

Chapter 7

Generalisation of the results

This thesis describes the extruder as a polymerisation reactor. Starting point of the research is the copolymerisation of styrene (St) with n-butylmethacrylate (BMA). Three different aspects are investigated, namely the effect of prepolymerisation, the effect of the polymer melt viscosity, and the effect of the polymerisation rate (chapters 4 to 6).

To understand reactive extrusion behaviour, a theory is developed by Ganzeveld et al (1992, 1993). The theory is schematically shown in the "Interaction diagram" (figure 7.1), which is a qualitative analysis of the influence of the several extruder parameters on, for example, the conversion. The diagram is very useful in understanding the global behaviour of the extruder reactor. However, this chapter shows some major discrepancies between the experiments and the predictions by the Interaction diagram. Therefore, we developed a new theory concerning reactive extrusion, which resulted in a new optimisation diagram for the extruder used as a polymerisation reactor.

7.1 The Interaction diagram

The Interaction diagram describes the effect of the primary parameters on the variables in the reactive extrusion process. Primary parameters are parameters that can be controlled externally. According to the Interaction diagram (figure 7.1), the primary parameters, which are indicated in double enclosed boxes, are the screw rotation rate, the die resistance, the barrel temperature and the throughput. The radical concentration is also considered as primary parameter, since the type and amount of initiator, which determine the radical concentration, can be chosen rather freely. The upper part of the diagram describes the process parameters, while the bottom part of the diagram shows the product parameters. For clarity reasons, not all parameters are taken into account. One aspect that is neglected is for example the termination reaction, which is an important feature of radical polymerisation reactions. An implication of this neglect is that according to the Interaction diagram, an increase in temperature results in a higher conversion. This is not always true, due to the decreasing initiator efficiency when the initiator is used at a too high temperature.

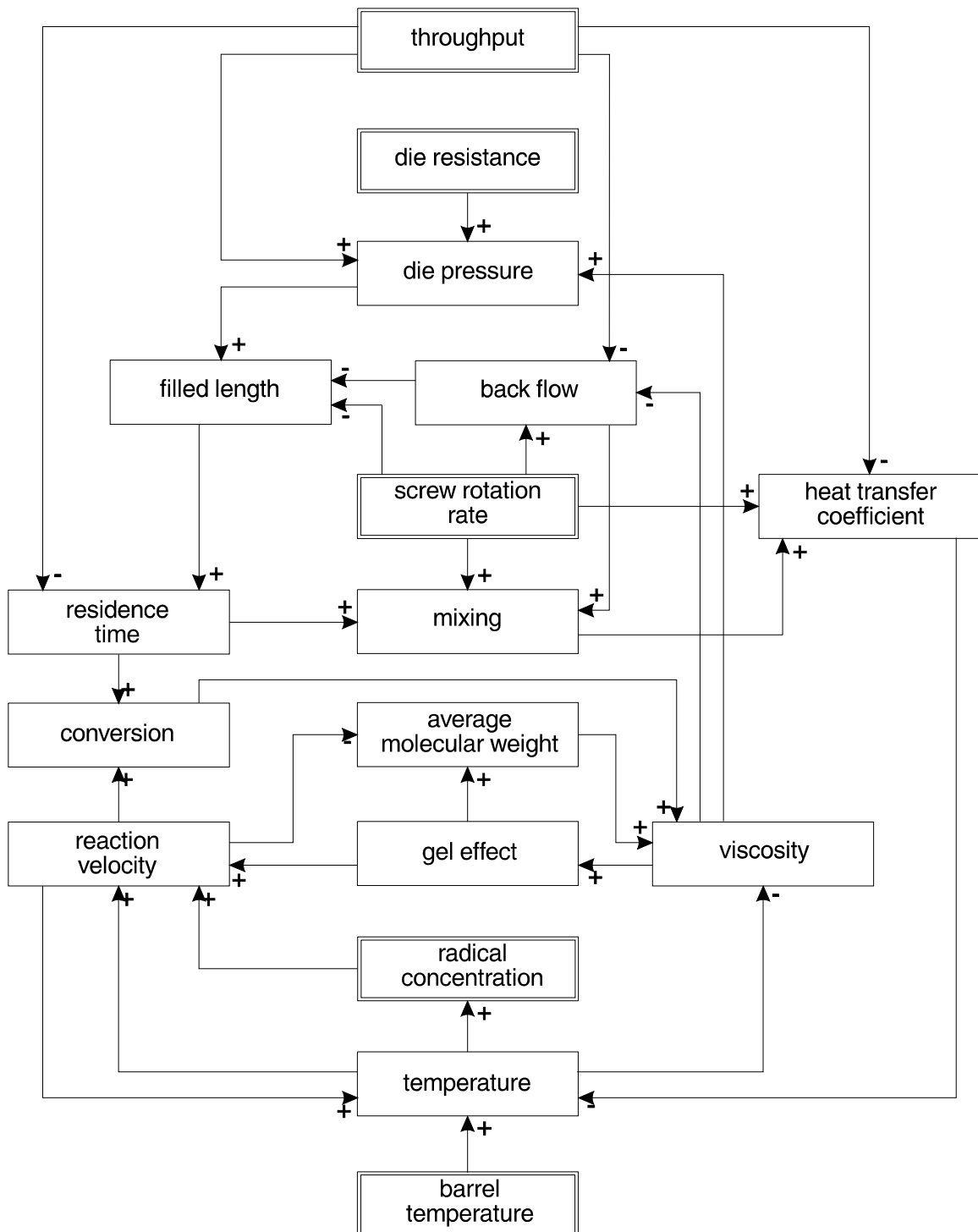


Fig. 7.1 Interaction diagram

7.2 Deviations from the Interaction diagram

The experiments, described in this thesis, show some situations in which the Interaction-diagram does not describe the experiments correctly. In itself, this is not very surprising, since the process of reactive extrusion is very complicated. However, the use of the extruder as a polymerisation reactor will only be interesting, if a stable extrusion process can be obtained, giving a product with sufficient conversion. Especially in that part of the working domain, the predictions by the Interaction diagram are usually not correct. Two of the main cases will be discussed below.

The first case is the influence of the screw rotation rate. The Interaction diagram predicts a decrease in conversion when the screw speed is increased, due to a decrease in residence time. This is not always true as can be seen in for example figure 6.9. It shows that a change in screw rotation rate hardly influences the conversion when 20% maleic anhydride (Mah) is added to the reaction mixture. This implies that an increase in screw rotation rate does not always lead to a decreased conversion. Sometimes, a constant conversion can be obtained when varying the screw speed. The second case concerns the throughput. The Interaction diagram conceives the throughput as primarily parameter, just as in normal extrusion processes. In reactive extrusion however, the maximum throughput will always be lower than the throughput in normal extrusion processes (figures 5.9 and 6.7). Furthermore, the figures show that the maximum throughput is dependent on material properties such as the polymerisation rate of the mixture in the extruder.

Besides the cases discussed above, the Interaction diagram does not take into account two other important aspects. The first aspect is that the extent to which the extruder parameters influence the process is dependent on the reaction mixture in the extruder. For example, more Mah leads to a decreased dependency on the extruder parameters (fig. 6.8 and 6.9). A second aspect is the fact that the magnitude of influence of the extruder parameters is dependent on the other extruder parameters (figure 6.10).

7.3 A new theory for reactive extrusion

A new theory for the process of reactive extrusion will be discussed in this section. This theory describes qualitatively the polymerisation in a closely intermeshing counterrotating twin screw extruder. Probably, the theory is also useful for other extruder types, e.g. the selfwiping extruder.

Crucial in the theory is the question whether or not an amount of non-reactive-material before the die exists. This material can be non-reactive, due to lack of monomer (100% conversion), lack of initiator, or the polymerisation has reached thermodynamic equilibrium (Dainton 1958). That non-reactive material is defined as a "plug" in this chapter. When a plug is present in the last part of the extruder, the process of reactive extrusion will be rather insensitive to changes in extruder variables, such as screw speed and die resistance. The reason for this phenomenon is that the material can not change anymore after complete

reaction. The theory can be expanded by stating that the bigger the size of the plug of material is, the less sensitive the reactive extrusion process is for any changes or disturbances. It should be noted that this plug is not the same as the fully filled length as described in chapter 2, but the plug is a part of that length. This situation is schematically shown in figure 7.2. If the plug is not present, the traditional theory, as given by the Interaction diagram, can be applied, since material that leaves the extruder still reacts. In that situation, an increase in screw rate results in a decrease in conversion due to a decrease in residence time, which corresponds with the prediction by the Interaction diagram.

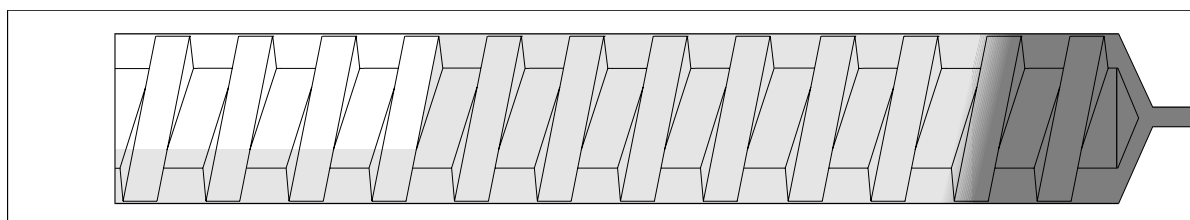


Fig. 7.2 Situation in which a plug (the darkest part) of completely reacted material is present before the die. This plug is part of the fully filled length.

The die resistance seems to be the most important (or at least mostly underestimated) extruder parameter, as it is a powerful tool to create a plug of completely reacted material. For an optimal use of the extruder, one should choose a die resistance that results in a plug of completely reacted material of minimal size. This die resistance can be defined as the minimum die resistance (MDR). If a die resistance larger than the MDR is applied, the size of the plug increases. This implies that the amount of mechanical energy added to the reacting material will be unnecessary high, as a result of which degradation may occur. Besides, when part of the extruder is filled with non-reacting material, the volume of the extruder is not used effectively. On the other hand, a too low die resistance leads to a conversion lower than the required conversion. It should be noted that the application of the MDR leads to an extrusion process that is very sensitive to disturbances. For stability reasons, one should apply a die resistance that is somewhat higher than the MDR, although the extruder volume is not used most economically in that situation.

The MDR is different for each monomer mixture. For instance, the amount of Mah determines the die resistance at which a conversion of 95% can be obtained in the St-BMA-Mah polymerisation (figure 6.8). Obviously, a faster polymerisation needs a lower die resistance for sufficient conversion. From experiments in which the polymer melt viscosity is increased by crosslinking (chapter 5), we can conclude that the MDR is also influenced by the polymer melt viscosity. Since the polymerisation rate and polymer melt viscosity are dependent on the temperature applied, the MDR will also depend on this temperature. The influence of the screw rotation rate is small, compared to that of the die resistance. As a result of this, the MDR will be slightly influenced by the screw rotation rate.

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The Interaction diagram states that the throughput can be adjusted at every value within the normal working domain of the extruder. The maximum throughput is determined by the theoretical throughput and the pressure needed at the die end. This die pressure determines the fully filled length of the extruder, over which the pressure rises from ambient to the pressure at the die entry. In an absolutely uniform screw system with an iso-viscous fluid this pressure development along the screw is linear. For a liquid system with a changing

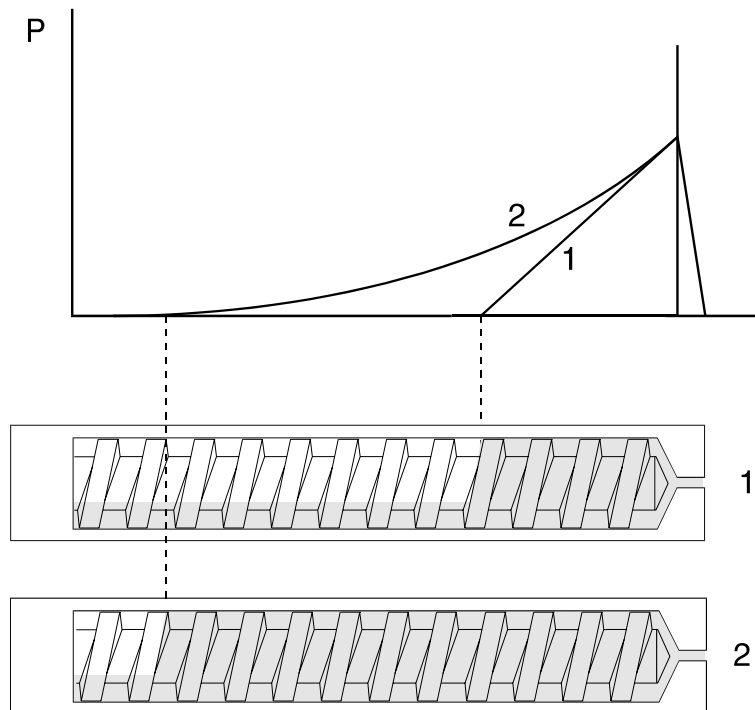


Fig 7.3 Pressure profiles 1. normal extrusion process, 2. reactive extrusion process

viscosity the pressure development is no longer linear, but curved (figure 7.3).

Suppose that we want to produce a certain amount of polymer. The die resistance needed is given by the MDR. This die resistance, together with the throughput and viscosity, determines the pressure at the die entry (chapter 2, Janssen 1978). If the extruder is fed with pure polymer, the pressure will increase linearly with the fully filled length, as indicated by line 1 for the ideal iso-viscous situation. The fully filled zone occupies only part of the extruder, so the throughput can be varied freely in a

quite large operating window. If the extruder is fed with monomer, the pressure profile as indicated by curve 2 will be obtained, provided that the throughput is similar and the conversion of the monomer is 100% resulting in an identical polymer as above. Since the product that leaves the extruder is similar for situation 1 and 2, the slope of the pressure profile at the die entry should be identical. Due to the decreased viscosity in the direction of the feedzone, the slope will decrease, which results in a larger fully filled length. In the situation as indicated in figure 7.3, the extruder is nearly fully filled, which implies that the throughput can not be increased anymore. So, in reactive extrusion, the maximum throughput is much smaller than the throughput in normal extrusion processes. For example, the maximum throughput described in this thesis was around 2 to 4% of the theoretical throughput. Even for a very fast polymerisation as performed by Jongbloed (1995a), the maximum throughput was limited to 10% of the theoretical throughput. Therefore, the throughput can better be considered as an extrusion variable rather than as a parameter that

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can be adjusted freely. However, it will be clear that when the polymerisation is very fast, the limitation in throughput will be less troublesome (chapter 6).

A method to increase the throughput is to perform a prepolymerisation. Figure 7.4 shows the effect of prepolymerisation, which is indicated by curve number 2. After prepolymerisation, the material fed to the extruder possesses already some viscosity, and is therefore able to create some pressure per chamber. This means that the slope of the pressure line does not go to zero, as in normal reactive extrusion processes (curve number 3) but it starts immediately with a slope significantly larger than zero. Although after prepolymerisation, the fully filled length is still larger than in the normal extrusion process (curve 1), it is significantly smaller than in a reactive extrusion process without prepolymerisation. This implies that larger throughputs can be obtained after prepolymerisation. Chapter 4 describes this effect experimentally.

With the theory described above, we can optimise the reactive extrusion process. The screw speed should be adjusted at a moderate speed; the temperature profile is especially in large extruders difficult to control, and sometimes necessary for adjusting the molecular weight of the polymer. This means that the temperature of the material in the extruder is not a real process parameter. The same holds for the initiator concentration. With this in mind the diagram as shown in figure 7.5 is developed. It optimises experimentally the process of reactive extrusion by searching for the lowest possible die resistance, combined with the maximum throughput, resulting in a high (for example more than 95%) conversion.

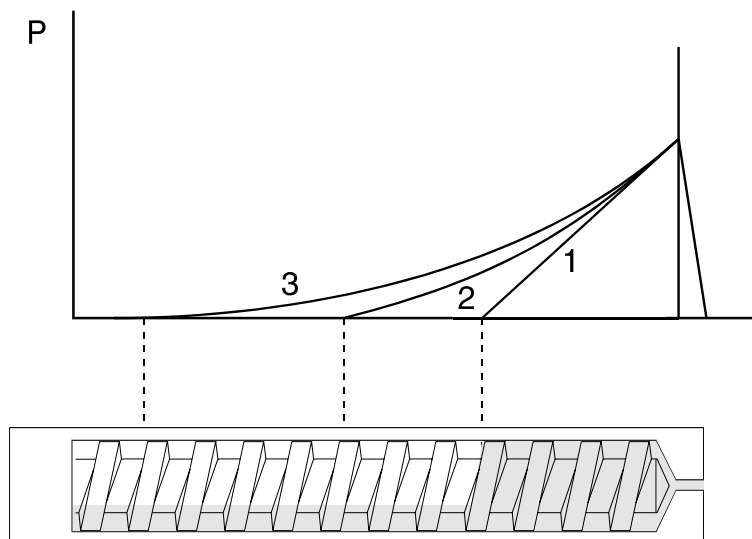


Fig 7.4 *The effect of prepolymerisation on the fully filled length*

Generalisation of the results

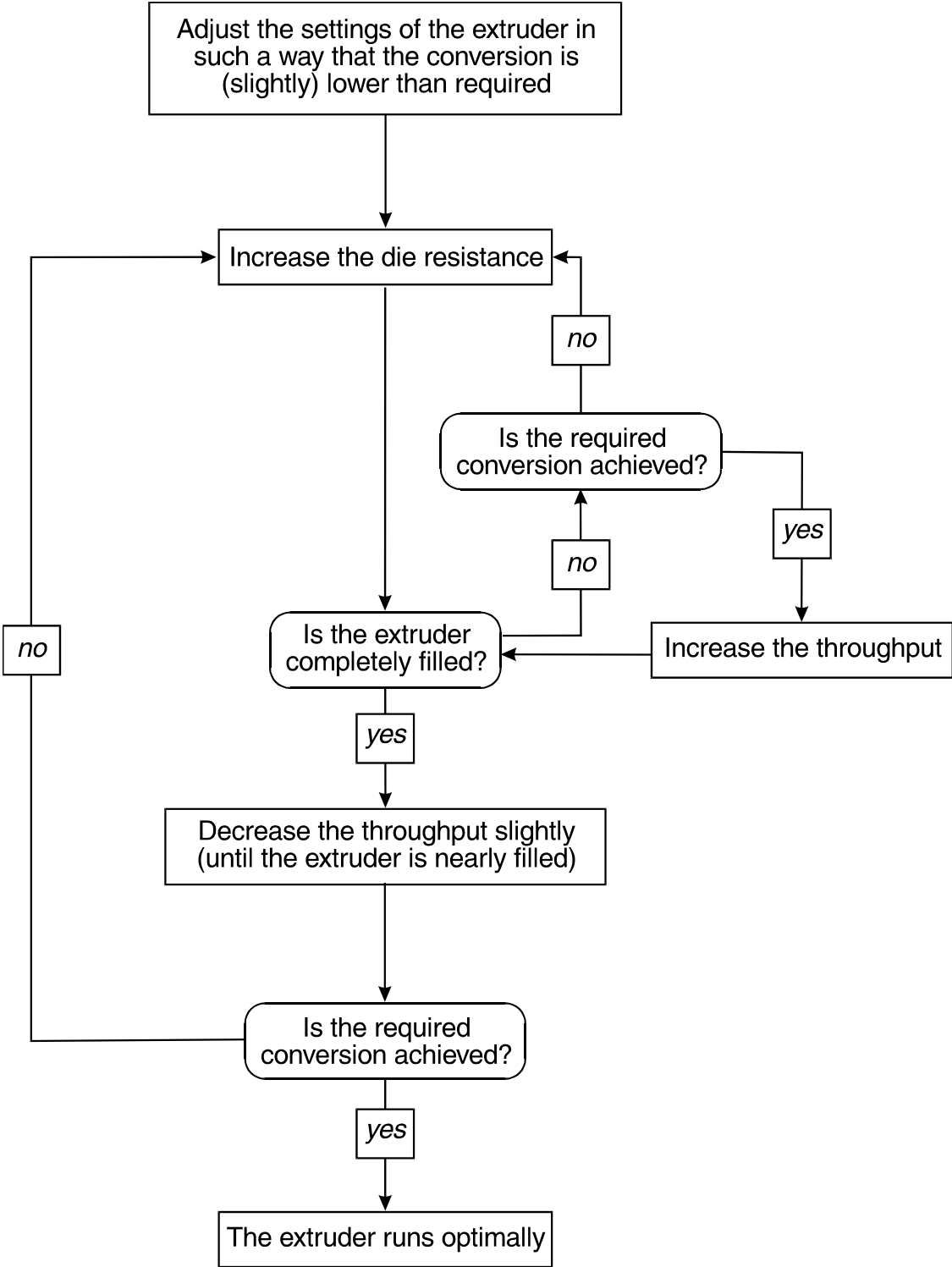


Fig 7.5 Optimisation diagram

7.4 Conclusions

The theory developed in this chapter explains most of the experimental results very well and is useful in optimising the process of reactive extrusion. The theory states that for a stable reactive extrusion process, the existence of a plug of completely reacted material just before the die is very important. If this plug is not present, the required conversion might not be achieved; if the plug is too small, a small disturbance in extruder parameters can lead to instabilities in the process. A too big plug leads to an unnecessary energy input into the material. The formation of the plug depends on either the extruder parameters and product properties, such as polymerisation rate and polymer melt viscosity.

The die resistance is the most powerful extruder parameter to create a plug. Moreover, it is a very useful tool to overcome stability problems. Nevertheless, the die resistance accounts for limitations in throughput, which results in the throughput being a variable instead of a standard process parameter. The die resistance needed for creating the plug is defined as the Minimum Die Resistance and is dependent on product parameters, and to a lesser degree on process parameters.

The limitation in throughput in reactive extrusion, when compared with normal extrusion processes, can be explained by the large change in viscosity of the material when it travels from feed zone to die end due to polymerisation. The limitations are less troublesome when the extruder is used as a polymerisation reactor for fast polymerisations or when a prepolymerisation is performed.

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