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Cross-linking of wheat starch and hydroxypropylated wheat starch in alkaline slurry with sodium trimetaphosphate[1]

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Wheat starch was cross-linked at 40°C and pH 11.0 by slurrying the starch (30% solids) in a solution of sodium trimetaphosphate (STMP), sodium hydroxide, and sodium sulfate. The extent of cross-linking was determined by an increase in alkaline fluidity or by a decrease in alkaline clarity. Response surface analysis showed that cross-linking increased with increasing levels of STMP (0.5–1.5%, based on starch, bos) and sodium sulfate (0–4.0%, bos) over a reaction period of 120–720 min. A regression equation with first and second order terms showed that STMP and sodium sulfate concentrations and the reaction time accounted for 99% of the variability in alkaline fluidity. Wheat starch (37% slurry) was hydroxypropylated by reaction with propylene oxide (8%, bos) for 24 h at 45°C in alkali (pH 11.5) containing 16.0% sodium sulfate (bos). The hydroxypropylated (4.5 wt%) wheat starch (DS 0.12–0.13) was not isolated but was cross-linked with STMP (0.1–0.5%, bos) over a 10–40 min reaction period. A comparison of pasting curves at pH 3.5 showed that some of the cross-links produced by STMP were less stable than those produced by phosphoryl chloride, indicating a low level of pyrophosphate as well as monophosphate cross-links. The less stable cross-links were diminished by changing reaction conditions with STMP. Copyright © 1997 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Cross-linked starches are used widely as thickeners in foods, particularly where a high and stable viscosity is needed. Cross-linking minimizes granule rupture, loss of viscosity, and formation of a stringy paste during cooking. Cross-linking is performed by treating granular starch with multifunctional reagents capable of forming ether or ester linkages with hydroxyl groups in starch (Rutenberg and Solarek, 1984; Wurzberg, 1986).

In the USA, the following agents may be used legally (CFR, 1995) to cross-link food grade starches: monosodium phosphate (SOP), sodium trimetaphosphate (STMP), sodium tripolyphosphate, epichlorohydrin, phosphoryl chloride ($POCl_3$), a mixture of adipic and acetic anhydrides, and a mixture of succinic anhydride and vinyl acetate. Two agents, $POCl_3$ and STMP, may be used alone to give singly modified (cross-linked) starches or in combination with other reagents to give doubly modified starches.

$POCl_3$ is an efficient cross-linking agent in aqueous slurry at pH > 11 in the presence of a neutral salt (Felton and Schopmeyer, 1943; Wetzstein and Lyon, 1956; Wu and Seib, 1990). But $POCl_3$ is a toxic chemical that fumes on contact with humid air. On the other hand, STMP is a solid of low toxicity with no reported adverse effects on humans. STMP is reported to be an effective cross-linking agent at high temperature with semidry starch and at warm temperature with hydrated starch in an aqueous slurry (Kerr and Cleveland, 1957, 1958, 1959, 1960, 1962; Srivastava and Patel, 1973).

Hydroxypropylation of starch improves the cold-temperature stability of its paste, decreases cooking temperature, and improves paste clarity (Tuschhoff *et al.*, 1969; Rutenberg and Solarek, 1984; Wurzberg, 1986). However, a hydroxypropylated starch that is not cross-linked swells excessively during cooking to

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produce a stringy paste that is unstable to shear and acid.

The level of cross-linking in a modified starch must be controlled carefully, yet quantifying phosphodiester cross-links in starch by chemical means is difficult. Attempts to determine the number of cross-links by increases in total phosphorus level in starch are confounded by endogenous phospholipids, and by the formation of phosphomonoesters (Kasemsuwan and Jane, 1994). Differential titration of phosphodiesters and monoesters is compromised by the presence of fatty acids, phospholipids, and proteins (Mitchell, 1972). For those reasons, cross-linking of starch often is measured by changes in physical properties, such as paste consistency, paste volume, and optical clarity in hot water or cold alkali (Jarowenco, 1971; Rutenberg and Solarek, 1984; Wurzberg, 1986). Alkaline fluidity (Tuschhoff and Smith, 1966; Tuschhoff *et al.*, 1969; Robinson *et al.*, 1973) and alkaline clarity (Craig *et al.*, 1989; Lim and Seib, 1993) are two convenient measures of cross-linking.

The objectives of this study were to determine the conditions to cross-link wheat starch and hydroxypropylated wheat starch in alkaline slurry with STMP and to determine the levels of STMP and $POCl_3$ that give equivalent cross-linking of hydroxypropylated wheat starch.

MATERIALS AND METHODS

Materials

Wheat starch (Midsol 50) was provided by Midwest Grain Products (Atchison, KS).

STMP was purchased from Sigma Chemical Company (St Louis); $POCl_3$ from Aldrich Chemical Company (Milwaukee, WI); and propylene oxide from Fisher Scientific (Fairlawn, NJ). All other chemicals were reagent grade unless otherwise specified.

Determination of phosphorus in starch

Phosphorus in wheat starch (5–10 g sample size) was determined by the procedure of Smith and Caruso (1964), and phospholipid content by the formula, lipids(%) = 16.4 × P(%) (Morrison, 1988). Endogenous phosphorus in wheat starch occurs as lysophospholipids with only traces of starch phosphates (Morrison *et al.*, 1984; Lim *et al.*, 1994).

Paste consistency

Pasting of starch was examined in a Brabender Viscograph-E (C.W. Brabender Instruments, Hackensack, NJ) at 700 cm g and 75 rpm. An aqueous slurry of starch (8%, dry basis) was heated at a rate of 1.5°C/min from 30 to 95°C, maintained at 95°C for 30 min, cooled to 50°C, and held at 50°C for 30 min (Mazurs *et al.*, 1957; Tipples, 1980). In some pasting experiments, an aliquot (3.0–3.5 ml) of aqueous HCl (0.1 M) was added to the slurry to give pH 3.5.

Degree of cross-linking

A funnel (mass 156 g) was fabricated from a 1 mm thick stainless steel sheet and a 27 mm diameter rod ($L = 23$ mm). The inverted 60° conical cavity had an inlet with a diameter of 104 mm, a height of 82 mm, and a capillary outlet at the bottom with a diameter of 2 mm and a length of 12 mm. Starch (2.000 g, dry basis) or hydroxypropylated starch (1.500 g, dry basis) was added slowly with mild stirring into 0.95% aqueous sodium hydroxide (100 ml) at 25°C. The paste was stirred for 5 min and transferred quantitatively into the plugged stainless steel funnel that had been equilibrated previously to 25°C. The plug was removed, and the volume (ml) of starch solution flowing through the funnel in 40 s was recorded, which was the time required for 100 ml of water at 25°C to flow through the funnel (Robinson *et al.*, 1973).

To measure paste clarity, an aliquot (0.5 ml) of the 1.5–2.0% alkaline paste was added to a test tube containing water (4.5 ml) at 25°C. The mixture was shaken gently by hand, and the transmittance (%T) at 650 nm was determined immediately. The tests for alkaline fluidity and clarity were replicated three times.

Cross-linking of wheat starch with $POCl_3$

Cross-linking of starch with $POCl_3$ was done essentially by the method of Felton and Schopmeyer (1943). Wheat starch (50 g, dry basis) was slurried for 1 h at 25°C in water (70 ml) containing sodium sulfate 1 g (2.0%, bos). The slurry was adjusted to pH 11.0 by slowly adding 1 M sodium hydroxide while maintaining temperature at 25°C. Phosphoryl chloride (5–50 μl, 8.2–82.3 mg or 0.016–0.168%, bos) was injected with a microliter syringe into the starch slurry. After 1 h, the slurry was adjusted to pH 5.5 with 1 M hydrochloric acid, and the starch was recovered by centrifuging (15,000 g, 10 min); washing with water (4 × 100 ml); and drying at 40°C. Fluidity and paste clarity were measured on the samples, and on a blank sample treated in the same manner without phosphoryl chloride.

Cross-linking of wheat starch with STMP

Cross-linking of starch with STMP was done by the procedure of Kerr and Cleveland (1957). A series of preliminary experiments were undertaken, all at 40°C, to determine cross-linking conditions. Wheat starch (30 g, dry basis) was stirred for 8 h in water (60 ml) containing sodium sulfate (0.6 g) and STMP (0.3, 0.6, 0.9, and 1.2 g) at pH 10.5, 11.0, and 11.5. In other reactions, cross-linking was done at pH 11.0 for 8 h with STMP (0.3 g) and 5 levels of sodium sulfate (0, 0.3, 0.6, 0.9, and 1.2 g), or with sodium sulfate (0.6 g) and STMP (0.6 g) at pH 11.0 and three temperatures (25, 35, 45°C) for 0–16 h. The pH of all reactions was adjusted by adding 1.0M sodium hydroxide. After a reaction, the pH of the slurry was recorded and then adjusted to 6.5 by adding 1.0M hydrochloric acid. The starch was washed with water (4 x 100 ml) and dried at 40°C. One blank sample was prepared by running at pH 11.0 for 6 h with sodium sulfate (0.6 g), but with no STMP.

Cross-linking conditions, also were modeled by response surface analysis using statistical software Version 6.10, SAS Institute (Cary, NC). Three independent variables were selected: level of STMP (0.5, 1.0, 1.5%, based on starch, bos); level of sodium sulfate (none, 2.0, 4.0%, bos); and reaction time (2, 4, 6 h). Three other variables were kept constant: initial starch solids at 30%, alkalinity at pH 11.0, and temperature at 40°C. Three dependent variables were monitored: the final pH of a reaction mixture and fluidity and clarity of the modified starch. Contour plots for each quality parameter were generated as a function of two variables, while the other variable was held constant.

Hydroxypropylated and cross-linked wheat starch

Hydroxypropylated and cross-linked wheat starch was prepared by the procedure of Tuschhoff *et al.* (1969). Wheat starch (31.4 g, dry basis) was slurried in water (48.2 ml) with sodium sulfate (4.5g) and a solution (5.2 ml) of 1.5 M sodium hydroxide and 0.75 M sodium sulfate was added to pH 11.5. Propylene oxide (2.96 ml, 2.51 g) was added, and the reaction vessel (200 ml glass bottle) was sealed with a screw cap and placed in a constant temperature bath at 45°C. After 24 h, the reaction was cooled to room temperature and $POCl_3$ (5–50 μl, 8.2–82.3 mg) was added with stirring at 25°C (Felton and Schopmeyer, 1943). If cross-linking was done with STMP, the hydroxypropylation mixture was maintained at 45°C, and STMP (94.2 mg) was added with continued stirring. After 10, 25, and 40 min, hydroxypropylated and cross-linked wheat starch samples were isolated as described previously. Each reaction was replicated four times.

Measurement of hydroxypropyl content of doubly modified wheat starch

The level of hydroxypropylation of starch was determined by high resolution ^{1}H-NMR spectroscopy of the starch's alpha-limit dextrin (Xu and Seib, 1996). The measurements were replicated four times.

RESULTS AND DISCUSSION

Cross-linking of wheat starch with $POCl_3$

Hudson and Moss (1962) investigated the reaction of $POCl_3$ in excess water. The first chloride ion is removed rapidly ($t_{1/2} \approx 0.01$ s) by water at 25°C, whereas the second and third chloride ions react relatively slowly and simultaneously ($t_{1/2} \approx 250$ s). Those results indicate that adding $POCl_3$ to a 30–40% starch slurry would produce mostly dichlorophosphate by its initial reaction with the large excess of water. The dichlorophosphate then would diffuse into starch granules, where it would react with the polymer chains.

Cross-linking of starch molecules to give a distarch monophosphate (Kasemsuwan and Jane, 1994) is favored by alkalinity above pH 10 and by the presence of a neutral sodium salt (Wetzstein and Lyon, 1956; Wu and Seib, 1990; Kasemsuwan and Jane, 1994). Otherwise, monostarch monophosphate esters are formed. Increasing the alkalinity in the cross-linking medium increases starch anion concentration, while increasing sodium ion concentration increases the uptake of alkali by starch as well as the ionic strength of the reaction medium. Those factors would be predicted to accelerate the bimolecular reaction between starch and dichlorophosphate (see discussion below).

Reaction of wheat starch with up to 0.07% (bos) $POCl_3$ at pH 11.0 in the presence of 2.0% sodium sulfate (bos) (approximately 0.05M in the aqueous phase) caused a rapid change in fluidity and clarity, but little additional change upon addition from 0.07 to 0.1% (bos) (Fig. 1). Wheat starches cross-linked with

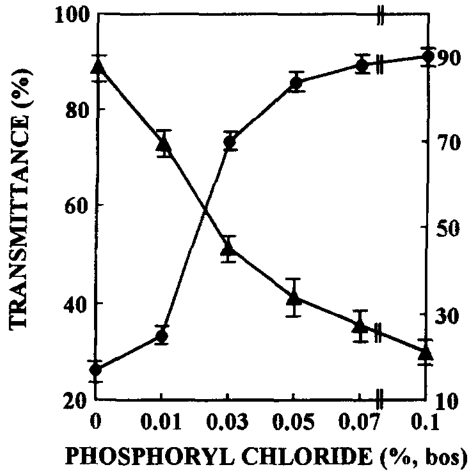

Fig. 1. Cross-linking of wheat starch with phosphoryl chloride for 1 h at 25°C and pH 11.0 in the presence of 2.0% sodium sulfate (bos, based on starch). Cross-linking was measured at 25°C by alkaline fluidity (●) of 2.0% starch in 0.95% sodium hydroxide and by alkaline clarity (▲) after a 9-fold dilution of the alkaline paste with water.

more than ≈0.07% $POCl_3$ could not be distinguished by either alkaline fluidity or clarity as measured in this investigation. The sensitivity of those tests for cross-linking with 0.07% $POCl_3$ might be increased by increasing the concentration of modified starch or alkali or both.

Maningat (1986) investigated the amylograph pasting curves of wheat starch that had been cross-linked with 0.005–0.3% $POCl_3$ at pH 11.0 in the presence of 15% sodium sulfate. Wheat starch that was reacted with 0.01–0.03% $POCl_3$ gave somewhat higher consistency pastes at 10% starch solids than did prime wheat starch, whereas those cross-linked with 0.05–0.30% $POCl_3$ gave ever-decreasing paste consistencies.

A wheat starch paste cooked at 90–100°C without high shear is a composite structure consisting of swollen granules (tiny beads of gel) suspended in a dilute solution of amylose (Doublier *et al.*, 1987; Steeneken, 1989). The consistency of the paste is considered directly proportional to the swollen volume of the gel beads and their stiffness (Evans and Haisman, 1979; Eliasson and Bohlin, 1982; Steeneken, 1989). The sensitivity of the amylogram pasting curve to cross-linking of wheat starch between 0.07 and 0.3% $POCl_3$ (Maningat, 1986) may be due to high shear in the amylograph compared to the low shear in the alkaline fluidity test.

Cross-linking of wheat starch with STMP

Cross-linking of wheat starch (30% starch) with STMP (0.5–2.0%, bos) in the presence of sodium sulfate (2.0%, bos) was accelerated with increasing alkalinity from pH 10.5 to 11.5 (Fig. 2) and by increasing temperature from 25 to 45°C (Fig. 3). Gelatinization of wheat starch in the warm alkaline reaction mixture was inhibited by adding sodium sulfate, which also promoted cross-linking (Fig. 4). In an 8 h reaction of wheat starch with 1.0% STMP (bos) at pH 11.0 and 40°C, doubling the concentration of sodium sulfate to 4.0% (bos) (approximately 0.1M) caused cross-linking to increase up to the limit of detection by either alkaline fluidity or clarity. Kerr and Cleveland (1957) and Kerr and Cleveland (1958) reported much faster cross-linking with STMP at alkaline pH 9–11 when the sodium ion concentration was increased from 0.15 to 0.4M. Other results in this study (see below) show that cross-linking with STMP is accelerated even more when sodium ion is increased above 0.1M.

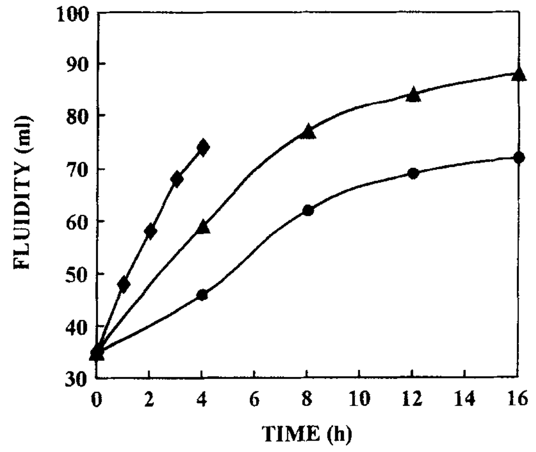

Fig. 3. Cross-linking (alkaline fluidity) of wheat starch with 2.0% STMP (bos) and 2.0% sodium sulfate (bos) at pH 11.0 and 25°C (●), 35°C (▲), and 45°C (◆).

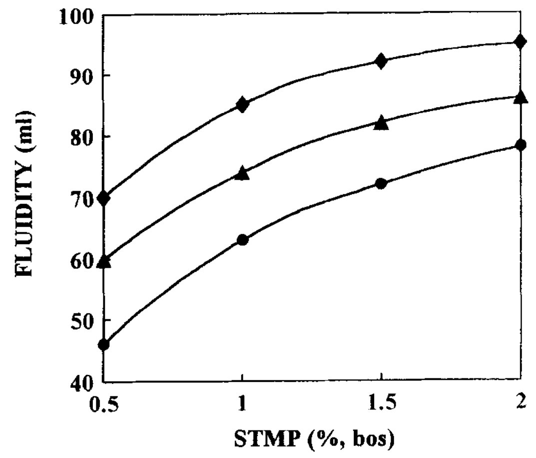

Fig. 2. Cross-linking (alkaline fluidity) of wheat starch (30% slurry) with sodium trimetaphospate (STMP) in the presence of 2.0% sodium sulfate (bos) at 40°C for 8 h at pH 10.5 (●), 11.0 (▲), and 11.5 (◆). The levels of 0.5–2.0% STMP (bos) in the reaction mixture were equivalent to 0.005–0.020M, and the 2.0% level of sodium sulfate (bos) to 0.02M.

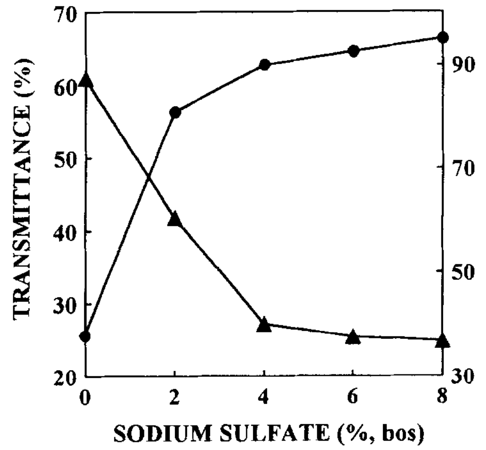

Fig. 4. Cross-linking of wheat starch (30% slurry) with 1.0% STMP (bos) at pH 11.0 and 40°C for 8 h. Cross-linking was measured at 25°C by alkaline fluidity (●) of 2.0% starch in 0.95% sodium hydroxide and by alkaline clarity (▲) after a nine-fold dilution of the alkaline paste with water.

Ionization of amylose in alkali at pH ≈ 11 has been detected by changes in the polarization of fluorescein-substituted amylose, in intrinsic viscosity, and in optical rotation (Kitamura *et al.*, 1982). The reaction of metaphosphate is faster with alkoxy anions than with non-ionized alcohols (Feldman, 1967; Liao and Seib, 1990), which explains the increased extent of cross-linking with STMP at high pH (Fig. 2). In contrast to cross-linking of granules in aqueous slurry, where the reaction was fast at an initial pH ≥ 11, cross-linking by roasting semidry starch with STMP was fast at an initial pH ≥ 10 (Lim and Seib, 1993). In the roasting reaction, where the amount of base present was small, the alkalinity of the reaction products decreased by 2–4 pH units. However, in the alkaline slurry cross-linking with STMP done in the present investigation, the alkalinity of the reaction mixture declined by no more than 0.3 pH units.

Why a high concentration of sodium sulfate in the slurry with STMP increased the extent of cross-linking is less clear (Fig. 4). As previously mentioned, this same phenomenon was observed first when cross-linking was done with $POCl_3$ (Wetzstein and Lyon, 1956; Rutenberg and Solarek, 1984; Wu and Seib, 1990). Rutenberg and Solarek (1984) suggested that sodium sulfate builds water structure and allows deeper penetration of reagent into the granule. Another possible explanation is that ionic strength promotes reaction between a starch alkoxide ion and an ionic phosphoryl reactant. Reactions between two negatively charged species are expected to increase with ionic strength (Gould, 1959; Hine, 1962). Moreover, ionization of weak acids (starch hydroxyls) is also promoted by ionic strength. Finally, sodium ions increase the alkali adsorbed by starch granules (Leach *et al.*, 1961), which has been attributed to the ion-exchange properties of starch (Oosten, 1990).

Response surface analysis yielded a regression equation expressing cross-linking (alkaline fluidity) of wheat starch as a function of the concentrations of STMP (X) and sodium sulfate (Y), and time (Z). In the cross-linking reaction at 40°C, pH 11.0, and 30% starch solids,

$$\begin{aligned}\text{Fluidity(ml)} &= -44.4 + 24.0X + 12.7Y + 22.0Z \\ &\quad - 2.1Y^2 - 2.1Z^2 + 1.3YZ (R^2 = 0.99).\end{aligned}$$

Contour plots calculated from the regression equation for alkaline fluidity are shown in Fig. 5. The higher rate of cross-linking with increasing concentration of sodium sulfate is immediately obvious by comparing Fig. 5 (A), (B) and (C). Nevertheless, Fig. 5 (A) shows that granular cross-linked wheat starch could be produced without the use of sodium sulfate at pH 11.0 and 40°C, provided extra reaction time or additional STMP were used. Figure 5 also shows that tripling the reaction time from 2 to 6 h was more effective in increasing cross-linking than tripling the concentration of STMP from 0.5 to 1.5% (bos).

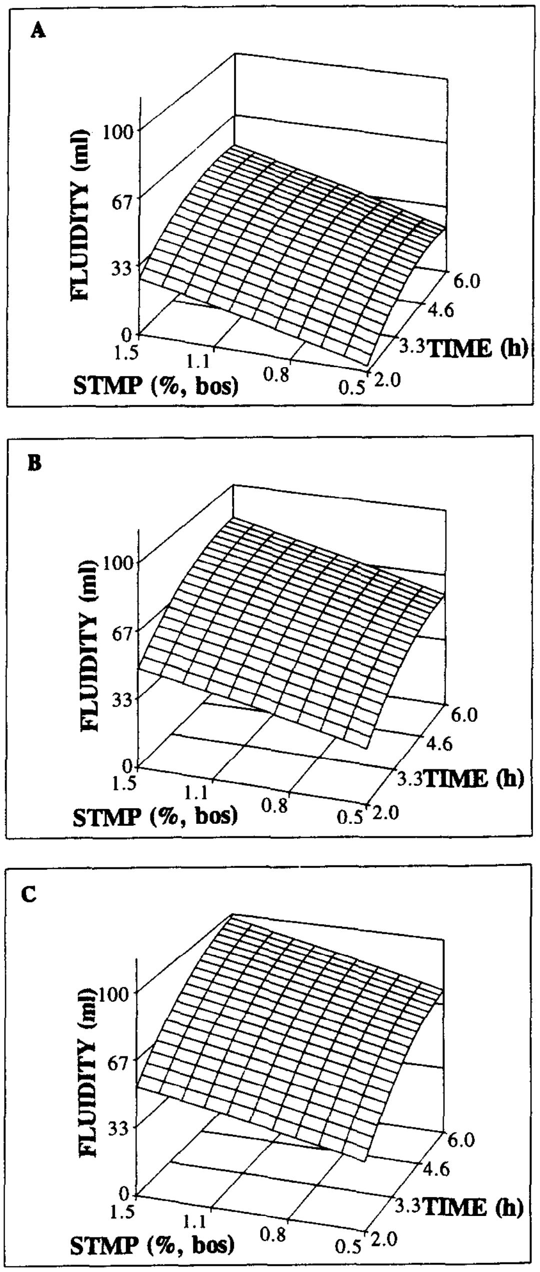

Fig. 5. Contour plots of the cross-linking of wheat starch (30% slurry) at 40°C and pH 11.0 with sodium sulfate concentration (bos) at (A) 0%, (B) 2.0%, (C) 4.0%. Cross-linking was measured by alkaline fluidity of 2.0% modified starch in 0.95% sodium hydroxide at 25°C.

The alkaline fluidity of prime wheat starch was 35 ml, and its phosphorus content 0.055%, almost all of which was lysophospholipid (0.90%). Stirring wheat starch at pH 11 with 2.0% sodium sulfate (bos) for 6 h at 40°C decreased fluidity to 28 ml, because the alkali/salt treatment reduced the phosphorus level to 0.033%, which is equivalent to 0.54% lysophospholipid. Under the same alkali treatment without sodium sulfate, the alkaline fluidity of the starch paste was 18 ml, indicating removal of even more lysophospholipids. A highly cross-linked wheat starch with fluidity near 100 ml, which was produced by reacting wheat starch with 2.0% STMP (bos) in 2.0% sodium sulfate (bos) at pH 11.0 for 6 h at 40°C, was found to contain 0.05% residual phosphorus. That level of residual phosphorus exceeds the limit of 0.04% in CFR (1995) for reacting starch with STMP alone, because no correction is made for indigenous phosphorus in the starch.

Cross-linking of hydroxypropylated wheat starch with STMP

The reaction of starch with propylene oxide is slow, and high temperature and high alkalinity are used to increase the reaction rate. But those conditions promote gelatinization of starch, which is countered by adding a salt that restricts starch swelling. In the case of wheat starch, hydroxypropylation was done at pH 11.5 and 45°C in the presence of 10.0–16.0% sodium sulfate (bos). A level of 16.0% sodium sulfate (bos) (approximately 0.7M in the aqueous phase) was chosen for the hydroxypropylation in this study, because many small reactions were run simultaneously. The small reactions were stirred with magnetic stir bars, which sometimes failed to keep the 37% starch granules suspended. Hydroxypropylations at 10.0% (bos) instead of 16.0% sodium sulfate (bos) sometimes gave an excessively gelatinized product. In reactions stirred with a paddle powered by an electric drive, hydroxypropylation (8% propylene oxide) and cross-linking at 10.0% sodium sulfate (bos) gave alkaline fluidity and a pasting curve identical with those obtained at 16.0% sodium sulfate. Alkaline fluidity in 0.95% aqueous sodium hydroxide again was used to determine the extent of cross-linking of hydroxypropylated wheat starch. However, because hydroxypropylation promoted swelling, the concentration of modified starch in the test was 1.5% instead of the 2.0% used for wheat starch. The hydroxypropylated wheat starch prepared with 8% (bos) propylene oxide at pH 11.5 and 45°C with 16.0% sodium sulfate (bos) was found to contain 4.5 ± 0.2% hydroxypropyl content (DS 0.12–0.13).

Response surface analysis yielded the regression equation expressing cross-linking (alkaline fluidity) of hydroxypropylated wheat starch as a function of the concentration of STMP (*X*), concentration of sodium sulfate (*Y*), and time (*Z*). In the cross-linking reaction at 45°C, pH 11.5 and 37% starch solids,

$$\text{Fluidity(ml)} = -4.1 - 1.5X + 2.1Z + 103.2X^2 + 1.0XZ - 0.016Z^2 (R^2 = 0.99).$$

Cross-linking was more rapid (Fig. 6) for the hydroxypropylated starch than for wheat starch (Fig. 5) because of four changes in reaction conditions: higher temperature (45 vs. 40°C), higher pH (11.5 vs. 11.0), higher sodium sulfate concentration (16.0 vs. 2.0%, bos), and increased starch concentration (37 vs. 30% starch). Low, moderate, and high levels of cross-linking of hydroxypropylated starch could be produced using 0.1–0.5% STMP (bos) and 5–50 min reaction time (Fig. 6). The changes in reaction conditions also promoted cross-linking with $POCl_3$; a high level of cross-linking of hydroxypropylated wheat starch was achieved with 0.016% $POCl_3$ (Table 1) compared with 0.07% for wheat starch (Fig. 1).

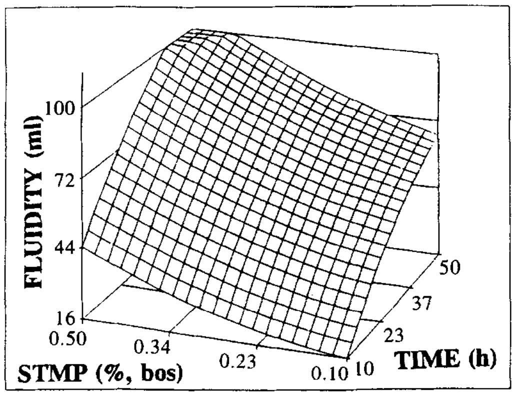

Fig. 6. Contour plot of cross-linking of hydroxypropylated wheat starch (37% slurry) at pH 11.5 and 45°C in the presence of 16% sodium sulfate (bos). Cross-linking was measured by alkaline fluidity of 1.5% modified starch in 0.95% sodium hydroxide at 25°C.

Pasting properties of doubly modified wheat starch prepared by cross-linking with $POCl_3$ and STMP

Hydroxypropylated (4.5 ± 0.2%) wheat starch was cross-linked with $POCl_3$ and with STMP to produce high, moderate, and low levels of cross-linking in the doubly modified starches. The conditions for cross-linking are given in Table 1. All phosphorus from the lysophospholipids was lost during the hydroxypropylation reaction (Table 2), so the residual phosphorus in the cross-linked hydroxypropylated wheat starches increased in direct proportion to their increased fluidity (Table 2). The phosphorus levels in the doubly modified starches were 1–3 mol% of the STMP phosphorus added in the cross-linking reaction (Table 2). The residual levels of phosphorus in the doubly modified wheat starches were well below the maximum allowable limit of 0.04% when cross-linking with metaphosphate alone. However, reaction of hydroxypropylated starch with STMP has not been approved for food-grade starch in the USA.

Table 1. Reaction conditions to produce three levels of cross-linking in hydroxypropylated[a] wheat starch with phosphoryl chloride ($POCl_3$) and sodium trimetaphosphate (STMP)

Cross-linking level(alkaline fluidity, ml)	$POCl_3$ reaction conditions (temperature, time, reagent[b])	STMP reaction conditions (temperature, time, reagent[b])
Low (32–36)	25°C, 1 h, 0.004%	45°C, 10 min, 0.3%
Moderate (54–57)	25°C, 1 h, 0.008%	45°C, 15 min, 0.3%
High (75–78)	25°C, 1 h, 0.016%	45°C, 40 min, 0.3%

[a] Hydroxypropylated (4.5 ± 0.2 wt%) wheat starch was prepared by reaction of a 37% starch slurry with 8% propylene oxide (bos) at 45°C, 24 h, and pH 11.5 in the presence of 16% sodium sulfate.

[b] Reagent level is wt% based on the dry weight of starch.

Table 2. Residual phosphorus content (%) in hydroxypropylated and cross-linked wheat starches prepared with STMP

Cross-linking level[a] (alkaline fluidity, ml)	Phosphorus in starch[b,c], %	Phosphorus reacted with starch, %
None (17–19)	0.0000A	—
Low (32–36)	0.0039B	1.3
Moderate (54–57)	0.0050C	1.7
High (75–78)	0.0097D	3.2

[a] Low, moderate, and high levels of cross-linking were achieved as described in Table 1.

[b] Average of two replicates.

[c] Averages with the same letter within the column are not significantly different at a 95% confidence level.

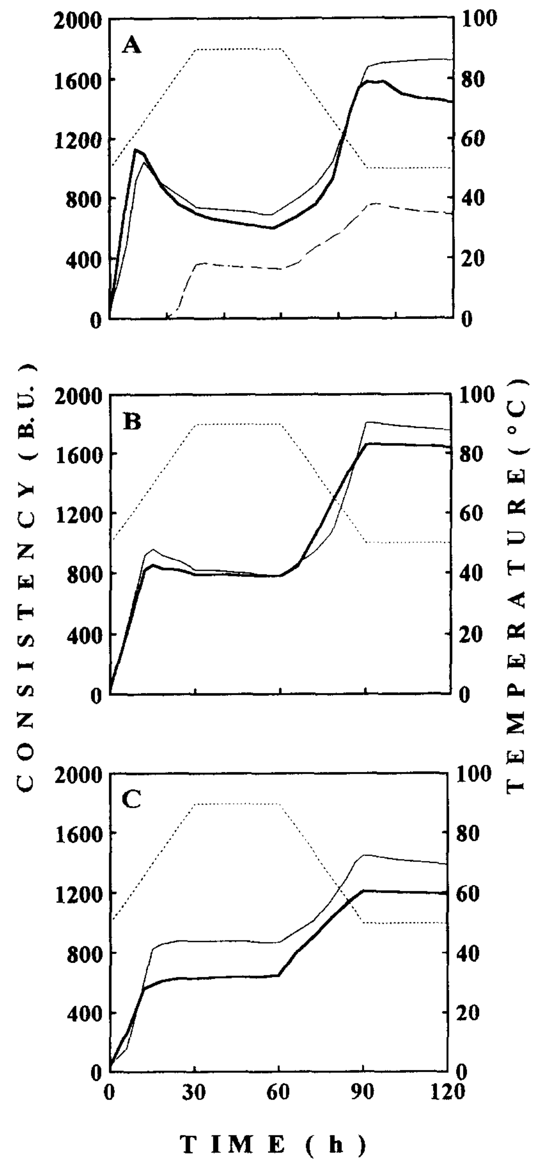

Fig. 7. Pasting curves (8.0% starch slurry) of wheat starch and cross-linked hydroxypropylated (HP) wheat starches. Wheat starch (---) and HP wheat starches cross-linked to a low (A), moderate (B), and high (C) level with phosphoryl chloride (———) and with STMP (———), respectively. The alkaline fluidity of the HP wheat starch before cross-linking was 1–2 ml. Reaction conditions are given in Table 1.

Pasting properties of cross-linked hydroxypropylated wheat starches

The pasting curves of the doubly modified wheat starches prepared to the same fluidities by cross-linking with STMP and $POCl_3$ (Table 1) were nearly the same, except at the high level of cross-linking (Fig. 7 (C)). We postulate that some of the cross-links formed from STMP at pH 11.5 and 45°C were due to distarch pyrophosphates (Fig. 7 (C)). Pyrophosphate cross-links are improbable when cross-linking with $POCl_3$. Pyrophosphate cross-links would likely be susceptible to hydrolysis during the alkaline fluidity test, which is done at $pH \approx 13$. For that reason, alkaline fluidity would underestimate the level of cross-linking at pH 11.0–11.5 with STMP. In contrast, the pasting curves of the starches are measured near neutral pH. Therefore, compared to $POCl_3$ cross-linked starch, STMP cross-linked starch would show a low consistency, especially at a high level of cross-linking.

Pasting curves of the doubly modified starches prepared to a moderate degree of cross-linking (Table 1) were also compared under acidic cooking conditions (Fig. 8). The modified starch made from STMP showed greater breakdown of its hot paste at pH 3.5 than the one made from $POCl_3$ (Fig. 8 (A)). A more stable pasting curve was obtained for hydroxypropylated wheat starch cross-linked with a low concentration of STMP over an extended reaction period as opposed to a high concentration of STMP and a brief reaction period (Fig. 8 (B)). This result is in accord with the occurrence of pyrophosphate cross-

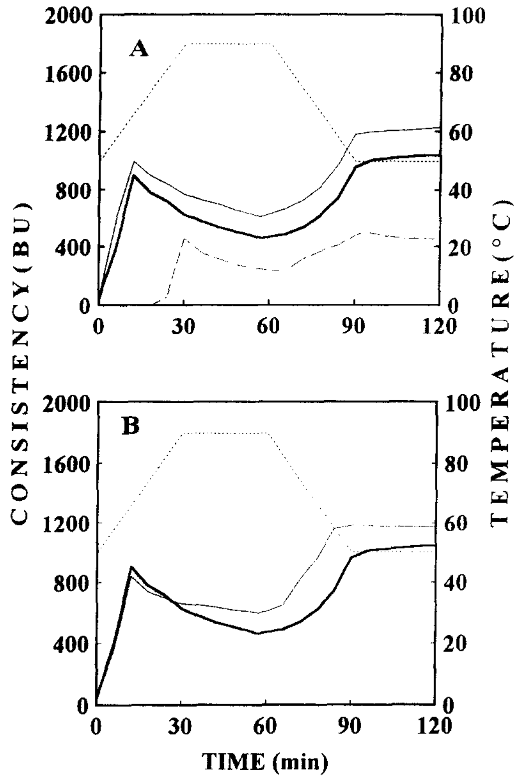

Fig. 8. Pasting curves of cross-linked hydroxypropylated (HP) wheat starches (8.0%) measured in an acidified medium at pH 3.5. (A) HP wheat starch moderately cross-linked with 0.3% STMP (bos) for 25 min (———) or with 0.008% phosphoryl chloride (———), and wheat starch (- - -); (B) HP wheat starch moderately cross-linked with 0.3% STMP (bos) for 25 min (———), or with 0.1% STMP (bos) for 100 min (———) at 45°C and pH 11.5.

links in STMP-treated wheat starch, because those cross-links would be less stable at pH 3.5 than phosphate cross-links. The pyrophosphate cross-links would be broken by mild acid hydrolysis of the anhydride bond (P–O–P) during pasting, whereas orthophosphate cross-links would be stable to mild acid. The pasting studies suggest that distarch pyrophosphate cross-links were less prevalent in hydroxypropylated wheat starch cross-linked at a long reaction time, probably because of their alkaline hydrolysis.

CONCLUSIONS

Wheat starch can be cross-linked in aqueous slurry (30% solids) to different degrees by reaction at 25–45°C with 0.5–2.0% STMP (bos) for 2–6 h at pH 10.5–11.5 in the presence of 0–4.0% sodium sulfate (bos). For a given level of cross-linking, a regression equation can be used to determine the minimum levels of reagents or the shortest reaction time. Hydroxypropylated wheat starch can also be cross-linked in aqueous slurry (37% solids) in the presence of 10.0–16.0% sodium sulfate (bos) to different degrees by reaction with 0.1–0.5% STMP (bos) for 10–40 min at pH 11.5 and 45°C. Some of the cross-links formed from STMP in a short reaction period appear less stable than those formed from $POCl_3$. More stable cross-links can be produced from STMP in an extended reaction period.

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