

Preparation and Properties of Starch Phosphates Using Waxy, Common, and High-Amylose Corn Starches. II. Reactive Extrusion Method

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ABSTRACT

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The structure and physicochemical properties of extruded waxy, common, and high-amylose corn starch phosphates prepared using slurry and dry-mixing treatments were studied. Extrusion parameters including moisture content and zone temperatures were optimized. All phosphorylated starches showed improved freeze-thaw stability, decreased retrogradation, and improved water binding relative to their parent starches. The extrusion process greatly increased the degree of phosphorylation compared with the conventional oven-heating method. The extrusion parameters of high pressure, temperature, and shear enhanced the efficiency of phosphorus incorporation. The slurry treatment was more

effective than dry mixing in incorporating phosphate groups because its higher moisture content allowed for better mixing under the reaction conditions studied. The phosphorylated starches prepared by the slurry treatment exhibited a lower gelatinization temperature and enthalpy, a higher pasting viscosity profile, and improved swelling and freeze-thaw stability compared with those prepared by the dry-mixing treatment. The amount and location of phosphorus incorporated into starches by extrusion varied with starch composition and sample treatment before extrusion. Waxy starch was more prone to phosphorylation, followed by common and high-amylose starches, respectively.

Starch provides various properties such as thickening and gelling in various processed foods. For industrial applications, it provides sizing, binding, adhesion, and other important functions. The food products and processing techniques require that starch be able to tolerate a wide range of handling, processing, and storage conditions. Modification of starches has been developed to extend the usefulness of starch in numerous food and industrial applications.

Phosphorylation is one of the techniques used to improve the functional properties of starch and to modify its behavior in terms of gelatinization, pasting, and retrogradation (San Martín-Martínez et al 2004). Starch is usually phosphorylated by heating in the presence of chemicals such as sodium tripolyphosphate (STPP) and sodium trimetaphosphate (STMP). The resultant starch phosphate gives a clear paste with increased solubility, swelling power, and freeze-thaw stability (Lim and Seib 1993; Jae et al 1994; Solarek 1995). The conventional oven process requires an excess amount of reagents, presents a fire hazard from starch dust, may cause environmental contamination from unreacted chemicals, and can be very expensive when removal of unreacted chemicals is considered. Efforts have been made to overcome these problems by using extrusion technology (Harper 1981; Kim et al 1999). The advantages of extrusion include simple construction, easy operation, low sample treatment cost, mass production, and uniform physical properties (Watano et al 2002).

Extrusion cooking conditions can convert starch from a granular and semicrystalline material into a highly viscous, plastic material (Brümmer et al 2002). This conversion is accompanied by disruption of the crystalline structure of starch polymers and their reduction to smaller molecules (Lengerich 1984; Vasanthan et al 2001). The starch granule disintegrates completely or partially, depending on the level of energy input, shearing effect, and pressure build-up during extrusion. Heating leads to starch granule swelling due to hydration of the amorphous regions and later the crystalline regions in starch granules (Rubens and Heremans 2000). A high pressure induces a reversible hydration of the amorphous phase followed by an irreversible distortion of the crystalline region during extrusion (Rubens and Heremans 2000).

Phosphorylation of starch by extrusion has progressed in recent years. Salay and Ciacco (1990) produced starch phosphate by extrusion and studied its physicochemical properties. Cunningham (1996) studied how the extrusion parameters affected the intrinsic viscosity of the extruded starch. Chang and Lii (1992) compared the physicochemical properties of starch phosphates prepared by oven heating and extrusion processes. However, little information is available on how starches with varying amylose-to-amylopectin ratios respond to phosphorylation through extrusion. No work has been reported to compare the efficiency of the slurry treatment with that of the dry-mixing treatment before extrusion. The objective of this study was to understand the effect of amylose-to-amylopectin ratio and sample preparation before extrusion on the efficiency of starch phosphorylation.

MATERIALS AND METHODS

Materials

Starch samples, including waxy corn starch ($\approx 0\%$ amylose), common corn starch (25% amylose), and two high-amylose corn starches ($\approx 50\%$ amylose [Hylon V] and $\approx 70\%$ amylose [Hylon VII]) were received from the National Starch and Chemical Company (Bridgegewater, NJ).

Optimization of Extrusion Parameters

A PolyLab laboratory-scale Rheomex twin-screw extruder with intermeshing counter-rotating screws (ThermoHaake, Karlsruhe, Germany) was used in the extrusion process. The barrel has a conical design with three heating zones and a maximum operating temperature of 400°C and pressure of 700 bar. It is equipped with an air-temperature-controllable system and operates at a maximum screw speed of 200 rpm. A rod capillary die attached at the end of the extruder barrel was used in this study. The extruder is attached to a computer system where extrusion parameters are monitored by PolyLab monitor software (ThermoHaake).

The extrusion temperature and sample moisture content were optimized before starch phosphate production. Starch was manually fed into the screw and the screw speed was maintained at 50 rpm because according to preliminary studies, a lower speed caused clogging while a higher speed caused plastic-like samples. Starch-phosphate mixtures were allowed to pass through the extrusion barrel and exit from the die. The three temperature zones of the extrusion barrel and the die were regulated. Three sets of extrusion temperatures were studied in this experiment: 70/96/130/135°C, 80/100/135/140°C, and 90/102/140/145°C, where the first, second, and third temperature represented the first, second,

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and third zone of the barrel, respectively, while the fourth temperature was the temperature of the die. These temperatures were based on the minimum temperature required for phosphorylation (130°C) and to minimize excessive evaporation inside the barrel. Pressure during extrusion averaged 275 psi. Moisture contents studied were 35, 40, and 45%, each of which was subjected to the three sets of extrusion temperatures. Samples with lower moisture contents (<35%) dried quickly, while higher moisture contents (>45%) resulted in excessive melting of the starch.

Preparation of Starch Phosphates

Each starch was mixed with phosphate salts using the slurry treatment described by Lim and Seib (1993) as well as the dry-mixing treatment described by Landerito and Wang (2005) before extrusion. For comparison purposes, this study used the same level of modification as in our previous study (Landerito and Wang 2005) using oven heating. The level of modification was chosen according to Lim and Seib (1993) to prepare starch phosphates with nearly the maximum phosphorus (0.4%) allowed by regulation (CFR 1991) using oven heating. Only one level of phosphorylation was conducted to study the effects of starch type and sample pretreatment. The reaction pH range 9.0–9.5 was chosen to achieve high stability to heat and shear and high consistency after cooling when using a combination of STMP and STPP (Lim and Seib 1993; Muhammad et al 2000). Unmodified starches as well as extruded, unmodified starches were included as references.

The slurry treatment involved the mixing of 15 g of sodium tripolyphosphate (STPP) and 6 g of sodium trimetaphosphate (STMP) in 300 mL of deionized (DI) water containing 15 g of sodium sulfate. The solution was adjusted to pH 9.0 with 10% NaOH before the addition of starch (300 g, db). After starch addition, the slurry was readjusted to pH 9.0 using 5% NaOH; water was then added to make the final dispersion of 45% solid. The slurry was stirred at room temperature for 1 hr and thereafter dried in a convection oven at 40°C overnight. The moisture content was readjusted to 35% (as is) before the extrusion process.

TABLE I
Phosphorus Content of Extruded Common Corn Starch Using Varying Moisture Contents (MC) and Extrusion Temperatures at a Screw Speed of 50 rpm^a

| Condition | MC (% , as is) | Zone Temp (°C) | Phosphorus Content (% , db) |
|-----------|----------------|----------------|-----------------------------|
| A1 | 35 | 70/96/130/135 | 1.182i |
| A2 | 35 | 80/100/135/140 | 1.470f |
| A3 | 35 | 90/102/140/145 | 1.525e |
| B1 | 40 | 70/96/130/135 | 1.230h |
| B2 | 40 | 80/100/135/140 | 1.535d |
| B3 | 40 | 90/102/140/145 | 1.581c |
| C1 | 45 | 70/96/130/135 | 1.341g |
| C2 | 45 | 80/100/135/140 | 1.590b |
| C3 | 45 | 90/102/140/145 | 1.635a |

^a Mean values of two replicates in a column followed by a common letter are not significantly different based on the Tukey test ($P < 0.05$).

TABLE II
Phosphorus Content of Extruded Starch Samples from Four Different Starch Types and Two Sample Treatments Using Extrusion^a

| Sample | Treatment | % Phosphorus (db) |
|-----------|------------|-------------------|
| Waxy | Slurry | 1.637a |
| | Dry-mixing | 1.600b |
| Common | Slurry | 1.516c |
| | Dry-mixing | 1.477d |
| Hylon V | Slurry | 1.346f |
| | Dry-mixing | 1.300h |
| Hylon VII | Slurry | 1.390e |
| | Dry-mixing | 1.340g |

^a Mean values of two replicates in a column followed by a common letter are not significantly different based on the Tukey test ($P < 0.05$).

Dry mixing involved the regulation of starch (300 g, db) moisture content to 35% (as is) before the extrusion process. The necessary additional water to reach 35% moisture content was used to dissolve 15 g of STPP, 6 g of STMP, and 15 g of sodium sulfate, and the solution was adjusted to pH 9.0 with 5% NaOH. The solution was added incrementally to the starch while mixing in a mixer (KitchenAid, St. Joseph, MI) and mixed for 30 min before proceeding to the extrusion process.

Phosphorus Content

The phosphorus content of starch phosphates was determined according to a standard analytical method (CRA 1999) as described in Landerito and Wang (2005).

Pasting Properties

Micro-viscoamylography (C.W. Brabender Instruments, South Hackensack, NJ) was used to measure the pasting properties of starch phosphates from waxy and common corn (7%, db), Hylon V (10%, db), and Hylon VII (15%, db). The slurries were first maintained at 50°C for 1 min, heated to 95°C at 3°C/min, held at 95°C for 3 min, and cooled to 50°C at 3°C/min. Pasting temperature, peak viscosity, breakdown, and total setback were obtained from the profile.

Thermal Properties

The effect of phosphate groups on the thermal stability of the starches was evaluated using differential scanning calorimetry (DSC) (Pyris-1, Perkin-Elmer Co., Norwalk, CT). Indium was used to calibrate the instrument and an empty pan was used as the reference. Starch (20.0 mg, db) was weighed into a standard stainless steel DSC pan and 40 µL of DI water was added using a microsyringe. The pan was hermetically sealed, allowed to stand for at least 1 hr before analysis, and scanned from 25 to 150°C at 10°C/min. Onset and peak temperatures and enthalpy were automatically computed. The gelatinized samples were stored at 4°C for 14 days and rescanned from 25 to 150°C at 10°C/min to obtain the enthalpy of the retrograded samples. The degree of retrogradation was calculated as the ratio of enthalpy change of retrograded starch to the enthalpy change of gelatinized starch.

Swelling Power

Swelling power was determined to study the effect of phosphate groups on the swelling characteristics of the starch granules. Starch suspensions (1.7%, 0.5 g of dry starch in 30 mL of DI water) in capped centrifuge tubes were placed in a water bath of 65, 85, or 95°C for 30 min. The heated samples were then rapidly cooled to room temperature in an ice water bath and centrifuged at 7,700 × *g* for 20 min. Each sedimented paste weight was measured and then divided by its initial weight to obtain its swelling power (Holm et al 1985).

Freeze-Thaw Stability

The starch pastes obtained after each micro-viscoamylograph run were used to determine freeze-thaw stability following the method of Wu and Seib (1990).

Structural Characteristics

The β-amylolysis limit was determined using the method of Hizukuri et al (1981) as described in our previous study (Landerito and Wang 2005). The precipitate from the β-amylolysis limit analysis (i.e., β-limits dextrin) was recovered for the structure characterization using a high-performance anion-exchange chromatography with pulse amperometric detection (HPAEC-PAD) (Dionex DX500, Sunnyvale, CA) (Landerito and Wang 2005). The system consisted of a LC20-1 chromatography organizer, GP50 gradient pump, ED40 electrochemical detector, 4×50-mm CarboPac PA1 guard column, 4×250-mm CarboPac PA1 analytical column, and AS40 automated sampler.

Statistical Analyses

All analyses were done in duplicate. Experimental data were analyzed by using ANOVA (SAS Institute, Cary, NC). Significant differences among treatments and starch types were identified using the Tukey test at the 95% confidence level.

RESULTS AND DISCUSSION

Optimization of Extrusion Parameters

The phosphorus contents of starch extrudates using a twin-screw extruder are listed in Table I. The results indicated that higher zone temperatures and higher moisture contents produced starch extrudates with higher phosphorus contents. Although the phosphorus content from each condition directly reflected the extrusion efficiency, there were other important qualities that needed to be taken into consideration when selecting the optimum extrusion parameters. Among the tested conditions, A3 produced starch phosphate extrudates with good quality in terms of color, texture, processibility, and reproducibility besides its high phosphorus content. The zone temperatures in conditions A1 and A2 were not sufficient to quickly gelatinize the starch at 35% moisture content, thus starch experienced a longer residence time that produced a burnt-like product. Conditions B1–B3 and C1–C3 incorporated a much higher moisture content where the plasticizing effect of water produced a plastic-like product that required subsequent drying before grinding, which might not be desirable in commercial production. Therefore, condition A3 was selected to produce starch phosphates in the following work.

Phosphorus Content

The phosphorus contents of extruded starch phosphates are presented in Table II. Waxy starch extrudates contained the highest phosphorus content, followed by common corn starch and then the two high-amylose starches. This trend was similar to that when using oven heating (Landerito and Wang 2005), except that the amounts of incorporated phosphorus by extrusion were approximately three to four times greater than those by oven heating, agreeing with Chang and Lii (1992) in a similar study, although they used only STPP and a single-screw extruder. The

high temperature, pressure, and mechanical shearing used in extrusion contributed to the enhanced phosphorylation. As a result, the waxy starch phosphates contained a larger amount of phosphorus than the other starch types, which suggests that starch with a higher amylopectin ratio is more susceptible to phosphorylation. It has been proposed that short chains in amylopectin were as reactive as amylose (Morrison et al 1984; Batres and White 1986; Schierbaum et al 1986; Eliasson and Ljunger 1988). Compared with amylose, the branching structure of amylopectin might help retain more phosphate salts for later phosphorylation, which otherwise would be distributed to amorphous regions where few starch molecules were present. However, it is not clear why Hylon VII showed better phosphorylation efficiency than Hylon V using extrusion, which was also observed when oven heating was used for phosphorylation (Landerito and Wang 2005).

The slurry treatment was slightly yet significantly more effective in incorporating phosphate groups into the starches compared with the dry-mixing treatment, possibly a result of better mixing. Starches prepared by the slurry treatment had an initial moisture content of 55% before being dried to 35% for the extrusion process. This amount of water was probably sufficient to hydrate most starch granules and at the same time to distribute the dissolved phosphate salts to all hydrated starch molecules for phosphorylation. In contrast, a smaller amount of water was added to starch in the dry-mixing treatment to a final moisture content of 35%, which might limit the distribution of water and phosphate salts, thus limiting phosphorylation efficiency (Landerito and Wang 2005).

Pasting Properties

The pasting properties of extruded native and phosphorylated starches from each starch type prepared by using the slurry and the dry-mixing treatment are presented in Figs. 1 and 2. The extruded starch phosphate exhibited a lower pasting temperature and higher peak and final viscosities compared with its unmodified, unextruded counterpart. Extruded starch phosphate was also characterized by an early swelling of starch upon heating. As suggested by Becker et al (2001), this is a common characteristic of extruded starches, in contrast to unextruded starches, due to partial gelatinization during extrusion. Moreover, extruded unmodi-

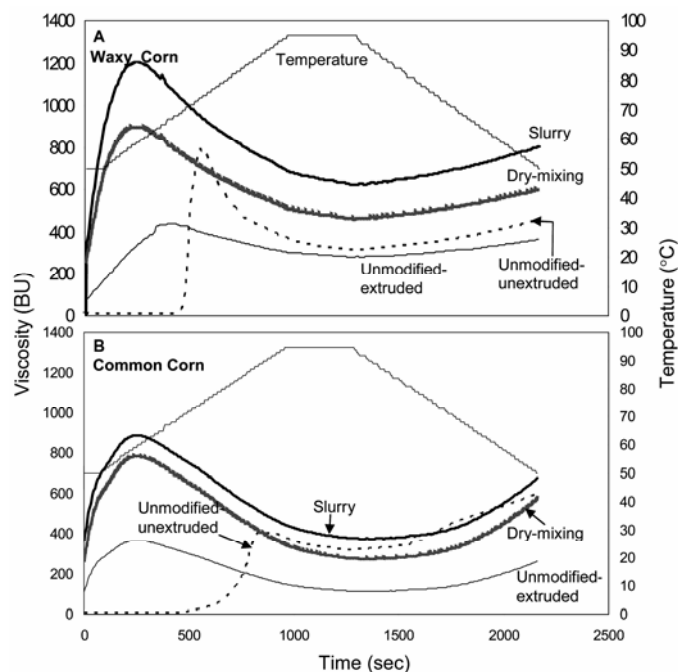


Fig. 1. Representative pasting curves of unextruded native starches and extruded phosphorylated starches using the slurry and dry-mixing treatments. **A**, Waxy corn (7%). **B**, Common corn (7%).

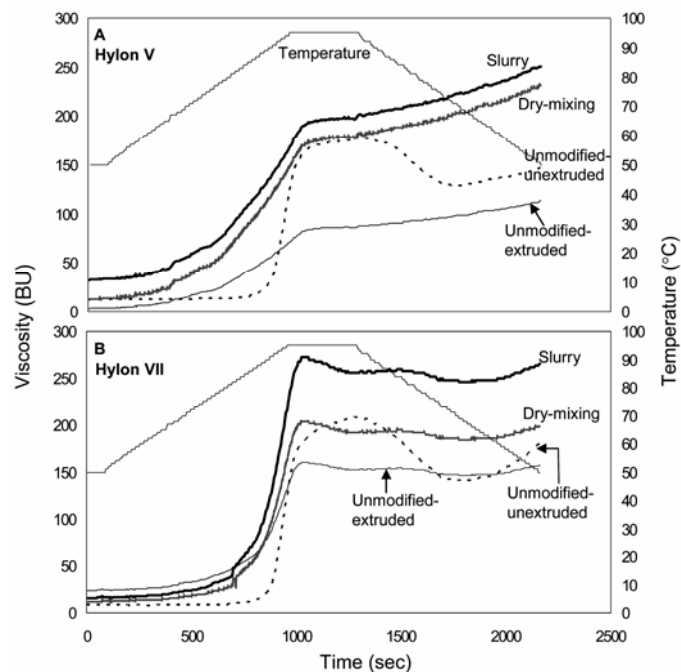


Fig. 2. Representative pasting curves of unextruded native starches and extruded phosphorylated starches using the slurry and dry-mixing treatments. **A**, Hylon V (10%). **B**, Hylon VII (15%).

fied or modified starches usually show a lower viscosity profile compared with unmodified or modified starches by conventional processes. This can be attributed to disintegration of starch structure from the high shearing, pressure, and temperature conditions in extrusion (Davidson et al 1984; Chang and Lii 1992). The damaged starch granules can be more easily penetrated by water, consequently decreasing the temperature of gelatinization, but producing a lower viscosity profile.

Among the phosphorylated starches, waxy starch phosphates produced the highest peak viscosity while the two high-amylose starches showed the lowest. Waxy corn starch phosphate also showed the largest breakdown among the phosphorylated starches. Extruded Hylon V and VII starch phosphates showed little or no breakdown, even with an increase in viscosity during holding at 95°C for Hylon V, compared with the oven-treated counterparts (Landerito and Wang 2005). These results indicate that extrusion helped expose the highly inhibited structure of high-amylose starches to become available to interact with water. An unmodified starch was also extruded for comparison to illustrate the effects of extrusion versus phosphorylation. The reduced pasting temperatures and increased pasting viscosities for all extruded starch phosphates when compared with unmodified extruded counterparts clearly demonstrated the influence of phosphate introduction.

Starches that were prepared using the slurry treatment exhibited a higher viscosity profile than those prepared using the dry-mixing treatment. This was attributed to the larger amount of phosphorus incorporated using the slurry treatment as previously discussed. The location where phosphorylation occurred might also be different, thereafter contributing to the observed difference in pasting properties. These results agreed with our previous study where slurry-treated starches gave a higher viscosity profile than the starches from the dry-mixing treatment using oven phosphorylation (Landerito and Wang 2005).

Thermal Properties

The thermal properties of unmodified and extruded phosphorylated starches are summarized in Table III. The extruded starch phosphates showed significantly lower onset and peak gelatinization temperatures and enthalpy from the addition of phosphate groups and the disruption of the crystalline structure during extrusion. Extruded, phosphorylated waxy starch had lower onset and peak temperatures, whereas those of phosphorylated high-amylose starch were higher, reflecting the inherent structure difference in parent starches. Phosphate groups assisted in destabilizing starch structure, which therefore was easily disrupted by an increase in temperature. The swelling starts in the amorphous region where amylose polymers are located; this region is considered to have weaker structures when compared with the crystalline region (Wang et al 1992; Yuan et al 1993; Zheng et al

1997). The majority of the crystalline structures in all starch types were disrupted by extrusion, as indicated by their very low gelatinization enthalpy.

After storage for 14 days, both waxy and common starches showed minimal retrogradation, whereas high-amylose starches retrograded to a greater extent, with Hylon VII showing >20% retrogradation. The higher phosphate content and fragmentation of starch molecules during extrusion contributed to the observed low degree of retrogradation in extruded starch phosphates when compared with starch phosphates prepared by oven heating (Landerito and Wang 2005).

Extruded starch phosphates produced by the slurry treatment showed lower onset and peak gelatinization temperatures, enthalpy, and degree of retrogradation than those produced by the dry-mixing treatment. The higher phosphorus content incorporated with the slurry treatment was assumed to contribute to these differences. The location of introduced phosphate groups might also differ for starch phosphates prepared by the two treatments, which in turn might result in a different extent of destabilization.

Swelling Power

The swelling power of native and phosphorylated starches are shown in Fig. 3. It is evident that all phosphorylated starches showed a greater swelling ability than native starches. Native starch requires water and heat to swell due to the packing and hydrogen bonding of the starch molecules within the granule (Becker et al 2001). After phosphorylation, the repulsive effects from incorporated phosphate groups facilitated water penetration, resulting in a greater swelling capacity. The availability of starch to interact with water, which controls starch gelatinization and swelling (Rubens and Heremans 2000), was greatly improved with extrusion. Extrusion might also enhance water distribution within the starch as opposed to unmodified starch.

Swelling power was higher for waxy starch phosphate but lower for high-amylose starch phosphates because swelling was essentially a property of amylopectin (Tester and Morrison 1990). Swelling power was slightly lower for phosphorylated starches from extrusion than from oven heating (Landerito and Wang 2005), agreeing with their pasting properties (Figs. 1 and 2). Samples prepared from the slurry treatment showed a better swelling ability than those prepared from the dry-mixing treatment, which was similar to the oven phosphorylation study (Landerito and Wang 2005). This was probably due to slightly higher phosphate contents or different phosphorylation locations.

Freeze-Thaw Stability

The freeze-thaw stability of both extruded native and phosphorylated starches from different starch types and sample treatments using extrusion is displayed in Fig. 4. Amylose content is the predominant factor controlling the degree of syneresis of

TABLE III
Thermal Properties of Unmodified and Extruded Phosphorylated Starches Using Slurry and Dry Mixing Treatments^a

| Samples | Treatment | Gelatinization | | | Degree of Retrogradation (%) 14 days |
|-----------|------------|-----------------|----------------|----------------|---|
| | | Onset Temp (°C) | Peak Temp (°C) | Enthalpy (J/g) | |
| Waxy | Unmodified | 70.3d | 76.1c | 12.7a | 35.2d |
| | Slurry | 46.4j | 51.2k | 1.5f | 4.1l |
| | Dry-mixing | 48.6i | 53.2j | 1.9f | 5.4k |
| Common | Unmodified | 71.0c | 74.5d | 11.0b | 37.9c |
| | Slurry | 50.3h | 55.8i | 2.2e | 5.7j |
| | Dry-mixing | 52.3g | 59.0h | 3.0d | 6.5i |
| Hylon V | Unmodified | 71.9b | 80.1b | 10.2c | 47.9b |
| | Slurry | 54.3f | 65.0e | 1.0f | 10.2h |
| | Dry-mixing | 56.6e | 63.9f | 1.6f | 11.5g |
| Hylon VII | Unmodified | 74.5a | 82.9a | 11.7b | 53.7a |
| | Slurry | 54.4f | 60.9g | 1.0f | 20.5f |
| | Dry-mixing | 56.8e | 63.1f | 1.2f | 21.9e |

^a Mean values of two replicates in a column followed by a common letter are not significantly different based on the Tukey test ($P < 0.05$).

starch pastes (Varavinit et al 2000). Thus, unmodified high-amylose starches had the largest amount of water separated within each cycle. Unmodified waxy starch showed better freeze-thaw stability among the native starches because of the entire highly branched structure of amylopectin, which hinders association of starch chains. Phosphorylated starches held water tighter than the native counterparts because the repulsion from the charged phosphates delayed starch reassociation. San Martín-Martínez et al (2004) found that water absorption of extruded starch increased under optimized extrusion conditions, which resulted in a higher degree of phosphorylation and less starch fragmentation.

Phosphorylated starch extrudates prepared from the slurry treatment exhibited improved freeze-thaw stability over those prepared from the dry-mixing treatment, presumably because of its higher phosphorus content. The difference could also be attributed to potentially different phosphorylation locations. Among the extruded phosphorylated starches, common corn starch showed the lowest syneresis within each cycle, agreeing with Schierbaum et al (1986). It was proposed that there was a heterogeneous melting in common corn starch where the remaining crystalline structure was more resistant to fragmentation from shear and heating compared with that of waxy corn starch.

Structural Characteristics

Table IV summarizes the structural characteristics of different starch phosphates. Starch phosphates produced by extrusion showed lower values of β -amylolysis limit when compared with their parent starches. The extent of decrease in β -amylolysis limit from extrusion, nonetheless, was not as large as that in the oven-heating process, assuming that fragmentation of starch increased β -amylolysis limit by creating more available starch molecules for β -amylase to hydrolyze. The introduced phosphate groups might exert a blocking effect against β -amylase by competing for metal ions that are essential to β -amylase activity (Feller et al 1996; D'Amico et al 2000) or the hydroxyl groups substituted by phosphates were essential for β -amylase activity (Evers et al 1997).

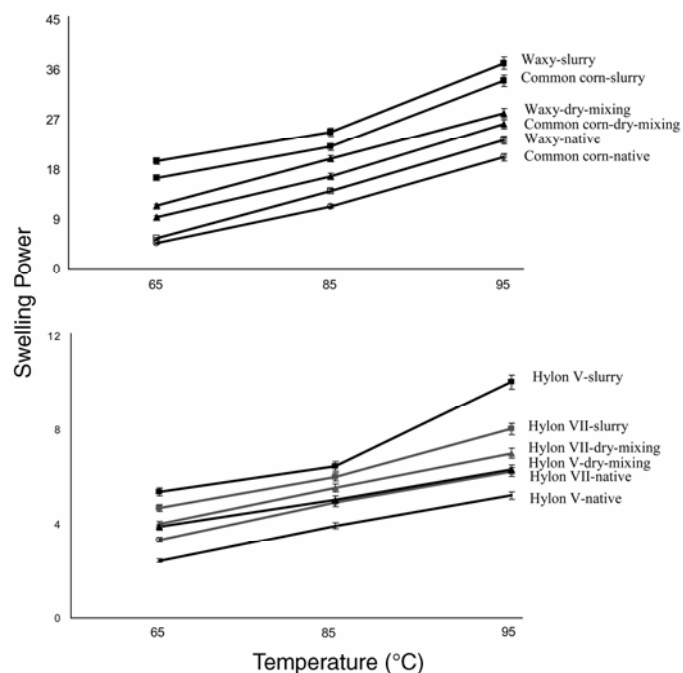


Fig. 3. Swelling power of native and phosphorylated starch from four different starch types and two sample treatments using extrusion. **A**, Waxy and common corn starches. **B**, Hylon V and VII high-amylose corn starches.

There were also differences in β -amylolysis limit between starch types and sample treatments, which was primarily attributed to the amount and possibly the location of incorporated phosphate groups. Extruded starch phosphates prepared by the slurry treatment had a lower β -amylolysis limit value compared with those prepared by the dry-mixing treatment. Again, better mixing during the slurry treatment improved the efficiency of phosphorus incorporation. The possible locations of phosphate groups in extruded starches were studied by HPAEC-PAD and expressed as distribution of percentage of degree of polymerization (DP). During β -amylolysis limit analysis, the β -amylase hydrolyzed the starch starting from the nonreducing end of the starch chain until it reached the phosphate group, where it blocked the enzyme's action. The remaining starch structure was then debranched by isoamylase and the degree of polymerization was determined. There were four major DP groups observed. A sample with a high amount of DP 1–2 was assumed to have phosphate groups located near the branching point, while more DP 3–4 suggested phosphate groups close to the nonreducing end. More phosphate groups in common and high-amylose starch phosphates prepared by the slurry treatment were located near the nonreducing ends as indicated by higher percentages of DP 4, whereas those prepared by dry mixing were closer to the branching points. Nevertheless, the opposite trend was observed for waxy starch phosphates using the two different sample treatments. These results were different from those reported in our previous study of oven heating (Landerito and Wang 2005), in which more phosphate groups were bound closer to the branching points in slurry-reacted starch phosphates when compared with starch phosphates from dry mixing, with the exception of Hylon V starch phosphates. There was no clear trend between β -amylolysis limit values and DP distribution of β -limit dextrin for different starch types and for different sample treatments in this study. The fragmentation of starch, particularly amylose, during extrusion might explain the inconsistency of these results with those by oven heating.

CONCLUSIONS

This study demonstrated that the extent of phosphorylation varied with starch type and for sample preparation in addition to extrusion conditions. Waxy and common corn starches were more susceptible to phosphorylation when compared with high-amylose corn starches. Extrusion was a very effective way to prepare starch phosphates. Its high temperature, shearing, and pressure allowed more efficient phosphorus incorporation into starch in a considerably shorter period of time. Phosphorylation improved the properties of the extruded starches with increased swelling, better water binding ability, reduced retrogradation, and greater resistance to β -amylase hydrolysis. The slurry treatment was more effective in incorporating phosphorus into starch when compared with the dry-mixing treatment. The slurry-reacted starch phosphates

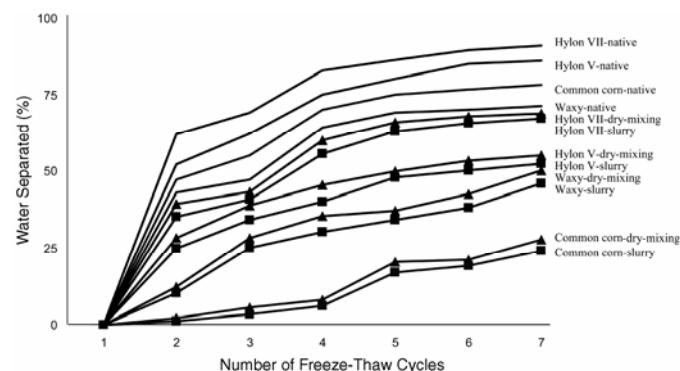


Fig. 4. Freeze-thaw stability of native and phosphorylated starches from four different starch types and two sample treatments using extrusion.

TABLE IV
Structural Characteristics of Unmodified and Phosphorylated Starches
from Four Different Starch Types and Two Sample Treatments Using Extrusion^a

| Samples | Treatment | β -Amylolysis Limit (%) | β -Limit Dextrin % Area | | | |
|-----------|------------|----------------------------------|-------------------------------|-------|-------|-------|
| | | | DP 1 | DP 2 | DP 3 | DP 4 |
| Waxy | Unmodified | 54.1b | 6.4f | 85.8a | 3.0j | 4.7k |
| | Slurry | 50.2f | 11.0c | 83.7b | 5.2i | 0.7l |
| | Dry-mixing | 52.7d | 10.6d | 12.5h | 7.5h | 69.4b |
| Common | Unmodified | 61.6a | 1.5i | 16.9e | 72.4b | 9.3i |
| | Slurry | 51.4e | 6.5f | 1.6k | 17.8e | 74.0a |
| | Dry-mixing | 53.1c | 27.3a | 14.6f | 53.0d | 5.1j |
| Hylon V | Unmodified | 50.1f | 2.8h | 6.0i | 76.3a | 14.7g |
| | Slurry | 42.3i | 10.6d | 13.5g | 7.6h | 68.2c |
| | Dry-mixing | 45.1g | 9.1e | 23.7d | 57.1c | 10.1h |
| Hylon VII | Unmodified | 43.5h | 3.2g | 5.2j | 72.9b | 18.7f |
| | Slurry | 34.2k | 6.9f | 17.0e | 10.0f | 66.2d |
| | Dry-mixing | 38.2j | 21.8b | 34.6c | 8.5g | 35.1e |

^a Mean values of two replicates in a column followed by a common letter are not significantly different based on the Tukey test ($P < 0.05$).

exhibited lower gelatinization temperatures and enthalpy, higher pasting viscosity profiles, and improved swelling and freeze-thaw stability. These treatments possibly also affected the location of introduced phosphorus in starch granules.

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