Cationic Oat Starch: Preparation and Effect on Paper Strength[1]

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ABSTRACT

Cationic ethers were prepared from oat starch by reaction with 2-chloro-3-hydroxypropyltrimethylammonium chloride at alkaline pH. The reaction of starch (~ 35% solids) in a mixture of 0.50*M* $Ca(OH)_2$ and 0.49*M* $CaCl_2$ at 25°C for 20 hr with 50 mmol of cationic reagent per millimole of anhydroglucose unit gave cationic oat starch with a degree of substitution (DS) of 0.014. When the reaction was done in 0.48*M* NaOH and 2.43*M* Na_2SO_4, the DS of the product was 0.042. In the calcium ion system, reacting beyond 8 hr at 35°C, 3 hr at 40°C, or 24 hr at 25°C caused gelation of the mixture. Cationic oat starch, corn starch, and wheat starch, all with DS of ~0.013, improved the dry strength of paper handsheets to a comparable degree. Cationic oat and wheat starches prepared in $CaCl_2/Ca(OH)_2$ gave higher Scott bond and burst indices than those prepared in $NaOH/Na_2SO_4$.

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A high demand for oat bran leads to a surplus of oat flour, because the milled bran accounts for approximately 35% of the oat groat compared with 65% for the flour. In recent work in our laboratory, oat starch from oat flour was isolated at 76% yield (86% of theory) using 0.03*M* calcium hydroxide. Oat starch isolated with either calcium hydroxide or highly turbulent water showed identical pasting curves, whereas oat starch isolated using sodium hydroxide gave a delayed pasting peak and increased paste consistency (Lim et al 1992). Cationic starch is widely used at the wet end of the paper machine to retain fines, fillers, and internal sizing agents; to increase paper strength; and to improve the running of the paper machine, especially with recycled fiber (Jensen and Winters 1986). The demand for cationic starch was increased in recent years because of the rapid shift from acidic to alkaline papermaking (Downs 1990).

The objectives of this investigation were 1) to establish conditions for cationic substitution of oat starch and 2) to compare the paper-strengthening effect of cationic oat starch with the effects of cationic wheat and corn starches.

MATERIALS AND METHODS

Materials

Corn starch was obtained from A. E. Staley Manufacturing Co. (Decatur, IL) and wheat starch from Midwest Grain Products, Inc. (Atchinson, KS). Oat starch was isolated from oat flour (ConAgra Grain Processing Co., Omaha, NE) using low shear in 0.03*M* $Ca(OH)_2$ (Lim et al 1992). The three starch samples contained 10–11% moisture and less than 0.4% protein and 0.3% ash. Quat 188, an aqueous solution of 3-chloro-2-hydroxypropyltrimethylammonium chloride, was supplied as 50% active amine with a density of 1.135 g/ml by Dow Chemical Company (Midland, MI). A commercial amphoteric corn starch, Cato 15, was obtained from National Starch Chemical Co. (Bridgewater, NJ). Nitrogen analysis indicated that Cato 15 had a degree of substitution (DS) of 0.029.

Preparation of Cationic Starch

Cationic starches were prepared using the general approach described by Carr and Bagby (1981). Oat starch (8.1 g, "as-is" basis equal to 45 mmol of anhydroglucose units [AGU]) followed by Quat 188 (0.41, 0.83, 1.24, or 1.66 ml), which was equivalent to 1.25–5.0 mmol of the cationic modifier, was added to a solution of calcium hydroxide (0.52 g) and calcium chloride (1 g) in water (13.3 ml) at 40°C. For one reaction, the oat starch had been isolated with $Ca(OH)_2$ and had not been neutralized, washed, or dried. Each reaction mixture, which contained 35% starch solids, was stirred for 3 hr at 40°C and then was stirred into a 1:3 (v/v) mixture of ethanol and water (400 ml). After being neutralized with 3*M* HCl, the slurry was centrifuged, and the sediment was washed with 1:3 (v/v) ethanol and water (5 × 200 ml). The last washing gave a negative test for chloride, using aqueous silver nitrate. Finally, the starch derivative was slurried in 95% ethanol, filtered, air-dried, and then assayed for nitrogen content.

An experiment was conducted to determine the concentration of calcium hydroxide that dissolved in the initial reaction mixture. A mixture of calcium hydroxide (0.52 g) and calcium chloride (1 g) in water (13.3 ml) was stirred at 40°C for 3 hr, the solids were removed by filtration using Whatman No. 1 filter paper, and the concentration of calcium hydroxide in the clear filtrate was titrated with standard hydrochloric acid. The concentration of calcium hydroxide was found to be 0.018*M*.

In a second series of reactions, calcium hydroxide (0.053, 0.13, 0.26, 0.53, or 1.06 g) and calcium chloride (1 g) were added to water (13.3 ml) and the mixtures were warmed to 40°C. Oat starch (8.1 g) and Quat 188 (0.83 ml) were added, the mixtures were stirred for 3 hr, and then the starch product was isolated as previously described and assayed for nitrogen.

In a third series of experiments, oat starch (8.1 g) was added to a solution of either a mixture of sodium hydroxide (0.28 g) and sodium sulfate (5 g) or a mixture of calcium hydroxide (0.52 g) and calcium chloride (1.0 g) in 13.3 ml of water. Quat 188 (0.83 ml) was added, and the mixtures were stirred for 0–20 hr at 25, 35, and 40°C. The starch products were isolated and assayed for nitrogen.

Cationic wheat and corn starches were prepared in a mixture of sodium hydroxide and sodium sulfate or a mixture of calcium hydroxide and calcium chloride in water. Quat 188 was added, and the mixture was stirred at the temperature and time to give the desired DS (Craig et al 1987).

Degree of Substitution

Nitrogen in starch was determined as described by Craig et al (1987). The DS was calculated from the increase in nitrogen content of a modified starch compared with that of the native starch, using the formula DS = 162 (%N)/[1,400 − 117 (%N)].

Paper Sheets and Paper Strength

Paper sheets were prepared from bleached Kraft pulp at the Department of Paper Science and Engineering, Miami University of Ohio, according to Method 205 of TAPPI (1981). The various cationic starches were cooked in water (1% solids) at 95° for 30 min using a double boiler, and the paste was mixed with the pulp slurry at a level of 4.5, 9.1, or 18.2 kg of starch per metric ton of dry pulp. Sample preparation before the strength tests on handsheets was done by Method 220 (TAPPI 1983). The standard tests included breaking length (Method T494, TAPPI 1981), burst index (Method T403, TAPPI 1985), and Scott bond (Reynolds 1974).

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RESULTS AND DISCUSSION

Substitution of Oat Starch with the Cationic Reagent

Preparation of a granular, cationic, oat starch using a cationic chlorhydrin reagent in water requires the presence of a base and a salt. The base accelerates the etherification reaction and neutralizes the by-product, hydrogen chloride, whereas the salt inhibits gelatinization of the granules. Previous investigations showed that oat starch isolated with calcium hydroxide had different pasting properties than oat starch isolated with sodium hydroxide (Lim et al 1992). That difference was thought to be attributable to the reduced solubility of the calcium salts of the starch lysophospholipids. Reduced solubility of the lysophospholipids also might enhance the paper-strengthening effect of a cationic starch by preventing the lipids from interfering with bonding at the interface between cellulosic fibers. Therefore, we decided to prepare the cationic oat starch in a mixture of calcium hydroxide and calcium chloride.

It is well known that starch dissolves in 2.5–3.5*M* aqueous calcium chloride at 25°C (Gough and Pybus 1973, Evans and Haisman 1982). But as the concentration of $CaCl_2$ increases from 0 to 1*M*, the gelatinization temperatures of corn and wheat starches rise 10°C (Gough and Pybus 1973; Jane, in press). We chose 0.49*M* $CaCl_2$ to inhibit gelatinization. We varied the concentration of calcium hydroxide from 0.05 to 1.00*M* in the mixture and then added 34.5–36.1 wt % oat starch. After adding 0.05 mmol of the cationic reagent per mole of AGU and stirring for 3 hr at 40°C, we found that a minimum concentration of 0.5*M* calcium hydroxide was needed to catalyze the etherification reaction (Table I). Perhaps this concentration of calcium hydroxide maintained saturation of the reaction mixture, because the solubility of calcium hydroxide in the presence of 0.49*M* $CaCl_2$ was 0.018*M* at 40°C as determined by titration.

Increasing the concentration of calcium hydroxide from 0.5 to 1*M* in the reaction mixture gave no further increase in reaction efficiency (i.e., the percentage of cationic reagent that reacted with the starch) (Table I). At 0.5 and 1*M* calcium hydroxide, the reaction mixture contained four- and ninefold excesses of hydroxide ion, respectively, compared with the maximum release of hydrogen chloride from the etherification reaction.

Etherification of oat starch in a mixture of approximately 0.5*M* $Ca(OH)_2$ and 0.49*M* $CaCl_2$, followed by neutralization with 3*M* HCl, gave a final reaction mixture that contained ~0.75*M* $CaCl_2$ and 26% starch solids. That level of $CaCl_2$ is below the level of 1–4*M* $CaCl_2$ that either swells or dissolves starch. When the level of cationic reagent was varied in reactions done in 0.49*M* $CaCl_2$/0.5*M* $Ca(OH)_2$, the best efficiency of substitution in a 3-hr reaction time was achieved using 0.05 mol of reagent per AGU. This gave a cationic oat starch with a DS of 0.008 (Fig. 1), whether or not the starch had been dried after isolation. The increase in the DS upon doubling the concentration of cationic reagent from 50 to 100 mmol per AGU was only 25%. It is not known why the increase in DS was lower than expected.

The reaction time and temperature were varied to improve the efficiency of etherifying oat starch with 50 mmol of reagent per

TABLE I
Reaction of Oat Starch with Cationic Reagent (0.05 mol per mole of Anhydroglucose Unit) in an Aqueous Mixture of 0.49*M* Calcium Chloride and Various Concentrations of Calcium Hydroxide for 3 hr at 40°C

Concentration of $Ca(OH)_2$ (*M*)	Starch Concentration in Reaction Mixture[a] (wt %)	Degree of Substitution	Reaction Efficiency (%)
0.050	36.1[b]	ND[c]	...
0.10	36.0	ND	...
0.20	35.7	0.001	2
0.50	35.3	0.008	16
1.00	34.5	0.009	18

[a] Cationic reagent: 3-chloro-2-hydroxypropyltrimethylammonium chloride.
[b] Starch solids calculated on "as-is" moisture basis.
[c] Nitrogen increase was not detected in the product.

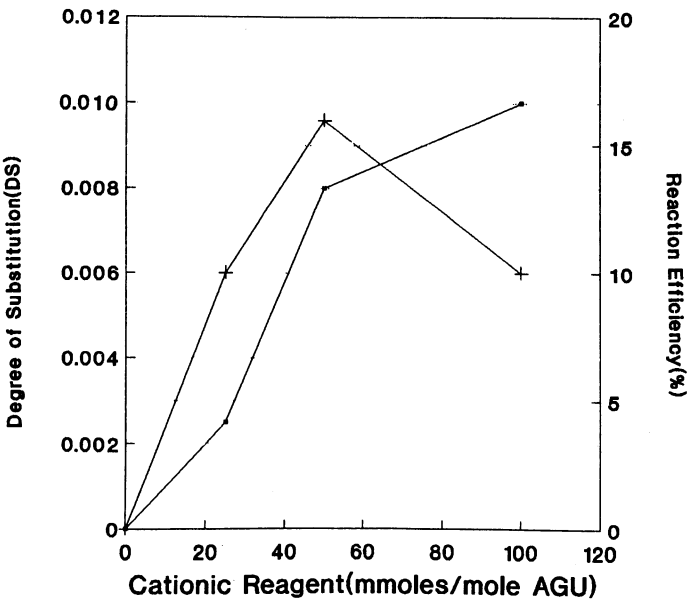

Fig. 1. Reaction of oat starch with cationic reagent. A 35 wt % slurry of oat starch in a mixture of 0.50*M* calcium hydroxide and 0.49*M* calcium chloride reacted with various levels of cationic reagent for 3 hr at 40°C. Reaction efficiency is the percentage of cationic reagent that reacted with the starch. ● = Degree of substitution; + = efficiency.

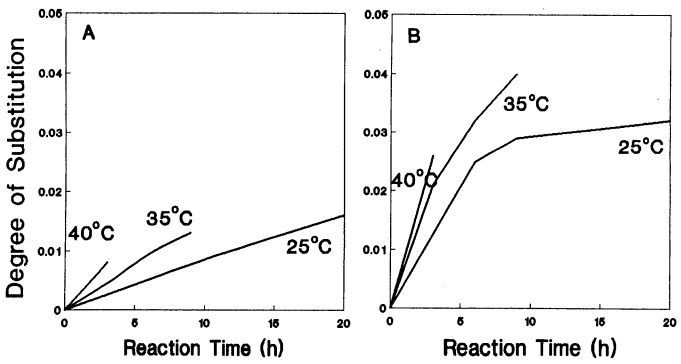

Fig. 2. Preparation of cationic oat starch at three temperatures. **A,** a 35 wt% slurry of oat starch in a mixture of 0.50*M* calcium hydroxide and 0.49*M* calcium chloride reacted with 50 mmol per anhydroglucose unit of cationic reagent. **B,** a 31 wt% slurry of oat starch in a mixture of 0.48*M* sodium hydroxide and 2.43*M* sodium sulfate with 50 mmol per anhydroglucose unit of cationic reagent.

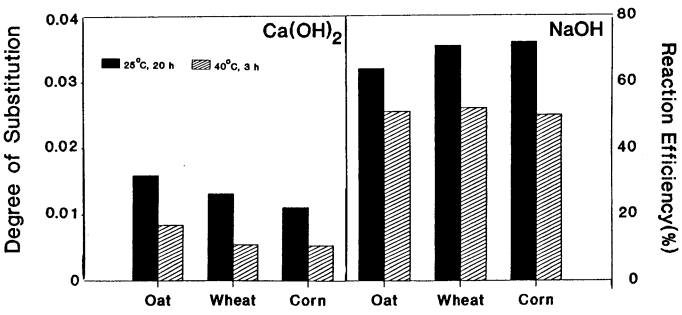

Fig. 3. Reaction of starch with cationic reagent. A 35% slurry of starch was prepared in either 0.50*M* $Ca(OH)_2$/0.49*M* $CaCl_2$ or 0.48*M* NaOH/2.43*M* Na_2SO_4 and reacted with 2-chloro-3-hydroxypropyltrimethylammonium chloride (50 mmol per anhydroglucose unit). Reaction efficiency is the percentage of cationic reagent that reacted with the starch.

TABLE II
Strength of Paper Handsheets Containing Cationic Starch

Cationic Starch			Property of Handsheets			
Native Starch	Base Used During Modification	Addition (kg/t)	Basis Weight (g/m^2)	Breaking Length (km)	Burst Index ($kPa \cdot m^2/g$)	Scott Bond (J/m^2)
Blank	...	0	75.3	3.3	2.0	43.6
Corn[a]	...	4.5	74.8	3.8	2.4	54.4
Corn[b]	NaOH	4.5	75.8	4.0	2.0	51.1
	$Ca(OH)_2$	4.5	74.7	3.7	2.3	57.3
Oat[b]	NaOH	4.5	75.4	4.1	2.1	46.7
	$Ca(OH)_2$	4.5	75.3	4.1	2.2	47.5
Wheat[b]	NaOH	4.5	74.7	3.9	2.2	45.6
	$Ca(OH)_2$	4.5	75.9	4.1	2.3	52.2
Corn[a]	...	9.1	75.2	4.3	2.6	62.2
Corn[b]	NaOH	9.1	74.9	4.4	2.5	67.5
	$Ca(OH)_2$	9.1	74.7	4.1	2.4	57.5
Oat[b]	NaOH	9.1	74.4	4.3	2.2	46.5
	$Ca(OH)_2$	9.1	75.5	4.5	2.5	60.1
Wheat[b]	NaOH	9.1	74.4	4.0	2.3	51.7
	$Ca(OH)_2$	9.1	75.6	4.2	2.5	55.9
Corn[a]	...	18.2	75.4	4.6	2.8	64.9
Corn[b]	NaOH	18.2	74.9	4.7	2.7	74.5
	$Ca(OH)_2$	18.2	74.9	4.6	3.0	57.9
Oat[b]	NaOH	18.2	79.0	4.5	2.9	57.2
	$Ca(OH)_2$	18.2	75.8	4.6	2.8	62.6
Wheat[b]	NaOH	18.2	74.7	4.6	2.8	63.8
	$Ca(OH)_2$	18.2	76.4	4.5	2.8	64.6

[a] Commercial amphoteric starch (Cato 15), nitrogen level indicated a degree of substitution of 0.029.
[b] Cationic starches prepared in this work with a degree of substitution of ~0.013.

AGU in 0.5*M* $Ca(OH)_2$/0.49*M* $CaCl_2$. Figure 2A shows that reducing the reaction temperature to 25°C and stirring for 20 hr gave a cationic oat starch with a DS of 0.014 (28% efficiency). It was not possible to further increase the efficiency at 25°C because the starch gelatinized after approximately 24 hr of stirring. When the etherification reaction was done at 35 and 40°C, the rate increased, but the reaction efficiencies remained low at 25 and 16% after 8 and 3 hr of stirring, respectively. Stirring beyond those times transformed the reaction mixture into a gel (Fig. 2A).

In contrast to etherification in the presence of 0.5*M* calcium hydroxide/0.49*M* calcium chloride, an oat starch slurry (31% solids) in 0.48*M* sodium hydroxide and 2.43*M* sodium sulfate gave 50–80% reaction efficiency (Fig 2B). This reaction mixture did gel at 40°C after a 3-hr reaction time, when the product had a DS of 0.025.

When the concentration of sodium sulfate was decreased from 2.5 to 0.5*M* in the presence of 0.5*M* alkali, adding oat starch to the mixture gave an immediate gel. The low solubility (~0.02*M*) of $Ca(OH)_2$ at 25°C prevents the gelatinization of oat starch but also leads to a relatively slow and inefficient etherification reaction (Fig. 3).

Strength of Paper Handsheet Containing Modified Starch

Paper handsheets containing any of the six cationic starches were stronger than a handsheet made with no added starch as determined by tensile strength (breaking length), burst index, and Scott bond (Table II). The Scott bond in paper was higher for cationic oat and wheat starches prepared with calcium ion than for those prepared with sodium ion, but the opposite was true for corn starch, except at the low level (4.5 kg/t) of usage. The cationic corn starch generally gave higher Scott bond than cationic wheat and oat starches at the low and medium (4.5 and 9.1 kg/t) levels in the paper sheets, but the differences narrowed at the high (18.2 kg/t) level.

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