Controlled peroxide-induced degradation of polypropylene in a twin-screw extruder: Change of molecular weight distribution under conditions controlled by micromixing

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ABSTRACT

Controlled degradation of polypropylene (PP) by peroxide was carried out in a laboratory twin-screw extruder ZSK 18 and the change in Molecular Weight Distribution (MWD) was measured using Size Exclusion Chromatography–Differential Viscosimetry (SEC–DV). The MWD results were compared to MWD predictions from a kinetic model developed and validated in earlier work (Iedema et al., 2001) assuming ideal mixing. Clear deviations were observed – the measured MWD was broader – that could only be explained by unaccounted heterogeneity in the extruder. Incorporating the relatively narrow Residence Time Distribution (RTD) in the twin-screw extruder did not lead to MWD broadening. In contrast, the exponential RTD of a Continuously Stirred Tank Reactor (CSTR) yielded a MWD widening that was too extreme. A new micromixing model, based on the striation thinning model by Ottino (1980), was constructed partly based on Monte Carlo sampling using a monomer scission probability (Tobita, 1996). This model was adapted to the geometry of the extruder entrance and the peroxide feed practice consisting of introducing a few per thousand peroxide-rich PP particles among pure PP particles. This micromixing model indeed allowed obtaining very good matches between measured and modeled MWD. Under different experimental conditions with respect to initial PP quality and amount of peroxide added, with a constant value for the striation thinning parameter the errors between measured and predicted MWD were around 5%.

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1. Introduction

The controlled degradation of Polypropylene (PP) using peroxides is extensively used in the Polyolefin industry to optimize both its processing capabilities and the end use properties desired by their customers. At the same time processing conditions form an interesting situation for Chemical Engineering from a selectivity point of view, since fast reactions of peroxide radicals are paired to a relative slow diffusion of these highly reactive initiator radicals through the polymer melt. It is interesting, since possibly the reactions proceed under spatially inhomogeneous conditions.

In the area of Polymer Reaction Engineering this problem has been addressed for macroscopically inhomogeneous systems (Wells and Ray, 2005; Schmidt et al., 2005), where flow conditions create compartments with different conditions. Distributed micro-structural properties such as the molecular mass, themselves possessing a certain spread in properties, are seen to

become even more distributed by such macroscopic inhomogeneities. The same holds for inhomogeneities at a more microscopic level, as shown by our earlier publications on the controlled degradation of Polypropylene in a Static Mixer Reactor (SMR) (Fourcade et al., 2001a,b). Both macroscopic and microscopic inhomogeneities originate from the joint effect of flow and diffusion, so attempting the detailed mathematical description of these phenomena using Computational Fluid Dynamics (CFD) is one serious manner in solving the problem (McKenna et al., 1998). However, this approach is still highly challenging as it is faced with a number of serious problems, like the non-Newtonian rheology of the polymer melt and the small scale of especially micromixing phenomena.

Dealing with micromixing in the framework of CFD requires sub-grid modeling, which has been applied to polymerization of low-density Polyethylene (ldPE) using probability density functions to describe the chemistry (Tsai and Fox, 1996; Kolhapure et al., 2005). Accounting for micromixing phenomena has not frequently been applied in Polymer Reaction Engineering. An early example using compartment modeling to describe the micromixing effect, again for ldPE, is given in Marini and Georgakis (1984), and a more recent one

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by Nele and Soares (2002), who suggest micromixing to be the cause of enhanced branching in metallocene-catalyzed Ethylene polymerization. Micromixing has scarcely been applied to polymer degradation. Note that the mixing addressed in a recent paper on PP degradation in a twin-screw extruder (Suresh et al., 2008) is concerned with macroscopic mixing. In a series of publications on the controlled degradation of PP in a Static Mixer Reactor (SMR) we did systematically address the micromixing phenomenon. There we followed – as we will do in the present publication – the approach developed by Ottino (1980) and Fields and Ottino (1987) using the concept of "striation thinning". According to it the complex 3-dimensional flow and convective diffusion problem is reduced to a one-dimensional problem with a limited number of parameters, like the striation thinning rate, α. At one point in the whole procedure we 'averaged' the 3D-flow (Newtonian) as computed by CFD and thus inferred the parameter α in a computational manner. In addition, α was experimentally determined by Laser Induced Fluorescence (LIF). When finally applied to experiments with controlled PP degradation in the SMR we employed α as an empirical parameter, obtained by fitting full MWD's on measured ones (SEC-DV). Micromixing turned out to have a strong impact on the MWD shape, which deviates considerably from the shape obtained under ideal mixing conditions.

The objective of this paper is to demonstrate the effect of micromixing on PP degradation in a twin-screw extruder. The experiments performed in the ZSK 18 are closer to the industrial practice than those with the SMR in our earlier work that has not been used in industry for PP degradation until today. However, here again a measurable effect of micromixing is not unimaginable, since the addition of the peroxide happens in solid form by a few pp particles possessing a peroxide coating, which may lead to locally high initiator radical concentrations (see Fig. 1). The modeling approach is comparable to the one followed in our earlier work, although we replaced the deterministic approach to compute MWD's by an extremely fast Monte Carlo sampling method (Tobita, 1996).

This paper is structured as follows.

First, a brief description of the laboratory extruder setup and the materials and measuring equipment used is given. The modeling chapter starts with the kinetic equations used culminating in the scission 'density' that is the central parameter of the Monte Carlo scission algorithm. This parameter possesses a distribution of values according to the RTD in a Continuously Stirred Tank Reactor (CSTR). Then the way the laminar micromixing model is applied to the twin-screw extruder is explained in terms of a 3-dimensional description of the entrance section of the extruder. Subsequently, the partial differential equations describing micromixing and reaction and their boundary conditions are presented. The solution of these equations provides the profiles of scission probabilities across the striations, which represent the input for the MC scission simulation procedure.

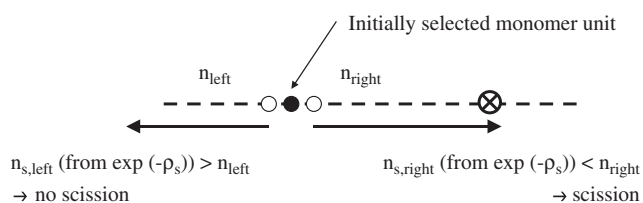Section 4 starts with a presentation of a quantitative measure of agreement between measured and predicted MWD. Then the effect of RTD in a CSTR and a twin-screw extruder on the scission probability distribution is shown as a reference to compare the micromixing results with. Finally, the effect of micromixing on the MWD is presented. Proper values for the striation thinning parameter α are obtained from the best fits of the MWD. These prove the broadening of the MWD due to micromixing as compared to ideal mixing.

2. Experimental

Polypropylene with molecular weights $M_w=370$, 470, 590 and 880 kg/mol and $M_n=70$, 105, 130, 245 kg/mole, respectively, were used as starting base powder obtained from Sabic Europe. This starting powder material was of high purity and contained no additives. The base powder was compounded adding 0.2 wt% Irganox B225 as antioxidant and Luperox 802PP40 as peroxide to control the molecular weight. The stabilizer and Luperox (concentrations of 0–0.5 wt%) were mixed with the pure PP base powder at SABIC-Europe using a Henschell mixer. This mixture was dosed to the hopper of a ZSK18 co-rotating twin-screw extruder with a length/diameter ratio of 40. In all experiments a throughput of 2.5 kg/h was maintained at a rotational speed of 200 rpm. The temperature of the barrel is measured at various places along the screw axis as shown in Fig. 4 and increases to 240 °C. The temperature profile shown is assumed to be kept during all experiments. The temperature of the polymer melt at extruder exit was also measured and turns out to be slightly higher: 242 °C. These temperatures were chosen to ensure high peroxide conversion. The residence time distribution was measured by introducing a PP grain with black colorant into the extruder and measure the time of first coloring of the exiting melt (τ_d in Eq. (14)) and observing the color intensity change. Typically, under experimental conditions the residence time varied from 37 to 70 s (see Fig. 7).

3. Modeling

3.1. Kinetics and ideally mixed batch reactor and CSTR

The kinetic model we use has been described in our previous publications. The reaction mechanisms involved are listed in Table 1, the pre-exponential factors and activation energies, if available, are listed in Table 2. In the previous work we employed a deterministic population balance approach to compute the MWD. Here, however, we decided to utilize a Monte Carlo sampling method, for reasons of computational speed. The method has been introduced by Tobita (1996). The method requires knowledge of the scission probability of each monomer–monomer bonding (probably at the secondary radical sites, Camara et al., 2006), also called the scission density, denoted by, ρ_s. The Monte Carlo sampling procedure will be explained for both a batch reactor and a CSTR. The latter reactor type, as it has a much broader residence time distribution (RTD)

Fig. 1. Scission procedure. A linear chain is sampled from the weight distribution p_n^w; on this chain an arbitrary monomer unit is selected; lengths left and right are compared to sampled values from the scission probability function $p_n^s=exp(-\rho_s n)$. Shortest pair of lengths decide whether scission event(s) took place and are added to yield final length.

Table 1
Reaction mechanisms.

Reaction	Equation
Initiation	$I \xrightarrow{k_d} 2I^\bullet$
Recombination of initiator radicals	$I^\bullet + I^\bullet \xrightarrow{k_c} IH$
Hydrogen abstraction followed by scission	$P_n + I^\bullet \xrightarrow{k_{ht}n} P_m^\bullet + P_{n-m} + IH$
Transfer to polymer followed by scission	$P_n^\bullet + P_m \xrightarrow{k_{tr}\cdot m} P_n + P_{m-l}^\bullet + P_l$
Disproportionation termination	$P_n^\bullet + P_m^\bullet \xrightarrow{k_{td}} P_n + P_m$