

Understanding the Mechanism of Cross-Linking Agents (POCl₃, STMP, and EPI) Through Swelling Behavior and Pasting Properties of Cross-Linked Waxy Maize Starches¹

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ABSTRACT

Cereal Chem. 79(1):102–107

The effects of cross-linking waxy maize starch with phosphorous oxychloride (POCl₃), sodium trimetaphosphate (STMP), or epichlorohydrin (EPI) on degree of swell and pasting properties were studied. As expected, increased concentration of cross-linking agent resulted in decreased granule swelling potential, Q (mL/g). The slower acting reagents, STMP (4-hr reaction time) and EPI (17-hr reaction time), showed a similar relation between Q value and molar concentration of agent, which was different from the faster-acting POCl₃ (30-min reaction time). Brabender viscoamylograph results show decreased peak viscosity with increasing amounts of cross-link agent due to increased inhibition to swelling. Brabender viscosities (BU) continued to increase after the time interval in which an uncross-linked sample would dissolve, which may be

a sign of flocculation. The magnitude of BU for all of the treatments after 41 min, plotted versus calculated molar concentration of cross-linking agent, showed a similar trend for all three reagents, indicating that type of reagent plays little effect on the overall pasting behavior of cross-linked waxy maize. However, when BU was plotted versus Q, starches treated with POCl₃ again separated themselves with much higher viscosities than the collectively grouped EPI- and STMP-treated starches. The combination of the reduced swell and higher viscosity indicates that POCl₃-treated granules have a more rigid external surface area, with hard crust formed on the outer layers of the granule. This information shows that the mechanism of action of the individual reagents plays a major role in the physicochemical behavior of the starches.

Cross-linked starch plays a major role in the manufacture of foods to thicken, stabilize, and provide texture. The invention of cross-linked starch stemmed from the need for starch granules that are tough enough to resist disintegration on cooking with water. To avoid a thick, pasty mass, Felton and Schopmeyer (1943) designed an inexpensive process to chemically treat native starch with acid chlorides including phosphorous oxychloride (POCl₃) in water. Other researchers followed suit with novel chemical approaches to cross-linking starch using other reagents such as epichlorohydrin (EPI) or sodium trimetaphosphate (STMP) (Konigsburg 1950; Hofreiter et al 1960; Lloyd 1970).

Waxy starches, which are made up almost entirely of amylopectin, are often used as the base for cross-linked starches because amylose retrogrades on cooling and forms an irreversible gel (Katzback 1972). Cross-linking agents bind neighboring anhydroglucose units (AGU) in the amorphous regions of the waxy maize amylopectin. Cross-links prevent the granules from fully swelling and ultimately disintegrating. The covalent cross-link network also makes the granules tolerant to pH extremes and high shear processes common to food manufacturing.

The extent of the effects of cross-linking on swelling and viscosity depends both on the treatment conditions of raw starch and on how the starch is prepared in the final application. Factors important in the cross-linking reaction include chemical composition of reagent, reagent concentration, pH, reaction time, and temperature (Rutenberg 1980; Lim and Seib 1993). Because the degree of cross-linking for food starches is very low, the extent of reaction and yield of cross-linked starch are difficult to measure chemically; hence the need for physical property measurement. Maximum extent of cross-linking reaction for EPI with corn starch, assuming that the percentage of reacted EPI that results in cross-links is constant, was reported at 90% (42 hr at 25°C) (Hamerstrand et al 1960). No such quantitative values are reported for POCl₃ or STMP.

In general, for preparation of cross-linked starches, unswollen, native granules are mixed in an aqueous system with reagents capable of reacting with at least two of the hydroxyl groups of neighboring molecules (Wurzberg and Szymanski 1970; Rutenberg and Solarek 1984). The type of reagent used and cross-linking conditions determine the ratio of mono and di-type bonds (esters with phosphorous based agents and glycerols with epichlorohydrin) due to cross-linking reaction mechanism and available starch hydroxyls (Koch et al 1982).

When phosphorous oxychloride (phosphoryl chloride, POCl₃; MW 153.5) is added to a starch slurry under alkaline conditions (pH 8–12), the hydrophilic phosphorous group immediately reacts with the starch hydroxyls, forming a distarch phosphate. In addition to phosphodiester linkages in POCl₃-treated corn starch, byproducts, including monophosphate derivatives and other types of phosphate esters, have been found in the insoluble starch fractions using phosphorous-31 nuclear magnetic resonance (NMR) spectroscopy (Kasemsuwan and Jane 1994). STMP (Na₃P₃O₉; MW = 305.9) has a ring structure that necessitates a bimolecular reaction that ultimately results in the formation of starch tripolyphosphate. The mechanism of the EPI (1-chloro-2, 3-epoxypropane; MW 92.5) reaction with starch occurs over a series of steps. With EPI, a multifunctional reaction can proceed whereby either one or two molecules of EPI are consumed to form a single cross-link. Regardless of cross-linking agent, diesters and diglycerols represent the cross-linked starch molecules (Kerr and Cleveland 1957).

It is possible to control starch thickening properties through changing the degree of cross-linking and manipulating the extent of swelling. Researchers have shown a relationship between rheological properties and swelling capacity of starch granules (Evan and Haisman 1979; Bagley and Christianson 1982). However, the relative effects of different cross-linking agents are not well understood. The flow behavior and textural properties of cross-linked starch are very complex due to the effects of starch concentration, heating rate, heating temperature, and amount of shear, as well as competition with other dissolved solutes and polymers (Doublie et al 1987; Steeneken 1989; Gluck-Hirsch and Kokini 1997).

Relative effects that the different cross-linking agents have on physical properties have been studied (Evans and Haisman 1979; Eliasson 1986; Steeneken 1989; Evans and Lips 1992). However, uncertainty remains as to how cross-linking is achieved at the macromolecular level of the three-dimensional granule structure. Therefore, microstructural differences have not been used to explain the

¹ Publication No. D10544-1-98 of the New Jersey Agricultural Experiment Station supported by state funds and the Center for Advanced Food Technology (CAFT).

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physical properties nor have physical measurements been used as a tool to help determine cross-linked granule architecture.

The objectives of this research are to contribute to the understanding of the mechanism of action of POCl₃, EPI, and STMP by comparing and quantifying the degree of swelling that different concentrations of POCl₃, STMP, and EPI independently have on waxy maize starch, and to relate the effects of swelling on pasting behavior. Such quantitative information is not available in the literature. The relative effects of the different agents are expected to give new insight as to how cross-linking is achieved within the starch granules.

MATERIALS AND METHODS

Materials

Native waxy maize starch (Amioca), was donated by National Starch and Chemical Co. (Bridgewater, NJ). Two different lots of waxy maize starch were used as the base starches for the cross-linking reactions. One lot was used for the POCl₃ and EPI-treated starches, and a different lot was used for the samples cross-linked with STMP.

POCl₃ (99%) and EPI (99%) solutions were purchased from the Aldrich Chemical Co. (St. Louis, MO), and STMP (powder) from Monsanto (St. Louis, MO). Blue dextran was purchased from Sigma. Other chemicals were reagent-grade.

TABLE I
Swell Factor (Q) for Waxy Maize Treated with Phosphorous Oxychloride (POCl₃)^a

Conc. (%)	Molecules/g of Starch (×10 ⁷)	Q (mL/g) POCl ₃
0.0050%	3.70	23.0 ± 0.67
0.010%	7.40	19.6 ± 1.0
0.015%	11.1	17.5 ± 0.82
0.020%	14.8	14.9 ± 1.3

^a Determined by dye exclusion of a 2% starch suspension.

TABLE II
Swell Factor (Q) for Waxy Maize Treated with Sodium Trimetaphosphate (STMP)^a

Conc. (%)	Molecules/g of Starch (×10 ⁷)	Q (mL/g) STMP
0.050%	18.6	19.4 ± 0.90
0.10%	37.1	19.3 ± 1.7
0.15%	55.7	16.8 ± 1.4
0.20%	74.3	16.3 ± 1.8

^a Determined by dye exclusion of a 2% starch suspension.

TABLE III
Swell Factor (Q) for Waxy Maize Treated with Epichlorohydrin (EPI)^a

Conc. (%)	Molecules/g of Starch (×10 ⁷)	Q (mL/g) EPI
0.005%	6.14	24.3 ± 0.76
0.010%	12.3	21.3 ± 2.1
0.015%	18.4	20.2 ± 0.31
0.020%	24.6	18.2 ± 1.1

^a Determined by dye exclusion of a 2% starch suspension.

Preparation of Cross-Linked Starches

Concentrations of cross-linking agents (% w/w) added to starch and the respective molar concentrations are shown in Tables I–III. A total of 12 starch treatments were analyzed (three cross-linking agents, each at four concentrations). For each of the 12 treatments, Amioca (1,000 g wb, 12% moisture) was suspended in 1,500 g of tap water under constant mixing (Boehm stirrer with three-blade propeller; Fisher Scientific Co., Fair Lawn, NJ). Before adding the reagent, 0.5 g of NaCl (0.5% wt of starch) was added, and the slurry was adjusted to pH 12 by adding a 3% NaOH solution. For the STMP reactions, in addition to the NaCl, 3 g of CaCl₂ (0.1% wt of starch) also was added.

The POCl₃ solution and STMP powder were added directly while the slurries were being stirred, covered with foil, and left to react. The starch with POCl₃ was reacted for 35 min at 25°C, and the starch with STMP was reacted for 5 hr at 30°C. The 30°C temperature for the STMP reactions was maintained by keeping the slurry beakers submerged in a 30°C water bath. For the EPI-treated starch, each of the slurries was transferred to a 1-gallon plastic container and the EPI was added using a syringe due to the low concentrations. The containers were immediately capped and inverted, and placed in a heated tumbler oven programmed to continuously rotate the slurry-filled containers end-over-end for the designated reaction time (17 hr) and temperature (40°C) (Table IV).

After the designated cross-linking time had elapsed, the starch slurries were brought to pH 5.25 ± 0.25 using a 3% HCl solution (Fisher Scientific) and then filtered using a Buchner funnel and filter paper (Reeve Angel grade 226 24-cm). The starch was then washed three times, air-dried overnight (50% rh at 30°C), and ground.

Moisture Determination

The weight of starch in the suspensions was confirmed using Approved Method 44-15A (AACC 2000). Weighed aliquots of the wet gelatinized starch samples, taken from the bottles after tempering, were put in aluminum moisture dishes, covered, cooled in a desiccator containing Hammond Drierite anhydrous calcium sulfate (≈1 hr), weighed, and dried overnight in an oven (14–16 hr) at 102°C. Dried samples were then cooled in the desiccator (≈1 hr) and weighed. Concentration of starch (1% moisture) was then calculated.

Determination of Maximum Granule Swelling Using Dye Exclusion

Maximum granule swelling potential (Q) of each of the starch treatments and the starch base was determined using a blue dye exclusion procedure described by Tester and Morrison (1990). Blue dextran, a HMW polysaccharide, (MW = ≈2,000,000) does not penetrate the swollen starch granules. As a result, this method enables the determination of the amount of intragranular water by measuring the concentration of the dye excluded from the starch granules into the supernatant.

Maximum granule swell was achieved by heating the starch through gelatinization. For each of the 12 starch treatments and the base starch, heating and mixing of the starch slurries were accomplished simultaneously using a spinning rotary evaporator (Bush Rotavapor RE121, Switzerland). Starch (1 g, wb) and 50 mL of distilled water were added to a 100-mL freestanding Pyrex round flask. The flask was immersed in a 110°C Buchi 471 oil

TABLE IV
Comparison of General Requirements for POCl₃, STMP, and EPI Cross-Linking Reactions^a

Cross-Link Agent	Reaction Time	Reaction Temperature	Final pH	Special Requirements
POCl ₃	35 min	25°C	5.25 ± 0.25	NaCl (0.5% wt of starch)
STMP	5 hr	30°C	4.75 ± 0.25	NaCl (0.5% wt of starch)
	...	Water bath	...	CaCl ₂ (0.1% wt of starch)
EPI	17 hr	40°C	5.50 ± 0.50	Tumbler oven

^a POCl₃ = phosphorous oxychloride, STMP = sodium trimetaphosphate, and EPI = epichlorohydrin.

bath and spun at 150 rpm. The benefit of using this apparatus is the absence of direct shear, whereby the flask spins, as opposed to a blade spinning in the slurry.

For all of the cross-linked treatments, the spinning flasks were heated for 30 min. Uncross-linked starch granules dissolve when heated to $>85^{\circ}\text{C}$, therefore a less severe heat treatment needed to be used for the base starch. Instead of heating for a given length of time, the unmodified starch was heated to the point where the suspension instantaneously changed from opaque to clear (approximate gelatinization point) at $\approx 70 \pm 10$ sec.

Each of the heated starch suspensions was then transferred to a 100-mL Nalgene test tube (Fisher Scientific). The tubes containing cross-linked starch were immediately cooled from 100 to 20°C by submersion into an ice bath. Before cooling on ice, the temperature of the uncross-linked starch slurries continued to rise, indicating that swelling continued to occur, even after they were transferred to test tubes. Optimal time to halt the heating and swelling process,

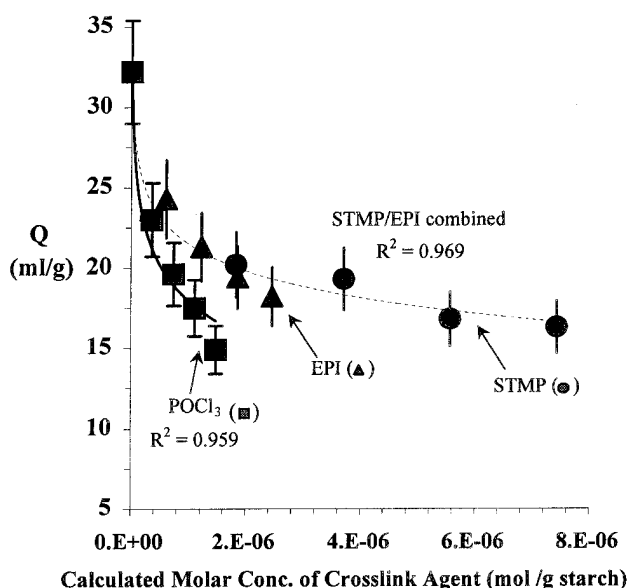


Fig. 1. Swelling potential (Q) versus cross-linking agent molar concentration; effect of cross-linking agent and cross-link agent concentration on granule swell

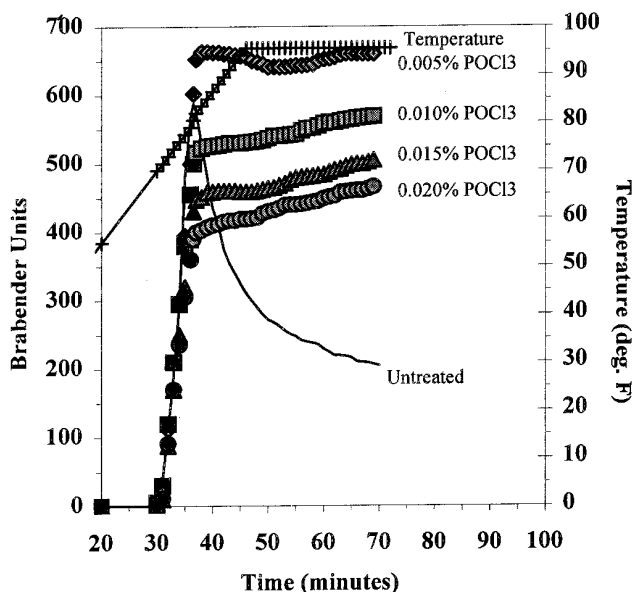


Fig. 2. Comparison of viscosity profiles for 5.5% starch slurries (wb) of phosphorous oxychloride-treated (POCl_3) waxy maize

before the granules started to dissolve, was once the uncross-linked starch temperature reached 87°C (≈ 45 sec after transfer to test tubes). Once cooled to 20°C , 5 mL of blue dextran (Pharmacia, 5 mg/mL) was added to each test tube, and the test tubes were gently inverted to mix the starch slurry and blue dextran. With the overall concentration of blue dextran $<0.05\%$, the osmotic pressure effects (deswelling) were assumed to be negligible (Bastide et al 1981).

The tubes were then centrifuged twice (Sigma Laborzentrifugen GmbH 2-15) at $1,500 \times g$ for 10 min. After the first centrifugation, 10 mL of the clear blue supernatant was pipetted out and added to a 5-mL centrifuge tube, then centrifuged again. Tester and Morrison (1990) centrifuged the samples once and then measured the absorption of the excluded supernatant. In this research, we centrifuged the samples twice to ensure no contamination from floating granules, as was confirmed by lack of turbidity in the supernatant.

The absorbance of the second and final supernatant (A_s) was measured spectrophotometrically at 620 nm (HP8452A diode array spectrophotometer). The excluded dye-water mixture was very clear (no turbidity), indicating that little or no low molecular weight fractions leached into the supernatant. Each experiment was performed in duplicate with errors $<10\%$. Reference tubes absorbances (A_r) with 5 mL of blue dextran and 50 mL of water also were measured at 620 nm.

Total swelling of the granules, swell factor Q (mL/g), was calculated as the ratio of the volume of swollen starch (V_2) per gram of dry starch (W). V_2 is calculated as the sum of the initial volume of starch (V_0) plus the absorbed, intragranular water (V_1): $V_2 = V_0 + V_1$. To determine V_2 , V_0 is calculated from a dry starch weight basis (W) in grams, using 1.49 g/mL as dry weight starch density, with V_0 (mL) = $W/1.49$. To determine V_1 , the free or interstitial plus supernatant water (FW), is first determined from the spectrometry results, where $FW = 55 (A_r/A_s) - 5$. (Note: 55 is the total volume, and 5 is the volume of the blue dextran solution). Then, the absorbed, intragranular water, V_1 , can be calculated as: $V_1 = 50 - FW$. Finally, Q (mL/g) can be determined as: $Q = V_2/W$.

Viscoamylograph Pasting Procedures

The effects of heating on starch behavior for all the starch treatments were compared using a viscoamylograph (C. W. Brabender Instruments, Inc., South Hackensack, NJ) with a 700-gm-cm transducer. Starch slurries (5.5%, wb) were each prepared by weighing 25.3 g (wb) of starch and 434.7 g of distilled water into a 600-mL beaker (pH ≈ 7.2). Each slurry was mixed with a glass stirrer, to suspend the starch and transferred to the amylograph sample cup. Slurries were heated at the rate of $1.5^{\circ}\text{C}/\text{min}$ through gelatinization (and pasting). Once the slurry temperature reached 95°C , it was maintained for a minimum of 30 min. All 12 cross-linked samples and the waxy maize base were run in duplicate.

RESULTS

Effect of Cross-Linking Agent and Agent Concentration on Granule Swell

The granule swell factor, Q (mL/g) for the 12 cross-linked samples are shown in Tables I–III. The Q values were 14.9–23.9 mL/g for the POCl_3 -treated waxy maize, 16.3–19.4 mL/g for STMP, and 18.2–24.3 mL/g for EPI. The Q value for the uncross-linked base starch was 32.2 mL/g. As expected, a higher concentration of cross-linking agent results in a lower degree of swell.

The degree of Q as a function of calculated cross-linking agent (molar) concentration for the three reagents at each concentration is plotted in Fig. 1. Theoretically, maximum granule swell can only be as high as would be achieved by the uncross-linked starch control. With all three curves originating from the same uncross-linked (or zero) cross-link agent concentration value, POCl_3 follows one decreasing swelling regime, and STMP and EPI seem

to follow another. The fast-acting POCl_3 results in a greater reduction in Q with increased molar concentration of reagent as compared with the slower acting STMP and EPI starches. Considering that the data are plotted as Q versus molar concentration of cross-link agent, accounts for the stoichiometry of the reactions. Therefore, the differences between the reagents may very well be due to a mechanistic difference in the cross-link reaction. This shows that the effect of cross-linking on granule structure of the very fast acting POCl_3 is different than the slower acting agents STMP and EPI.

The dependence of Q on starch treatment best fit with a logarithmic model of the data because $r^2 = 0.983$ for POCl_3 and the combined fit of the STMP and EPI treated starches is $r^2 = 0.929$. There is remarkable superposition of the EPI and STMP data in the range where the data are superimposable.

The swelling factor represents an important physical parameter because it defines the maximum swelling potential of a starch granule heated through gelatinization. Decreases in Q with increasing concentration of cross-linking agent directly show the constraints imposed by cross-links on swelling behavior. There is a much stronger negative correlation of degree of swell with cross-linking agent concentration for POCl_3 -treated starches compared with STMP- and EPI-treated starches. The cross-links appear to be much more effective in preventing the swelling action of POCl_3 -cross-linked starches compared with STMP- and EPI-treated starches.

One explanation for this is that there is a large concentration of POCl_3 cross-links at the surface of the granule that cause a hard crust on the outer layer (Gluck-Hirsch 1997; Huber and BeMiller 2001). The slower acting cross-linking agents, STMP and EPI, penetrate further into the interior of the granule, and the cross-links have a much more diffuse impact because they are essentially evenly distributed throughout the granule volume.

Effect of Degree of Cross-Linking on Viscosity

A comparison of four concentration levels of POCl_3 , EPI, and STMP and their untreated waxy maize counterparts is shown in Figs. 2–4. For all of the samples, there is a bimodal response to heating consisting of a sharp initial rise in viscosity at 30 min, and then either a sharp decline in viscosity for the uncross-linked samples or a continual rise in viscosity for all the cross-linked samples. The deviation between the uncross-linked and cross-linked samples becomes apparent at 30–35 min. The exponential viscosity decline of the uncross-linked starch at 36.5 min is the result of starch granules breaking down.

Conversely, there is a gradual rise in the viscosity of the cross-linked samples. The strength of the additional covalent bonds of the cross-linked starch enables the granules to withstand the 95°C temperature and not dissolve at >30 min.

With increasing concentration of cross-linking agent, the peak viscosity decreases for all three cross-linking agents (Figs. 2–4). The lower peak viscosity of the more highly cross-linked samples can be attributed to the higher density of cross-links, and is consistent with the decreasing swelling behavior with increasing cross-linking agent concentration (Fig. 1). The greater the degree of cross-linking, the smaller the granule volume, which precludes the more highly cross-linked starches from coming into contact with each other as much as the granules with a higher volume (i.e., more lightly cross-linked starches with a greater Q). As a result, the maximum viscosity observed for the highly cross-linked starches is lower than the lesser cross-linked starches at this starch concentration.

Note that the peak viscosity of the POCl_3 cross-linked samples at 0.005% concentration is considerably larger than the uncross-linked starch, and the peak of the 0.005% EPI-treated starches is approximately equal to its uncross-linked counterpart. The rate of swelling of the starch granules and their dissolution into a dispersed, polymeric phase may determine the peak viscosity (Kokini et al 1992). It is therefore possible that very small amounts of cross-linking agent such as 0.005% POCl_3 may inhibit dissolution. How-

ever, the relatively high degree of swell enables a strong interaction between granules, resulting in a larger peak viscosity than with an uncross-linked starch. The slight decrease in viscosity of the 0.005% POCl_3 with time indicates that some granules are not sufficiently cross-linked and are most likely dissolving (Rutenberg and Solarek 1984).

Although the applied rate of heating is equal for all the samples (1.5°C/min), the time interval of the exponential increase in viscosity seems to be a little longer for the less cross-linked samples. The gelatinization temperature does not change (Rutenberg 1980) but with a higher density of cross-links the larger granules appear to require more time to swell. This is also expected because the increasing number of cross-links could be posing a diffusional resistance to water penetration. This is most apparent in the EPI-treated starches (Fig. 4), whereby the start of the continual rise begins at 37, 38, 39, and 41 min for the 0.005, 0.010, 0.015, and 0.020% treatments, respectively.

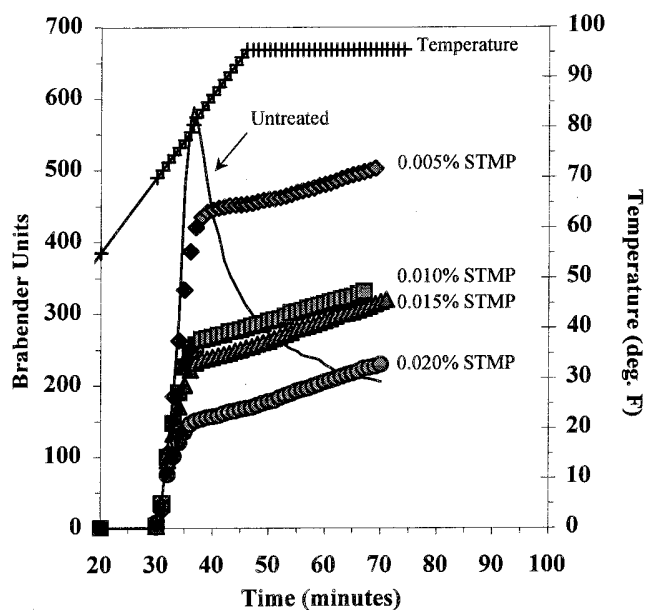


Fig. 3. Comparison of viscosity profiles for 5.5% starch slurries (wb) of sodium trimetaphosphate-treated (STMP) waxy maize

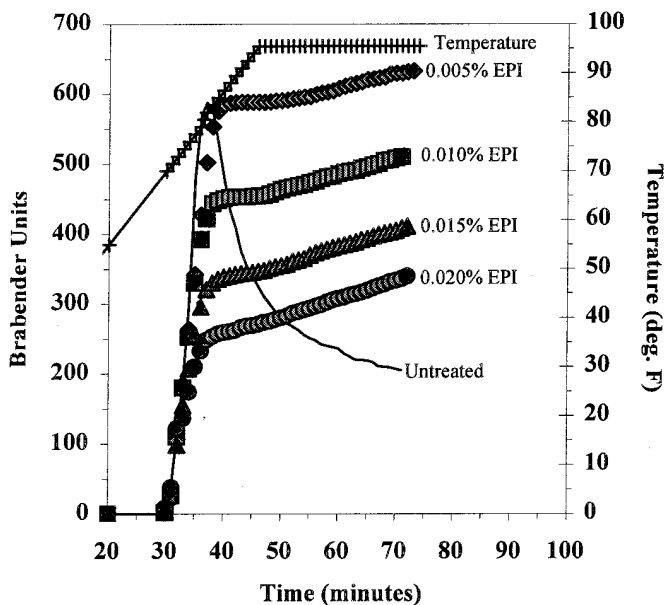


Fig. 4. Comparison of viscosity profiles for 5.5% starch slurries (wb) of epichlorohydrin-treated (EPI) waxy maize

By 41 min, all of the treated samples are well into the secondary regime, with viscosity increasing with time. A plot of viscosity values at 41 min versus calculated molar cross-linking agent concentration (Fig. 5) shows excellent correlation ($r^2 = 0.943$) for all three cross-linking treatments combined. This relationship of viscosity and degree of cross-linking shows that these very different chemical reagents enact similar macromolecular functionalities using this type of measurement comparison. Wolfe (1987), who found that cross-linked latex particles with different degrees of cross-linking fall along the same curve, attributed such a relationship to volume fraction effects, with swelling as the primary influence on dispersion viscosity for such microgels. Certainly, in this case, it is possible to do separate regression analyses on the effect of amount of cross-linking of each individual agent on suspension viscosity, with very good individual correlations (POCl₃ $R^2 = 0.944$; STMP $R^2 = 0.967$; EPI $R^2 = 0.991$). Thus, one can contend that each agent generates a unique relationship between viscosity and cross-linking concentration. However, a more interesting picture develops for the physical behaviors, expressed as degree of cross-linking of

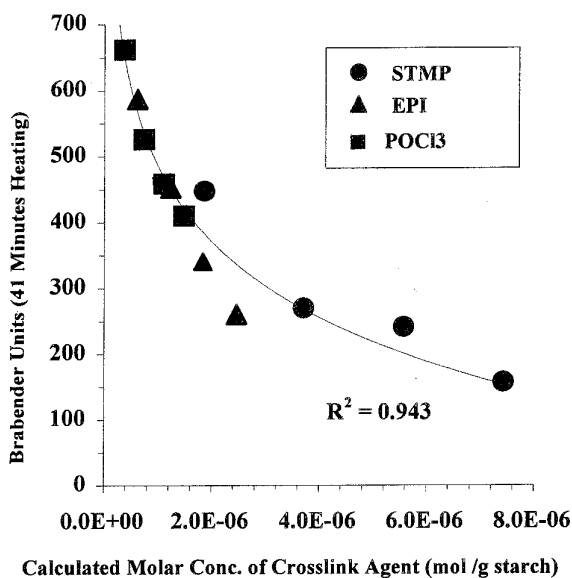


Fig. 5. Comparison of the effects of cross-link agent and cross-link agent concentration on viscosity

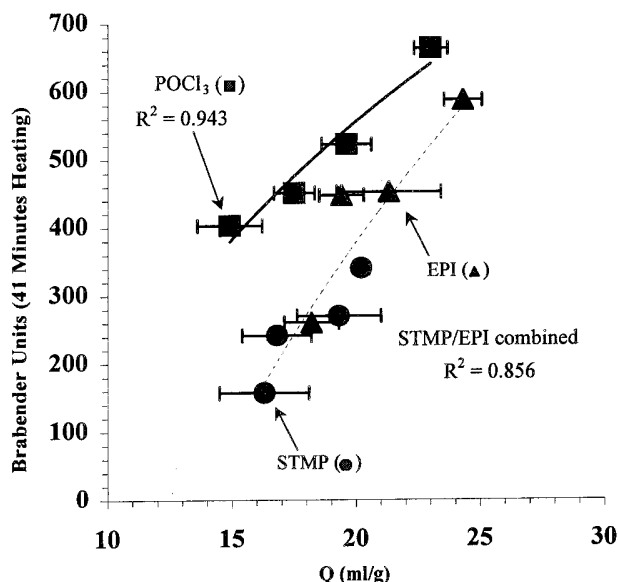


Fig. 6. Effect of degree of swell on viscosity; comparison of three cross-linking agents

these three different reagents and combined to show that they are all actually very similar.

A comparison of viscosity at 41 min versus degree of swelling (Fig. 6) shows that suspension viscosity for each agent increases with increased degree of swelling (Q). Increasing cross-linking agent decreases the degree of granule swell, thereby reducing granule interaction at low starch concentrations. At low concentrations, the smaller the granules, the further away they will be from each other in a suspension. Therefore, decreasing cross-linking agent is comparable to increasing starch concentration because, in both cases, the granules are closer together. With lightly cross-linked starch, as with a more concentrated suspension, granules are in close proximity to each other and are sterically confined, requiring a greater force to deform enough to move past each other (Ketz et al 1988).

Individually, the treated starches all have decreased swell and decreased viscosity as cross-linking increases (Figs. 1 and 6).

The information in Fig. 6 (viscosity vs. calculated molar cross-link concentration) is consistent with that presented in Fig. 1 (Q vs. calculated molar cross-link concentration). The slower reacting agents STMP and EPI effectively regressed as one, showing similar dependence of viscosity on Q, whereas POCl₃ follows a different trend. Each of the cross-linking agents help maintain the granular integrity, but how the cross-links occur in or on the granules affects both the swelling and suspension viscosity.

All of the POCl₃ cross-linked starches have higher viscosities than the STMP and EPI treatments (Fig. 6). However, surprisingly, the POCl₃-treated granules generate a higher viscosity with swelling values that are lower than the others. The EPI- and STMP-treated granules occupy a larger volume than the POCl₃-treated starches but have lower viscosity. Although the POCl₃ cross-linked granules are smaller than the granules treated with STMP and EPI, they have a higher viscosity.

Due to the high reactivity of POCl₃, cross-links predominate on the outer layer of the cross-linked granules, forming a hard shell (Gluck-Hirsch 1997; Huber and BeMiller 2001). The ability of the POCl₃-treated granules to generate a higher viscosity than both EPI- and STMP-cross-linked starches at a given swelling ratio suggests that the POCl₃ granules are more rigid than the other treated granules. Maximum packing fraction (ϕ_m) is a measure of how well a particle compacts and has an inverse relationship with viscosity (Metzner 1985; Willett 2001). In general, hard spheres ($\phi_m = 0.64$) generate higher viscosities than deformable microgels ($\phi_m \geq 0.64$), due to their inability to compact (Wolfe 1987). The surface crust of the POCl₃-treated granules may contribute to inhibition of swelling of the individual granules, but it enables a greater overall suspension viscosity than the softer, more deformable STMP or EPI at the same molar concentration of cross-linking agent. The surface crust that develops from POCl₃ cross-linking causes the granules to swell less but, because they are more rigid, the granules compress and compact less and occupy a greater total volume (lower degree of maximum packing) than the other treated starches. In addition, consistent with more deformable granules having lower viscosities, the STMP- or EPI-treated granules may be softer due to a loss of crystallinity from the long reaction time of the starch at pH 12 and 30–40°C.

Another factor that may explain the contradictory behavior of POCl₃ suspensions is surface friction. As a result of deformation during shear, the granules may exude water, which acts as a lubricant and enables the granules to slide more easily past each other (Ketz et al 1988; Willett 2001). Viscosity is the integral of all frictional resistances to flow and deformation. Therefore, the more rigid POCl₃-treated granules may exude less fluid than the more deformable STMP- and EPI-cross-linked granules, thereby generating less lubricity and a greater frictional resistance, leading to a greater viscosity.

As a final explanation, it may be possible that the POCl₃-treated granules flocculate during mixing, perhaps due to surface entangling or attractive forces, whereas the STMP- and EPI-treated starches

either do not, or not to the same extent. A higher POCl_3 system viscosity may be due a greater effective volume of the aggregates. The viscosity of the suspensions continue to rise over time, although very slightly, which is consistent with the physical properties of colloidal gels (Figs. 2–4). The surfaces of unmodified starch granules are very complex, containing graininess, holes, pores, and deep depressions (Hall and Sayre 1970; Fannon et al 1992, 1993; Huber and BeMiller 2001). Therefore, cross-linking derivitization sites on the surface may enhance intergranular friction and granule bridging.

CONCLUSIONS

Through the determination of swell values (Q), swelling and cross-link agent concentration have a decreasing power law relationship. As expected, a higher concentration of cross-linking agent resulted in a lower degree of swell for each of the three cross-linking agents at four concentration levels of cross-linking agent.

The POCl_3 -cross-linked starches have a greater dependence of Q on molar concentration than waxy maize starches cross-linked with STMP and EPI, which together show a very similar dependence of Q on molar concentration. This suggests that the mechanism through which STMP and EPI cross-link causes similar effects of swelling.

Viscosity measurements reveal for the individual agents that higher degrees of cross-linking cause lower peak viscosities, due to the lower degree of swell, and thus less intergranular interaction. However, a comparison of viscosity values of the three cross-linking agents at 41 min versus molar cross-link agent concentration shows that EPI- and STMP-treated starches fall on one curve, and POCl_3 starches on another. In each case, decreasing logarithmic relationships are observed between viscosity and molar concentration of cross-linking agent. At equal swell ratios, POCl_3 has the ability to impart the greater viscosity because the granules are more rigid due to the concentration of cross-links at the surface of the granule or due to increased friction between granules or flocculation. This research shows that there is a strong relation between cross-linking agent and degree of swell, and verifies that the cross-linking mechanism, including reagent and reaction time, plays an important role in the physical properties of cross-linked starch.

ACKNOWLEDGMENTS

We would like to thank Dan Solarek and Jeanne Paulus of National Starch for their technical assistance and help in preparing the cross-linked starch samples.

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[Received February 28, 2001. Accepted September 4, 2001.]