking on functional properties of legume starches. *Starch/Stärke, 38*, 149–155.

Janzen, G. J. (1969). Digestibility of starches and phosphatized starches by means of pancreatin. *Stärke, 21*, 231–237.

Li, X., Wen, Q., & Chen, L. (2002a). Biodegradability of cross-linked tapioca starches with $POCl_3$. *Huaxue Gongcheng (Xi'an, China), 30*, 45–48 55; Chemical Abstracts 141, 6093 (2004).

Li, X., Chen, L., Wen, Q., & Li, L. (2002b). Study on biodegradability of tapioca starch crosslinked with phosphorus oxychloride. *Shipin Kexue (Beijing, China), 23*, 25–28; Chemical Abstracts 142, 96230 (2004).

Lim, S.-T., Han, J.-A., Lim, H. S., & BeMiller, J. N. (2002). Modification of starch by dry heating with ionic gums. *Cereal Chemistry, 79*, 601–606.

O'Dea, K., Snow, P., & Nestel, P. (1981). Rate of starch hydrolysis in vitro as a predictor of metabolic responses to complex carbohydrate in vivo. *American Journal of Clinical Nutrition, 34*, 1991–1993.

Seal, C. J., Daly, M. E., Thomas, L. C., Bal, W., Birkett, A. M., Jeffcoat, R., & Mathers, J. C. (2003). Postprandial carbohydrate metabolism in healthy subjects and those with type 2 diabetes fed starches with slow and rapid hydrolysis rates determined in vitro. *British Journal of Nutrition, 90*, 863–864.

Sekine, M., Otobe, K., Sugiyama, J., & Kawamura, Y. (2000). Effects of heating, vacuum drying and steeping on gelatinization properties and dynamic viscoelasticity of various starches. *Starch/Stärke, 52*, 389–405.

Shih, F. F., & Daigle, K. W. (2003). Gelatinization and pasting properties of rice starch modified with 2-octen-1-ylsuccinic anhydride. *Nahrung, 47*, 64–67.

Shin, M., Woo, K., & Seib, P. A. (2003). Hot-water solubilities and water sorptions of resistant starches at 25 °C. *Cereal Chemistry, 80*, 564–566.

Shin, S. I., Choi, H. J., Chung, K. M., Hamaker, B. R., Park, K. H., & Moon, T. W. (2004). Slowly digestible starch from debranched waxy sorghum starch: preparation and properties. *Cereal Chemistry, 81*, 404–408.

Shin, S. I., Kim, H. J., Ha, H. J., Lee, S. H., & Moon, T. W. (2005). Effect of hydrothermal treatment formation and structural characteristics of slowly digestible non-pasted granular sweet potato starch. *Starch/Stärke, 57*, 421–430.

Trubiano, P. C. (1986). Succinate and substituted succinate derivatives of starch. In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 131–147). Boca Raton: CRC Press.

van Amelsvoort, J. M., & Weststrate, J. A. (1992). Amylose-amylopectin ratio in a meal affects postprandial variables in male volunteers. *American Journal of Clinical Nutrition, 55*, 712–718.

Villwock, V. K., & BeMiller, J. N. (2005). Effect of salts on the reaction of normal corn starch with propylene oxide. *Starch/Stärke, 57*, 281–290.

Viswanathan, A. (1999). Effect of degree of substitution of octenyl succinate starch on enzymic degradation. *Journal of Environmental Polymer Degradation, 7*, 185–190.

Wang, Y.-J., & Wang, L. (2000). Effects of modification sequence on structures and properties of hydroxypropylated and crosslinked waxy maize starch. *Starch/Stärke, 52*, 406–412.

Wolever, T. M. S. (2003). Slow digestible carbohydrates. *Danone Vitapole Nutritopics, 28*, 1–17.

Wolf, B. W., Bauer, L. L., & Fahey, G. C., Jr. (1999). Effects of chemical modification on in vitro rate and extent of food starch digestion: an attempt to discover slowly digested starch. *Journal of Agricultural and Food Chemistry, 47*, 4178–4183.

Wolf, B. W., Wolever, T. M. S., Bolognesi, C., Zinker, B. A., Garleb, K. A., & Firkins, J. L. (2001). Glycemic response to a food starch esterified by 1-octenyl succinic anhydride in humans. *Journal of Agricultural and Food Chemistry, 49*, 2674–2678.

Woo, K. S., & Seib, P. A. (2002). Cross-linked resistant starch: preparation and properties. *Cereal Chemistry, 79*, 819–825.

Wootton, M., & Chaudhry, M. A. (1979). Enzymic digestibility of modified starches. *Starch/Stärke, 31*, 224–228.

Xie, X., & Liu, Q. (2004). Development and physiochemical characterization of new resistant citrate starch from different corn starches. *Starch/Stärke, 56*, 364–370.

Yeh, A.-I., & Yeh, S. L. (1993). Some characteristics of hydroxypropylated and cross-linked rice starch. *Cereal Chemistry, 70*, 596–601.