

Preparation of Cationic Starch Containing Quaternary Ammonium Substituents by Reactive Twin-Screw Extrusion Processing*

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SYNOPSIS

Cationic starch, an important additive for papermaking and other uses, was prepared from native cornstarch and 3-chloro-2-hydroxypropyltrimethylammonium chloride in aqueous sodium hydroxide using a twin-screw extruder as the reactor. The effects of physical and chemical reaction variables on reaction efficiency (RE) and degree of substitution (DS) of up to 0.05 were studied. RE was based on nitrogen content contributed by cationization of the starch after the products were exhaustively washed to remove unreacted monomer. Under certain reaction conditions, exceptionally high RE (90%+) was achieved, exceeding maximum values previously reported using laboratory-batch reaction procedures. The combined effects of high reaction temperature (90°C), intense mixing, high-starch solids (65%), and appropriate levels of catalyst contributed to the unusually high RE values achieved by the reactive extrusion process. © 1994 John Wiley & Sons, Inc.[†]

INTRODUCTION

The reaction of cornstarch with a cationic chlorohydrin monomer to form cationic starch ether derivatives in a twin-screw extruder is presently reported. Cationic starches with low degrees of substitution (DS 0.02–0.05) are widely used in the papermaking industry, particularly as wet-end paper-strengthening additives.¹ These derivatives are also important for sizing paper and textiles, coatings, flocculation of organic and inorganic matter, separation of oil from aqueous emulsions, preventing loss of oil-well drilling fluids, and for other applications.² The usefulness of these positively charged starch derivatives arises primarily from their affinity for negatively charged polymers, pigments (e.g., clay), salts, and other anionic materials. The effectiveness

of cationic starches is related particularly to their DS, charge density, charge distribution, molecular weight, and dispersion characteristics.

Cationic starches with amino, ammonium, sulfonium, phosphonium, and other groups have been produced.^{1–3} Currently, monomers such as 2-diethylaminoethyl chloride, 2-dimethylaminoethyl chloride (or bromide), and 2-diisopropylaminoethyl chloride are important for the preparation of tertiary aminoalkyl cationic starch ethers. However, the most widely used monomer is probably 3-chloro-2-hydroxypropyltrimethylammonium chloride under the trade name Quat 188.⁴ Reaction of the latter monomer with starch and an alkaline catalyst yields a quaternary ammonium cationic starch ether. The scheme for this reaction in aqueous media is shown in Figure 1. Reaction of the monomer with NaOH forms the epoxide ring, which reacts readily with starch hydroxyl groups. This reaction occurs slowly with ungelatinized starch granules but relatively rapidly with gelatinized starch. Conventional batch reaction procedures employ temperatures of about 35–40°C, starch in water concentrations of 25–35%, and, generally, a salt such as Na₂SO₄ to maintain

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Journal of Applied Polymer Science, Vol. 54, 1855–1861 (1994)
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CCC 0021-8995/94/121855-07

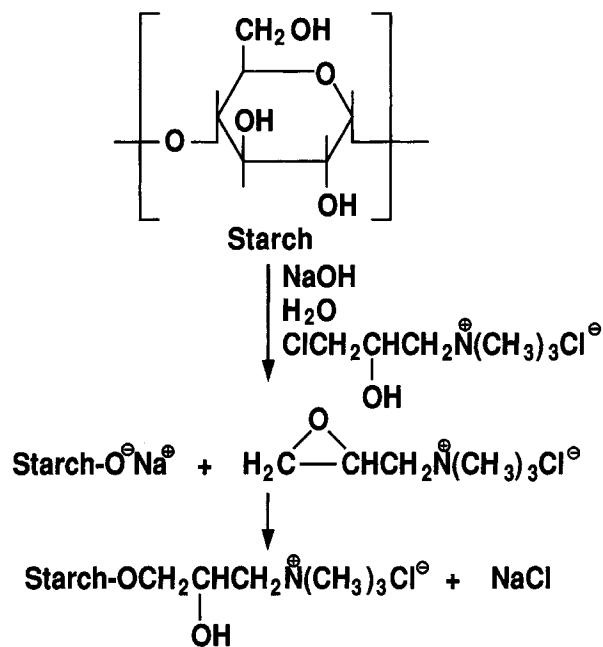


Figure 1 Reaction scheme for preparation of cationic starch ether from native unmodified cornstarch and 3-chloro-2-hydroxypropyltrimethylammonium chloride and sodium hydroxide catalyst in aqueous media.

integrity of the unswollen granule over a reaction period of 2 or more hours. A DS of not more than 0.05 (one monomer substitution/60 hydroxyl groups) is suitable for most widely used applications such as papermaking and sizing. However, DS levels of 0.2–0.7 are more effective for flocculation applications.^{5,6}

A reaction efficiency (RE) of 85% would be considered excellent for the reaction shown in Figure 1. RE refers to the percentage of the monomer that covalently bonds to starch. Previously, a maximum RE of 88% was achieved in a study that used a typical type of laboratory-batch procedure using reaction periods of several hours.⁷ Wheat starch and QUAT 188 have been reacted in a Clextal BC45 twin-screw extruder.⁸ However, in that study, a maximum RE of 82% was achieved only after aging the extrudate for 24 h, concurrently with brown-color formation. In the present study, unmodified cornstarch was reacted with Quat 188 and NaOH in aqueous media in a ZSK 30 twin-screw extruder under a number of conditions not achievable in conventional batch reaction systems or previously reported. This report provides basic information for the preparation of cationic starch with maximum DS levels of 0.025 and 0.050 by continuous reactive extrusion procedures at conditions that resulted in RE values of up to 90% or more.

The potential for the extruder as a reactor for achieving high-efficiency cationization of starch has been demonstrated in the present study. Although the process was continuous with respect to cationization, downstream processing equipment and procedures would need to be developed for removing unreacted monomer and salts of neutralization for some applications. However, the crude cationic starch may be suitable as extruded for applications such as waste water treatments, particularly when 90% of the monomer is covalently bonded to starch and the residual monomer is rendered inactive.

EXPERIMENTAL

Materials

The materials included native unmodified cornstarch (Buffalo 3401, CPC International, Englewood Cliffs, NJ), Quat 188 (65% active monomer, 5% inactive monomer, and 30% water, Dow Chemical, Midland, MI), sodium hydroxide (97% purity, EM Science, Gibbstown, NY), and distilled water.

Equipment

The extruder was a ZSK 30 twin-screw extruder (Werner & Pfleiderer, Ramsey, NJ) with corotating, fully intermeshing screws previously described.^{9,10} The intense mixing screw was composed of 61 individual slip-on mixing elements on each shaft. Various types of kneading blocks (12 each shaft including two reverse-flow blocks) and screws of various designs for feeding, conveying, compressing, reverse-flow, and pumping purposes were intermittently spaced along the shafts. Left-handed (reverse pitch) elements were spaced closely following injection of the Quat 188 monomer. A less intense mixing screw design was also used. This design used 50 elements each shaft, of which only four of each shaft were kneading blocks. Two of these blocks were placed just after injection of aqueous NaOH, and two were placed just after injection of Quat 188. The total length of the processing section was equivalent to an L/D ratio of 43 (length of processing section \div screw diameter). The die-head assembly was equipped with a die containing two 4 mm-diameter holes.

Procedures

Starch with 10% moisture was fed into barrel section number 1 (BS-1) using a K-TRON loss-in-weight

feeder. Aqueous solutions of NaOH were metered into BS-3, while Quat 188 (65% active monomer in aqueous solution, used as shipped) was metered into BS-5 using LEWA high-pressure, reciprocating, piston pumps. Reaction temperatures were either 70, 80, or 90°C in all zones (eight zones) except zone 1, which was kept at 70°C for all experiments. After steady-state conditions were achieved, the extrudate was collected directly in a Waring Blendor cup containing 500 mL of methanol and sufficient HCl to bring the pH to about 5. Each sample was collected at the die for 1 min and then rapidly and vigorously blended with the methanol/HCl to simultaneously neutralize and precipitate the product. The methanol/HCl supernatant was decanted and the product was washed twice more in the blender with 500 mL portions of ethanol. The precipitate was collected on Whatman #54 filter paper and again washed with methanol and then acetone. The products were allowed to dry to about 10% moisture at room conditions under a hood. All samples were milled to pass a screen containing 0.5 mm-diameter holes using a Wiley-type mill before analyzing the granular products for moisture and nitrogen. Nitrogen contents of the dried samples were determined basically by the Kjeldahl method using a Kjeltac distilling unit system (Model 1026, Hoganas, Sweden), a titration stirrer/Burette (Model 400, Fischer Scientific), and a computer scientific titrimeter/printer (Model 465, Fisher Scientific).

Calculations

The formula for calculating the degree of substitution (DS) of the starch derivative is as follows:

$$DS = \frac{162 \times \left\{ \frac{\% \text{ substituent}}{152.5} \right\}}{100 - \left\{ \frac{151.5}{152.5} \times \% \text{ substituent} \right\}}$$

where 162 = average molecular weight (MW) of the starch anhydroglucose unit; the substituent is $-\text{CH}_2\text{CHOHCH}_2\text{N}(\text{CH}_3)_3\text{Cl}$ with an MW of 152.5. The denominator accounts for the loss of one hydrogen atom from a starch hydroxyl for each substitution (see Fig. 1). The % substituent by weight was calculated from nitrogen content of the cationic starch after corrections for moisture and a small amount of nitrogen present in the unmodified starch before derivatization (0.035%). Reaction efficiency (RE) was calculated by dividing the DS found by the theoretical DS (0.050 for most experiments).

Table I Primary Formulation for Preparation of Low DS Cationic Starch By Reactive Extrusion^a

Materials	Feed Rate	
	(g/min)	(Mol/Min)
Starch, dry basis (d.b.)	81.0	0.500
Moisture of starch	9.0	N/A
NaOH, pure basis	2.0	0.050
Water of NaOH solution	34.6	N/A
Monomer (Quat 188)	4.7	0.025
Monomer, inactive, d.b.	0.4	N/A
Water in monomer solution	2.2	N/A

^a Cornstarch, NaOH solution, and Quat 188 monomer solution were fed into barrel sections 1, 2, and 5, respectively. N/A = not applicable.

RESULTS AND DISCUSSION

Formulation

The primary formulation for present work is shown in Table I. This formulation was chosen because cornstarch, Quat 188, and sodium hydroxide are the major raw materials for producing cationic starches in the United States and because the DS is generally not greater than 0.05 for major applications such as in papermaking. The level of the catalyst (NaOH) in this formulation was based on previous results in which laboratory batch-preparation procedures were used.⁷ The starch feed rate was primarily based on previous studies using the ZSK 30 twin-screw extruder as a reactor.⁹⁻¹¹ Another reason for choosing the rates shown in Table I was to easily express these rates in terms of mol ratios. For example, 81 g of starch (d.b.) is exactly 0.5 mol, and 4.7 g of Quat 188 is exactly 0.25 mol. Thus, mol ratios of the three reactants can be expressed as 1 : 2 NaOH/monomer, 1 : 10 NaOH/starch, and 1 : 20 monomer/starch. The amount of water in the formulation gives a starch concentration of 65%, expressed as (g starch, d.b. ÷ g starch with moisture + water added) and a total solids concentrations of about 60%. Also, other concentrations were evaluated. Results for these and other feed rates are discussed below.

Mixing

Two screw configurations were investigated using the formulation in Table I. The mixing capability of one was considerably more intense than was the

Table II Effect of Screw Profile Arrangement on Reaction Efficiency (RE) and Degree of Substitution (DS)^a

Screw		Quenched Reaction, Yes/No	Nitrogen Content (%)	RE (%)	DS
Mixing Intensity	Speed (rpm)				
Weak	100	Yes	0.29	69	0.034
Strong	100	Yes	0.32	76	0.037
Strong	100	No	0.39	93	0.045
Weak	50	Yes	0.34	81	0.039

^a Reaction temperature = 80°C. Cornstarch concentration = 65%. Maximum DS possible = 0.050. Maximum nitrogen possible = 0.42%. Monomer = Quat 188.

other as indicated in the Experimental section. Table II shows the results that were obtained using the two screw configurations at screw speeds of 50 and 100 rpm and at a reaction temperature of 80°C. The reaction was quenched in about 2–3 min after sampling for 1 min at the die in order to estimate the extent of reaction occurring primarily within the extruder. In some cases, unquenched samples were allowed to stand 20 h before determining the extent of the reaction (see Experimental). Data show that fairly high RE and, therefore, high reaction rates occurred using both intense and weak mixing screws at 100 rpm. However, RE was significantly higher for the stronger mixing screw (76% vs. 69%). This may have been primarily because the residence time of material in the extruder was about 1 min greater for the stronger mixing screw. Data clearly show the importance of residence time in the extruder using the weak mixing screw at 50 rpm (81% RE). The average residence time was about 2 min longer at 50 rpm than at 100 rpm. Data also show that exceptionally high RE (93%) was obtained when unquenched samples were allowed to stand 20 h at room temperature without further mixing. In general, data suggest that, although good mixing is important, residence time is much more important. All subsequent experiments were conducted with the use of the strong mixing screw.

Sample Replication

Data in Table III show RE values of unquenched samples collected at 10–15 min intervals at the die. These samples were aged at room temperatures for 20 h after collection. The primary formulation was used in the reaction. Starch concentration was 65%, reaction temperature was 80°C, and screw speed was

400 rpm. RE values ranged from 90 to 95%, of which four were 93%. The range in values reflects all possible errors involved in the processing, precipitation/washing procedures, and moisture/nitrogen analyses.

Starch Concentration/Temperature

The effect of reaction temperature and starch concentration on RE is somewhat dramatic, as shown in Figure 2. These experiments were conducted using the primary formulation of Table I and the intense mixing screw at 200 rpm. In all cases, the reaction was quenched immediately after sampling, as previously described. Data indicate that the quantity of water in the formulation is probably the most important variable affecting the reaction rate. At 35% starch concentration, the RE values were 8–40% (70–90°C), compared to 70–92% at 65% starch concentration. Reaction temperature was also a very important variable. At 70°C, the extrudate was less gelatinized at 35% starch concentration than at either 50 or 65%. The reaction rate would be expected to be slower for the less gelatinized starch, presumably because the hydroxyl groups are less readily available. The true effect of temperature on the reaction rate is unclear since the extent of gelatinization, and, hence, hydroxyl availability, is a function of temperature as well as of starch concentration. The effect of temperature at 70–90°C appeared to be greatest at 50% starch concentration (36–84%

Table III Sampling Replication Data in Preparation of Cationic Starch by Reactive Extrusion^a

Sampling Time	Nitrogen Content (%)	Product Constituents (g/100 g of Product) ^b		RE ^c (%)	DS
		Monomer	Starch		
9 : 50	0.38	5.1	94.9	90	0.045
10 : 00	0.39	5.3	94.7	93	0.047
10 : 17	0.39	5.3	94.7	93	0.047
10 : 32	0.40	5.4	94.6	95	0.048
10 : 45	0.39	5.3	94.7	93	0.047
11 : 00	0.39	5.3	94.7	93	0.047

^a Reaction temperature = 80°C. Cornstarch concentration = 65%. Screw speed = 400 rpm. Maximum degree of substitution (DS) possible = 0.050. Monomer = Quat 188.

^b Product = cationic cornstarch, dry basis.

^c RE was determined after aging the unquenched samples about 20 h.

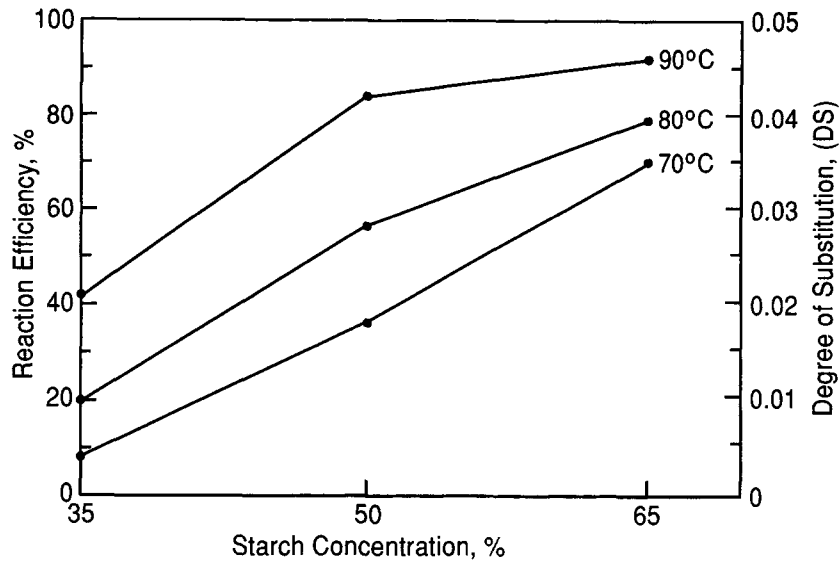


Figure 2 Effect of starch concentration and reaction temperature on RE and DS using a ZSK 30 twin-screw extruder reactor. Screw speed = 200 rpm. Intense mixing screw. Maximum DS possible = 0.050.

RE) compared to either 35 or 65%. It is worth mentioning that higher reaction rates may be achievable at 50% starch concentration by optimization of the physical, mechanical, and chemical variables.

Screw Speed

The effect of screw speed on RE is shown in Figure 3. The primary formulation was employed, except

that various amounts of water were used. The reaction temperature was 80°C, and samples were quenched as previously discussed. These data show that increases in screw speed produced moderate increases in RE and DS. As screw speed was increased from 100 to 400 rpm at various starch concentrations, RE increased from 11 to 20%, 48 to 59%, and 75 to 85% at 35, 50, and 65% starch concentrations, respectively. This effect occurred even though losses

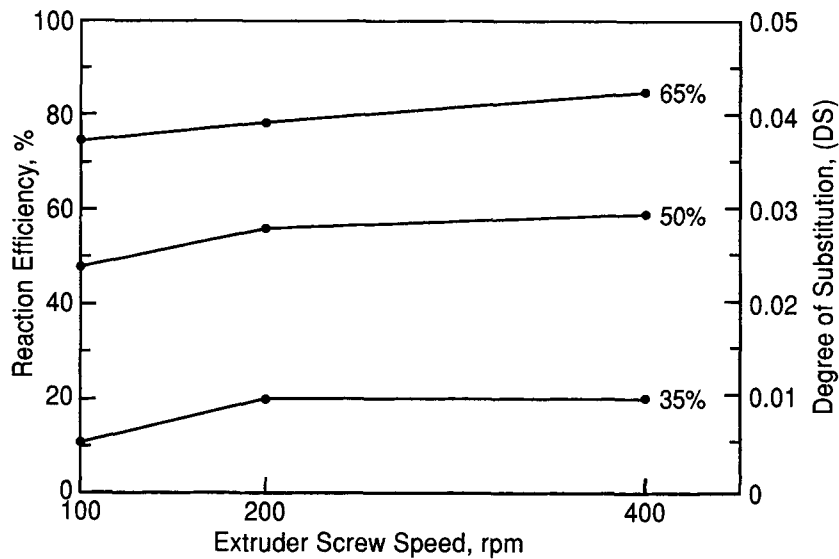


Figure 3 Effect of screw speed at various starch concentrations on RE and DS in a ZSK 30 twin-screw extruder reactor. Reaction temperature = 80°C. Intense mixing screw. Maximum DS possible = 0.050.

in RE would be expected as a result of concomitant reductions in residence time of 2 min at 400 rpm compared to 100 rpm (average 3 min vs. 5 min). However, another factor to be considered is the mechanical heat generated at 400 rpm at high starch concentrations. The extruder chiller system could not maintain material temperature at 80°C in zones 5–8. Thus, at 65% starch concentration, the material temperature at the die reached about 85°C. It is worth noting that 400 rpm is not a realistic screw speed for the feed/production rates used in this formulation, but, nevertheless, provided useful information.

Monomer/NaOH Mol Ratios

Figure 4 shows the results that were obtained by altering the mol ratios in the formulation. The intense mixing screw was used at 100, 200, and 400 rpm for each of the conditions shown. All samples were quenched as previously described. Curve 1 shows that high RE values (88–91%) were achieved at 65% starch concentration using exactly one-half the quantities of NaOH catalyst and Quat 188 that were used in the primary formulation. Based on the results discussed above, this could be expected since the NaOH/monomer ratio was identical to that of the primary formulation. However, the NaOH/starch ratio of the curve 1 experiment was one-half

that of the primary formulation. Hypothetically, this would reduce the number of hydroxyl groups available in the ionized form (starch- $\bar{O}Na$). Nevertheless, slightly higher RE values were obtained at 100 and 200 rpm with this formulation (curve 1) than with the primary formulation (curve 2). Curve 3 shows the results obtained by increasing NaOH 50% over that of the primary formulation. A temperature of 70°C and a starch concentration of 50% was used to reduce the extent of side-reaction products that can occur at higher temperatures and concentrations using this level of NaOH. Data reveal that RE values for the latter experiment were significantly higher than those in which the primary formulation was used at a higher temperature (70°C, curve 3 vs. 80°C, curve 4). However, there was a concomitant yellow/brown color of the extrudate, indicating side-reaction components. Curve 5 shows that a NaOH/Quat 188 monomer ratio of 50% less than was used in the primary formulation resulted in a relatively slow reaction rate, even though the screw speed was 400 rpm, the starch concentration was 65%, and the reaction temperature was 80°C.

Feed Rate/Production Rate

Very brief experimentation indicated that the total feed rate in the primary formulation can be doubled without loss of RE. The comparison was made using

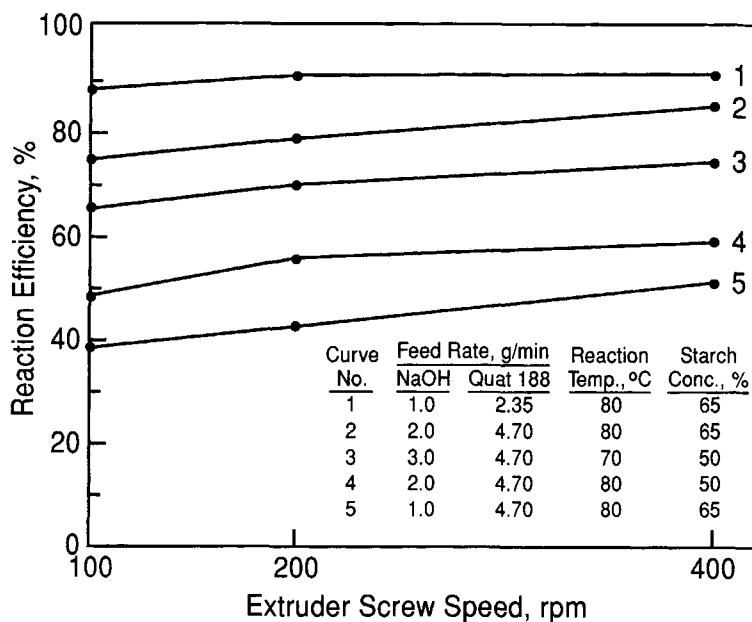


Figure 4 Effect of monomer and sodium hydroxide concentrations and mol ratios on RE and DS in a ZSK 30 twin-screw extruder reactor. Maximum DS possible for curve 1 = 0.025; for curves 2–5 = 0.050.

Table IV Effect of Feed Rate on RE and DS in Preparation of Cationic Starch by Reactive Extrusion^a

Starch	Feed Rate (g/min)		Reaction Temp (°C)	Starch Concn (%)	Nitrogen (%)	RE (%)	DS
	Water/NaOH	Monomer					
90	34.6/2.0	4.7/2.2	90	65	0.348	83	0.042
180	64.8/4.0	9.4/4.4	90	65	0.360	86	0.043

^a Cornstarch contained 10% moisture. Monomer = Quat 188 as shipped (4.7 g active monomer + 2.2 g water). Screw speed = 200 rpm.

the intense mixing screw, a screw speed of 200 rpm, a starch concentration of 65%, and a reaction temperature of 90°C. Table IV shows that high RE values were obtained (83–86%) in both instances. The difference in RE values of 83 and 86% is probably not significant considering all possible factors in the replication process. With respect to the important economic implications related to production rate, this area of investigation needs considerably more attention.

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Received February 23, 1994

Accepted May 4, 1994