The extruder as a polymerisation reactor for styrene based polymers
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Chapter 1

Introduction

1.1 Reactive extrusion

Since the 1980's, the interest in reactive extrusion is growing. This growing interest is based on the fact that the extruder can handle highly viscous materials, which makes it suitable as a chemical reactor for the production of polymers. From the beginning of the polymer industry, extruders have been used for melting, pumping, mixing and devolatilising polymers. Besides, extruders find applications in food industry.

Historically, polymerisation- and modification reactions of polymers were carried out in diluted systems. After completion of the reaction, solvent had to be removed, which was rather energy consuming. Because of environmental restrictions issued over the last 20 years, the reduction of energy consumption and solvent emission became very important. The environmental advantages of an extruder used as a reactor becomes clear when the extruder is compared with the traditional reactors, which need solvents to dilute the viscous polymer liquid. Extruders need no diluent, which eliminates the energy for a solvent recovery. Furthermore, no energy is necessary to heat or cool the solvent, and when no solvents are used, there will be no emission of these chemicals. The potential of these advantages is very large, because in traditional reactors, the polymer is diluted 5 to 20 times.

Reactive extrusion can be used for a lot of reactions. The main reactions are (Lambla 1994, Xanthos 1992, Brown 1988, Wielgolinski 1983):
- bulk polymerisations;
- graft- or functionalisation reactions;
- coupling- or branching reactions;
- degradation reactions.

In a clear article Todd (1992) describes the advantages and limitations of reactive extrusion. Besides the advantages already mentioned, Todd states that the extruder provides good mixing, that the thermal homogenisation is better than in traditional reactors and that the residence time distribution can be controlled quite well. Furthermore, the extrusion process is continuous and the extruder does not have stagnant zones. Due to its high plug flow character, the extruder volume can be smaller than the volume of traditional reactors.

Restrictions are the limited residence time, the limited heat transfer through the barrel and the poor ability to handle low-viscous materials.
1.2 The extruder as a polymerisation reactor

The possibilities for the use of an extruder as a polymerisation reactor were already recognised in 1950. A patent of Dow Chemical Company (Stober 1950) described the use of a single screw extruder as a main polymeriser. After a prepolymeriser with a mean residence time of 90 hours, a screw conveyor was used as a polymerisation reactor, in which a residence time of 18 hours was necessary for the thermal polymerisation of styrene. The first polymerisations described in open literature were the polymerisation of nylon (Illing 1969) and several polycondensation reactions (e.g. Mack 1972). In the mid-seventies, the first theoretical considerations concerning reactive extrusions appeared. Meyuhas (1973) stated that the 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. This study advised a prepolymerisation to avoid low viscous material fed to the extruder. Mack (1976) proposed twin screw technology for reactive extrusion because of difficulties in scaling up single screw extruders that can be avoided in twin screw extruders. Furthermore, the residence time and its distribution can be controlled better in twin screw extruders. Residence times of half an hour were possible in a self-wiping twin screw extruder. Finally, Mack 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.

In more recent years, the radical polymerisation of several methacrylates was studied in a counterrotating twin screw extruder (Stuber 1985, Dey 1987, Ganzeveld 1993, Jongbloed 1995a). Stuber and Dey studied the radical polymerisation of methylmethacrylate, Ganzeveld the polymerisation of n-butylmethacrylate, while Jongbloed studied a copolymerisation of n-butylmethacrylate and 2-hydroxy-propylmethacrylate. Jongbloed and Ganzeveld found maximum conversions of roughly 93% in one step, while Dey claimed complete conversion after prepolymerisation. Jongbloed (1995b) used also a selfwiping corotating twin screw extruder for the copolymerisation of n-butylmethacrylate and 2-hydroxy-propylmethacrylate. Apart from the polymerisations already mentioned, the counterrotating extruder was also used for the polycondensation of urethanes (Ganzeveld 1992) and the anionic polymerisation of e-caprolactam (Speur 1988). The possibilities for reactive extrusion of urethanes were also recognised by several other authors (Bouilloux 1991, Coudray 1994, Uhland 1994).

Recent articles describe the use of a corotating twin screw extruder for the anionic polymerisation of e-caprolactam (Hornsby 1994, Kye 1994, Michaeli 1995). Kye successfully integrated the anionic polymerisation of e-caprolactam in a corotating twin screw extruder with a melt spinning of a polyamide 6 fiber. The anionic polymerisation of styrene was investigated by Michaeli (1993, 1995), who also published on the copolymerisation of styrene with isoprene (Michaeli 1994). The processes, described by Michaeli, seems very promising, since complete conversion was easily obtained in one step. The radical polymerisation of styrene in an extruder was described in a patent by Kelley (1993). In a two-stage process, styrene was polymerised and devolatilised in a corotating twin screw extruder (Berstorff ZE180). The patent claimed a throughput up to 8000 kg per hour. The patent also describes several copolymerisations with styrene as the main
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component and the synthesis of high-impact polystyrene (HIPS). Since this process resembles our process, it will be evaluated in chapter 4 and compared with the process studied in this thesis.

1.3 Classification of extruders

An extruder is an apparatus that consists of one or more screws enclosed by a barrel. A schematic picture is given in figure 1.1. When the screw of an extruder rotates, material inside the extruder is transported from the feed zone to the die end. The barrel of an extruder, and thereby the material in the extruder, can be heated.

Fig. 1.1 Schematic representation of an extruder

Single screw extruders are most widely used in industry, since it is a simple and cheap extruder type. The extruder consists of one screw in a barrel of circular cross-section. The transport mechanism is based on drag flow, which originates from the contact effects between the material, the barrel and the moving screw. No-slip conditions are essential for the functioning of the extruder. Due to the pressure built up at the die end of the extruder, a pressure flow in a opposite direction of the drag flow arises. The throughput of the single screw extruder can be calculated by subtracting the pressure flow from the drag flow.

Twin screw extruders consist of two screws that are placed parallel in a barrel with a eight shaped cross-section. Twin screw extruders can be divided into two main groups: corotating and counterrotating. Corotating extruders can be divided into self-wiping (the shape of the screws results in a cleaning of the screws) or closely intermeshing (the channel of one screw is blocked by the flight of the other screw). Counterrotating extruders can be divided in closely intermeshing or non-intermeshing. Non-intermeshing means that the distance between the two screw axes is at least equal to the outer screw diameter (Janssen 1978). Figure 1.2 represents the classification of twin screw extruders.

Material inside a closely intermeshing twin screw extruder is transported by volumetric displacement. This volumetric displacement is relatively independent of rheological behaviour of the material inside the extruder. This results in a stable transport mechanism. In
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non-intermeshing or selfwiping extruders, the transport mechanism stands midway between
the transport mechanisms of single screw extruders and closely intermeshing extruders.

Fig. 1.2 Classification of twin screw extruders

1.4 About this thesis

The objective of this study is the production of styrene based polymer blends by means of
reactive extrusion. The blends will be obtained by dissolving a polymer in a monomer
(mixture) that will be polymerised in an extruder in order to obtain a fine dispersion of the
dissolved polymer in the newly formed polymer. Before the polymer blends can be
synthesised, the production of polystyrene and styrene copolymers (mainly the styrene-n-
butylmethacrylate copolymer) through reactive extrusion has to be investigated thoroughly.
This part of the study is more extensive than expected in advance, but it has resulted in a
new theory concerning reactive extrusion. Apart from reactive extrusion, the theory of the
counterrotating twin screw extruder will be evaluated, and supplemented where necessary.

The contents of the chapters are as follows:
Chapter 2 gives an extensive description of the counterrotating twin screw extruder. It
evaluates traditional theories concerning this type of extruder. This chapter shows how to
determine of the degree of fill in the partially filled zone and the length of the fully filled
zone.
Chapter 3 gives information about the applications and synthesis of polystyrene and styrene
copolymers. Furthermore, it gives some theoretical considerations about polymer kinetics of
homo- and copolymerisations. After that, the results of kinetic experiments are discussed.
Chapter 4 shows the experimental set-up. The results of the extrusion polymerisation of
styrene (St) with n-butylmethacrylate (BMA) are described. Finally, this chapter outlines the
effect of prepolymerisation on the process and the product properties.
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In chapter 5, the effect of the polymer melt viscosity on the working domain is investigated by slightly crosslinking the St-BMA-copolymer. The crosslink agent used is divinylbenzene (DVB). The influence of the crosslink agent on the product properties is also described in this chapter.

The effect of the polymerisation rate on the working domain is studied in chapter 6. By replacing a certain part of the BMA by maleic anhydride (Mah), the polymerisation rate is increased. Furthermore, this chapter describes the influence of Mah on several product properties.

Chapter 7 gives a theory that explains the results of the previous chapters. By using this theory, an optimisation diagram is developed for extruders used as polymerisation reactors.

In chapter 8, the production of polymer blends is described. In order to obtain the best polymer properties, only styrene is used. Therefore, this chapter starts with the extruder polymerisation of styrene, followed by the production of the polymer blends based on this monomer. The polymers used are poly-2,6-dimethyl-1,4-phenylene oxide (PPE) in order to increase the glass transition temperature, and SBS (a styrene-butadiene-styrene triblock-polymer) to increase the impact strength.

Chapter 9 gives the main conclusions of this thesis.

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