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Françoise Berzin, Bruno Vergnes

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Françoise Berzin*[1], Bruno Vergnes[2]

[1] UMR FARE (Fractionnement des AgroRessources et Environnement), Université de Reims Champagne-Ardenne, INRA, 2 esplanade Roland-Garros, 51686 Reims (France)

[2] MINES ParisTech, PSL Research University, CEMEF (Centre de Mise en Forme des Matériaux), UMR CNRS 7635, CS10207, 06904, Sophia Antipolis Cedex (France)

francoise.berzin@univ-reims.fr

Starch is one of the most common polysaccharides from natural and renewable resources. It is increasingly used in place of synthetic polymers for industrial applications and can be chemically modified to obtain products having specific properties. For example, cationic starches are largely used in the paper industry. They are generally prepared using conventional batch reactors, but they can also be obtained using reactive extrusion. In this chapter, after a brief introduction to the twin-screw reactive extrusion process, experimental results of starch cationization are presented. Then, a model based on flow simulation coupled to a kinetic equation is developed, allowing a clear understanding of the influence of the processing parameters on the extent of the cationization reaction. This model, experimentally validated, is then used to solve optimization and scale-up problems.

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Introduction

Starch is a polysaccharide derived from natural and renewable resources. It is increasingly used in place of petroleum-based polymers for industrial applications, for example in packaging industry. However, starch properties are not always well adapted to the desired applications and it must thus be chemically modified to obtain wanted specific properties. There are many types of stach chemical modifications (1, 2). In this chapter, we focus on cationic starches, which are largely used in paper industry. Indeed, they can increase strength, filler and fines retention, and drainage rate of the pulp. They can also lower biological oxygen demand of the white water when used as wet-end additives. These cationic starches are produced from starch with reagents which are able to carry a positive charge. They are usually prepared using conventional batch reactors. However, such processes present some drawbacks, like discontinuous process with low yield, residual reactive agent elimination, and environment pollution. To overcome these drawbacks, some tentatives have been made in the early nineties to develop starch cationization using reactive extrusion (3-5). However, without the help of flow modeling, it was difficult to define optimal conditions for real industrial applications.

Reactive extrusion has largely developed during the last decades (6). Compared to a classical batch process in solution, it provides many advantages:

- the reaction is carried out in the melt, in the absence of any type of solvent, what avoids environmental issues;
- an extruder can work with very viscous products, what is not always the case for batch reactors;
- processing conditions are very flexible in a twin-screw extruder (modular geometry, mixing capacities, high temperatures, etc).

However, some drawbacks exist:

- the residence time is very short in an extruder (typically, of the order of a few seconds to a few minutes). Therefore, only fast reactions can be carried out in reactive extrusion, even though temperature and concentration of reagents may be higher in molten state than in solution;
- the cooling capacity of an extruder is limited and high exothermic reactions could be difficult to control.

Among the various extrusion systems (single screw extruders, counter- and co-rotating twin-screw extruders, co-kneaders), the co-rotating twin-screw extruders are the most popular in reactive extrusion, in reason of many advantages that are described in the next Section. Afterwards, an experimental study of the starch cationization in a twin-screw extruder is presented. The following Section is devoted to the modeling of the process and, finally, the last Section shows how this modeling can help to optimize the processing conditions

and the screw profile, and to solve the problems of scale-up, when moving from a laboratory scale to an industrial one.

Basics on co-rotating twin-screw extrusion and reactive extrusion

Description of the twin-screw extrusion process

The first particularity of a twin-screw extruder is the complexity of the geometry. Indeed, these machines are modular, i.e. they consist of small elements of fixed length, which can be arranged on a splined shaft to obtain a certain screw profile (Figure 1).

Figure 1. Screw elements and splined shafts (Clextral documentation)

These elements are essentially of two types:
- screw elements, either direct (right-handed) or reverse (left-handed);
- blocks of kneading discs.

The kneading discs (Figure 2) are elements without helicity but a certain thickness, with the same cross section as that of screw elements. They are assembled in blocks of a few elements and mounted on the shafts being offset by a certain angle with each other. This configuration creates complex flows during rotation, leading to efficient mixing, both dispersive and distributive. The offset is called direct (or right-handed) if the tips tend to push the material downstream. Otherwise, it is question of reverse (or left-handed) staggering.

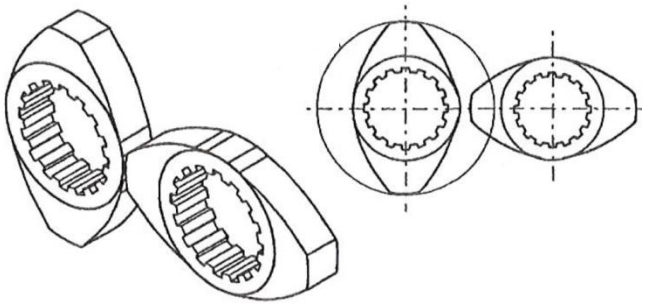

Figure 2. Example of two tips kneading discs (Clextral documentation).

Blocks of kneading discs and left-handed screw elements are restrictive elements that tend to oppose to the "natural" polymer flow downstream of the extruder. In contrast, right-handed screw elements are conveying elements.

Between the entry and the exit of the extruder, different functional areas are encountered: solid conveying, melting and melt flow. Figure 3, taken after stopping the machine in steady state conditions, cooling and extracting the barrel, illustrates this situation.

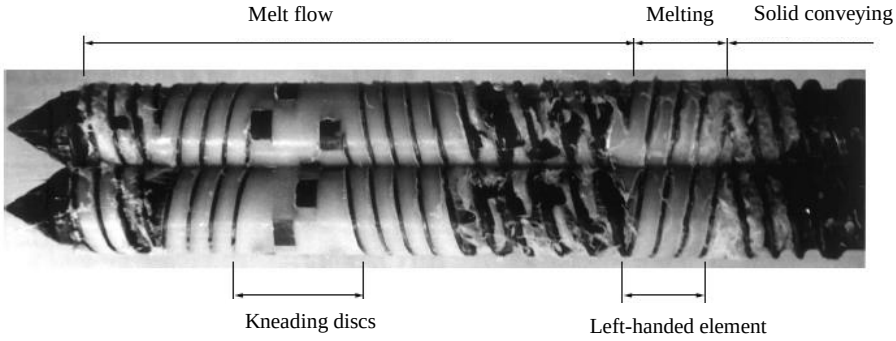

Figure 3. State of the material inside a twin-screw extruder (reproduced with permission from ref. 7. Copyright 2014 ISTE-Wiley).

It can be observed in Figure 3 that the melting zone is very short and that the twin-screw extruder is only partially filled. This is because the feed rate is controlled by a volume or gravimetric feeder, which allows to decouple the two main control parameters, which are the mass feed rate Q and the screw speed N. It follows that the feed zone, and more generally the conveying zones along the screws (except in the restrictive elements) may be only slightly filled. The independence of feed rate Q and screw speed N gives the twin-screw extrusion

process a high flexibility. In practice, the *Q*/*N* ratio is used to characterize the overall filling ratio of the extruder.

The main parameters of the extrusion process controlling the quality of the product are the temperature, the residence time, and the specific mechanical energy (*SME*). When the screw speed is increased at constant flow rate, the temperature increases by viscous dissipation, the residence time is reduced and the *SME* is increased. When the feed rate is increased at constant screw speed, the temperature is quite unaffected, but the residence time is largely reduced and the *SME* is decreased (7). Therefore, by choosing adequately screw speed and feed rate, it is possible to tune the thermomechanical treatment imposed to the product. As a rule of thumb, *SME* is roughly proportional to *N*/*Q* and the mean residence time can be calculated as:

$$\bar{t} = \frac{A}{Q} + \frac{B}{N} \tag{1}$$

where *A* and *B* only depend on the screw geometry.

Fundamentals of reactive extrusion

In the reactive extrusion process, the extruder is used as a continuous chemical reactor. The objective may be to perform polymerization (or polycondensation), chemical modifications (starch cationization is an example), controlled degradation (specifically for polypropylene), dynamic vulcanization (producing thermoplastic elastomers), etc (6). The major advantages over conventional batch reactor processes are to have a continuous and very flexible solvent-free process. The use of twin-screw extruders is justified by the following reasons:

- the modular screw and barrel geometries allows one to adapt the screw profile to the reaction to be carried out. The profile can be divided into successive independent sections, with specific functions like feeding and melting of the polymer, injection of the reagents, mixing, reaction development, devolatilization, pumping and shaping;
- as the filling ratio of the screws is only partial, different ingredients may be easily introduced or removed along the barrel, either in liquid or solid form;
- mixing capacities are generally important, and the mixing conditions (distributive or dispersive) can be easily controlled according to the geometry of the blocks of kneading discs (number of discs, number of tips, disc thickness, staggering angle) (7).

However, a reactive extrusion process may be difficult to master due to the many interactions between the various parameters. For example, flow conditions (residence time, temperature, mixing conditions) govern the development of the reaction, which in turn modifies the polymer properties (viscosity, elasticity),

leading to changes in flow conditions. Changing only one parameter of the process (e.g. screw speed) will affect all other parameters and, due to the complexity of the interactions, it is very difficult for the operator to predict what would be the impact of a such change. Therefore, it is of primary importance to develop dedicated theoretical models, able to provide predictive tools in order to help to understand the process and to define the best conditions for conducting an operation of reactive extrusion.

Starch cationization in a twin-screw extruder

Chemical reaction

Cationic starches are industrially used for many applications, including paper making and water treatment. These modified starches are produced with reagents containing amino, ammonium, sulfonium, or phosphonium groups, which are able to carry a positive charge (1). Starch cationization consists in substituting the hydroxyl groups of the glycosyl units by one of these functional groups. In the following, we focus on a wheat starch and two ammonium-based reagents: 2,3-epoxypropyl-trimethylammonium chloride (called hereafter Quab 151®) and 3-chloro 2-hydroxypropyl-trimethylammonium chloride (called Quab 188®). The reaction of cationization involves two stages with the Quab 188®, the first one for transforming the reagent (in alkaline medium) into an active epoxy form, and the second one for operating the substitution on starch backbone (Figure 4) (8, 9). With the Quab 151®, which is initially under epoxy form, the first stage is eliminated.

The degree of substitution (*DS*) indicates the average number of sites per anhydroglucose unit on which there are substituent groups. Thus, if only one hydroxyl has been cationized, *DS* is equal to 1. At the maximum, three hydroxyls can been substituted. The maximum value of *DS* is therefore equal to 3. Industrial cationic starches usually have low *DS*, in the range 0.02-0.10.

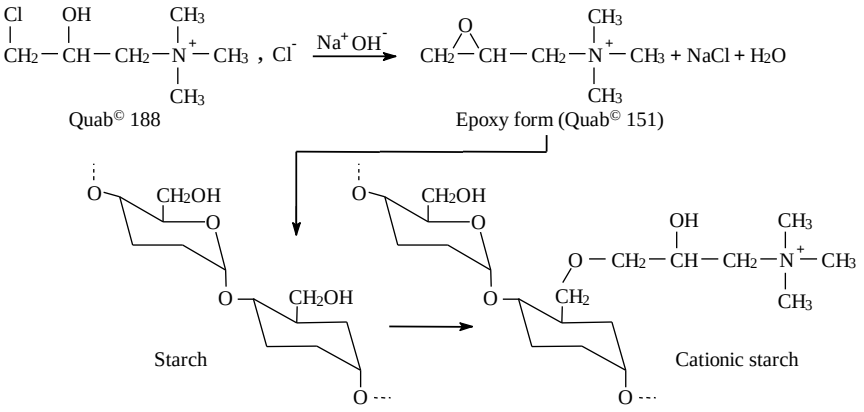

Figure 4. Reaction scheme of starch cationization
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Experimental results

Experiments were performed on a laboratory scale co-rotating twin-screw extruder (Clextral BC 21, Firminy, France), with the following characteristics: centerline distance = 21 mm, screw diameter = 25 mm, length/diameter ratio = 36 (10). Two screw profiles were tested. They are shown in Figure 5. Profile 1 was composed of two-flighted conveying screw elements of various pitches, and a block of eight kneading discs, negatively staggered (-45°). Profile 2 was more restrictive, with two blocks of kneading discs with the same configuration. The barrel was made of nine sections of 100 mm each, regulated at a fixed temperature (50°C for the first section, 80°C or 90°C for the others). Starch was plasticized with 40 % water. It was fed in the first barrel element, when water and reagent were mixed together and injected downstream (barrel 2 or 5), using a pump.

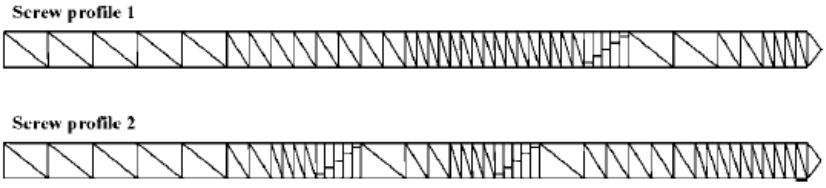

Figure 5. Screw profiles used for starch cationization
(reproduced with permission from ref. 10. Copyright 2007 Wiley).

After extrusion, the nitrogen content (% *N*, value between 0 and 100) of each sample was determined by Kjeldahl method (Kjeldatherm, Gerhardt GmbH., Oberdollendorf, Germany). The degree of substitution *DS* was then calculated by:

$$DS = \frac{M_S \, \% N}{100 M_N - M_R \, \% N} \tag{2}$$

where M_S, M_N and M_R are the molar masses of starch anhydroglucose monomer (162 g.mol^{-1}), nitrogen (14 g.mol^{-1}) and reagent once fixed on glycosyl unit (152.5 g.mol^{-1}), respectively (9). The theoretical degree of substitution, noted DS_{th}, is the theoretical value that would be obtained for a reaction efficiency of 100 %. It corresponds to the molar ratio between reagent and anhydroglucose monomer. In the experiments, it defines the target and allows to adjust the values of the starch and reagent flow rates, according to:

$$DS_{th} = \frac{\rho_r Q_r}{Q_S} \frac{M_S}{M_{fr}} \frac{I_{pr}}{I_{ps}} \tag{3}$$

where Q_r (L.h^{-1}) and Q_S (kg.h^{-1}) are the flow rates of reagent and starch, as fed in the extruder. M_{fr} is the molar mass of free reagent, ρ_r the reagent density, I_{pr} and I_{ps} the purity indices of reagent and starch. The reaction efficiency *RE* is logically defined as:

$$RE = \frac{DS}{DS_{th}} \tag{4}$$

As the reaction is an exchange reaction, its influence on starch viscosity is expected to be low. In-line measurements using a slit die fixed to the extruder were performed to check this assumption (12). It is shown in Figure 6 that there is no difference between starch and cationized starch. However, as starch is sensitive to the mechanical energy received during the extrusion process, it is necessary to take into account this parameter (13). According to Figure 6, the plasticized starch viscosity is thus expressed by a power-law:

$$\eta = K \exp\left[\left(\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right) + \beta\left(SME - SME_0\right) + \gamma\left(WC - WC_0\right)\right)\right] \dot{\gamma}^{n-1} \tag{5}$$

where *K* is the consistency, *n* is the power-law index, *E* is the activation energy, *R* is the gas constant, T_0 is the reference temperature, SME_0 is the reference

specific energy, WC_0 is the reference plasticizer amount, β and γ are constants, and $\dot{\gamma}$ is the shear rate. In our case, starch was plasticized with water and the following values were obtained: K = 1920 Pa.s, n = 0.53, E = 22.7 kJ/mol, T_0 = 363 K, β = -0.0028 t.kWh^{-1}, SME_0 = 325 kWh.t^{-1}, γ = -10.91 and WC_0 = 0.40.

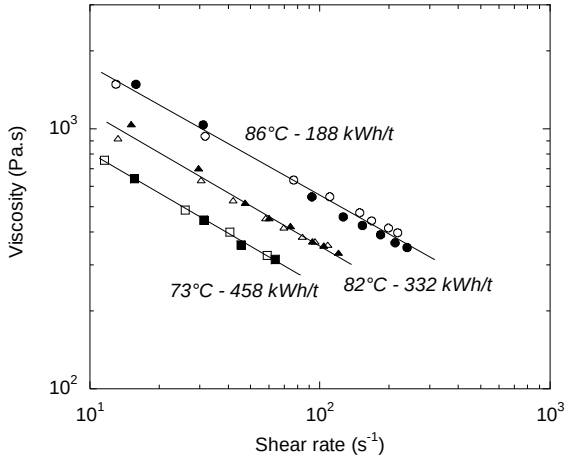

Figure 6. Viscosity curves for different processing conditions (product temperature and specific energy). Comparison between starch (full symbols) and cationic starch (open symbols) (adapted with permission from ref. 12. Copyright 2007 Kerschensteiner Verlag).

The effect of screw speed on the degree of substitution *DS* for profile 1 is shown in Figure 7. An increase in *DS* up to 400 rpm, followed by a decrease at higher speeds is observed. A slight increase in *DS* with screw speed (100-400 rpm) was reported by Carr (3). The same shape of curve is obtained whatever the reagent or the targeted DS_{th}. As expected, in identical conditions, Quab 151® is more efficient and leads to higher *DS*. The efficiency follows obviously the same trends, but is lower for higher DS_{th}, as already reported by Della Valle et al. (9). For Quab 151®, it increases from 50 to 62 % for DS_{th} = 0.04 and from 33 to 55 % for 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, but the residence time decreases (7). 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 when the product temperature exceeds 100°C.

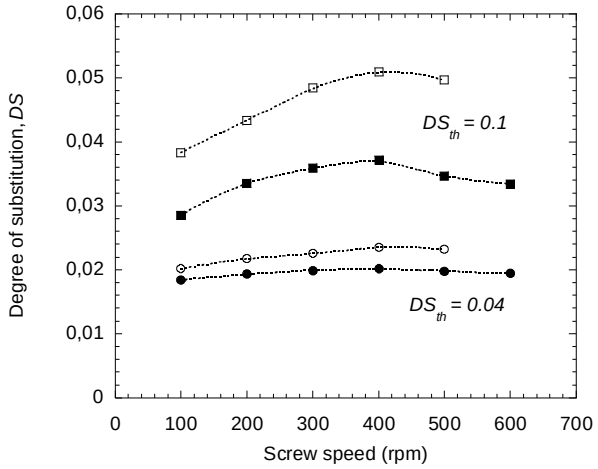

Figure 7. Variation of DS with screw speed at constant feed rate (Q = 1.9 kg/h) for different theoretical degrees of substitution and reagents (Profile 1, DS_{th} = 0.04: ○ Quab 151®, ● Quab 188®; DS_{th} = 0.10: □ Quab 151®, ■ Quab 188®) (adapted with permission from ref. 11. Copyright 2004 Wiley).

The influence of feed rate at constant screw speed (400 rpm) is shown in Figure 8. In this case, a continuous decrease of *DS* is observed, mainly explained by the reduction of residence time. 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 due to the fact that, starting directly from the epoxy form, the reaction is faster.

The influences of NaOH/Quab molar ratio, starch plasticizer and barrel temperature have also been characterized by Tara et al. (10), but these effects remain limited compared to those of screw speed and feed rate.

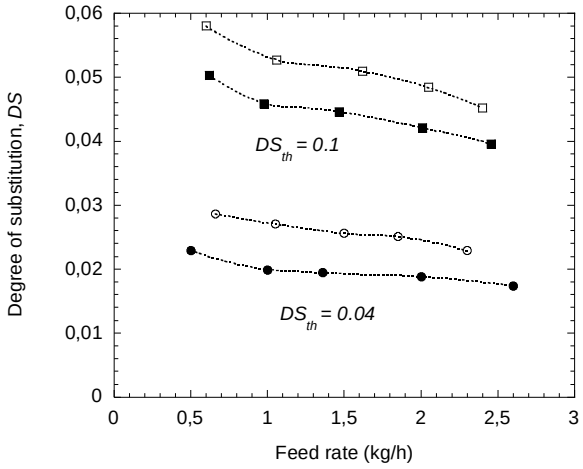

Figure 8. Variation of DS with feed rate at constant screw speed (N = 400 rpm) for different theoretical degrees of substitution and reagents (Profile 1, DS_{th} = 0.04: ○ Quab 151®, ● Quab 188®; DS_{th} = 0.10: □ Quab 151®, ■ Quab 188®) ((adapted with permission from ref. 11. Copyright 2004 Wiley).

Modeling of starch cationization in a twin-screw extruder

Principles of modelling

For modelling a reactive extrusion process using an approach based on continuum mechanics, three modules are necessary:

- a module for the calculation of the flow conditions in the twin screw extruder;
- a module for the calculation of the chemical reaction development, as function of local values of time, temperature, concentration of reagents, etc;
- a module for the calculation of the physical and rheological changes induced in the polymer by the reaction development. This last module is only necessary when the studied reaction significantly modifies the structure of the polymer, and thus its rheological behavior. For the cationization reaction, we have seen previously that the use of such a module is not necessary.

All these modules have then to be coupled in order to provide the desired results.

In the following, we will use as flow model a software called Ludovic©, developed by Vergnes et al. (14) from initial studies on the extrusion-cooking of

cereal products (15). It is a global model, which allows to consider the entire process, since the introduction of the solid material in the hopper to the die exit, and to quickly calculate the main flow parameters (pressure, temperature, residence time, shear rate, strain, etc) in an industrial configuration. It is based on a simplified approach, favoring 1D methods and calculating average values. This software has been of course largely validated, both in comparison with experiments, but also with the results of more sophisticated 3D numerical models (16).

Besides the flow module, a kinetic equation is necessary to model the cationization reaction. Therefore, a specific study has been performed to define an overall kinetic law (17). Figure 9 shows an example of experimental results. The reaction efficiency *RE* increases with time and temperature and tends to a limit at long times. In these conditions, the development of the reaction takes a few minutes, which is compatible with the residence time in the extruder.

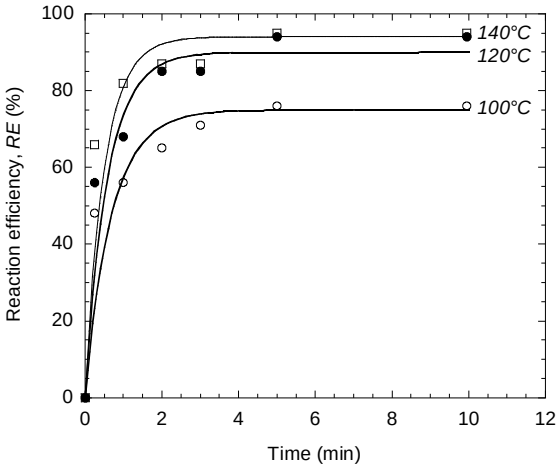

Figure 9. Comparison between calculated (lines) and experimental (symbols) kinetics for Quab 151® at three different temperatures: ○ 100°C, ● 120°C, □ 140°C (adapted with permission from ref. 17. Copyright 2004 Wiley)..

From this experimental study, it was possible to deduce, for each reagent, the change in degree of substitution as function of time and temperature:

$$DS = \frac{DS_{th}}{[B]_0}\left([A]_0 - [A]_t\right) \tag{6}$$

where $[A]_0$ and $[B]_0$ are the initial concentrations in starch and reagent, respectively. The starch concentration at time t is given by:

$$[A]_t = \frac{\frac{[A]_0}{[B]_0}\left([A]_0 - [B]_0\right)\exp\left[\ k\left([A]_0 - [B]_0\right)t\right]}{\frac{[A]_0}{[B]_0}\exp\left[\ k\left([A]_0 - [B]_0\right)t\right] - 1} \quad (7)$$

where k is the kinetic constant, depending on temperature through an Arrhenius law:

$$k = k_0 \exp(-\frac{E_a}{RT}) \quad (8)$$

where k_0 is a constant, E_a is the activation energy and R is the gas constant. Figure 9 shows that Eqs. (6) to (8) allow to describe correctly the kinetic of the cationization reaction with the following values: k_0 = 10.92 L.mol^{-1}.min^{-1}, E_a = 11.3 kJ.mol^{-1} for Quab 188®, and k_0 = 8.10 L.mol^{-1}.min^{-1}, E_a = 10.2 kJ.mol^{-1} for Quab 151®.

These equations have been implemented in Ludovic© software to calculate the evolution of the degree of substitution along the screws (10).

Influence of feed rate

Figure 10 shows an example of results for various feed rates at 400 rpm and 80°C. With the screw profile 2 and the Quab©151 at 400 rpm, for a targeted DS_{th} of 0.04, the feed rate has been varied between 2.7 and 5.4 kg.h^{-1}. In these conditions, the computed residence time greatly decreases (from 80 to 48 s) when the temperature remains quite unchanged. Consequently, the final *DS* and the efficiency decrease (from 0.0308 to 0.0231 and from 77.0 to 57.8 %, respectively) when the feed rate increases. The main variations in *DS* occur in the two blocks of kneading discs, where the residence time is maximum. The symbols represent experimental values of *DS* measured at the die exit. They are in good agreement with the computed data.

Influence of screw speed

At 2.7 kg.h^{-1}, for the same targeted DS_{th} (0.04), the screw speed has been varied between 150 and 400 rpm. This case is particularly interesting because an increase in screw speed induces both a decrease in residence time and an increase

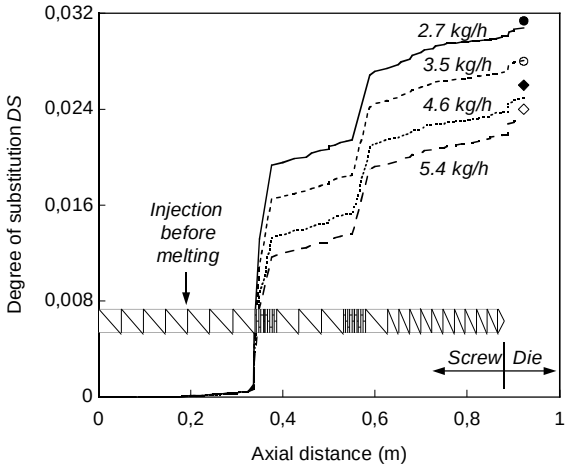

Figure 10. Evolution of the degree of substitution DS along the twin-screw extruder for different flow rates (Profile 2, Quab©151, N = 400 rpm, T_b = 80°C, DS_{th} = 0.04). Symbols are experimental points, lines are calculated results (adapted with permission from ref. 10. Copyright 2007 Wiley).

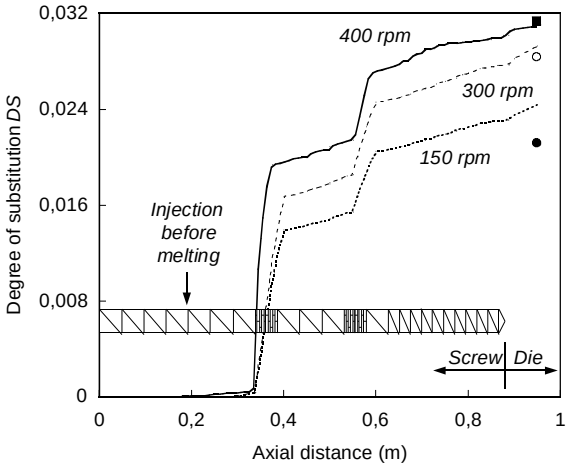

Figure 11: Evolution of the degree of substitution DS along the twin-screw extruder for different screw speeds (Profile 2, Quab©151, Q = 2.7 kg h^{-1}, T_b = 80°C, DS_{th} = 0.04). Symbols are experimental points, lines are calculated results (adapted with permission from ref. 10. Copyright 2007 Wiley).

in temperature by viscous dissipation (7). In other words, the two parameters which control the chemical reaction vary in opposite direction, making impossible to foresee the final effect. As it can be seen in Figure 11, the model indicates that, when the screw speed increases from 150 to 400 rpm, the computed *DS* increases from 0.0244 to 0.0308 and *RE* from 61.0 to 77.0 %. The benefit due to the temperature increase (approximately 13°C) largely compensates the decrease of residence time (approximately 16 s). The experimental values at the die exit validate the computed results.

Influence of barrel temperature

As the reaction is accelerated by the temperature, it is expected that an increase in barrel temperature improves the degree of substitution. Obviously, this leads to a global increase in product temperature (die exit temperature at 136°C instead of 92°C), but without modification of the residence time, as the latter is totally independent of the viscosity of the extruded product (7). Consequently, as observed in Figure 12, a more advanced reaction is obtained at 130°C: a *DS* of 0.0331 is reached, instead of 0.0244 at 80°C, and *RE* increases also from 61.0 to 82.8 %. The agreement with the experiments remains satisfactory.

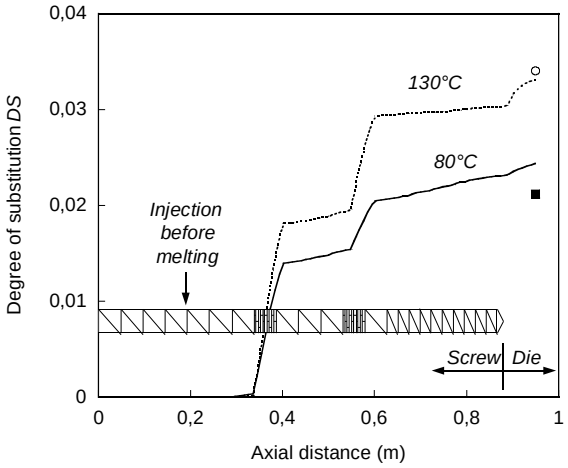

Figure 12. Evolution of the degree of substitution DS along the twin-screw extruder for different barrel temperatures (Profile 2, Quab© 151, Q = 2.7 kg h^{-1}, N = 150 rpm, DS_{th} = 0.04). Symbols are experimental points, lines are calculated results (adapted with permission from ref. 10. Copyright 2007 Wiley).

Influence of injection point

The injection of the reagents can be made before or after the melting of the starch, i.e. before or after the first block of kneading discs. On profile 2, two different points were tested, located either before or after the melting zone. The computation was carried out for Quab©151 at 400 rpm and 2.7 kg.h^{-1}. It can be seen in Figure 13 that the computed *DS* values are higher when the reagent is injected before the melting zone. The *DS* and *RE* are respectively 0.0308 and 77.0 %, instead of 0.0239 and 59.8 % when the reagents are injected after melting. These results are principally due to the increase in residence time (around 30 s) when the material is flowing through the first block of kneading discs. A similar result was also experimentally observed by Della Valle et al. (4), but not explained by the authors.

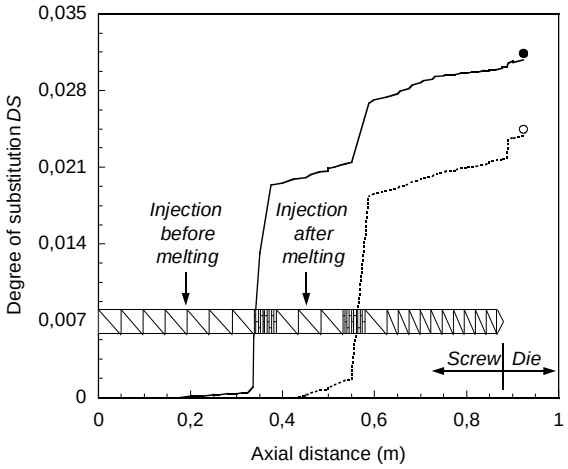

Figure 13: Evolution of the degree of substitution DS along the twin-screw extruder for different injection points of the reagents (Profile 2, Quab©151, Q = 2.7 kg h^{-1}, N = 400 rpm, T_b = 80°C, DS_{th} = 0.04). Symbols are experimental points, lines are calculated results
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A systematic comparison has been made between experiments and computed results, for all tested conditions. It can be seen in Figure 14 that, whatever the reagent, its amount and the processing conditions (feed rate, screw speed, barrel temperature, injection point), the agreement is good on a wide range of values (efficiency between 30 and 90 %).

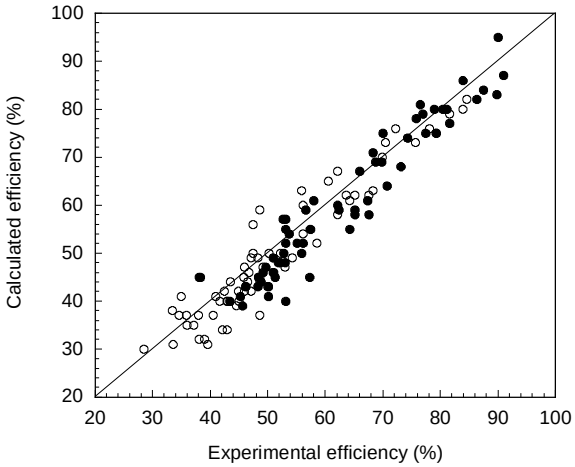

Figure 14: Comparison of calculated and experimental efficiency for the whole experimental points (●: Quab©151, ○: Quab©188)
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Application of modeling to optimization and scale-up

We have just seen that modelling is a great help to both understand what happens during the process and try to improve it. Another important problem in industrial applications is the scale-up, i.e. the passage from a laboratory test (flow rate of a few kg/h on a small machine) to an industrial one (several tons/h, on a machine with a diameter more than ten times larger). This can be done on the basis of trial and error, but this is very expensive in terms of time, immobilization of machines and personnel, and consumption of raw material. Again, the use of a modelling approach can be largely beneficial. In this last section, we will see, without going into details, some examples of the use of a software like Ludovic© to solve these types of problems.

Principles of process optimization

A computer code can obviously directly be used to optimize a process by trial and error, just as it could be done experimentally (but faster and cheaper!). But it is also possible, if the numerical solution is fast enough, to implement more sophisticated optimization techniques. For example, Genetic Algorithms (GA) were used by Gaspar-Cunha et al. (18) to optimize extrusion conditions in

the case of a fixed screw profile. GA mimic the natural evolution processes in which an initial population evolves over successive generations by different operations (selection, crossover, mutation, etc.). The optimization procedure then necessitates three modules:

- an objective function that quantifies the performance of each individual (i.e. each case of extrusion) with respect to the target performance;
- a calculation module, here Ludovic©, which calculates the value of the objective function for each individual;
- an optimization algorithm, which controls the evolution of the population towards the goal. The initial population is randomly chosen (e.g., by varying screw speed, flow rate and barrel temperature). With each new generation, the algorithm selects the best individuals and generates new ones.

A global objective function cab be defined, comprising several different targets, possibly conflicting, with associated weights:

$$F_o = \sum_i w_i \ f_i \tag{9}$$

where w_i are the weights ($\sum_i w_i = 1$) and f_i are specific functions defined to maximize, minimize or keep a parameter in a fixed interval. The problem of screw profile optimization was also studied with more advanced optimization techniques (multi-objective evolutionary algorithms), but the optimizations performed often led to many solutions, more or less equivalent, among which it is often difficult to discern the best (19). It is possible that the simplified assumptions used in Ludovic© software are sometimes too important to get the best of these sophisticated techniques.

Optimization of screw profile and processing conditions

Anyway, besides dedicated algorithm, it is always possible to go back to a "manual" optimization. This will be illustrated in the case of the optimization of the screw profile of a laboratory extruder (Clextral BC 21) (20). First, various screw profiles are defined, as shown in Figure 15. The first one was already used in Section "Starch cationization in a twin-screw extruder". Starch cationization is all the more difficult as the targeted *DS* is high (11). Therefore, we have chosen to optimize the process for a targeted DS_{th} of 0.1. The objective is to obtain a modified starch with the highest possible efficiency, at the highest possible flow rate. For that, both temperature and residence time inside the extruder have to be increased. This could be achieved by substituting along the screw profile screw conveying elements by left-handed screw elements or blocks of kneading discs. This is what is shown in Figure 15, with the screw profiles numbered 2, 3, 4 and 5. The first part of the profile, where starch is conveyed and melted, remains unchanged. The severity of the profile is

progressively increased by adding, after the first block of kneading discs, supplementary mixing elements: a third block of kneading discs for profile 2, a third block of kneading discs and a left-handed screw element for profile 3, three blocks of kneading discs and two left-handed screw elements for profile 4 and, finally, three blocks of kneading discs and three left-handed screw elements for profile 5.

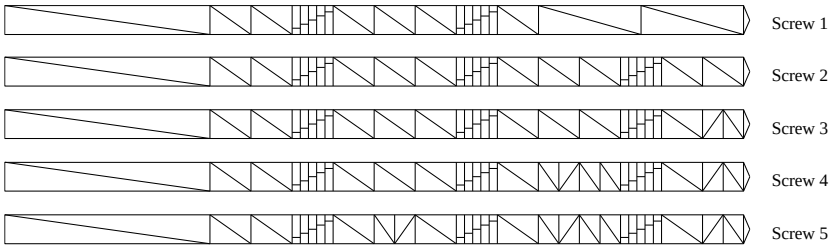

Figure 15. Screw profiles used in the optimization study (Clextral BC 21). Each vertical line indicates a change of pitch (reproduced with permission from ref. 20. Copyright 2007 Wiley).

For each screw profile, the degree of substitution and the reaction efficiency are calculated for various feed rates between 2.5 and 40 kg/h, at the maximum screw speed of 400 rpm (this choice allows to maximize the flow rate). The barrel temperature is fixed at 130°C (which is a good compromise between reaction enhancement and possible thermal degradation). Figure 16 shows the change in the reaction efficiency for the different profiles and flow rates. As expected, at a fixed feed rate, *RE* increases with the severity of the screw profile. Moreover, *RE* is more important when the feed rate is low, because of the higher residence time: for example, residence time of screw 1 increases from 15 to 90 s when the feed rate is decreased from 40 to 2.5 $kg.h^{-1}$; for screw 5, it increases from 23 to 262 s in the same conditions. As a consequence, *RE* increases from 22 to 86 % for screw 1 and from 39 to 86 % for screw 5.

By considering these results, we could imagine that screw 5 is the best one. But other parameters have to be considered. For example, it can be seen in Figure 16 that the specific mechanical energy (*SME*) increases also with the severity of the profile and is lower at high feed rate. *SME* is an important parameter in twin-screw extrusion of starchy products (13). It controls the molecular weight of the extruded starch, and thus some end-use properties like water solubility. Let us assume that the desired solubility of the cationic starch corresponds to a *SME* of 200 $kWh.t^{-1}$ maximum. Then, a *RE* of 77.5% could be reached at 3.4 $kg.h^{-1}$ with screw 1, or 76% at 5 $kg.h^{-1}$ with screw 2, or 75% at 7 $kg.h^{-1}$ with screw 3, or 71.5% at 10.5 $kg.h^{-1}$ with screw 4, or finally 70% at 13.5 $kg.h^{-1}$ with screw 5. The optimal profile can thus be chosen by the user as func-

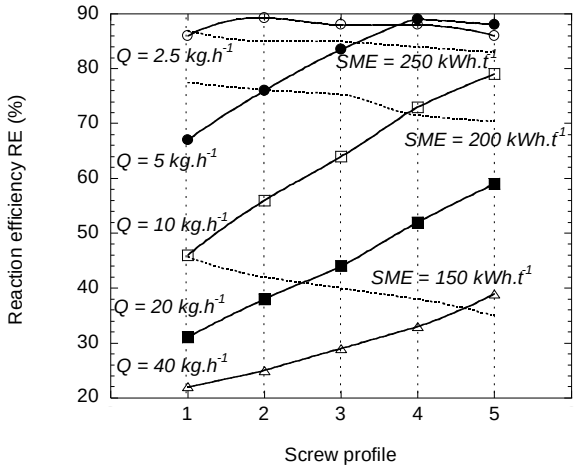

Figure 16. Variation of reaction efficiency (RE) as function of screw profile, for different feed rates (○ = 2.5 kg.h^{-1}, ● = 5 kg.h^{-1}, □ = 10 kg.h^{-1}, ■ = 20 kg.h^{-1}, ∆ = 40 kg.h^{-1}). Isovalues represent specific mechanical energy (SME). Full and doted lines are just here to guide the eyes: there is no interpolation between discrete values (adapted with permission from ref. 20. Copyright 2007 Wiley).

tion of his priorities, that is to say whether the reaction efficiency or the feed rate is preferred.

If it is assumed now that the maximum temperature experimented by the starch along the extruder T_{max} must be lower than 165°C to avoid degradation and browning and that the maximum shaft torque C_{max} must be lower than 50 mN, new limitations appear and reduce the processing window (Figure 17).

For a fixed screw profile, the maximum feed rate is limited by the torque at around 25-35 kg.h^{-1}. Similarly to *SME*, at constant flow rate, the maximum temperature increases with the severity of the screw profile. The best conditions for maximizing *RE* and feed rate are thus 64% at 5.5 kg.h^{-1} with screw 1, or 63% at 8 kg.h^{-1} with screw 2, or 62% at 11 kg.h^{-1} with screw 3, or 55% at 18 kg.h^{-1} with screw 4, or finally 52% at 25 kg.h^{-1} with screw 5. Once again, the final choice has to be defined by the user in function of his priorities.

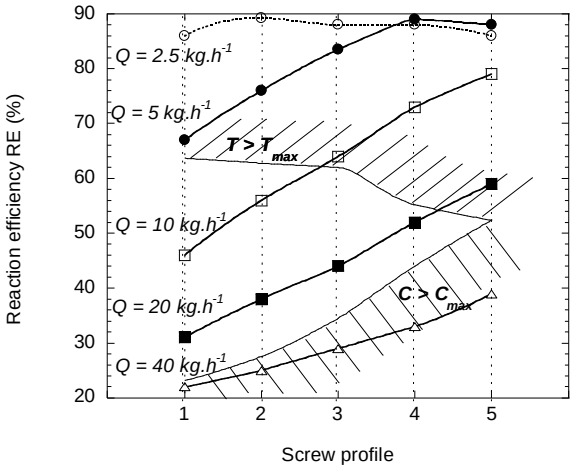

Figure17. Variation of reaction efficiency (RE) as function of screw profile, for different feed rates (○ = 2.5 kg.h^{-1}, ● = 5 kg.h^{-1}, □ = 10 kg.h^{-1}, ■ = 20 kg.h^{-1}, ∆ = 40 kg.h^{-1}). Isovalues represent the limits for maximum temperature T_{max} = 165°C and maximum shaft torque C_{max} = 50 Nm (adapted with permission from ref. 20. Copyright 2007 Wiley).

Example of scale-up

Before to decide any investment at an industrial scale, it is important to foresee the performances that could be reached. Classical rules of extrapolation exist for twin-screw extruders, generally based on geometrical ratios between the machines (21). But these simple rules cannot be applied to a complex process involving chemical reactions, as starch cationization. Therefore, scale-up has to be performed with the same modeling approach. The idea is to repeat the previous procedure with an industrial machine. As example, a machine of the same series, but with larger capacities will be considered. The Clextral BC 72 extruder has a diameter of 82 mm, a centerline distance of 72 mm and a total length of 2700 mm. The barrel is composed of nine elements, each of 300 mm long. The first step is to build screw profiles similar to those of the laboratory scale extruder (Clextral BC 21). “Similar” means with the same type of elements (screw elements and blocks of kneading discs), at the same relative location (according to the total length), but of course with the dimensions (pitch, diameter, etc.) of the new machine. The maximum screw speed (here, 360 rpm) and a barrel temperature of 130°C are selected. Then, the feed rate is varied in the operating range. In a first guess, this range is estimated from a volume scale-up rule:

$$\frac{Q_2}{Q_1} = \left(\frac{D_2}{D_1} \right)^3 \quad (10)$$

where Q is the feed rate and D the screw diameter. Subscript 1 refers to the small machine, 2 to the large one. As feed rate was varied between 2.5 and 40 kg.h^{-1} for the BC 21, a feed rate range of 90-1400 kg.h^{-1} can be expected for the BC 72.

The results of the simulations put in evidence important points. First, the maximum flow rate estimated at 1400 kg/h cannot be reached, whatever the screw profile, indicating that the volume scale-up rule (Eq. (10)) is not completely verified. The maximum possible feed rate is 1200 kg.h^{-1} for screws 1, 2 and 3, and 1000 kg.h^{-1} for screws 5 and 6. Second, the range of *RE* (30 to 90%) and *SME* (140 to 340 kWh.t^{-1}) is the same as for the BC 21, indicating that products of similar quality could be obtained. But the ranges of temperatures and torques are different. Obviously, the torque is much higher on a bigger machine with important flow rates. In the tested conditions, the maximum temperature of the product varies between 143 and 189°C, and is in the major cases higher than 160°C. Consequently, according to the previous criteria, the operating window is highly reduced. If a maximum temperature of 165°C and a maximum torque of 1500 m.N are assumed, only screws 1 and 2 could be used (Figure 18), with following optimal results: Q = 240 kg.h^{-1} and *RE* = 51% for screw 1 and Q = 400 kg.h^{-1} and *RE* = 45.5% for screw 2.

The obtained *RE* are low, compared to the results obtained on the lab-scale extruder. As the main limitation is the product temperature, this parameter must be reduced. Temperatures are higher on the industrial extruder because, at the considered screw speed, shear rates are much higher, leading to higher viscous dissipation. However, as the cooling capacities are better on a bigger machine because the exchange surface is larger, the product temperature can be reduced by a simple decrease of the barrel temperature. Accordingly, the previous simulation procedure has been repeated with a barrel temperature of 100°C instead of 130°C. As it can be seen in Figure 19, the new processing window is much larger and screws 1, 2, 3 and 4 could now be used, with the following best cases: Q = 155 kg.h^{-1} and *RE* = 60% for profile 1, Q = 225 kg.h^{-1} and *RE* = 58% for profile 2, Q = 310 kg.h^{-1} and *RE* = 58% for profile 3, and finally Q = 560 kg.h^{-1} and *RE* = 49% for profile 4. However, screw 5 remains too severe, due to both limitations in temperature and torque.

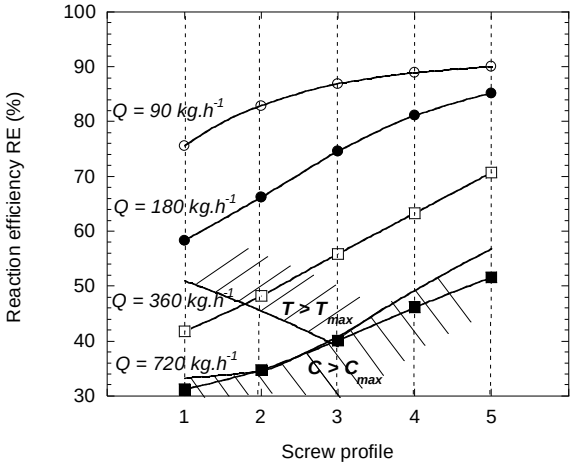

Figure 18: Variation of reaction efficiency (RE) as function of screw profile, for different feed rates. Isovalues represent the limits for maximum temperature T_{max} = 165°C and maximum shaft torque C_{max} = 1500 Nm (adapted with permission from ref. 20. Copyright 2007 Wiley).

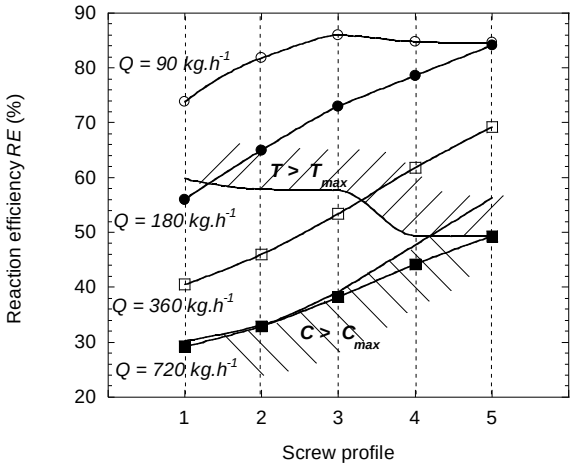

Figure 19: Variation of reaction efficiency (RE) as function of screw profile, for different feed rates, at a barrel temperature of 100°C. Isovalues represent the limits for maximum temperature T_{max} = 165°C and maximum shaft torque C_{max} = 1500 Nm (adapted with permission from ref. 20. Copyright 2007 Wiley).

To summarize, for screws 1 to 4, the scale-up leads to similar results for the two extruders in terms of *RE* (55-65% and 50-60% for BC21 and BC72, respectively), with feed rates varying according to the following rule:

$$\frac{Q_2}{Q_1} = \left(\frac{D_2}{D_1} \right)^{2.8} \tag{11}$$

Conclusion

We have shown in this chapter that it is possible to prepare cationic starches by twin-screw reactive extrusion and to model the process with a good accuracy. Predictive models without any adjustable parameter can be derived if accurate kinetic data are available. These models are very useful to understand the conditions of the process and to optimize it, for example by modifying screw profile and/or processing conditions. Moreover, we have shown that the difficult scale-up problems can be more easily solved by using such a theoretical approach. Even though these models may present some limitations, they appear as efficient tools on such complex systems, compared to systematic trial and error procedures.

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