University of Groningen

The hydroxypropylation of starch in a self-wiping twin screw extruder

de Graaf, R.A.; Janssen, L.P.B.M.

Published in:
Advances in Polymer Technology

DOI:
[10.1002/adv.10034](https://doi.org/10.1002/adv.10034)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2003

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
de Graaf, R. A., & Janssen, L. P. B. M. (2003). The hydroxypropylation of starch in a self-wiping twin screw extruder. *Advances in Polymer Technology*, 22(1), 56 - 68. <https://doi.org/10.1002/adv.10034>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

The Hydroxypropylation of Starch in a Self-Wiping Twin Screw Extruder

ROBBERT A. DE GRAAF

Akzo Nobel Chemicals, 7400 AA Deventer, The Netherlands

LEON P. B. M. JANSSEN

Department of Chemical Engineering, The University of Groningen, 9747 AG Groningen, The Netherlands

Received: February 5, 2002

Accepted: April 13, 2002

ABSTRACT: Potato starch was chemically modified in an APV self-wiping twin screw extruder to produce hydroxypropylated starch. The product obtained had a molar degree of substitution (MS) between 0.06 and 0.26. The selectivity of the hydroxypropylation reaction varied between 50 and 95%, yields varied between 15 and 95%, and conversions between 30 and 91%. Using viscosity data of native and hydroxypropylated starch, together with extruder parameters like temperatures, residence time distribution, and shear rates, a model was set up to predict the MS values, conversions, and selectivities. With this model, interactions between temperature, reaction, and viscosity can be understood and predicted.

© 2003 Wiley Periodicals, Inc. *Adv Polym Techn* 22: 56–68, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/adv.10034

KEY WORDS: Modified starch, Processing, Reactive extrusion, Screw configuration

Introduction

Starch and its derivatives are used in many industrial processes nowadays. Their usage is no longer limited to food processing, but there are also

Correspondence to: Robbert A. de Graaf; e-mail: Robbert.deGraaf@akzonobel.com.

Contract grant sponsor: Dutch National Innovation Oriented Program Carbohydrates (IOP-k).

applications in the paper, textile, pharmaceutical, and adhesive industry, which are becoming more numerous every year. In order to maintain this position, continuous innovation of the processes and products is essential. One important group of starch derivatives are the starch ethers. In this work we focus on the modification of starch by propylene oxide forming hydroxypropylated starch. Hydroxypropyl starch (HPS) is a chemically modified starch with a wide range of applications. In HPS, part of the hydroxyl groups of the glucose monomers have been converted into *o*-(2-hydroxypropyl) groups. A measure of the number of propylene oxide moles substituted to an anhydroglucose unit (AGU) is the molar substitution (MS). Since an AGU has three hydroxyl groups available for reaction, the maximum possible MS is 3. If substituent groups are able to react further with the reagent, thus forming oligomeric substituents, higher MSs are possible. MSs < 1 are produced by reaction of starch with hydroxypropyl at temperatures below 320 K in aqueous slurries of starch granules. NaCl or Na₂SO₄ is used as a swelling inhibiting salt, and NaOH is used as a catalyst. Producing HPS with MSs > 1 in aqueous slurry becomes increasingly difficult. Increasing the MS lowers the gelatinization temperature of the starch granules.

This type of reaction is performed in batch or continuous stirred tank reactors to overcome mixing problems. Starch polymers dissolve from their granular structure into water, forming a highly viscous paste. This process is initiated at temperatures above 60°C. As a consequence, starch suspensions are used with high salt and water concentrations and low reaction temperatures. The salt is used to inhibit the gelatinization process, allowing higher process temperatures. These mixing solutions give rise to extra costs because

- the salt has to be removed from the end product;
- a long residence time is needed to complete the reaction because of the low reaction temperatures;
- the excess of water used during the reaction results in low reaction selectivities.¹

A reactor that does not have these drawbacks is the extruder. Twin screw extruders can be used to produce modified starches continuously with a more constant product quality. Moreover, the extruder has the advantage of a good mixer for highly viscous fluids, enhanced heat transfer, and good plug flow

characteristics. This paper describes how to perform the hydroxypropylation of starch in a self-wiping twin screw extruder. In order to understand the results of the measurement, a model is presented describing the interactions between extruder parameters, reaction, and viscosity.

Theory

KINETICS

The following reactions take place when gelatinized starch, NaOH, and propylene oxide are mixed:

The acidity constant of the hydroxyl groups on the starch molecules regulates the amount of RO[−] formed. These RO[−] groups are able to react with propylene oxide in the following way:

Catalyzed reaction with starch:

When no base is present the *noncatalyzed reaction* can occur:

Also the propylene oxide is able to react with both NaOH (catalyzed reaction) and water (noncatalyzed reaction):

Catalyzed hydrolysis:

Uncatalyzed hydrolysis:

The reactions proceed according to an $\text{S}_{\text{N}}2$ reaction mechanism.^{1,2} The reactants involved in the slow reaction step determine the reaction rate. The fast reaction steps are rapid, establishing acid-base reactions.^{1,3} The reaction rate equations of the reactions (b)–(e) can be written as

Catalyzed hydroxypropylation: $-R_{\text{PO}} = k_{1,0}c_{\text{RO}^-}c_{\text{PO}}$

Uncatalyzed hydroxypropylation:

$$-R_{\text{PO}} = k_{1,1}c_{\text{ROH}}c_{\text{PO}}$$

Catalyzed hydrolysis: $-R_{\text{PO}} = k_{2,0}c_{\text{OH}^-}c_{\text{PO}}$

Uncatalyzed hydrolysis: $-R_{\text{PO}} = k_{2,1}c_{\text{H}_2\text{O}}c_{\text{PO}}$

In principle propylene oxide can react with 1,2-propanediol in a consecutive reaction to form 1,1'-oxybis-2-propanol in both hydroxide catalyzed and uncatalyzed conditions. According to measurements performed by Lammers et al.^{1,4} in a static mixer, less than 1% of the propylene oxide reacted towards 1,1'-oxybis-2-propanol. Therefore the contribution of this reaction to the overall conversion rate of propylene oxide was neglected.

The reaction constants of the above reactions have been determined by Lammers et al.¹ The selectivity of the reaction towards HPS can be calculated from

$$\sigma_{\text{hps}} = \frac{k_{1,0}c_{\text{RO}^-} + k_{1,1}c_{\text{ROH}}}{k_{1,0}c_{\text{RO}^-} + k_{1,1}c_{\text{ROH}} + k_{2,0}c_{\text{OH}^-} + k_{2,1}c_{\text{H}_2\text{O}}} \quad (1)$$

Figure 1 shows that the selectivity decreases at higher temperatures. Moreover there is an optimum in the selectivity curve depending on the amount of NaOH (catalyst) added.

From these kinetics the following overall conclusions can be drawn. Increasing the starch concentration gives an increase in the selectivity. Increasing the temperature will result in an increase in the total conversion of propylene oxide but a decrease in the selectivity towards HPS and the amount of propylene oxide which will dissolve into the highly viscous starch paste. This last effect is a result of the pronounced evaporation of propylene oxide out of the reaction medium (propylene oxide boils at 305 K). Increasing the process pressure reduces this problem.

FIGURE 1. Selectivity vs. catalyst concentration at different temperatures.¹ — $T = 363$ K, --- $T = 333$ K, ... $T = 303$ K.

Finally the ratio water to propylene oxide is of importance.⁵ Certain ratios are unfavorable, and so the degree of substitution is a function of the temperature, the water concentration, the NaOH concentration, the extruder pressure, and the propylene oxide concentration.

THE COROTATING SELF-WIPING TWIN SCREW EXTRUDER

The geometry of the screws of this extruder type can be described as an “eight”-shaped chamber with a rather large tetrahedral gap. Because of this gap, the mean transport mechanism in a corotating self-wiping twin screw extruder is drag flow^{6,7} implying that back pressure can have a large effect on the actual throughput. The simplest approximation considers the channel to have a rectangular cross-sectional shape, with average height H and width W . The barrel wall is treated as moving with a velocity U_w over the screw channel under an angle φ , the pitch angle. The real throughput equals the sum of the maximum drag flow and the pressure flow^{7,8}:

$$Q_{\text{real}} = Q_d - Q_p$$

or

$$Q_{\text{real}} = \frac{1}{2}(2m-1)U_w H W F_d - (2m-1)\frac{W H^3}{12\eta}\left(\frac{dp}{dz}\right)F_p \quad (2)$$

For a given extruder geometry and an iso-viscous fluid, the drag flow and pressure flow are therefore

determined by the screw rotation rate and the real throughput. In case of rectangular screw channels, analytical solutions for the shape factor F_d and F_p can be obtained.^{9–11} However, for the complex screw geometry of a self-wiping extruder, F_d and F_p can only be calculated numerically⁶ or measured.^{12,13}

VISCOSITY

An important aspect is the influence of the viscosity. Usually non-Newtonian flow behavior of starchy materials is to be expected in extruders. Not only the starch materials but also the chemical reactions performed with these materials influence the viscosity function. In our case two viscosity functions were derived, describing the behavior of concentrated starch pastes¹⁴ and of the hydroxypropylated starch.

In case of a concentrated starch paste the viscosity is a function of strain, strain history, temperature, and the amount of water. The strain history $W(t)$ is introduced into the viscosity equation, using an exponential dependency of the apparent viscosity on the amount of work performed on the paste:

$$W(t) = \frac{1}{\rho_p w_{\text{starch}}} \int_0^t \eta(t) \dot{\gamma} dt \quad [\text{kJ kg}^{-1} \text{ dry starch}] \quad (3)$$

The viscosity equation is a modified version of that presented by van Zuilichem and Janssen¹⁵ and Dolan and Steffe,¹⁶ and reads as follows:

$$\eta_{\text{app}} = \eta_0 e^{\left\{ \frac{A}{T} + B w_{\text{starch}} - C W(t) + (n-1) \ln \dot{\gamma} \right\}} \quad (4)$$

Here η_0 , A , B , C , and n are fit parameters as noted in the literature,¹⁴ w_{starch} is the amount of pure starch in the gel, $\dot{\gamma}$ is the shear rate, $W(t)$ is the amount of work performed on the starch granule, and T is the temperature of the gel. The viscosity of hydroxypropylated starch was described in the same way as for the concentrated starch pastes. From our own measurements it was observed that the η_{app} of hydroxypropylated starch ($MS > 0.25$) is not dependent on the strain history, which reduces Eq. (3) to

$$\eta_{\text{app,hps}} = \eta_{0,\text{hps}} e^{\left\{ \frac{A_{\text{hps}}}{T} + B_{\text{hps}} w_{\text{hps}} + (n_{\text{hps}} - 1) \ln \dot{\gamma} \right\}} \quad (5)$$

The parameters were measured using a Brabender Rheotron Couette Viscometer. The samples were prepared by dissolving hydroxypropylated starch ($MS = 0.25$) in water. Samples with a total starch concentration of 5.2, 10.0, 14.8, 20.0, and 24.8 mass%

were tested in the viscometer thermostated at 27.54, 35.14, and 40.14°C. The samples were completely gelatinized. In Table I the measurements are tabulated. Experimental data were fitted with Eq. (5), using the Marquadt–Levenberg method.¹⁷ In Table II the parameters of the fit are shown.

TABLE I
Experimentally Determined Hydroxypropylated Potato Starch Paste Viscosities for ($MS = 0.25$) $0.052 < w_{\text{starch}} < 0.25$, $20^\circ\text{C} < T < 45^\circ\text{C}$, $10 < \dot{\gamma} < 245 \text{ s}^{-1}$

w_{starch} (–)	T (°C)	$\dot{\gamma}$ (s ^{–1})	η_{app} (Pa s)
0.052	21	10.82	0.097
0.052	21	15.38	0.101
0.052	21	21.71	0.088
0.052	21	30.71	0.087
0.052	21	61.20	0.083
0.10	21	10.82	0.75
0.10	21	15.38	0.73
0.10	21	21.71	0.71
0.10	21	30.71	0.66
0.10	21	61.20	0.64
0.148	21	10.82	2.207
0.148	21	15.38	2.147
0.148	21	21.71	2.17
0.148	21	30.71	2.21
0.148	21	61.20	2.3
0.20	21	10.82	4.5
0.20	21	15.38	4.31
0.20	21	21.71	4.56
0.20	21	30.71	4.89
0.20	21	61.20	5.06
0.248	21	10.82	16.39
0.248	21	15.38	14.65
0.248	21	21.71	13.60
0.248	21	30.71	13.43
0.248	21	61.20	13.45
0.20	21	21.97	4.5
0.20	21	43.22	5.06
0.20	21	87.11	5.35
0.20	40	21.97	3.42
0.20	40	43.22	2.52
0.20	40	87.11	2.15
0.20	44	21.97	2.97
0.20	44	43.22	2.28
0.20	44	87.11	1.96

TABLE II
Values and Standard Deviations of the Parameters
 $\eta_{0,hps}$, A_{hps} , B_{hps} , η_{hps} as Measured for HPS in the
 Couette Rheometer

Parameter	Value	Standard Deviation
$\eta_{0,hps}$	4.52×10^{-7}	1.23×10^{-8}
A_{hps}	2.277×10^3	3.2
B_{hps}	22.4	1×10^{-2}
η_{hps}	0.835	1.3×10^{-3}

A plot of the apparent viscosity versus strain and HPS concentrations is given in Fig. 2. The viscosity dependency of hydroxypropylated starch having MS values lower than 0.25 is assumed to behave in an exponential way. The η_{app} can be calculated from

$$\eta_{app} = \eta_{hps} [\eta_{MS=0.25} / \eta_{MS=0}] e^{[MS/0.25]} \quad (6)$$

HEAT TRANSFER

Knowledge of heat generation and transfer during reactive extrusion is essential for obtaining good products. Several processes like heat transfer through the barrel wall, generation of heat due to viscous dissipation, and generation of heat by the reaction take place. In order to determine which process has the largest influence on the reaction, dimensionless numbers can be used. The Brinkman number determines the ratio between mechanical energy by viscous dissipation and the heat due to conductive

heat transfer. It is given by

$$Br = \frac{\eta_{app} u^2}{\lambda \Delta T} \quad (7)$$

Here η_{app} is the apparent viscosity of the material, u is the velocity, λ is the thermal conductivity, and ΔT is the temperature difference between the barrel and the material. By Lammers et al. found that λ is independent of the starch concentration and the viscosity.¹⁸ The ratio between the heat generated by the reaction and the heat generated by viscous dissipation is equal to the Br number divided by the Damköhler IV number (ratio of heat generated by the reaction and the conductive transport of heat):

$$R \text{ number} = \frac{Br}{Da \text{ IV}} = \frac{\eta_{app} u^2}{\Delta H_r (-R_{PO,ov})} \quad (8)$$

Here ΔH_r is the reaction enthalpy ($\Delta H_r = 88 \text{ kJ mol}^{-1}$ at 25.15°C).¹⁴ Based on the similarity of the functional groups involved in the reaction, the reaction enthalpy, ΔH_r , of the hydroxypropylation reaction was assumed to be equal to ΔH_r of the hydrolysis reaction. $R_{PO,ov}$ is the reaction rate of propylene oxide.

$$\begin{aligned} -R_{PO,ov} = & c_{PO}(k_{1,0}c_{RO^-} + k_{1,1}c_{ROH} \\ & + k_{2,0}c_{OH^-} + k_{2,1}c_{H_2O}) \end{aligned} \quad (9)$$

In Figs. 3 and 4 both dimensionless groups are shown. It can be concluded that during the reaction the heat generation process changes. In the case of a high material temperature and a low shear

FIGURE 2. Viscosity of hydroxypropylated starch (MS = 0.25) as a function of the shear rate. $T = 27^\circ\text{C}$.
 —: Fitted lines; $\circ$: $w_{hps} = 0.248$; $+$: $w_{hps} = 0.200$;
 $\bullet$: $w_{hps} = 0.148$; $\triangle$: $w_{hps} = 0.100$; $\square$: $w_{hps} = 0.052$.

FIGURE 3. R number as a function of total shear opposed on the starch gel. The shear rate increases from 1, 10, 100 to 1000 s^{-1} .

FIGURE 4. R number as a function of the MS of the processed material (MS from 0.25 to 0).

rate (Fig. 3), heat generated by the reaction is the main heat source (assuming that when the R number equals 1 both processes are equally important). Not only the temperature and the shear rate are important, but also the MS of the end product (Fig. 4).

HEAT TRANSFER FROM THE BARREL TO THE PROCESSED MATERIAL

During the last decades, different heat transfer theories have been proposed. They mostly depend on the one-dimensional diffusion equation for stationary heat transfer in a stagnant medium, as proposed by Jepson.¹⁹ Recently Tenge and Mewes²⁰ and Todd²¹ have proposed newer concepts concerning heat transfer in extruders. In our case the extruder is assumed to behave as a scraped heat exchanger. This means that after every pass of a screw flight along the barrel a new polymer layer is deposited at the barrel wall. This layer is penetrated by heat for a certain time after which it is renewed and mixed with the bulk. Another approach is to consider the heat transfer to a semi-infinite flowing medium. Both approaches have been used in our model.

Heat is also generated because of viscous dissipation. Yacu²² and van Zuilichem²³ describe a method for modeling this heat generation. The extruder is divided into a solid conveying zone, a melt-pumping zone, and a melt-shearing zone. It is assumed that in the first section because of the reasonably good mixing in self-wiping twin screw extruders, heat transfer is controlled by convection. A pseudo heat transfer coefficient U_s is used to replace the characteristic conductivity property of the granular material in the feed section.

The change of material in the second section from solid powder to a fluid melt is assumed to take place abruptly. In the third section four regions are defined where energy is converted. For every region an energy term can be defined:

- the screw channel (E_{screw})
- between the flight tip and the screw barrel (E_{fb})
- between the flight tip of one screw and the bottom of the channel of the other screw (E_{fbo})
- between the flights of opposite screws parallel to each other (E_{ff})

Per screw turn the total energy converted per channel can be expressed as

$$E_{\text{tot}} = E_{\text{screw}} + E_{\text{fb}} + E_{\text{fbo}} + E_{\text{ff}} = E_{\text{pt}} \eta N^2 \quad (10)$$

DETERMINATION OF THE AMOUNT OF SHEAR DURING PROCESSING

The shear imposed on the processed material is assumed to take place in the screw channel (γ_c) and between screw flights and the barrel wall (γ_f). The shear rate over the flight and in the screw channel can be approximated by

$$\dot{\gamma}_f = \frac{u}{\delta} = \frac{\pi DN}{\delta} \quad \dot{\gamma}_c \frac{u}{H} = \frac{\pi DN}{H} \quad (11)$$

in which δ is the flight clearance and H is the channel height. The residence time in the screw channel is $t_{\text{channel}} = L_{\text{channel}} S_{\text{channel}} / \phi_v$, while the residence time in the flight section is

$$t_{\text{flight}} = \frac{V_{\text{flight}}}{\phi_{\text{flight}}} \quad (12)$$

The (averaged) total shear on the material, together with the number of (tangential) passes over the tip of the kneading flight $\nu (=mN t_{\text{flight}})$, is

$$\dot{\gamma}_t = (\dot{\gamma}_{\text{flight}} \bar{t}_{\text{flight}} + \dot{\gamma}_{\text{channel}} \bar{t}_{\text{channel}}) \nu \quad (13)$$

MODELING

The reactor hydrodynamics in a self-wiping twin screw extruder has a plug flow character, as has been verified by van Zuilichem²³ and de Graaf.²⁴ Assuming that all materials are perfectly mixed in the radial direction of the channel the following balances can

be derived:

$$\text{Mass balance: } \frac{dc_{\text{PO}}}{dz} = \frac{-R_{\text{PO,ov}}S}{\phi_v} \quad (14)$$

Heat balance:

$$\frac{dT}{dz} = \frac{-R_{\text{PO,ov}}\Delta H_r S - \alpha S(T - T_b) + E_{\text{tot}}\eta_{\text{app}}}{\rho C_p \phi_v} \quad (15)$$

$$\text{Pressure buildup: } \frac{dp}{dz} = \frac{(-1.5\eta_{\text{app}}(Q_{\text{real}} - A))}{B} \quad (16)$$

$$\text{Total shear: } \frac{d\gamma}{dz} = \dot{\gamma}_z \quad (17)$$

The axial temperature profile, pressure buildup, MS, and selectivity can be calculated by solving the above set of differential mass and heat balances using a fourth-order Runge-Kutta procedure.¹⁷ During this process the viscosity of the material has to be corrected for the amount of work performed on the material and the increased shear rate. The amount of work performed on the starch over a small part of the channel is assumed to be

$$W = \frac{\Delta p}{\rho_{\text{reaction mixture}} m_{\text{starch}}} \quad (18)$$

in which Δp is the pressure drop over a small part of the extruder channel. Using Eqs. (5) and (6) the viscosity of the material is calculated as function of the MS, shear, and work performed. The die used consisted of two round capillaries. During the experiments a fixed diameter was used. In the model the die pressure was calculated according to the following equation:

$$P_{\text{die}} = Q_{\text{real}}\eta_{\text{app}}/K \quad (19)$$

in which K (2×10^{-11}) is the die resistant and η_{app} is the viscosity in the die. Furthermore, it was assumed that the reaction in the partially filled zone is negligible and that no diffusion limitation between the propylene oxide phase and the starch gel exists.

M.P.F. 160) has an L/D of 24 and a length of 122.5 cm. It was mounted with three pressure transducers with a range of 0–50 bar. Two different heat profiles were imposed on the barrel (Fig. 5). The potato starch was delivered by AVEBE (The Netherlands) (Food grade, production year 1991). Merck manufactured the propylene oxide and the NaOH. Because propylene oxide is a gas at 32°C and the extruder operating conditions are above 32°C, a special screw configuration was chosen (Fig. 5). After starch, water, and NaOH had been fed, a pressure was build up by means of pressure-inducing elements. This pressure was reduced using 4D of kneading discs in a staggered position. Because there was no transport action in these kneading discs, this part of the extruder could be fully filled with gelatinized starch. Propylene oxide was injected after this gel slot. Because of the gel slot, gasified propylene oxide could not leak back to the starch inlet. From this point on two different screw geometries were used. The first, low shear, geometry (Screw I) consisted of only transporting elements. The second, high shear, geometry (Screw II) consisted of transporting elements and kneading elements. Besides this screw geometry, the screw rotation, the PO throughput, the amount of NaOH, the starch throughput, and the temperature could be varied. In Tables III and IV an overview is given of the parameters during the extruder runs with Screws I and II.

ANALYSIS

The extrudate was analyzed on the molar degree of substitution (MS) and the conversion of propylene oxide into propylene glycol. The MS was determined as described by de Graaf et al.²⁵ To calculate the selectivity of hydroxypropyl towards starch, the amount of propylene oxide left and the amount of propylene glycol formed has to be measured. This was done using gas chromatography. Part of the extrudate was dissolved in water and neutralized with HCl (0.1 mol l⁻¹). As an internal standard propanol was added.

Experimental

EXTRUSION

During the experiments a self-wiping twin screw extruder was used. This APV Baker extruder (type

Results and Discussion

In this section, experimental results on MS values, propylene oxide conversions, and selectivities toward the desired product HPS are compared with results obtained from model calculations.

FIGURE 5. Screw I (upper screw) and Screw II (lower screw) geometry together with the temperature profiles used. The die is situated at 122.5 cm.

MODEL

In order to determine the importance of viscous dissipation, MS values as modeled both with and without viscous dissipation are compared with experiments (Figs. 6 and 8). By examining these graphs it becomes obvious that viscous dissipation has a pronounced effect on the reaction and cannot be neglected. Besides the effect of viscous dissipation it was also examined which heat transfer model predicted MS values the best. In Fig. 6 the outcomes for both models are set out in a parity plot of the calculated MS values versus the measured MS values. Both models do not differ much from each other, leading to the conclusion that both models can be used in this particular case.

EXPERIMENTS

In Fig. 7 the influence of temperature (constant temperature along the barrel) and screw speed on

the MS values is set out. An increased temperature means a higher reaction velocity and thus a higher MS. The screw speed does not have a pronounced effect on the MS. In this case the model predicted the same MSs and did not show an effect of the screw speed on the MS as well. In Fig. 8 the modeled values of Experiment 1 (Table III) are set out versus the dimensionless reaction length. A steep decline in the viscosity is noticed as a result of the increase of the temperature and the MS (a higher MS results in a lower viscosity, Eq. (6)). In this case the viscosity drop influences the reaction rate by influencing the temperature.

Changing the total throughput (Fig. 9, constant barrel temperature and concentration ratios) results in a small increase in the measured MS at higher throughputs. The model predicts the opposite. At an increased throughput and a constant screw speed, the leakage flow decreases ($Q_{\text{leak}} = Q_{\text{th}} - Q_{\text{real}}$) resulting in a decreasing mean residence time (MRT)

TABLE III
Extruder Parameters Used for Screw I Configuration

No	N (rpm)	$\phi_{m, \text{starch}}$ (g min ⁻¹)	$\phi_{m, \text{water}}$ (g min ⁻¹)	$\phi_{m, \text{PO}}$ (g min ⁻¹)	c_{NaOH} (mol dm ⁻³)	T (°C)
1	214	100	40	5.88	4.125	80
2	324	100	40	5.88	4.125	80
3	404	100	40	5.88	4.125	80
4	135	100	40	5.88	4.125	80
5	188	100	40	5.88	4.125	90
6	269	100	40	5.88	4.125	90
7	378	100	40	5.88	4.125	90
8	135	100	40	5.88	4.125	90
9	135	100	40	5.88	4.125	70
10	214	100	40	5.88	4.125	70
12	297	100	40	5.88	4.125	70
13	351	100	40	5.88	4.125	70
14	214	100	40	0.00	4.125	80
15	214	100	40	5.88	4.125	80
16	214	100	40	8.82	4.125	80
17	214	100	40	11.76	4.125	80
18	214	100	40	17.65	4.125	80
19	214	100	40	23.53	4.125	80
20	214	100	40	29.41	4.125	80
21	214	70	28	5.88	4.125	70
22	214	80	32	5.88	4.125	70
23	214	90	36	5.88	4.125	70
24	214	100	40	5.88	4.125	70
25	214	110	44	5.88	4.125	70
26	214	120	48	5.88	4.125	70
27	214	130	52	5.88	4.125	70

TABLE IV
Extruder Parameters Used for Screw II Configuration

No	N (rpm)	$\phi_{m, \text{starch}}$ (g min ⁻¹)	$\phi_{m, \text{water}}$ (g min ⁻¹)	$\phi_{m, \text{PO}}$ (g min ⁻¹)	c_{NaOH} (mol dm ⁻³)	T (°C)
28	270	100	40	8.7	1.5	70
29	380	100	40	8.7	1.5	70
30	160	100	40	8.7	1.5	70
31	270	100	40	8.7	1.5	110
32	325	100	40	8.7	1.5	110
33	215	100	40	8.7	1.5	110
34	270	100	40	8.7	1.5	70
35	270	100	40	17.4	1.5	70
36	270	100	40	26.5	1.5	70
37	270	100	40	30.5	1.5	70

FIGURE 6. Parity plot of the measured and modeled MS values (Table III). $\square$: Model without viscous dissipation taking into account; $\diamond$: modeled values with penetration theory; $\circ$: modeled values with Leveque solution.

and conversion. Still the measured and calculated MS values are within the accuracy of the analysis method. In this graph also the modeled selectivity, conversion, and mixture end temperature are set out. The calculated lines agree to what is expected from theory: a decreased reaction time due to a decreasing MRT results in a decreasing conversion. There is almost no influence on the selectivity and the reaction end temperature.

Increasing the throughput of propylene oxide (Fig. 10) results in a higher MS because of an increased concentration in the starch gel and a lower initial viscosity. Furthermore the temperature rises

FIGURE 7. MS of HPS as a function of the extruder screw speed. $\diamond$: $T = 70^\circ\text{C}$; $\blacktriangle$: $T = 80^\circ\text{C}$; $\blacksquare$: $T = 90^\circ\text{C}$. Modeled values (only for $T = (70^\circ\text{C})$ and (90°C)).

FIGURE 8. Simulated PO conversion, starch viscosity, and reaction temperature vs. the dimensionless reaction length.

because of the increased reaction heat, which in turn lowers the viscosity. A lower viscosity means that the fully filled length increases, resulting in an increased MRT. All these effects lead to higher MS values and conversions.

Until now only transport elements have been used in the screw geometry. In Figs. 10–12 measurements with the Screw II geometry are shown. The alkali amount was 1.5 mol l^{-1} , which is about three times lower than the alkali amount in the former screw geometry. Also a different temperature profile was used (Fig. 5). In the first kneading section, the temperature profile was kept the same for all experiments. From that point on the temperature profile

FIGURE 9. The MS of HPS as a function of the throughput; the screw speed remained constant (Screw I). $\diamond$: Measured MS of HPS; $---$: modeled MS; $\square$: ζ to HPS; $\circ$: σ of PO; $\triangle$: end T .

FIGURE 10. The MS of HPS as a function of the propylene oxide throughput, with constant screw speed. $\blacklozenge$: Measured MS/Screw I; —: modeled MS/Screw I; $\blacksquare$: measured MS/Screw II.

was changed for the different experiments. Because of the neutral elements in the first kneading section (Fig. 5) the filled length was significantly larger in comparison to the case where only transport elements were used. This resulted in almost the same MS values compared to the MS values obtained with a Screw I configuration despite the lower alkali concentration. Figure 10 indicates that MS increases with an increase in $\phi_{m,PO}$ (all other parameters remained constant). The decay of MS values at increasing propylene oxide throughputs is a result of the demixing of propylene oxide and water at higher propylene oxide concentrations.²⁶ Figures 11 and 12 show the effect of increasing screw speeds.

FIGURE 11. The MS, selectivity, and conversion of the HPS reaction with the Screw II configuration as a function of the screw speed ($T = 70^\circ\text{C}$). $\blacktriangle$: ζ of PO; $\blacksquare$: MS; $\blacklozenge$: σ to HPS.

FIGURE 12. The MS, selectivity, and conversion of the HPS reaction with the Screw II configuration as a function of the screw speed ($T = 110^\circ\text{C}$). $\blacktriangle$: ζ of PO; $\blacksquare$: MS; $\blacklozenge$: selectivity towards HPS.

Again no significant influence was found on the conversion, the selectivity, or the MS. (It should be noted that during these measurements both the MS and the conversion of propylene oxide into propylene glycol were determined.) By comparing the measured selectivities and conversions with the calculated selectivities and conversions a good similarity becomes apparent.

Conclusions

The reaction rate of the hydroxypropylation of starch is relatively slow. Besides that, propylene oxide is also a gas at 40°C . As is proven in this article, these two factors are no problems for the process. Choosing the right screw design, extruder type, and extruder parameters, the process is able to reach high MSs, high selectivities, and conversions. Examining the extruder experiments and the modeling more thoroughly, it can be concluded that besides reactant concentrations, heat transport and material viscosity are major parameters influencing the conversion. Instead of using high extruder temperatures it is also possible to use the viscous dissipation to heat the reaction mixture.

Increasing the alkali molality increases the reaction rate considerably, giving high conversions while the selectivity drops only slightly. Both experiments and calculations show selectivities above 50% (these values can be higher at different extruder conditions), which is good compared to selectivities

reached with processes used nowadays (<50%). Complete conversion of propylene oxide can be achieved. This is very important because of the price and toxic character of this reactant. Comparing the results of using extra kneading elements, it can be concluded that they have no significant effect on the selectivity or conversion.

Nomenclature

c	Concentration (mol m^{-3})
E_a	Activation energy (J mol^{-1})
ΔH_r	Molar reaction heat (J mol^{-1})
k	Reaction rate constant ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$)
m	Mass (kg)
M	Molar mass (kg kmol^{-1})
MS	Molar degree of substitution (–)
n	Amount of screw threads (–)
N	Screw speed (s^{-1})
P	Pressure (bar)
Q_d	Drag flow ($\text{m}^3 \text{s}^{-1}$)
Q_{real}	Real throughput ($\text{m}^3 \text{s}^{-1}$)
R number	Ratio (–)
R_s	Screw radius (m)
R	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
R_{PO}	Reaction rate of propylene oxide (mol m^3)
r^2	Regression coefficient (least-squares method) (–)
S	Cross-sectional channel area (m^2)
T	Temperature ($^{\circ}\text{C}$)
t	Time (s)
u	Velocity (m s^{-1})
U_s	Pseudo heat transfer coefficient ($\text{J s}^{-1} \text{m}^{-2} \text{K}^{-1}$)
V_c	Chamber volume (m^3)
w	Weight fraction (–)
W	Channel width (m)
x	Mole fraction (–)
x	x -Coordinate channel (m)
α	Heat transfer coefficient ($\text{J s}^{-1} \text{m}^{-2} \text{K}^{-1}$)
α	Filling degree (–)
β	Distance between screw axis (m)
$\dot{\gamma}$	Shear rate (s^{-1})
δ	Flight clearance (m)
ε	Clearance between flight tip and channel bottom of 2 opposite screws (m)

λ	Thermal conductivity ($\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$)
ν	Number of fully filled chambers (–)
ζ	Conversion (%)
η	Viscosity (Pa s)
ρ	Density (kg m^{-3})
σ_{hps}	Selectivity towards hydroxypropylated starch (–)
σ	Clearance between flights of opposite screws parallel to each other (m)
φ	Pitch angle (rad)
ϕ_m	Mass feed rate (kg s^{-1})
ϕ_v	Volumetric feed rate ($\text{m}^3 \text{s}^{-1}$)
ϕ'_w	Heat flux (J m^{-1})
τ_{xz}	Shear stress (N m^{-2})
NaOH	Sodium hydroxide
OH^-	Hydroxide ion
HPS	Hydroxypropyl starch
PO	Propylene oxide
PG	Propylene glycol
ROH	Starch hydroxyl group
RO^-	Dissociated starch hydroxyl group

References

- Lammers, G.; Beenackers, A. A. C. M. *Ind Eng Chem Res* 1993, 32, 835-737.
- Parker, R. E.; Isaacs, P. *Chem Rev* 1959, 59, 737.
- Chlebicki, J. *Ann Soc Polonorum* 1975, 49, 925.
- Lammers, G.; Stamhuis, E. J.; Beenackers, A. A. C. M. *Ind Eng Chem Res* 32, 835-842.
- Gilbert, R. G. *J Polym Sci, Part C: Polym Lett* 1988, 26, 293-297.
- Rauwendaal, C. J. *Polymer Extrusion*; Hanser Publishers, Munchen, 1986.
- Meyer, H. E. H.; Elemans, P. H. M. *Polym Eng Sci* 1988, 28, 275-302.
- Denson, C. D.; Hwang, B. K. *Polym Eng Sci* 1980, 20, 965.
- Booy, M. L. *J Eng Ind, Trans ASME, Ser B* 1964, 86, 22.
- Booy, M. L. *Polym Eng Sci* 1978, 18, 725-733.
- Booy, M. L. *J Basic Eng Trans, AME Ser D* 1966, 88, 725.
- Todd, D. B. *Int Polym Process* 1991, 2, 143.
- de Graaf, R. A. The use of twin screw extruders as starch modification reactors. Ph.D. Thesis, RU Groningen, The Netherlands, 1996.
- Lammers, G.; Beenackers, A. A. C. M. *Carbohydr Polym* 1994, 24, 55.
- van Zuilichem, D. J.; Janssen, L. P. B. M. In *Rheology*; Astarita, G.; Marcus, G.; Nicolais, L. (Eds.); Plenum: New York, 1980; Vol. 3.
- Dolan, K. D.; Steffe, J. F. *J Texturizer Stud* 1990, 21, 265.

HYDROXYPROPYLATION OF STARCH IN A SELF-WIPING TWIN SCREW EXTRUDER

17. Press, W. H.; Flannery, B. P.; Teukolsky, S. A.; Vetterling, W. T. Numerical Recipes in Pascal; Cambridge University Press: Cambridge, UK, 1989; p. 574.
18. Lammers, G.; Beenackers, A. A. C. M. Trans Inst Chem Eng 1994, 72, 728.
19. Jepson, C. H. Ind Eng Chem 1953, 45(5), 992.
20. Tenge, S.; Mewes, D. Polym Eng Sci 2000, 40(2), 277.
21. Todd, D. SPE ANTEC 1988, 54.
22. Yacu, W. A. In: Thermal Processing and Quality of Foods; Zeuthen, P.; Cheftel, J. C.; Eriksson, C. Elsevier: London, 1983.
23. van Zuilichem, D. Extrusion Cooking, Craft or Science ? Thesis, LU Wageningen, The Netherlands, 1992.
24. de Graaf, R. A.; Rohde, M.; Janssen, L. P. B. M. A Novel Model Predicting the Residence Time Distribution during Reactive Extrusion, Chem Eng Sci 1997, 52, 4345–4356.
25. de Graaf, R. A.; Lammers, G.; Janssen, L. P. B. M.; Beenackers, A. A. C. M. Starch/Stärke 1995, 47(12), 469–475.
26. Morcow, K. W.; Smith, R. W. J Chem Eng Data 1971, 6(12), 197–200.