Preparation of Cationic Wheat Starch by Twin-Screw Reactive Extrusion

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ABSTRACT: Cationic starches were prepared in a corotating twin-screw extruder by using wheat starch and two different reagents: 2.3-epoxypropyltrimethylammonium chloride (Quab 151®) and 3-chloro 2-hydroxypropyltrimethylammonium (Quab 188®) in aqueous sodium hydroxide (NaOH). The different factors affecting this reaction were investigated. These factors include the extrusion conditions (feed rate, screw speed, barrel temperature), the reagent chemical structure, the starch plasticizer, and the molar ratio between Quab and NaOH. Degree of substitution (DS) and reaction efficiency (RE) were characterized, as well as starch transformation. High reaction efficiency (90%) can be reached for a low degree of substitution. It appears that the epoxy form of the reagent (Quab 151®) is more efficient in all processing conditions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 201–208, 2004

Key words: cationic starch; efficiency; degree of substitution; reactive extrusion; twin-screw extruder

INTRODUCTION

Cationic starches are produced from starch with reagents containing amino, ammonium, sulfonium, or phosphonium groups, which are able to carry a positive charge.[1] Starch cationization consists of substituting the hydroxyl groups of the glycosyl units by one of these functional groups. The degree of substitution (DS) indicates the average number of sites per anhydroglucose unit on which there are substituent groups. Thus, if one hydroxyl on each of the anhydroglucose units was cationized, DS is equal to 1. If all three hydroxyls were cationized, DS is maximum and is equal to 3. Cationic starches used in industry usually have DS in the range of 0.02–0.10.

These modified starches are used in various fields. In papermaking, cationic starches can increase strength, filler and fines retention, and drainage rate of the pulp. They can also lower biological oxygen demand (BOD) of the white water when used as wet-end additives. Sizing agents based on cationic starches offer unique advantages because of their electrochemical attraction to cellulosic fibers. Moreover, because of the tenacity of the ionic bonding, these modified starches are not removed during repulping of broke. As a result, the BOD and chemical oxygen demand (COD) of mill effluents are lower than with other starches. Cationic modification is typically combined with reactions that degrade starch, leading to various viscosity grades.[2] Cationic fluid starches are useful paper binders that provide high strength, ink holdout, and gloss at lower levels than other starches.[3,4] In the textile industry, cationic starches containing hydrophobic groups clean and absorb soils from carpets and upholstery.[5] They are excellent flocculants for suspensions of inorganic or organic matter having a negative charge. Their effectiveness is related to molecular weight and degree of substitution.[6] In adhesives, bottle-labeling adhesives were made by using mixtures of quaternary ammonium starch ether, hydroproxypyl derivatives of oxidized starches, and maize starch.[7] Uniform aqueous dispersions of manganese dioxide were produced by reduction of potassium permanganate in the presence of cationic starch. This system was used in making annihilation layers for photographic film.[8] Cationic starches also showed improved performance over conventional starch as fluid loss control agents for drilling fluids having high-calcium (200 to 1000 ppm) and high-salinity concentrations.[9]

Usually, cationic starches are prepared by using conventional batch reaction procedures. Carr and Bagby[10] studied the cationization of maize starch in such systems. The reagent was 3-chloro-2-hydroxypropyltrimethylamonium chloride (Quab 188®) and catalyst was sodium hydroxide. They obtained a DS ranging between 0.01 and 0.07. The parameters influencing this reaction were sodium hydroxide concentration, temperature, starch concentration, and reaction time. For example, with a DS of 0.044, they

TABLE I
Physical Properties of the Reagents

	Quab 151®	Quab 188®
Active monomer (%)	72	69
Inactive monomer (%)	5	1
Water (%)	20	30
Molecular weight (g/mol)	151.6	188.1
Density	1.129	1.166
Viscosity at 20°C (mPa s)	80	20

could obtain an efficiency of reaction (RE) of 84%, at 25°C in 48 h. At 50°C, the reaction time falls to 4 h.

However, the cationization by chemical process in a batch reactor presents some drawbacks, such as discontinuous process with low yield, residual reactive agent elimination, and environment pollution. Thus, to overcome these drawbacks, some attempt was made to develop starch cationization by using reactive extrusion process.

Della Valle et al.[11,12] extruded cationic maize starch by using a pilot scale twin-screw extruder (Clextral BC 45). Processing conditions were as follows: added water, 20%; barrel temperature, 120°C; screw speed, 200–250 rpm; feed rate, 20–26 kg/h. The position where reagents were injected had an influence on the reaction. RE increased from 60 to 71% under the same operating conditions just by modifying injection position, from a location after the melting zone to an upstream one. Reagent concentration had an influence on DS and RE. When reagent concentration increased, final DS increased (from 0.04 to 0.09), while RE decreased (from 72 to 64%). Last, these authors showed that the low viscosity of cationic starches, due to starch degradation during extrusion, was an advantage for papermaking.

Carr[13,14] resumed his early work by using reactive extrusion and studied the influence of temperature, starch concentration, and screw speed. He noticed that RE and DS increased with starch concentration and temperature (between 70 and 90°C), and less markedly with screw speed.

Reactive extrusion is becoming more popular because cationization by batch process in reactors presents numerous drawbacks. However, this new technology presents some problems related to the mastering of the process, arising from the multiple interactions between properties of raw materials, operating conditions, and properties of the final product.[15] The present study deals with the development of wheat-starch cationization process in a corotating twin-screw extruder. We focused the study on the influence of the different processing parameters, such as feed rate, screw speed, and barrel regulation temperature. Moreover, two reactive agents were tested. The substitution degree of starch and its structural changes were characterized and related to the processing parameters of the twin-screw extrusion process. Compared to the previous studies of Della Valle et al.[11,12] and Carr,[13,14] this work presents results with two different reagents and offers a more detailed experimental study on the influence of processing parameters which were not previously characterized, such as feed rate, for example. Moreover, the results of the cationization reaction are interpreted in terms of processing parameters, such as residence time and specific energy.

EXPERIMENTAL

Materials

Native wheat starch, with 13 wt % initial moisture content, was provided by Chamtor (F-51110 Bazancourt, France). It contained 74% amylopectin and 26% amylose, with residual protein and lipid contents < 0.2 and 0.7%, respectively. Glycerol (Chamtor) with a 99.5% purity was used as a plasticizer (at a constant amount of 20 wt %). The following two reagents were used: 2,3-epoxypropyltrimethylammonium chloride (Quab 151®) and 3-chloro 2-hydroxypropyl-trimethyl-ammonium (Quab 188®). Both reagents, the properties of which are given in Table I, were supplied by Degussa (Courbevoie, France). Solid sodium hydroxide (NaOH) was purchased under anhydrous pellets from Sosa Caustica Aragoneses (Spain).

Extrusion equipment

We used a laboratory scale corotating twin-screw extruder (Clextral BC 21, Firminy, France). Its main characteristics are as follows: centerline distance, 21 mm; screw diameter, 25 mm; length/diameter ratio, 36. The profile used is depicted in Figure 1. It is composed of
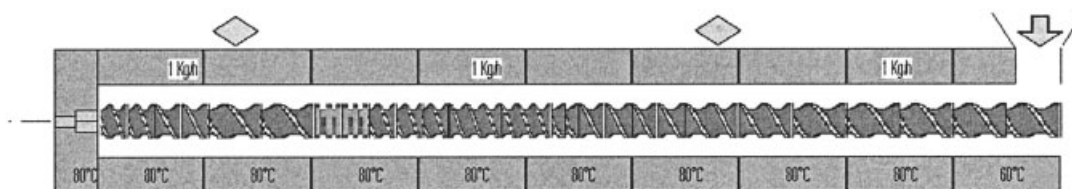

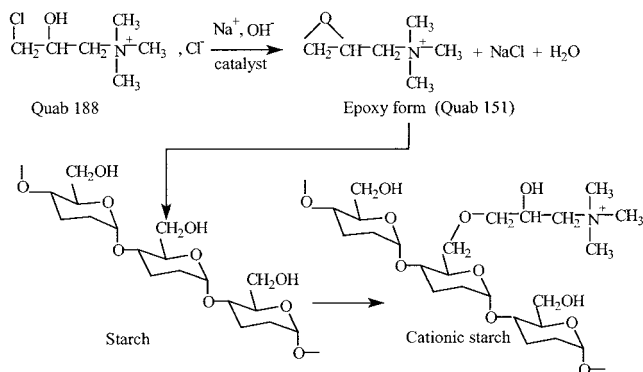**Figure 1** Screw profile (Clextral BC 21).

Figure 2 Reaction scheme of starch cationization.

two-flighted conveying screw elements of various pitches, and a block of eight kneading discs, negatively staggered ($-45°$), to ensure the melting of the starch. The barrel is made up of nine sections of 100 mm each, regulated at a fixed temperature ($50°C$ for barrel section one and, depending on the experiments, 80 or $90°C$ for the others).

Processing conditions

In a first series of experiments, wheat starch was plasticized with 20% water and 20% glycerol (on a dry basis). The reaction of cationization involves two stages with the Quab 188®, the first stage for transforming the reagent in alkaline medium under an active epoxy form, and the second stage for operating the substitution on starch backbone. With the Quab 151® being initially under epoxy form, the first stage is eliminated (Fig. 2). The materials (starch, water, glycerol, Quab, sodium hydroxide) are mixed together in a turbo-mixer (SCAMIA, France) and fed into barrel section 1 by using a volumetric K-TRON feeder. The screw speed is controlled with a variable speed motor. After steady-state conditions are achieved, extrudates are collected directly at the die exit, stored (for 24 h at $25°C$ and 50% relative humidity), and crushed.

A second series of experiments was carried out without glycerol, using 40% water as starch plasticizer. All the tests performed are summarized in Table II. Typically, for the different formulations, we varied screw speed at constant feed rate, and feed rate at constant screw speed, in the range of variations indicated in the table.

The influence of screw speed, feed rate, barrel temperature, type of Quab, Quab concentration, type of plasticizer, and molar ratio (NaOH/Quab) was studied. For each experiment, processing parameters such as specific mechanical energy (SME), mean residence time (by colored tracer), and product final temperature were recorded. SME is directly deduced from the motor torque C following the expression

$$SME = \frac{C\Omega}{Q} \qquad (1)$$

where Ω is the screw rotation speed and Q is the mass flow rate.

Mean residence time is roughly estimated by introducing a colored tracer in the hopper and by measuring the time necessary to obtain at the die exit the maximum of coloration in the extrudate. Product temperature is obtained by introducing a thermocouple in the extrudate at the die exit. Each experiment is repeated two to three times to assess the reproducibility.

Sample analysis

Degree of substitution and reaction efficiency

Ten grams of sample are washed in a blender with 400 mL ethanol, blended for 5 min, filtered on Whatman paper, and dried at $100°C$ for 2 h under a hood. The nitrogen content (%N, between 0 and 1) of each sample of cationic starch was determined by Kjeldahl method (Gerhardt, Kjedatherm). DS is then calculated by

$$DS = \frac{M_S \times (\%N)}{M_N - M_R \times (\%N)} \qquad (2)$$

TABLE II
Processing Conditions for Preparation of Cationic Starch

	Without Quab	—	
Series 1			
20% glycerol	Quab 151®	$DS_{th} = 0.04$	Constant feed rate: 1.9 kg/h
		$DS_{th} = 0.10$	$N = 100/600$ rpm
+20% water	Quab 188®	$DS_{th} = 0.04$	Constant screw speed: 400 rpm
		$DS_{th} = 0.10$	$Q = 0.6/2.5$ kg/h
	Without Quab	—	
Series 2			
40% water	Quab 151®	$DS_{th} = 0.01$	Constant feed rate: 1.9 kg/h
		$DS_{th} = 0.04$	$N = 100/350$ rpm
	Quab 188®	$DS_{th} = 0.01$	Constant screw speed: 400 rpm
		$DS_{th} = 0.04$	$Q = 2/3.5$ kg/h

where M_S, M_N, and M_R are the molar masses of starch anhydroglucose monomer (162 g/mol), nitrogen (14 g/mol), and reagent once fixed on glycosyl unit (152.5 g/mol), respectively. For a reaction efficiency of 100%, the theoretical degree of substitution, noted as DS_{th}, is computed as

$$DS_{th} = \frac{Q_r}{Q_s} I_{pr} \frac{\rho_r M_s}{M_{fr} I_{ps}} \qquad (3)$$

where Q_r (L/h) and Q_s (kg/h) are the flow rates of reagent and starch, as fed in the extruder, M_{fr} is the molar mass of free reagent (151 or 188 g/mol), ρ_r is the reagent density (1.129 or 1.166), and I_{pr} and I_{ps} are the purity indices of reagent (72 or 69%) and starch (87%), respectively. The theoretical degree of substitution corresponds to the molar ratio between reagent and anhydroglucose units. The RE is logically defined by:

$$RE = \frac{DS}{DS_{th}} \qquad (4)$$

Intrinsic viscosity

Starch transformation is evaluated by measurements of both intrinsic viscosity, using Ubbelohde viscometer (length: 100 mm; diameter: 1 mm), and apparent viscosity in solution.[16] We have checked that these two measurements were correlated. Consequently, in the following, we will limit the presentation to intrinsic viscosity. Samples are prepared from native and extruded crushed starch by suspension and mixing (3 h) at 75°C (in 50 mL distilled water containing 2.8 g KOH and 0.5% of extruded starch, i.e., 0.25 g). Four concentrations (0.1–0.4 wt %) are prepared at 25°C. Extrapolation of the reduced viscosity to zero concentration gives the intrinsic viscosity [η] (mL/g).
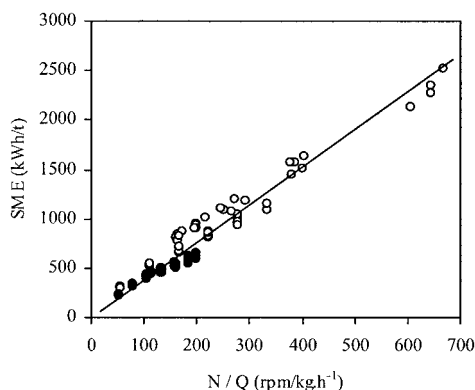

Figure 3 Variation of SME with ratio of screw speed to feed rate ($\bigcirc$, Series 1, 20% glycerol + 20% water; $\bullet$, Series 2, 40% water).
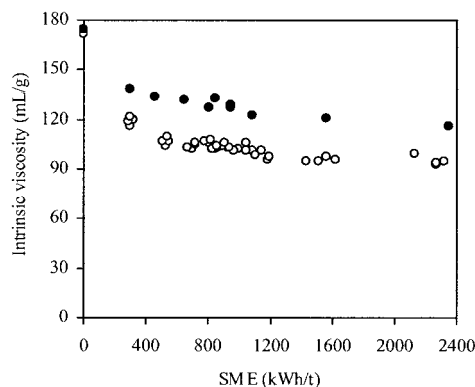

Figure 4 Variation of intrinsic viscosity with SME for experiments of Series 1, without ($\bullet$) and with ($\bigcirc$) cationization.

RESULTS AND DISCUSSION

Extrusion conditions and starch transformation

It is well known that the specific mechanical energy increases with screw speed N and decreases with feed rate Q.[17,18] In fact, we observe in Figure 3 that the specific mechanical energy varies linearly with the ratio of screw speed to feed rate (N/Q), whatever the experimental conditions (different Quabs, plasticizers, and concentrations). As starch transformation is directly correlated to SME,[19] it is possible to control directly this parameter, and therefore, starch intrinsic viscosity, by controlling extrusion parameters (Fig. 4).

Without reaction (meaning without introducing the reagents and extruding only starch and plasticizer), intrinsic viscosity decreases from 174 (native starch) to 120 mL/g for an SME equal to 1560 kWh/t. At the same energy level, the cationized sample has a much lower viscosity, equal to 97 mL/g. Apparently, for cationized starch, starch transformation depends neither on the type of reagent (Quab 151® or Quab 188®) nor on their concentration. Indeed, open symbols in Figure 4 gather data for the two Quabs and the two DS_{th}. From these results, we can express the two following hypotheses. First, the starch degradation is more important with the cationization reaction; hence, it leads to a lower intrinsic viscosity. Second, with or without cationization, the starch degradation induced by specific mechanical energy is the same. However, there could be some attraction forces between charges of cationic starch, which provoke a decrease of hydrodynamic volume of macromolecular chains. This fact could induce lower values of intrinsic viscosity. Analyses of the molar mass by size exclusion chromatography are in progress and will permit us to confirm the right assumption.

Figure 5 shows the influence of screw speed and feed rate on the product temperature at the die exit. Temperature increases quite linearly with both screw
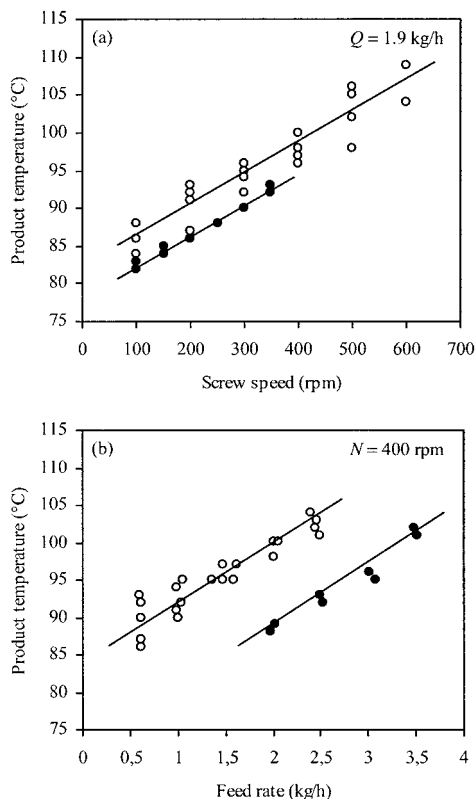
Figure 5 Variations of product temperature with screw speed (a) and feed rate (b) (○, Series 1, 20% glycerol + 20% water; ●, Series 2, 40% water).
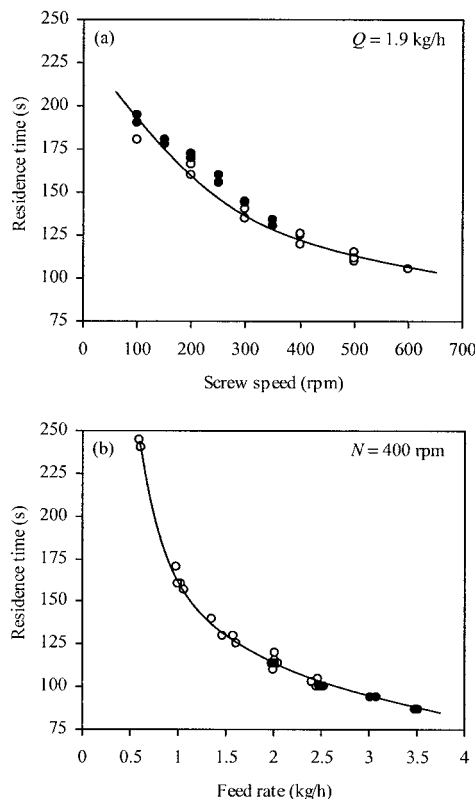

Figure 6 Variations of mean residence time with screw speed (a) and feed rate (b) (○, Series 1, 20% glycerol + 20% water; ●, Series 2, 40% water).

speed and feed rate, due to viscous dissipation. At high speed, the final temperature can be very different (around 30°C) from the barrel temperature (80°C). This evolution is quite independent of the reaction (i.e., it is similar with Quab 151® and with Quab 188®). However, temperature increase is more limited for series 2, which indicates that the starch is more viscous for series 1. Contrary to the temperature, the mean residence time decreases when increasing feed rate or screw speed (Fig. 6). It decreases markedly at low feed rate. There is no influence of the type of plasticizer, as residence time in a twin-screw extruder is independent of the viscosity.[20] All these results show that the parameters controlling the reaction kinetics (time and temperature) depend directly on the operating conditions (screw speed and feed rate). However, unlike SME, there are no simple relationships relating the temperature and the mean residence time to screw speed and feed rate.

Cationization results

The reaction efficiency was measured after 24 h of storage of extruded samples. It was checked (Fig. 7) that kinetics after extrusion was quite stopped and additional reaction rates were very limited. Della Valle

et al.[11] reported that reaction still went on during storage, but reached a plateau after 24 h.

Influence of screw speed

The effect of screw speed on DS is shown in Figure 8. We observe an increase in DS up to 400 rpm, followed by a decrease at higher speeds. A slight increase in DS with screw speed (100–400 rpm) was reported by
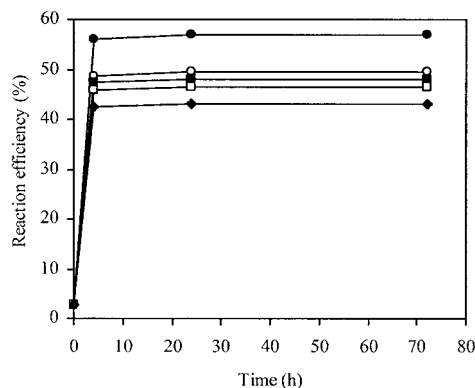

Figure 7 Change in reaction efficiency with storage time for different flow rates (N = 400 rpm; ●, 0.5 kg/h; ○, 1 kg/h; ■, 1.4 kg/h; □, 2 kg/h; ◆, 2.6 kg/h).
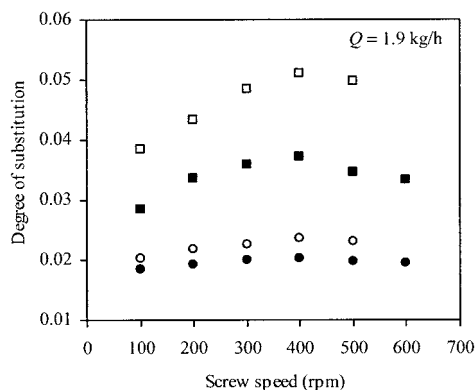
Figure 8 Variation of DS with screw speed at constant feed rate (Q = 1.9 kg/h) for different theoretical degrees of substitution and reagents (Series 1, DS_{th} = 0.04: ○, Quab 151®, ●, Quab 188®; DS_{th} = 0.10: □, Quab 151®, ■, Quab 188®).

Carr,[14] whereas Della Valle et al.[12] noticed no influence, but in a more limited range (200–250 rpm). The same shape of curve is obtained whatever the reagent or the targeted theoretical degree of substitution. As expected, at identical conditions, Quab 151® leads to higher DS. The efficiency obviously follows the same trends, but is lower for higher DS_{th}, as already reported by Della Valle et al.[12] For Quab 151®, it increases from 50 to 62% (DS_{th} = 0.04) and from 33 to 55% (DS_{th} = 0.10), when the screw speed increases from 100 to 400 rpm. These results could probably be explained by the contradictory effects of temperature and residence time. Indeed, when screw speed increases, temperature increases by shearing effects, but the residence time decreases [Figs. 5(a) and 6(a)]. We can imagine that the temperature effect is dominant at low screw speed, whereas the residence time becomes preponderant at high screw speed. This specific effect of screw speed is often observed in reactive extrusion.[21,22] Moreover, it is known that the epoxy form of the reagent is sensitive to high temperatures. Consequently, the decrease of DS at high screw speed could also be due to the thermal degradation of the reagent.

Influence of feed rate

Figure 9 shows the influence of feed rate at constant screw speed (400 rpm) on the degree of substitution. In this case, we observe a continuous decrease of DS, mainly explained by the reduction of residence time indicated in Figure 6(b). If temperature increases also when feed rate is increased, it remains too moderate compared to the important decrease in residence time. In our experiments, feed rate appears as an important factor. However, by multiplying the feed rate by 2, Carr[14] observed no effect on DS or RE. We have too few details on his processing conditions (screw profile,

product temperature, SME, etc.) to explain this difference. The effects of the type of reagent and of the targeted DS_{th} are identical to the preceding case. The higher efficiency obtained with Quab 151® is certainly due to the fact that we start directly from the epoxy form and thus the reaction is more rapid.

Influence of NaOH/Quab molar ratio

Starch cationization is catalyzed by sodium hydroxide (NaOH). Consequently, the molar ratio NaOH/Quab influences the reaction kinetics. It has been shown by Ayoub and Bliard,[23] using a micro-compounder, that an increase from 1 to 2 in molar ratio induced an increase in DS from 0.02 to 0.03, and in RE from 40 to 60% (for a DS_{th} equal to 0.05). It can be seen in Figure 10 that, in our experimental conditions, DS increases only slightly with molar ratio, whatever the processing conditions. RE is also only increased by 2.5 to 3.5% when the molar ratio increases from 1 to 2. These results are also different from those of Carr,[14] who reported an increase in RE of a factor of 2 on a similar twin-screw extruder (but with different operating conditions).

Influence of starch plasticizer

It has already been shown that cationized starches are similarly transformed when using water instead of glycerol as plasticizer (Fig. 4). However, it can be observed in Figure 11 that slightly higher DS are obtained with glycerol. Moreover, without glycerol, maximum screw speed is limited to 350 rpm. Above this value, starch is too degraded and begins to be brown colored. The increase in DS observed with glycerol could be explained by the fact that the starch plasticized with glycerol is more viscous than the starch plasticized with water (Fig. 5).
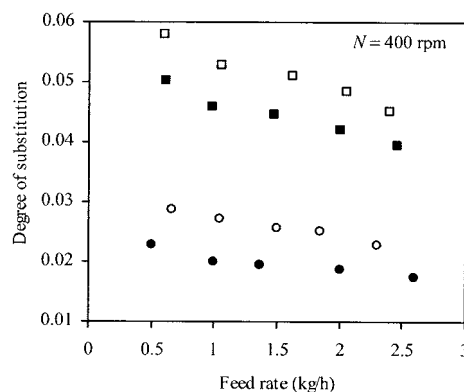

Figure 9 Variation of DS with feed rate at constant screw speed (N = 400 rpm) for different theoretical degrees of substitution and reagents (Series 1, DS_{th} = 0.04: ○, Quab 151®; ●, Quab 188®; DS_{th} = 0.10: □, Quab 151®; ■, Quab 188®).
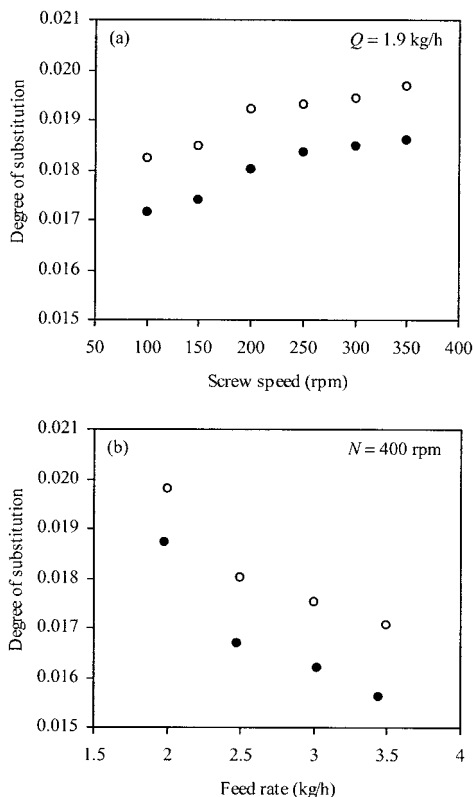
Figure 10 Variation of DS (DS_{th} = 0.04) with screw speed (a) and feed rate (b) for different molar ratios (Series 2, Quab 188®; ●, molar ratio: 1; ○, molar ratio: 2).

This leads to a higher product temperature, which could result in a more advanced reaction. Anyway, even if glycerol seems to be a better plasticizer for wheat-starch cationization, water could be preferred for economical reasons.

Influence of barrel temperature

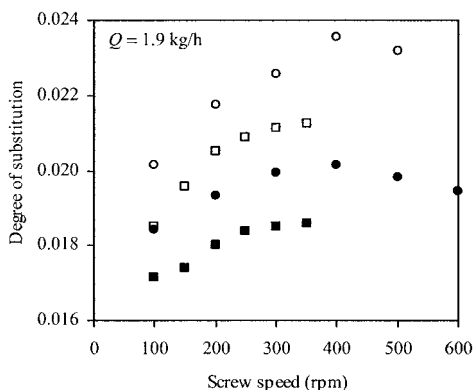Figure 12 shows the influence of barrel temperature on DS. We observe a small increase in DS, and conse-

Figure 11 Variation of DS (DS_{th} = 0.04) with screw speed for different plasticizers at constant feed rate (Series 1: ○, Quab 151®; ●, Quab 188®; Series 2: □, Quab 151®; ■, Quab 188®).
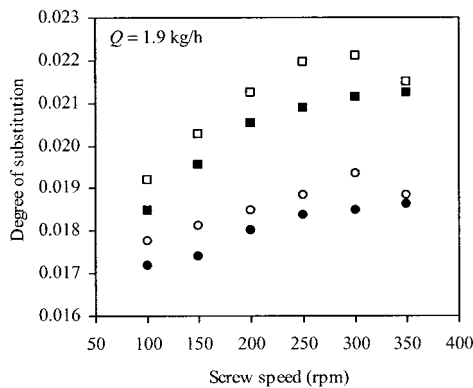

Figure 12 Variation of DS (DS_{th} = 0.04) with screw speed for different barrel temperatures at constant feed rate (Series 2; Quab 151®: ■, 80°C; □, 90°C; Quab 188®: ●, 80°C; ○, 90°C).

quently in RE, when the temperature of the eight barrel sections is increased from 80 to 90°C. However, a rapid decrease appears when the screw speed is higher than 300 rpm. This is due to the degradation of the epoxy form when the product temperature exceeds 100°C. In all cases, for an increase of 10°C in barrel temperature, RE is increased by 1 to 2%.

Processing window

The DS, the theoretical one DS_{th} and the reaction efficiency RE, are interdependent, according to eq. (3). For a targeted DS_{th}, the resulting DS will vary between 0 and DS_{th}; hence, RE varies between 0 and 100%. On the theoretical line linking RE and DS, resulting DS will move between two extreme points depending on operating conditions (Fig. 13). Consequently, it is possible, from the different series carried out, to define a processing window defining the properties of the cationized starches which are likely to be obtained. We can see that, in our experimental conditions, high RE (80–90%) can only be obtained for low DS_{th} (< 0.03)
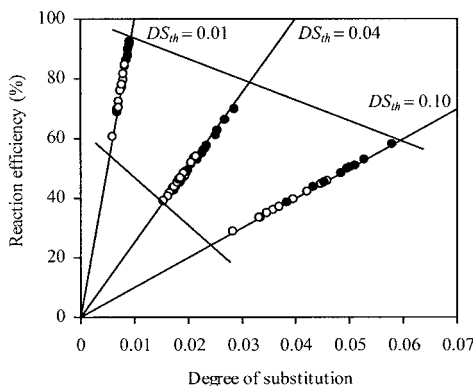

Figure 13 Processing window: variation of reaction efficiency with degree of substitution (●, Quab 151®, ○, Quab 188®).

TABLE III
Variation of *DS* with Feed Rate at Constant Screw Speed (*N* = 400 rpm) for Different Theoretical
Degrees of Substitution and Reagents (series 2)

| | DS_{th} = 0.01 | | | | DS_{th} = 0.04 | | | |
| | Quab 151® | | Quab 188® | | Quab 151® | | Quab 188® | |
Feed rate (kg/h)	DS	RE (%)	DS	RE (%)	DS	RE (%)	DS	RE (%)
2	0.0092	92.21	0.0085	84.56	0.0215	53.71	0.0187	46.81
2.5	0.0086	86.32	0.0078	78.10	0.0208	51.91	0.0167	41.72
3	0.0082	81.62	0.0072	72.23	0.0193	48.31	0.0162	40.53
3.5	0.0079	79.27	0.0070	70.47	0.0182	45.61	0.0156	39.04

(Table III). To widen this window, it would be necessary to modify the screw profile in order, for example, to increase the residence time without increasing too much the product temperature.

CONCLUSION

The cationization of wheat starch by reactive extrusion was investigated, using both Quab 151® and Quab 188®. The use of the epoxy form (Quab 151®) leads to higher efficiency. At optimum extrusion conditions, RE of 90% was obtained for a targeted DS_{th} of 0.01. Effects of screw speed, feed rate, and barrel temperature on DS and RE were characterized and interpreted in terms of product temperature and residence time. It was shown how to define a processing window, which can be used for conducting the extrusion process. In a next step, the modeling of this reactive process will be developed, based on the previous studies carried out on synthetic polymers.[22,24]

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