Summary

The extruder as a polymerisation reactor for styrene based polymers

This thesis describes the counterrotating twin screw extruder as a polymerisation reactor for styrene based polymers. The use of the extruder as a polymerisation reactor offers new possibilities for synthesising polymers and polymer blends without using any solvents, which makes the process environmentally friendly. Since previous research showed the closely intermeshing counterrotating twin screw extruder to be the most stable polymerisation reactor, this type of extruder was used during the whole study. Furthermore, the average shear level is low in a counterrotating twin screw extruder, which prevents degradation of the newly formed polymer to occur. Styrene is chosen as main component since it is a well-known and versatile monomer.

The study described in this thesis covers three different subjects:

1. The general theory of counterrotating twin screw extruders;
2. The extruder as a polymerisation reactor: The product properties;
3. The extruder as a polymerisation reactor: The process characteristics.

The counterrotating twin screw extruder

The counterrotating twin screw extruder can be considered as series of C-shaped chambers that move towards the die due to the rotation of the screws. The transport of the material through the extruder is by positive displacement, which is a mechanism that is relatively independent of the rheological behaviour of the material. Leakage flows, which are partly pressure driven and partly mechanically induced, account for interaction between the chambers. Characteristic for this extruder is the fact that it is starved fed, which leads to a partially filled zone.

Besides a partially filled zone, a fully filled zone exists. This zone is the pump zone of the extruder. Its length is determined by throughput, geometry of the screws and die pressure. This die pressure is dependent on viscosity, throughput and die resistance.

Until now, the die resistance was derived from theory. However, to be able to validate theory by experiments, the die resistance has to be measured. Therefore, the die resistance was determined experimentally. Based on these results, the residence time measurements show that the theory underestimates the length of the fully filled zone by roughly 30%.

Also the degree of fill in the partially filled zone is studied. It appeared that a good estimation of the degree of fill can be obtained if all non-pressure driven leakage flows are taken into account. This result, combined with the newly determined length of the fully filled zone, makes a good prediction of the mean residence time possible.

The extruder as a polymerisation reactor

The extruder is studied as a polymerisation reactor in chapters 4 to 8. Starting point of the research is the radical copolymerisation of styrene (St) and n-butylmethacrylate (BMA). Kinetics investigations show that this copolymerisation is slower than the bulkpolymerisation of BMA, but faster than the polymerisation of St.

The product properties

The copolymer consisting of St and BMA has a slightly alternating tendency. The polymer is transparent and possesses a glass transition temperature of 30 °C. Dependent on reaction conditions, it was possible to synthesise St- or St-BMA-polymers that possess a weight average molecular weight varying from 30 to 200 kg/mol. The molecular weight was mainly influenced by the initiator concentration and by the temperature profile along the barrel. Furthermore, it turned out that the extruder can be used for making slightly crosslinked polymers. The maximum conversion for St was almost 99%, while for St-BMA the maximum conversion was 96%. This difference is most likely due to differences in thermodynamic limitations in the two polymerisations mentioned.
Besides St and St-BMA, also a terpolymer consisting of St-BMA-Mah (maleic anhydride) was investigated. The maximum conversion was approximately 97%, while the molecular weight of the polymer was higher than the molecular weight of the St-BMA copolymer, when it was produced under similar conditions. The addition of Mah resulted in a faster polymerisation, and the polymer formed was pale white.
Apart from the polymerisations mentioned above, the extruder was used for synthesising polymer blends based on styrene. To improve the thermal properties of polystyrene, PPE (poly-2,6-dimethyl-1,4-phenylene oxide) was added to the monomer St. After the polymerisation of St, a homogeneous blend was obtained with a higher glass transition temperature than polystyrene. In order to improve the impact strength, some rubber was added to St. However, due to the fine dispersion of the rubber after polymerisation, the effect of the rubber on the impact strength was negligible.

The process characteristics

As the previous section suggested, the extruder can be used as a polymerisation reactor for the aforementioned polymers and polymer blends. The starting point of the research was the copolymerisation of St and BMA. Due to its relatively low polymerisation rate, the process of reactive extrusion was rather difficult to perform. For sufficient conversion, a high die resistance was needed as a result of which the throughput was strongly limited. This severely restricted the working domain of the extruder.

The operating window of the extruder could be enlarged by performing a prepolymerisation, by crosslinking the St-BMA-copolymer, and by the addition of Mah to the monomer mixture. The effect of crosslinking is most remarkable, since crosslinking did not influence the polymerisation rate. The larger working domain after prepolymerisation or in the case of a faster polymerisation, which was obtained by replacing BMA by Mah, was more or less expected. A larger working domain meant higher throughputs and a decreased dependence on extruder parameters, such as die resistance and screw speed.

A stable reactive extrusion process that yields sufficient conversion will be obtained if a plug of completely reacted material exists in and before the die. If the plug is not present, the required conversion will not be achieved. The most economical use of the extruder is when a plug of minimal size is present. However, stability problems are very likely to occur in that situation.

The die resistance is a the most powerful tool in creating a plug. The minimum die resistance needed for creating a plug is mainly dependent on product properties. For reasons of comparison the various processes, this die resistance should be known quantitatively.

The limitations in throughput can be explained by the large viscosity differences of the material when it travels from feed zone to die end. However, prepolymerisation or a fast polymerisation reduce the limitations in throughput.