

# Mathematical Modelling of Rheological Properties of Low-density Polyethylene Produced in High-Pressure Tubular Reactors

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Abstract: Low-density polyethylene (LDPE) is a commodity polymer widely used in a variety of applications. Due to the complexity of its molecular structure, which includes molecular weight distribution and randomly distributed long-chain branching, its rheological behavior is varied. In the present work, a mathematical model is used to predict molecular and rheological properties of LDPE produced in a high-pressure tubular reactor under different operating conditions. The agreement between flow curve predictions and experimental data is very good, demonstrating the potential of this model as a predictive tool for industrial producers.

*Keywords:* Low-density Polyethylene, Tubular Reactor, Rheology, Mathematical Model.

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## 1. INTRODUCTION

Low-density polyethylene (LDPE) produced by radical polymerization in high-pressure tubular reactors usually has a broad molecular weight distribution (MWD) and contains a considerable number of long-chain branches (LCB). Characterizing and controlling properties such as the MWD and the long-chain branching distribution (LCBD) is crucial for the industrial processing of the material because both of them affect the rheological behavior and the end-use properties of the polymer (Gabriel and Münstedt 1999). Numerous investigations have been carried out to understand the effects of the MWD and the LCBD on rheological properties. In general, long-chain branched polyethylenes present increased melt strength and shear-thinning behavior under shear-flow compared to linear ones (Vega, Santamaria et al. 1998, Lohse, Milner et al. 2002, Malmberg, Gabriel et al. 2002). Usually, branching in polyethylene is associated with broadening in the MWD. However, it is sometimes complex to separate the effects of the MWD from those of the LCBD.

Additionally, the effect of LCB content may vary at low or high shear-rate conditions. For example, Yan, Wang et al. (1999) measured rheological properties of polyethylene with low LCB content and concluded that sparsely branched

structures resulted in higher viscosities at low shear rates and lower viscosities at high shear rates. Mendelson, Bowles et al. (1970) reported that increasing LCB in LDPE at constant weight-average molecular weight  $\overline{M}_w$  and MWD yielded a reduction in zero shear viscosity and elasticity. Bersted (1985) studied the effect of very low LCB levels on the rheological behavior of high-density polyethylene (HDPE) and LDPE. This author observed large variations of the zero-shear viscosity with the degree of branching and found a correlation between the shear viscosity and the relative amount of linear and branched species. A maximum value of zero-shear viscosity was observed as a result of two competing effects: on the one hand, at low LCB content, the increase of the amount of the highly viscous branched species produces an increase of zero-shear viscosity up to a maximum; on the other hand, at high LCB content, the reduction of the radius of gyration produces a reduction of zero-shear viscosity.

Due to the complex relationship between molecular characteristics such as the MWD and the LCBD with rheological properties like the shear viscosity ( $\eta(\dot{\gamma})$ ), processing behavior is deeply affected. Computational techniques able to connect polymerization conditions with the molecular structure, and this with rheological parameters, may be very useful for industrial polymer producers. In the literature, there are few comprehensive models able to provide

detailed information on the distributed molecular properties of LDPE produced in high-pressure tubular reactors, and even fewer that use this information to predict the rheological behavior of the LDPE melt. Pladis, Meimaroglou et al. (2015), for example, developed a kinetic-molecular Monte Carlo algorithm to predict the exact molecular architecture of nonlinear LDPE produced in a high-pressure tubular reactor. Subsequently, they applied a molecular approach, developed for highly branched molecules, to predict the viscoelastic behavior of LDPE expressed as  $\eta(\dot{\gamma})$ , storage and loss moduli and relaxation modulus. Read, Auhl et al. (2011) modeled the LDPE polymerization process with a Monte Carlo model coupled with another algorithm that applies a rheological approach based on several relaxation processes.

Polymer rheology information is useful during both polymer production and for designing end-use properties. Nowadays, polymer industry employs sophisticated methods for product characterization and quality control. Nevertheless, the well-known melt flow index (MI) is one of the most commonly used rheological parameters due to its fast, easy, and low-cost measurement. This parameter can also be estimated through mathematical models using  $\eta(\dot{\gamma})$  as input. From the above discussion, it becomes clear how important it is to have a comprehensive modeling approach detailing the effects of reactor operating conditions on the molecular and branching properties and their connection with the polymer rheology, as well as with industrial control parameters such as the MI.

In the present work, we applied a rheological model developed by Bersted (1975) and subsequently adapted by Pedersen and Ram (1978) to branched LDPE, to predict the shear viscosity flow curve ( $\eta(\dot{\gamma})$ ) of several samples of LDPE. This model uses as input the MWD as well as LCB information expressed as the branching index ( $g$ ). This rheological model was added to a deterministic model of the high-pressure ethylene polymerization process in tubular reactors previously developed by the authors (Dietrich, Sarmoria et al. 2019). This new comprehensive model is capable of predicting not only the MWD, the bivariate molecular weight-long chain branching distribution (MWD-LCBD), the bivariate molecular weight-short chain branching distribution (MWD-SCBD), and average molecular properties such as the weight-average molecular weight ( $\overline{M}_w$ ), number-average molecular weight ( $\overline{M}_n$ ), number of long-chain branches every 1000 carbon atoms (LCB/1000C) and branching index ( $g$ ), but also the shear viscosity curve ( $\eta(\dot{\gamma})$ ).

## 2. MODEL DESCRIPTION

Bersted (1975) developed an empirical model relating the shear dependence of the steady shear melt viscosity  $\eta(\dot{\gamma})$  of linear HDPE melts to the MWD. Pedersen and Ram (1978) extended this model to branched LDPE melts using the mean-square radius of gyration  $\overline{S}_{0,branch}^2|_M$  instead of  $\overline{M}_w$  to describe the melt viscosity behavior. For linear polymers, the mean-square radius of gyration  $\overline{S}_{0,linear}^2|_M$  is proportional to the molecular weight  $M$  of a given molecule; for branched polymers, a relationship for  $\overline{S}_{0,branch}^2|_M$  may be established from the definition of  $g$ :

$$g = \frac{\overline{S}_{0,branch}^2|_M}{\overline{S}_{0,linear}^2|_M} \quad (1)$$

Then, considering the proportionality of  $\overline{S}_{0,linear}^2|_M$  with  $M$ :

$$\overline{S}_{0,branch}^2|_M \propto gM \quad (2)$$

the authors proposed that the relationship between  $\eta(\dot{\gamma})$ ,  $M$  and  $g$  could be:

$$\log \eta(\dot{\gamma}) = A + B \log \left( \overline{gM} \right)_w^* (\dot{\gamma}) \quad (3)$$

where  $\left( \overline{gM} \right)_w^* (\dot{\gamma})$ , the weight average of  $gM$ , is defined as:

$$\left( \overline{gM} \right)_w^* (\dot{\gamma}) = \sum_1^{c-1} w_i g_i M_i + (gM)_c (\dot{\gamma}) \sum_c^\infty w_i \quad (4)$$

Here  $w$  is the molecular weight distribution (MWD) expressed in weight fraction, and  $w_i$ ,  $g_i$  and  $M_i$  are the particular values of weight fraction, branching index and molecular weight of the polymer molecule  $i$ , respectively. The model has three fitting parameters:  $A$ ,  $B$  and  $(gM)_c(\dot{\gamma})$ ; the latter is a shear rate dependent parameter.

The model by Bersted (1975), developed for linear HDPE, requires a shear-rate dependent parameter  $M_c(\dot{\gamma})$ , which separates molecular weights into two classes: molecules with molecular weight below  $M_c$  contribute to the viscosity as they do at zero shear rate, and molecules with molecular weight above  $M_c$  contribute to the viscosity as if they had the same relaxation times as molecules of molecular weight  $M_c$ . Each molecular weight species contributes according to its weight fraction. In the extended model by Pedersen and Ram (1978),  $M_c$  is replaced by  $(gM)_c$ , which is also a function of the shear rate.

The rheological model was added to a high-fidelity reactor model developed by the authors (Dietrich, Sarmoria et al. 2019), which uses the deterministic probability-generating function (pgf) technique to obtain uni- and bivariate distributions of molecular properties and average molecular properties. Besides, it calculates the branching index  $g$  using the correlation developed by Zimm and Stockmayer (1949) in terms of the weight-average number of long-chain branches per molecule, as explained in the previous work by the authors (Dietrich, Sarmoria et al. 2019). The model was implemented in gPROMS ModelBuilder software. It calculates the values of the molecular weight distribution  $w_i$  and the branching index  $g_i$  and uses equations (3) and (4) to compute  $\eta(\dot{\gamma})$ . Model parameters  $A$ ,  $B$  and  $(gM)_c(\dot{\gamma})$  were fitted against experimental data of  $\eta(\dot{\gamma})$ , as described in the following section. Summarizing, the full reactor model uses operating conditions and design reactor features as input to predict the molecular properties described in the previous section as well as the flow curve  $\eta(\dot{\gamma})$  of the LDPE.

## 3. RESULTS AND DISCUSSION

The predictive ability of the proposed integrated model was tested against experimental data of LDPE produced in a high-pressure tubular reactor. Ten different sets of reactor operating

conditions were analyzed, named M01, M02, M05, M06, M07, M08, M09, M10, M11, M18, for which experimental data on rheological properties of the produced LDPE was available.

Figure 1 shows the MWD prediction for each of them. Additionally, Figure 2 depicts the corresponding  $g$  curves. The branching index is commonly used to reflect the degree of LCB in highly branched polymers: the lower the value of  $g$  at a given molecular weight, the greater the presence of branches is in those molecules. Figure 2 shows that all the curves are similar at low molecular weights, but they vary significantly at high molecular weights. This may indicate that the longer molecules are responsible for changes in the LCB content between samples. The LDPE produced under M11 operating conditions exhibits the highest values of  $g$  at high molecular weights, suggesting that longer molecules are less branched in this sample. On the contrary, for operating condition M07, the polymer exhibits the lowest values of  $g$  at high molecular weights, which indicates that this LDPE contains highly branched long molecules. It has been well studied that even small amounts of long highly-branched molecules in a polymer affect the rheological behavior of polymer melts, so it is important to quantify them.

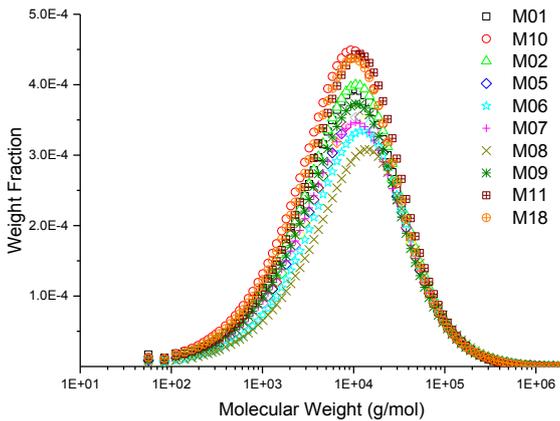


Fig. 1. Molecular weight distribution of LDPE samples.

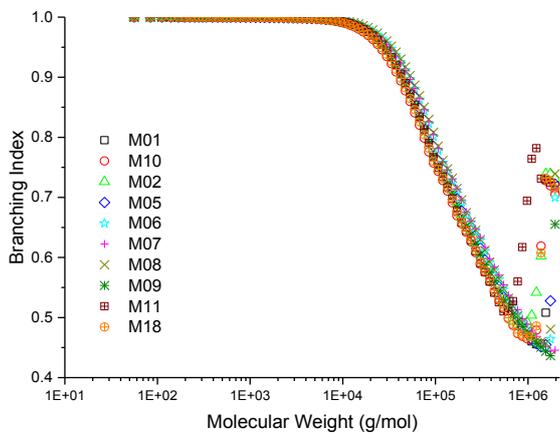


Fig. 2. Branching index of LDPE samples.

For the estimation of the model parameters of equations (3) and (4), in a first step  $w_i$  and  $g_i$  were calculated for each set of

operating conditions. Then, these data were used together with the experimental information of  $\eta(\dot{\gamma})$  at 190°C to perform a parameter estimation of  $A$ ,  $B$ , and  $(gM)_c(\dot{\gamma})$ . Figure 3 plots the  $(gM)_c$  vs.  $\dot{\gamma}$  curves estimated for each sample. It may be seen that these curves share approximately the same tendency. The linear fit that best represents all the samples is:

$$\log(gM_c) = 16594 - 0.101 \log(\dot{\gamma}) \quad (5)$$

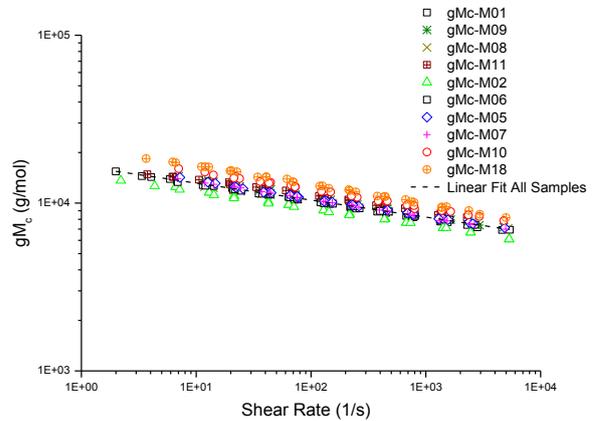


Fig. 3. Estimated values of  $(gM)_c(\dot{\gamma})$  for the different LDPE samples and a linear fit to represent them.

Parameters  $A$  and  $B$  were also fitted for each sample, and an average value of them was then calculated. Average values of  $A$  and  $B$  were used together with equation (5) to calculate  $\eta(\dot{\gamma})$  for the different samples. However, the agreement with experimental data was poor. After analyzing different fitting alternatives, the best results were found using the average value of  $B$  and a linear fit of  $A$  as a function of  $\overline{M}_w$  of the samples. This linear fitting function is shown in equation (6) while Figure 4 shows the fitted data. Besides, the average value of  $B$  was 7.944.

$$A = 5 \times 10^{-5} \overline{M}_w - 36.944 \quad (6)$$

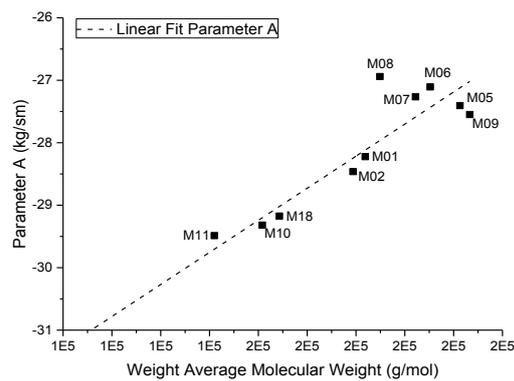


Fig. 4. Values of model parameter  $A$  for the different LDPE samples of LDPE as a function of the corresponding weight average molecular weight  $\overline{M}_w$ .

Figures (5)-(12) show the viscosity curves of some of the samples calculated with equations (3) to (6) compared to the corresponding experimental data. A capillary rheometer was used to obtain the high shear rate portions of the experimental curves at 180, 200, and 220 °C, which were subsequently

unified at 190°C using the time-temperature superposition principle (Ferry 1980). This is the temperature specified by standard test method ASTM D-1238 to measure MI.

In most cases, the predicted curve is in good agreement with the experimental data. The worst results were obtained for samples M06, M07, and M08. Indeed, Figure 4 shows that these samples deviate significantly from the linear tendency proposed for model parameter A, especially M08 which presents the worst viscosity fit. Although experimental data are available for shear rates greater than 1.0 s<sup>-1</sup>, model results are extended to lower shear rates to show that the model predictions follow the expected tendency for LDPE.

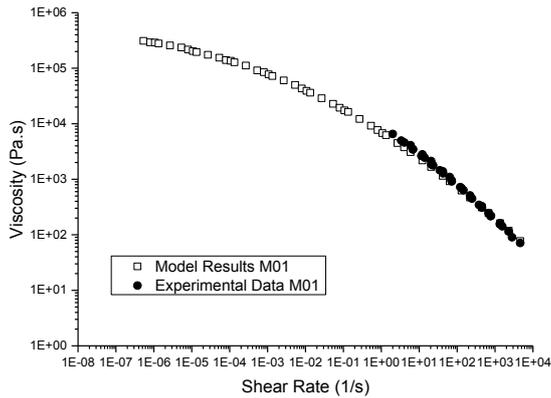


Fig. 5. Comparison between model results and experimental data of shear viscosity of LDPE sample M01 at 190°C.

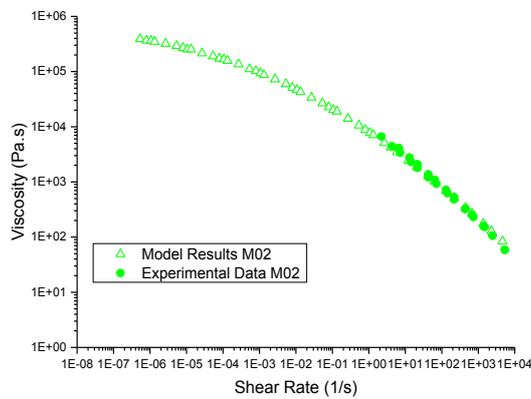


Fig. 6. Comparison between model results and experimental data of shear viscosity of LDPE sample M02 at 190°C.

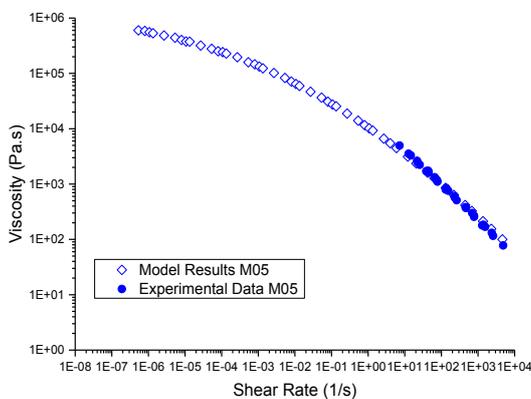


Fig. 7. Comparison between model results and experimental data of shear viscosity of LDPE sample M05 at 190°C.

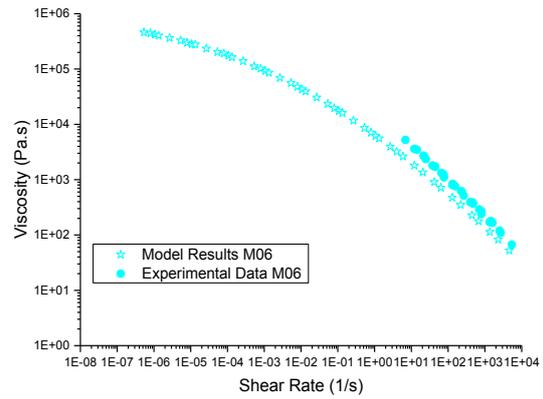


Fig. 8. Comparison between model results and experimental data of shear viscosity of LDPE sample M06 at 190°C.

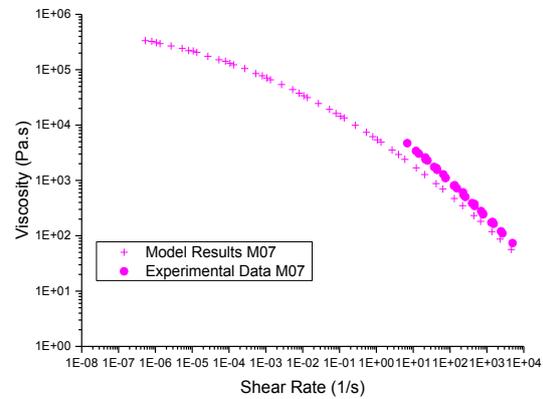


Fig. 9. Comparison between model results and experimental data of shear viscosity of LDPE sample M07 at 190°C.

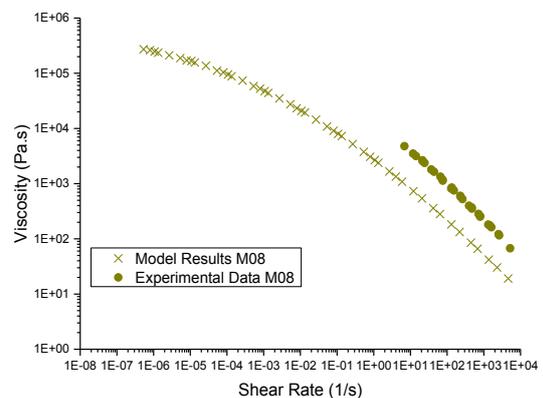


Fig. 10. Comparison between model results and experimental data of shear viscosity of LDPE sample M08 at 190°C.

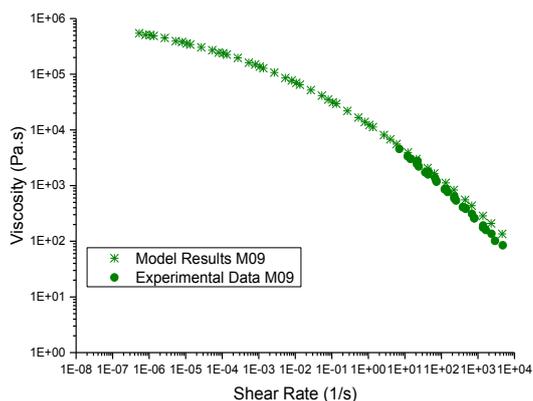


Fig. 11. Comparison between model results and experimental data of shear viscosity of LDPE sample M09 at 190°C.

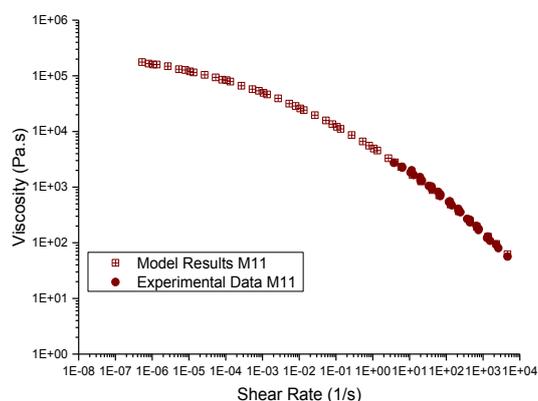


Fig. 12. Comparison between model results and experimental data of shear viscosity of LDPE sample M11 at 190°C.

#### 4. CONCLUSIONS

A mathematical model of a high-pressure tubular reactor for LDPE production was extended to be able predict the flow curve  $\eta(\dot{\gamma})$ . Model predictions were compared against experimental data showing a good agreement. This model represents a very attractive tool to connect reactor operating polymerization conditions to the polymer flow curve, which is usually used as input for the prediction of some important end-use properties, such as the melt index.

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