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Short-chain branching distribution oriented model development for Borstar bimodal polyethylene process and its correlation with product performance of slow crack growth

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HIGHLIGHTS

- A process model coupled with an updated structure–performance model is developed.
- The predicted SCBD and MWD are in good agreement with the plant data.
- Consideration of SCBD is key to estimate slow crack growth (SCG) performance.
- The effects of operating conditions on the SCBD-MWD and the SCG of BPE are assessed.

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ABSTRACT

This work aims to develop a model that can predict the short-chain branching distribution (SCBD) of bimodal polyethylene (BPE) for an industrial Borstar process and correlate it with an updated structure–performance model (SPM) to estimate the slow crack growth (SCG) performance of the product. To calculate the SCBD and molecular weight distribution (MWD) simultaneously, a rigorous process model (i.e., kinetic model, thermodynamic model, reactor model) combined with a specific calculation method is established. The predicted SCBD and MWD of BPE are in good agreement with the plant data. An updated SPM that allows the estimation of the SCG resistance of BPE from its molecular architecture is developed, taking the effect of SCBD into account. The SPM reveals that the predicted SCG performance of BPE will be underestimated when only the average SCB content will be considered. The process model is coupled with the updated SPM, and it is capable of a full assessment on the effects of various operating conditions on the SCBD link with the MWD and, in turn, the SCG performance of BPE produced in the Borstar process. The underlying relationships are also discussed.

1. Introduction

The end-use properties of a polymer material are closely related to the polymer chain microstructure, including molecular weight distribution (MWD), copolymer composition distribution, short-chain branching distribution (SCBD), and long-chain branching distribution, etc. Understanding and controlling these molecular architectures are prerequisites for the successful development of polyolefins with desired application characteristics. Bimodal polyethylene (BPE), as an example, is widely used in many high performance applications, such as durable gas pipes and high-strength packaging film, because of its outstanding slow crack growth (SCG) resistance, stiffness, and processability (Bohm et al., 1992; Alt et al., 2001; Bohm, 2003). The excellent properties of BPE is believed to originate from the well-defined MWD and SCBD (Hubert et al., 2001, 2002; Shan et al., 2002, 2003). Considerable scientific and industrial interest in developing new catalysts (Jiang et al., 2013; Kurek et al., 2013; Liu et al., 2013; Li et al., 2014; Zhao et al., 2014) and new processes (Covezzi and Mei, 2001; Chadwick, 2009; Tian et al., 2013a, 2013b) exist with a view of tailoring the chain microstructures of BPE and expanding its applications.

In the polyolefin industry, the cascade of two reactors at extremely different conditions to produce BPE with a high-activity Ziegler–Natta catalyst is common. Generally, the first reactor in the presence of high hydrogen concentration forms a low molecular weight homopolymer, whereas the second reactor with a comonomer (1-butene, 1-hexene, or 1-octene) with a much

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less hydrogen concentration generates a high molecular weight copolymer. This cascade process allows the incorporation of a comonomer in the long polymer chains within the latter reactor. The final polymer blend products exhibit a remarkable combination of properties caused by the bimodal MWD and inverse comonomer distribution. On-line monitoring of chain microstructures is very difficult, if not impossible; thus, the control of polymer quality in industrial reactors is still a challenging work (Kiparissides, 2006; Mueller et al., 2011).

Modeling offers a powerful tool for process control and optimal operation of polymerization reactors. The prediction of the polymer chain microstructures has a key function in the development of the model. Considerable effort has been devoted to the development of models for catalytic olefin polymerization cascade processes. The reactor configurations include a series of stirred tank reactors (Khare et al., 2002; Luo et al., 2009; Meng et al., 2013), loop reactors (Reginato et al., 2003; Touloupides et al., 2010; Zheng et al., 2011), fluidized bed reactors (FBRs) (Zacca et al., 1997), and horizontal stirred bed reactors (Khare et al., 2004; Tian et al., 2012). In the case of ethylene polymerization, Khare et al. (2002) developed a general process simulator to describe the steady-state and dynamic operation of a slurry high-density polyethylene (HDPE) process. The effect of the operating conditions on the production rate and the average molecular properties (i.e., M_n, PDI) were analyzed. Meng et al. (2013) also built up a steady-state model for that same process and studied the influence of the various feed rates (i.e., catalyst, comonmor, etc.) on the average molar mass and MWD. Touloupides et al. (2010) established a comprehensive model to simulate the dynamic behavior of an industrial ethylene polymerization loop reactor series at different operation conditions (i.e., start-up, grade transition). The model studied the effects of the operating conditions on the dynamic evolution of average molecular properties and MWD of polyethylene (PE). In a previous work (Chen et al., 2014b), a model was developed to simulate the MWD of BPE produced in the Borstar process based on a modified thermodynamic model. In addition to the mentioned modeling works, researchers have attempted to determine the optimal operating conditions to produce polymers with a target average molar mass or MWD. Pontes et al. (2008, 2011) formulated and solved an optimization problem to find the optimal operating policies to produce PE resins with pre-specified melt index and MWD for an ethylene solution polymerization process. More recently, different optimization approaches for an industrial slurry HDPE process at steady (Gu et al., 2013; Zhang et al., 2013) and dynamic state (Weng et al., 2014) with target MWD were developed.

Most of the models were observed to focus on the prediction of the average polymer properties or MWD. However, the SCG resistance, a crucial long-term property for high performance pipe applications, is strongly affected by the placement of SCB on the polymer chains (DesLauriers et al., 2005; Deslauriers and McDaniel, 2007; Krishnaswamy et al., 2008). To the best of the authors' knowledge, there are no reports to date on the modeling of PE processes in predicting SCBD. Furthermore, although many accelerated tests have been developed to evaluate the SCG performance, several tests are still time consuming, specifically for high-performing pipe materials. As an example, the SCG failure time of PE100+ or PE100RC pipe resins exceeds 10,000 h (> 1 year). Note that the SCG performance of BPE is directly related to its MWD and SCBD and, in turn, is determined by the operating conditions of the original polymerization process for a given catalyst. The cycle time for the development of new materials can be remarkably reduced with the knowledge on how process operating conditions affect the MWD, SCBD, and the resulting SCG performance of BPE. A process model coupling with a structure–performance model (SPM) can satisfy this requirement. However, developing a quantitative SPM is difficult because of the complex SCG failure mechanism at the molecular level (Krishnaswamy et al., 2008; Cazenave et al., 2006; Deblieck et al., 2011). Recently, DesLauriers and Rohlfing (2009, 2010, 2011) proposed a method to estimate the SCG performance of PE resins rapidly by formulating a single parameter-Primary Structural Parameter (PSP2) from polymer chain structures. The PSP2 correlated well with the SCG resistance (e.g., Pennsylvania Notch Test (PENT), Single Point Notched Constant Tensile Load) in all types of PE resins that they studied. This method was also employed to relate PSP2 to the PENT failure time of the other PE pipe resins (Garcia et al., 2011; Adib et al., 2014). However, in the calculation of density reduction by the presence of SCB, DesLauriers and Rohlfing (2009) assumed that all SCB contents have the same effect (i.e., average SCB content). Despite this assumption, the PSP2 method allows a better understanding of the SCG failure mechanism and the improvement of the effectiveness of the product design.

This work aims to develop a comprehensive model to predict the SCBD, as well as the SCG performance of BPE, for an industrial Borstar process. A process model comprising different sub-models (i.e., kinetic model, thermodynamic model, reactor model) was combined with an updated SPM. A four-site kinetic model was used to describe the homopolymerization of ethylene in the first reactor and the copolymerization of ethylene with 1-butene in the second reactor over a same Ziegler–Natta catalyst. To calculate SCBD, a specific method was presented. The predicted SCBD and MWD of the different polymer grades were validated by experimental data. In the development of the updated SPM, a method accounting for the distribution of SCB across the whole MWD was proposed to estimate PSP2. Consequently, the effect of SCBD on SCG performance was investigated. The effects of operating conditions on the SCBD linking with the MWD and the SCG resistance of BPE produced in the Borstar process were also assessed using the integrated model. The underlying relations were discussed.

2. Model development

Fig. 1 shows the framework in developing a process model coupled with an updated SPM for the Borstar bimodal polyethylene process. The process model consists of three basic modules, namely, kinetic model, thermodynamic model, and reactor model.

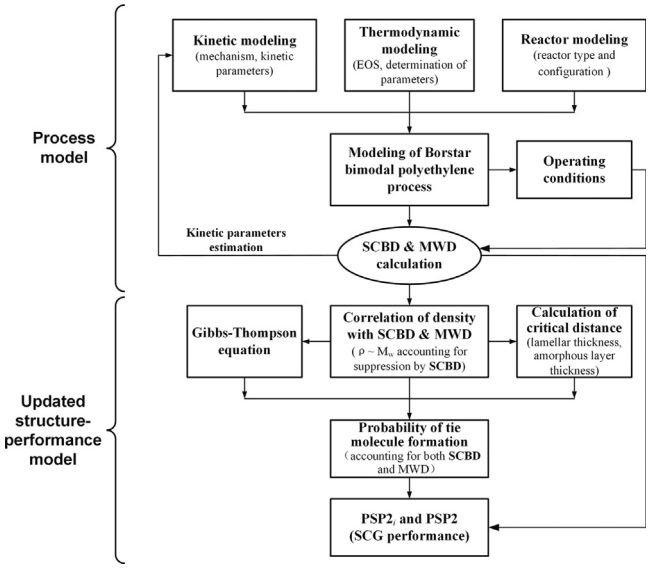

Fig. 1. Framework for the model development of a process model coupled with an updated SPM for the Borstar bimodal polyethylene process.