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On the Stability of Reactive Extrusion*

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Interest in reactive extrusion has grown considerably during the last decade. The instabilities that may occur during polymerization in extruders can pose severe limitations on the process and on its scalability. They manifest themselves as severe fluctuations in throughput and product quality or as dual steady states, one at low conversion and one at high conversion. These instabilities may be of thermal, hydrodynamic, or chemical nature. In this paper the possible sources of instabilities are identified in a qualitative way and some possibilities to prevent them are given. Because some of the instabilities are dependent on the scale of the equipment, experiment design is important when a reactive extrusion process has to be developed on laboratory equipment and successively scaled up to larger machines.

INTRODUCTION

The possibilities of using an extruder as a polymerization reactor were already recognized in 1950. A patent of Dow Chemical Company (1) described the use of a single screw extruder as a main polymerizer. After a pre-polymerizer with a residence time of 90 hours, a screw conveyor was used as a polymerization reactor in which a residence time of 18 hours was necessary for the thermal polymerization of styrene. The first polymerizations described in open literature were the polymerization of nylon (2) and several polycondensation reactions (e.g. 3). In the mid-1970s, the first theoretical considerations concerning reactive extrusions appeared. Meyuhas *et al.* (4) stated that an extruder is the best plug flow reactor for viscous materials, but that some distribution in molecular weight of the polymer formed can not be prevented. In this study, a pre-polymerization is advised to avoid low viscous material to be fed to the extruder. Mack and Herter (5) proposed twin screw technology for reactive extrusion because of difficulties in scaling up single screw extruders that can be avoided in twin screw extruders. Residence times of half an hour were possible in a self-wiping twin screw extruder. Finally, Mack and Herter concluded that a combination of a stirred tank reactor, a single screw extruder, and a twin screw extruder is most suitable for the production of polyesters.

More recently, the radical polymerization of several methacrylates was studied in a counter-rotating twin

screw extruder (6–9). Stuber and Tirrel (6) and Dey and Biesenberger (7) studied the radical polymerization of methylmethacrylate, Ganzeveld and Janssen (8) described the polymerization of n-butylmethacrylate, while Jongbloed *et al.* (9) also studied a copolymerization of butylmethacrylate and 2-hydroxy-propylmethacrylate. Jongbloed and Ganzeveld found maximum conversions of roughly 96% in one step, while Dey claimed complete conversion after pre-polymerization. Jongbloed *et al.* (10) also used a self wiping co-rotating twin screw extruder for the copolymerization of n-butylmethacrylate and 2-hydroxy-propylmethacrylate. Apart from the polymerizations already mentioned, the counter-rotating extruder was also used for the polycondensation of urethanes (11) and the anionic polymerization of ϵ -caprolactam (12). The possibilities for reactive extrusion of urethanes were also recognized by several other authors (13–15).

Recent articles describe the use of co-rotating twin screw extruders for the anionic polymerization of ϵ -caprolactam (16–18). The anionic polymerization of styrene was investigated by Michaeli *et al.* (19), who also published on the copolymerization of styrene with isoprene (20). The radical polymerization of styrene was described in a patent by Kelley (21). This patent also describes several co-polymerizations with styrene as the main component and the synthesis of high impact polystyrene (HIPS). Van der Goot and Janssen (22) investigated the polymerization of styrene and the influence of pre-polymerization on the maximum stable throughput. Despite all reactions performed in extruders, the stability of reactive extrusion processes is still barely understood. Although instabilities can pose severe restrictions on the use of an extruder as a polymerization reactor, hardly anything on this sub-

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ject has been reported in literature. The purpose of this paper is to identify—mainly qualitatively—the factors that have an influence on the stability of reactive extrusion.

INSTABILITIES IN OPERATION

The unstable operation of an extruder can manifest itself in two different ways:

- Upon changes in one of the operating parameters, the conversion quickly drops to a much lower value, which indicates the possibilities of dual steady states.
- Rigorous fluctuations of the throughput and the conversion may occur.

Figure 1 shows a typical example of such fluctuations during the polymerization of styrene in a counter-rotating twin screw extruder (23). A constant period of approximately 15 minutes can clearly be distinguished. Because the extruder was operated with a constant feed stream, these instabilities can only be interpreted as a filling of the machine up to a certain level, followed by a sudden release of its contents. The fluctuations in throughput were accompanied by large fluctuations in conversion. This type of instability often occurs at the transition of an operating region with high conversion to a region with low conversion.

A central feature in understanding the instabilities is the filled length. Only in part of the extruder the channel is fully filled (Fig. 2). In this fully filled zone, the pressure is generated that is needed to convey the material through the die or over a kneading section. Mathematical expressions for the length of this zone both in co-rotating and in counter-rotating extruders for iso-viscous materials have been described elsewhere (24). For a qualitative understanding of the stability of reactive extrusion processes, it is important to know the dependence of the length of this zone on the different process parameters. Figure 3 gives an interaction diagram for reactive extrusion. A (+) sign in this diagram indicates a positive correlation between the parameters; a (-) sign stands for a negative correlation (25). If only the extruder part of the diagram is

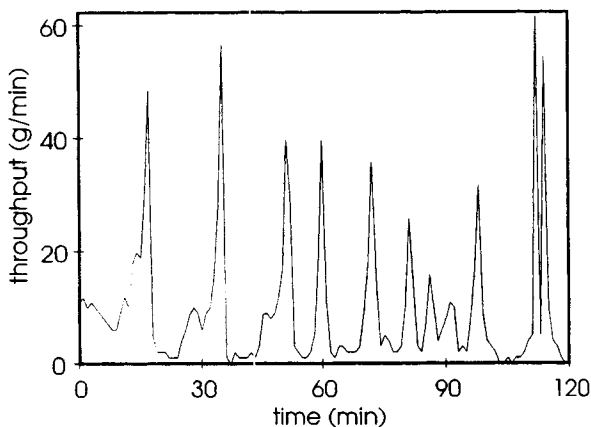


Fig. 1. Instabilities in throughput for the reactive extrusion of styrene.

considered, four dependencies of the fully filled length can be distinguished:

- An increase in die resistance demands that a larger pressure be built up in the extruder, which leads to a longer fully filled length.
- An increase of the screw rotation rate at constant throughput increases the back flow and therefore decreases the filled length.
- An increase of throughput increases the die pressure and decreases the back flow, both leading to an increase of the filled length.
- An increase in the viscosity both increases the die pressure and the pressure buildup abilities of the extruder. In the simplified case of an iso-viscous process, the filled length remains constant. In reactive extrusion, where the material is generally far from iso-viscous, the filled length may increase or decrease, depending on the viscosity changes along the screw.

Figure 2 also shows the influence of the changing viscosity on the pressure built up in the extruder. For a simple screw with uniform geometry, this pressure buildup is uniform in the simplified case of an iso-viscous material (a). For reactive extrusion the viscosity increases in the direction of the die and the low viscosity in the filling region results in poor local pressure buildup abilities (b). This makes the extruder more sensitive to disturbances, and small fluctuations in pressure will result in large changes in the fully filled length and therefore in residence time. Moreover, overfilling of the extruder can occur.

In Fig. 3, several positive feedback loops can be distinguished. As a result of these positive feedback loops, a disturbance in a process parameter can be amplified, which may lead to an unstable operation. In this way three different possible sources of instabilities can be distinguished:

- The thermal instability, where an increase in temperature leads to an acceleration of the reaction, which, for exothermic reactions, again leads to an extra increase in temperature.

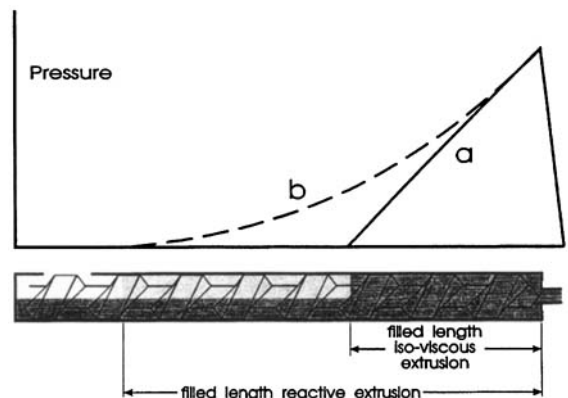


Fig. 2. The filled length and the pressure buildup in a twin screw extruder: a) iso-viscous material, b) reactive polymerization.

THERMAL CONSIDERATIONS

Local Heat Balances

Although viscous dissipation may play a role in the temperature balance, we consider here only a system where the change in temperature of the reactive polymer is basically determined by the heat of reaction and the heat removed to the wall. For a Lagrangian coordinate system, moving with a fluid element, the classic graphical representation given in Fig. 4 can be used. If the cooling effect of the wall is large compared with the heat produced by the reaction, as is the case for slow reactions in small extruders, one unique solution of the heat balance is possible. It should be noted that small fluctuations in temperature may result in large fluctuations in conversion. However, the situation changes drastically in large extruders, where the surface to volume ratio decreases and the cooling effect of the surface diminishes (Fig. 5). Upon scale-up, a transition occurs to a situation where in general three solutions of the heat balance are possible. Because the middle one is unstable, the extruder has

- The hydrodynamic instability, where a small increase in die pressure leads to a larger local residence time, which in turn, through conversion, results in a larger viscosity. This viscosity increase will successively increase the die pressure even further. The positive feedback will be counterbalanced by the back flow, since an increased viscosity also increases the pressure buildup ability of the extruder, and an influence on the stability may be expected if the interaction parameters and the local viscosities are such that the positive feedback dominates.
- The chemical instability that can be distinguished is based on the gel effect or Trommsdorff effect (26). An increased reaction velocity increases the local conversion and the viscosity. The resulting decrease in mobility of the polymer chains decreases the termination velocity and hence increases reaction speed and average molecular weight. Although this is the primary chemical instability, as follows from the interaction diagram, several other effects may also influence the stability of the process, as will be discussed later in this paper.

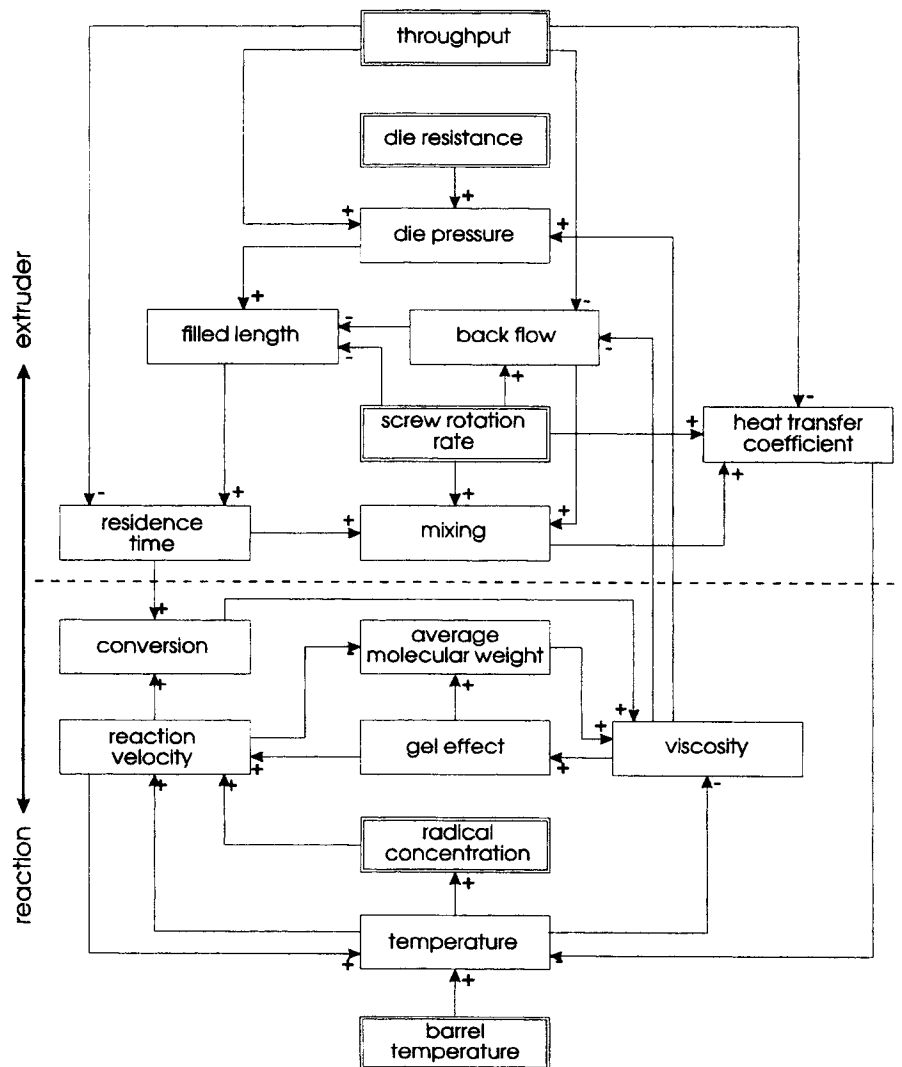


Fig. 3. The interaction diagram.

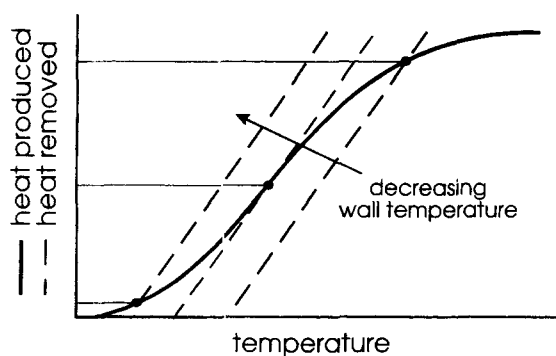


Fig. 4. Local heat balance for reactions with a low exotherm or in small extruders.

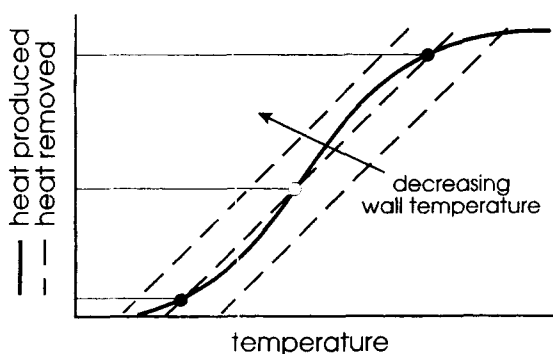


Fig. 5. Local heat balance for reactions with a high exotherm or in large extruders. ● stable working point; ○ unstable working point.

a stable working point either in a region of low conversion or in a region of high conversion, depending on local temperatures. This last situation corresponds to local run-away conditions. It is clear that this effect imposes strong limitations on the possibility of scaling up reactive extrusion from too small laboratory equipment to plant sizes.

Local thermal runaway conditions do not need to create problems as long as the reaction exotherm is such that no severe degradation occurs. A good estimation of the behavior of the material in large scale extrusion equipment is given by the adiabatic temperature rise (ΔT_{ad}):

$$\Delta T_{ad} = \frac{\Delta H_p}{\rho C_p} \quad (1)$$

where ΔH_p is the heat of reaction, ρ is the density, and C_p stands for the specific heat of the material. If this temperature rise is too large to be accepted, several possibilities exist to compensate for the decreasing surface to volume ratio:

1. Part of the polymer can be fed back or an inert material may be added to decrease the reaction heat per kilogram throughput.
2. Devolatilization of part of the monomer or of an inert material will decrease the effective heat released by the phase change enthalpy of the volatiles removed.

3. Several side feeds of deep-cooled monomer will lower the base temperature to which the adiabatic temperature rise has to be added.

Wall Temperature Fluctuations

If the extruder is electrically heated, fluctuations of the wall temperature may also have an effect on the stable operation of reactive extruders. In general, many extruders are equipped with large heating elements to shorten the start-up time. Because the heat has to penetrate to the thermocouple in the wall, a certain time elapses before this thermocouple reacts and the heaters are switched off. With a large heating capacity, this implies that a considerable amount of heat is released into the barrel wall, resulting in temperature fluctuations. The typical time constant of these fluctuations is in the order of several minutes; typical temperature differences are in the order of several degrees. It is clear that this effect may influence the onset of the reaction.

Thermal Inhomogeneities

A special complication is formed by the thermal inhomogeneities. As shown in Fig. 6, the polymer follows a circular path in the cross-channel direction. This implies that, depending on the size of the thermal boundary layer, only a certain amount of polymer passes this boundary layer where it is cooled directly. Therefore, for deep-cut channels, the heat of reaction released by the polymer in the middle of the channel is difficult to remove. Janeschitz-Kriegl and Schijf (27) derived a criterion for thermal homogeneity in a single screw extruder by comparing the channel depth (H) with the thickness of the thermal boundary layer (δ_T):

$$\delta_T = \sqrt{\pi a t} = \sqrt{\frac{\pi a}{N}} \quad (2)$$

N is the rotational speed and a the thermal diffusivity. This can be adapted to twin screw extruders with m thread starts per screw. It can be concluded that thermal inhomogeneities become important if:

$$\frac{mNH^2}{a} > 120 \quad (3)$$

It can be seen that thermal inhomogeneities increase strongly for larger-scale extruders, where the channels are deeper cut. This is especially the case for continuous channels, as in self wiping co-rotating machines operating with materials with a large heat of reaction. A reliable scale-up, in terms of thermal homogeneity, is possible only if mixing elements are used at regular intervals to homogenize the radial temperature differences.

HYDRODYNAMIC CONSIDERATIONS

As stated before, the basis of the hydrodynamic instability can be found in a competition between die

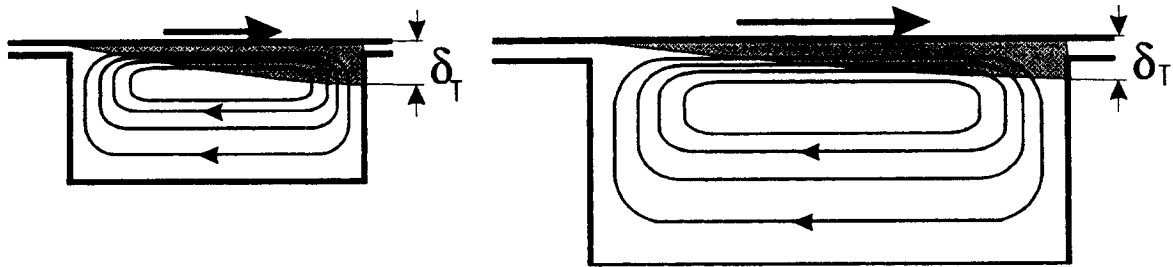


Fig. 6. The influence of the thermal boundary layer thickness (δ_T) in small and in large extruders.

effects and pressure buildup abilities in the screw. These instabilities can be explained by assuming an initial situation where the reaction comes to completion in the die, resulting in a high local viscosity at the die and a lower viscosity in the rest of the extruder. Owing to the resulting low throughput, the extruder fills itself while the reaction proceeds and the viscosity is built up, until the extruder is capable of emptying itself. The resulting short residence time after this period leads again to low viscosities in the extruder and a higher viscosity in the die. It is clear that a more stable operation can be achieved if a certain amount of high viscosity material is permanently present at the end of the screws, ensuring a good pumping ability at all times. This can be obtained by increasing the reaction speed or by increasing the viscosity levels.

The reasoning above can also be illustrated graphically. The dependencies that cause the hydrodynamic instability are qualitatively shown in Fig. 7. The die pressure (P) is linearly proportional to the local viscosity (η) and because of the changing viscosity along the screw, the filled length (L_f) is more than proportional to the end viscosity. Because the total residence time (rt) has a component in the partially filled zone and a component in the fully filled zone, it already has a certain value if no fully filled zone is present and from there on increases linearly with an increasing length of the fully-filled zone. The conversion (χ) as a function of the residence time shows the familiar "S" shape, while the viscosity is a power function of the conversion (e.g. 28, 29). These dependencies are combined in Fig. 8, where for the sake of convenience the residence time is eliminated. In this Figure, a stationary (but unstable) working point is shown by the solid line. Small deviations from this working point will cause the extruder to deviate to a working point of high conversion or a working point of low conversion. From a practical point of view, only the point of high conversion is of interest. From Fig. 9 it can be seen

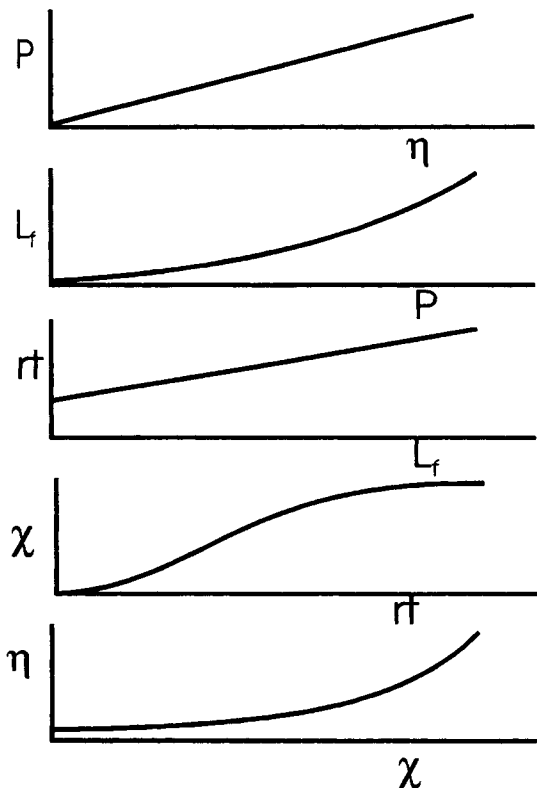


Fig. 7. Mutual influences during reactive extrusion.

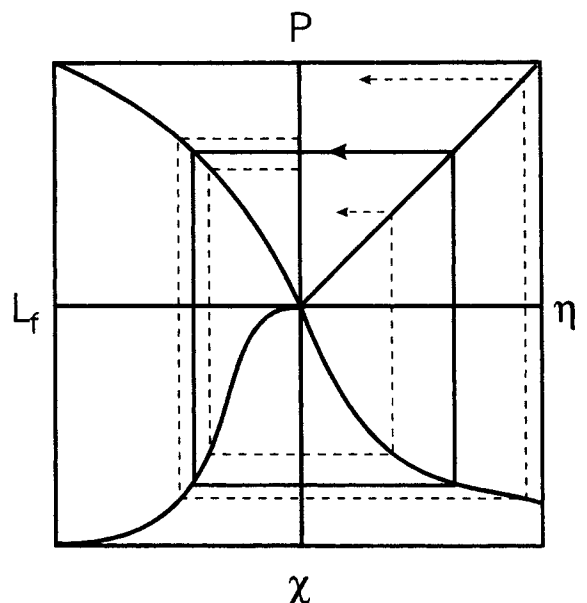


Fig. 8. Circle diagram, ——— unstable working point, - - - - result of small deviations from the working point.

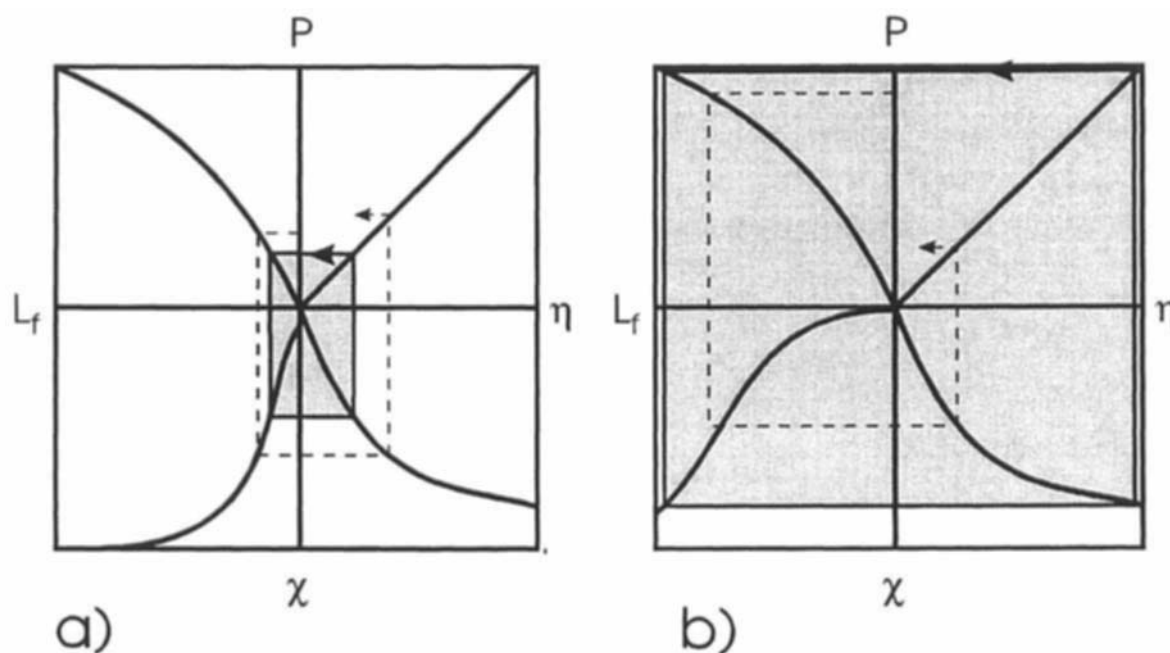


Fig. 9. The effect of increasing reaction speed (a) fast reaction (b) slow reaction. Shading indicates the region of convergence to low conversion.

that an increase in reaction speed facilitates the convergence to high conversion. In Fig. 9a, the reaction is fast and starts already in the partially filled zone; convergence to a working point at high conversions is nearly everywhere possible. The opposite is true in Fig. 9b for slow reactions; nearly every initial situation leads to low conversions. The same reasoning can be applied to viscosity changes. If the viscosity increases gradually to its end value, the pressure buildup ability of the extruder screws increases and stability is enhanced. If, on the other hand, the viscosity increases sharply only toward the end of the extruder, the pressure buildup ability is poor in the major part of the screws and nearly every initial situation will converge to a low conversion. This is consistent with the reasoning at the beginning of this paragraph.

CHEMICAL CONSIDERATIONS

From the interaction diagram as given before (Fig. 3), the gel effect is identified as a possible source of chemical instabilities. Nevertheless, there are also other chemical effects that influence the stability of reactive extrusion. The two other effects identified here are the ceiling temperature and phase separation. The stability of the reactive extrusion process is influenced by these three factors because they have a direct influence on the viscosity and reaction speed and therefore on the hydrodynamic instabilities.

The Gel Effect

The gel effect was first identified by Trommsdorff *et al.* in 1948 (26). During a bulk polymerization reaction the viscosity gradually increases and the diffusiv-

ity decreases. At a certain point in time the diffusivity of the growing polymer chains reaches a value where the termination speed drops considerably, while, owing to the higher mobility, the diffusivity of the monomer molecules is still large. This results in an increase in reaction speed and in higher molecular weights of the polymer formed. Figure 10 shows a differential scanning calorimetry (DSC) experiment of butyl-methacrylate at 110, 120 and 130°C. An enhancement of the reaction speed due to the gel effect can be seen at 110°C, but is totally lacking at 130°C, where the mobility of the polymer chains is still sufficient. The influence of the gel effect depends on its location. If it occurs entirely in the screws, the resulting

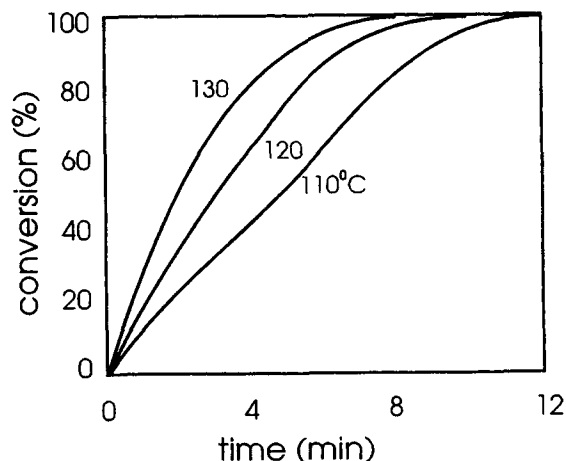


Fig. 10. DSC experiments at different temperatures for butyl-methacrylate.

increase in reaction velocity and viscosity will enlarge the pressure buildup abilities and it will stabilize the process. However, if the onset of the gel effect occurs close to the die, it mainly will increase the viscosity in the die, and destabilization will happen.

The Ceiling Effect

Many addition polymerization reactions are equilibrium reactions. At elevated temperatures this equilibrium shifts toward a higher monomer concentration (30), which implies that above a certain temperature no net polymerization occurs. This so-called ceiling temperature, T_c , follows directly from the Gibbs free energy equation:

$$\Delta G = \Delta H_p - T\Delta S_p \quad (4)$$

Equilibrium occurs when ΔG equals zero, so:

$$T_c = \frac{\Delta H_p}{\Delta S_p} = \frac{\Delta H_p}{\Delta S_p^0 + R \ln\{c_m/c_m^0\}} \quad (5)$$

where ΔH_p is the polymerization enthalpy, ΔS_p the entropy change due to polymerization, R the gas constant, and c_m the monomer concentration. For instance, for pure polymethylmethacrylate, this ceiling temperature has a value of 220°C. Again, for large-scale equipment, the effect of the ceiling temperature can be estimated by comparing it with the adiabatic temperature rise (Eq 1). Apart from the negative effect on conversion, the occurrence of a ceiling temperature slows down the reaction and therefore enhances hydrodynamic instability.

Phase Separation

During reactive extrusion a polymer-monomer mixture exists that changes from pure monomer to (nearly) pure polymer. Several systems can go through a region of phase separation during polymerization. Malkin (31) has studied the influence of this type of phase transition on the viscosity. One of the systems is polydodecaneamide from dodecalactam, which shows this effect at 160°C but remains a homogeneous mixture at 180°C. Figure 11 shows the increase in viscosity with time and is adapted from Malkin's experimental results. At high temperatures, the slope of the curve equals 3.3, as expected from theory. However, at low temperature, the slope is only 2.3. The viscosity of the mixture (η) can be described in general terms by:

$$\eta = K.M_n^\alpha.c_p^\beta \quad (6)$$

where K is a constant, M_n is the number averaged molecular weight (in kg/kmole), and c the concentration of the polymer. α and β are interaction parameters. By fitting the measurements to the theory, Malkin found that at 160°C, α was equal to zero and β was 2.3, while at 180°C, α was found to be 1 and β was 2.3. This difference can be attributed to the fact that, if phase separation occurs, the entanglements between the polymer molecules are hindered and the

viscosity buildup slows down. This effect can enhance instability. An extra complication is that high shear forces stretch the molecules and decrease their internal entropy (32, 33). Therefore, high-shear fields increase the concentration region where phase separation occurs, and, because they mainly exist in the screw, this effect enhances instability even further.

EXPERIMENTAL SUPPORT

Experiments were performed in a closely intermeshing counter-rotating twin screw extruder with a screw diameter of 40 mm and a screw length of 60 cm and in a self-wiping co-rotating twin screw extruder with a diameter of 50 mm and a screw length of 125 cm. The reactions performed were the polymerization of styrene and the co-polymerization of butyl-methacrylate with hydroxy-propyl-methacrylate. The monomers were pre-mixed with a combination of two initiators (dibenzoyl peroxide and Trigonox C or Trigonox T (AKZO-Nobel)) and fed to the extruder at a constant flow by means of a pump. In order to detect the instabilities, the feed stream or the screw rotation speed was increased gradually. The extruders could also be equipped with a die with variable resistance.

Figure 12 shows a typical stability diagram in terms of throughput versus rotation rate as found in an APV 50 mm self-wiping extruder for the copolymerization of butyl-methacrylate with hydroxy-propyl-methacrylate. The (+) signs indicate experiments where a stable process at high conversions was obtained, the (-) signs represent unstable operation (fluctuations or low conversion). Increasing the throughput or the rotational speed enhances unstable operation. This can be understood by realizing that both an increase in throughput and an increase in rotation speed (at constant throughput) decrease the residence time. Once

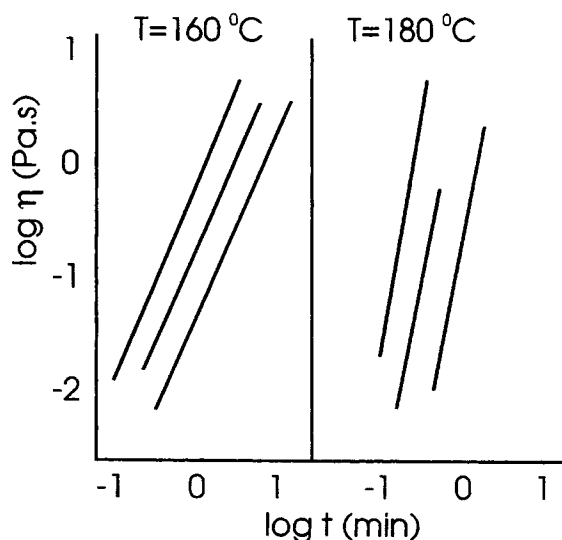


Fig. 11. Viscosity built up during the polymerization of dodecalactam to polydodecaneamide. At 160°C phase separation occurs (after Malkin).

this residence time falls below a critical value, the viscosity profile drops and a fluctuating operation or a transition to low conversions occurs.

Figure 13 shows the conversion as a function of the reciprocal die resistance for the polymerization of styrene in a counter-rotating extruder. If only styrene and an initiator are used, the conversion suddenly drops to a lower value if the die resistance is below a critical value. This is consistent with the arguments on two steady states as given in the section on hydrodynamic instabilities. The effects of increasing viscosity and increasing reaction speed were also investigated. Maleic anhydride was added to increase the reaction velocity or divinylbenzene was added to promote crosslinking and therefore increasing the viscosity. The addition of maleic anhydride resulted in a four-fold increase in reaction speed (23), while the addition of divinylbenzene caused a viscosity rise of a factor 50

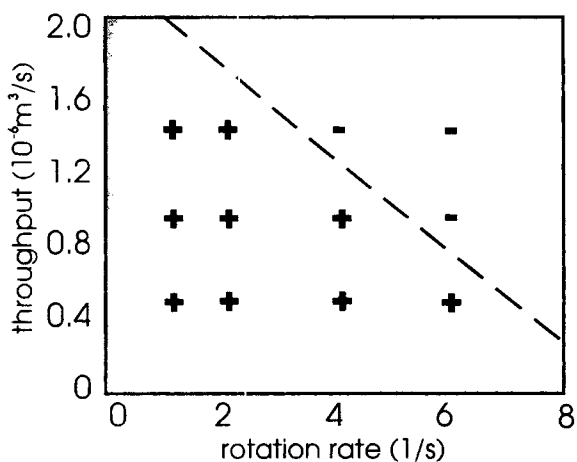


Fig. 12. Stability of a 50 mm self-wiping extruder during the polymerization of butylmethacrylate. + stable working point, - unstable working point, shading indicates the unattainable region.

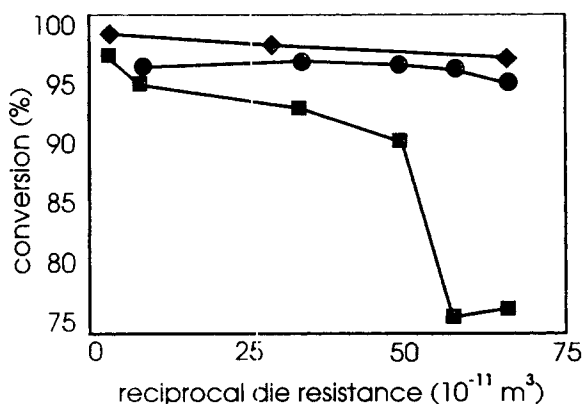


Fig. 13. Conversion as a function of reciprocal die resistance during polymerization of Styrene in a 40 mm counter-rotating twin screw extruder. ■ pure styrene with initiator; ◆ increased viscosity by DVE addition; ● increased reaction speed by MAH addition.

at relevant shear rates (10 s⁻¹) (34). Both additions had a stabilizing effect.

This stabilizing is further illustrated in Figs. 14 and 15. The addition of both maleic anhydride and of divinylbenzene increased the maximum stable throughput at a high conversion level substantially. The counter-rotating and the co-rotating extruder are compared in Fig. 16 for the reactive extrusion of butylmethacrylate with hydroxy-propyl-methacrylate. For this reaction it can be concluded that, at lower throughputs, the extruders are comparable in performance, but at higher throughput the conversion in the counter-rotating machine drops to a lower value. Here the co-rotating extruder performs much better, even when the differences in screw diameter are considered (50 mm vs. 40 mm) This behavior may be attributed to the much larger screw length of the co-rotating machine and therefore to the longer residence time and to its better distributive mixing abilities.

A closer look at the two types of extruders shows that the closely intermeshing counter-rotating twin screw extruder has a better ability to build up pressures, even in an environment with low viscosity liquids. This is due to the nearly closed C-shaped chambers, which provide a positive displacement action

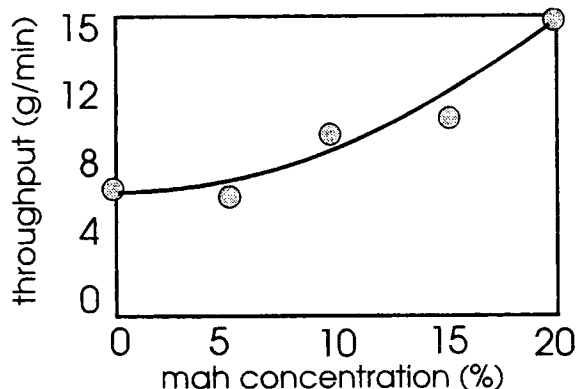


Fig. 14. The influence of the reaction speed (MAH addition) on the maximum stable throughput.

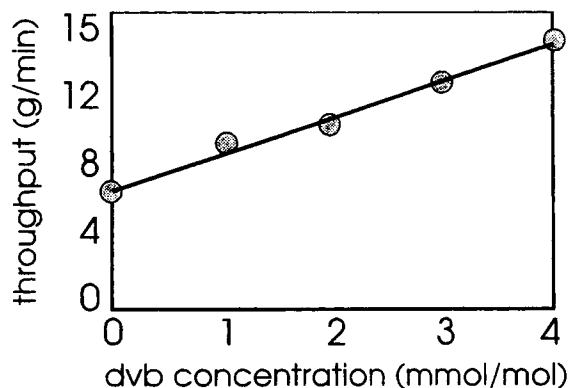


Fig. 15. The influence of viscosity buildup (DVB addition) on the maximum stable throughput

that enhances stability. Self-wiping extruders, on the other hand, are generally capable of much larger throughputs at comparable residence times. This leads to a preference of counter-rotating extruders for relatively slow (and therefore potentially unstable) reactions, while self-wiping machines can be used for faster polymerizations.

CONCLUSIONS

Reactive extrusion is a promising area for polymerization processes; however, its applications are still severely hampered by the possible occurrence of instabilities, resulting in a sudden transition to an operating mode with low conversions or in severe oscillations during the process. The interaction diagram reveals three possible sources of instabilities: of thermal origin, of hydrodynamic origin, and of chemical origin.

Thermal considerations reveal that most extrusion polymerization processes occur under local runaway conditions. This is especially the case for large equipment and should be considered when designing an experimental program. Experiments on a small scale may easily lead to results that cannot be scaled up successfully. If the barrel wall is heated electrically, small temperature fluctuations may be enhanced by the reaction, leading to severe fluctuations in the filled length and the residence time. Especially in large-scale equipment, large radial thermal inhomogeneities can build up. Machines with continuous channels, such as single screw extruders or self-wiping twin screw extruders, are sensitive to this phenomenon that may lead to an erroneous scale-up. It is advisable to introduce small mixing elements at regular distances in the screw for good thermal homogenization.

Hydrodynamic considerations lead to the contention that there are two stable operating points in reactive extrusion, one with a high conversion and one with a low conversion. In the region in between, severe oscillations in throughput and conversion may occur. The stability, and as a consequence the maximum attainable throughput at high and stable con-

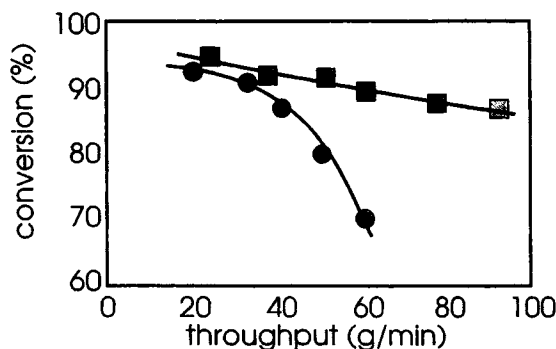


Fig. 16. Conversion as function of the throughput for BMA polymerization. ■ Self-wiping co-rotating extruder ($D = 50\text{mm}$); ● Closely intermeshing counter-rotating extruder ($D = 40\text{mm}$).

version, can be improved by increasing the reaction speed, increasing the viscosity built up in the screws and by increasing the residence time. For slow reactions a closely intermeshing extruder is preferred; for faster reactions, co-rotating self-wiping machines give a higher stable throughput.

Chemical considerations lead to three effects that influence the stability of reactive extrusion: the gel effect, the ceiling temperature, and phase separation. Gel effects increase the conversion by an "autocatalytic" behavior. If the gel effect occurs completely in the screws it stabilizes the process; if it occurs near or in the die it may create destabilization. The occurrence of a ceiling temperature slows the reaction and thus has a direct negative influence on the hydrodynamic stability. Phase separation can decrease the effective viscosity and enhance the hydrodynamic instability. It should be realized that even in systems or at temperatures where under stationary situations no phase separation occurs, high shear forces can change the entropy such that flow induced phase separation is possible.

Concluding remarks: A good understanding of the factors that determine the stability in reactive extrusion processes is important for further development. The most important role in these instabilities is played by the changes in the filled length in the extruder, which are determined by a complex mutual interaction involving residence time, conversion, and viscosity buildup. Other factors of thermal or chemical origin influence these interactions. Research into a further quantification and mathematical modeling of the stability has been started.

NOMENCLATURE

α, β	Interaction parameter in Equation 6.
χ	Conversion, %.
ρ	Density, kg/m^3 .
η	Viscosity, Pa.s.
δ_T	Thermal boundary layer thickness, m.
a	Thermal diffusivity, m^2/s .
c_m	Monomer concentration, kmole/m^3 .
C_p	Specific heat, $\text{J}/\text{kg}\cdot\text{K}$.
c_p	Polymer concentration, kmole/m^3 .
H	Channel depth, m.
K	Constant.
L_f	Filled length, m.
M_n	Number averaged molecular weight, kg/kmole .
m	Number of thread starts per screw.
N	Rotation rate of the screws, s^{-1} .
P	Pressure, Pa.
R	Gas constant, $\text{J}/\text{kmole}\cdot\text{K}$.
T	Absolute Temperature, K.
rt	Residence time, s.
t	Time, s.
ΔG	Gibbs free energy, J/kmole .
ΔH_p	Heat of polymerization, J/kmole .
ΔT_{ad}	Adiabatic temperature rise, K.
ΔS_p	Polymerization entropy, $\text{J}/\text{kmole}\cdot\text{K}$.

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