

# The application of the multipass rheometer to time-dependent capillary flow measurements of a polyethylene melt

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## Synopsis

This communication presents experimental data on the time-dependent capillary flow measurements for a high-density polyethylene using a newly developed multipass rheometer (MPR). The experimental data consist of precision pressure measurements on the MPR, which has well-defined fully constrained boundary conditions. A model developed previously by Molenaar and Koopmans [Molenaar, J. and R. J. Koopmans, *J. Rheol.* **38**, 99–109 (1994)] and incorporating melt compressibility has been adapted to suit the MPR boundary conditions and is shown to give good agreement with the experimental data without necessitating the use of any arbitrary adjustable parameters. The results, in particular, show that the experimentally observed pressure relaxation on cessation of the piston movement can be almost entirely attributed to the compressibility of the melt alone and this conclusion is consistent with the findings reported by Hatzikiriakos and Dealy [Hatzikiriakos, S. G. and J. M. Dealy, *Polym. Eng. Sci.* **34**, 493–499 (1994)] for related time-dependent extrusion experimental observations using a conventional capillary rheometer. © 1999 *The Society of Rheology*. [S0148-6055(99)00802-0]

## I. INTRODUCTION

Capillary rheometry techniques are being increasingly used to perform time-dependent rheological measurements on a variety of materials including polymer melts. In capillary flows involving polymer melts, compressibility effects are significant and can have a major influence on the time-dependent pressure changes in the system as described recently by Dealy (1995) and also earlier by Pearson (1969) in a review about melt flow instabilities. Molenaar and Koopmans (1994) and Hatzikiriakos and Dealy (1994) have developed models to quantitatively predict the pressure changes during the capillary flow of a polymer melt using the principles of mass conservation and compressibility effects. The model presented by Molenaar and Koopmans (1994) was initially formulated by Weill (1980) and describes the flow of a polyethylene melt through a simple capillary rheometer assembly using two coupled differential equations. Durand *et al.* (1996) have subsequently solved this model and compared the solution with experimental results for high density polyethylene (HDPE) in a capillary rheometer. Hatzikiriakos and Dealy (1994) have also developed a model along similar principles to estimate the power-law parameters of a linear low-density polyethylene melt using the pressure buildup data obtained from capillary flow experiments. Both Hatzikiriakos and Dealy (1994) and

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Durand *et al.* (1996) have highlighted the importance of melt compressibility in describing the time-dependent pressure changes encountered in the capillary flow of polymer melts and acknowledge that very small changes in the compressibility of the melt can be translated into significant differences in their time-dependent behavior.

This paper presents the time-dependent experimental data of a high-density polyethylene melt measured using a recently developed multipass rheometer (MPR) and the data are compared with a model of the kind described above that includes the melt compressibility. A limitation of the model as presented by Molenaar and Koopmans (1994) is its reliance on arbitrary undefined variables in order to obtain a quantitative prediction of the flow. In this paper, the multipass rheometer for which the boundary conditions of flow are fully defined is used for experimentation. The MPR is a double-piston capillary rheometer developed at the University of Cambridge by Mackley *et al.* (1995). In the context of this paper, the fully defined upstream and downstream boundary conditions coupled with a reformulation of the problem, enables modeling the flow of HDPE without having to resort to the use of any semiarbitrary adjustable parameters.

## II. EXPERIMENT

The polyethylene used for experimental purposes is a high-density polyethylene (HDPE 1003 is manufactured by The Dow Chemical Company Ltd.) and was studied using the multipass rheometer. The MPR configuration of two pistons with a fully contained sample was initially used by Westover (1961) to measure the pressure dependence of the viscosity of polyethylene melts. The MPR is made of stainless steel and consists of a top and a bottom barrel through which two servohydraulically driven pistons enter the rheometer assembly with a capillary test section positioned between the barrels. Pressure transducers and temperature thermocouples located in the top and bottom barrel sections are used to monitor the system temperature and pressure. The experiments were carried out using a capillary of 10 mm length and 1 mm diam with a 45° entry angle. All the experiments were performed at 180 °C.

After the MPR was loaded with HDPE at 180 °C, experiments were carried out by moving both the pistons together at a certain velocity (corresponding to a certain wall shear rate) and amplitude (corresponding to a certain shear strain). The resulting pressure difference across the capillary was followed as a function of time. In general, the pressure difference builds up to reach a steady state. When the pistons stop moving, this pressure difference across the capillary undergoes relaxation. Experiments were repeated for a range of piston velocities in order to obtain an experimental flow curve of HDPE (mean steady pressure difference across the capillary versus piston velocity), which is shown in Fig. 1. The flow curve is discontinuous and consists of two branches with a section in between where the HDPE is unstable and the data reported here are consistent with the previously reported data by Durand *et al.* (1996). The instability manifests itself in terms of periodic pressure oscillations and, hence, the regime of this form of instabilities is referred to as the “*periodic oscillations*” regime. The two monotonically increasing branches of the flow curve can be fitted as power-law fluids. The flow curve is divided into four different flow regimes which have been identified from the time-dependent pressure data obtained for a certain shear rate over a range of shear rates (Figs. 3–6). These are (1) the stable flow regime, (2) the periodic oscillations regime, (3) the overshoot regime, and (4) the high-velocity regime.

In order to model these time-dependent pressure difference traces, it is necessary to determine the compressibility of HDPE. The compressibility  $\chi$  of the melt under isothermal conditions can be defined as

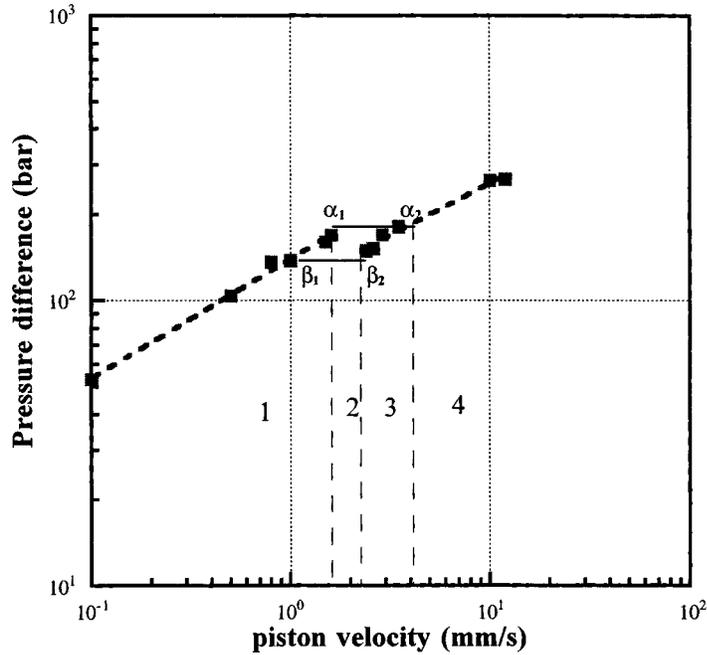


FIG. 1. Steady state flow curve of HDPE.

$$\chi = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T, \quad (1)$$

where  $V$  is the volume occupied by the melt and  $P$  is the pressure in the system. Using a capillary of the same radius as that of the barrel in the test section, the compressibility of the HDPE melt was determined using the MPR by measuring the pressure and volume changes in the system caused by moving one of the pistons inwards while keeping the other stationary. The compressibility of HDPE over a pressure range of 1–25 MPa was measured to be  $1.38 \cdot 10^{-9} \text{ (Pa)}^{-1}$  at  $180^\circ\text{C}$ .

### III. MODELING THE FLOW OF THE HDPE IN THE MULTIPASS RHEOMETER

The model proposed by Molenaar and Koopmans (1994), incorporates a mass balance across the system, the material compressibility, and a function for the flow curve of the melt. For solving the equations, it was necessary to assume some form of function for the flow curve and an arbitrary adjustable parameter was introduced in an equation of motion for the material in the system.

A schematic diagram of the MPR flow configuration is given in Fig. 2. The geometry is fully constrained with the top and bottom pistons moving at the same velocity  $v_p$  imposing a flow rate of  $Q_{in}$  on the melt.  $P$  and  $V$  represent the pressure and volume of the barrels and subscripts  $t$  and  $b$  refer to the top and the bottom barrels, respectively, which are connected by a capillary of radius  $r$  and length  $L$ ; the internal radius of both the barrels is  $R$ .  $Q_c$  is the flow rate of the polymer melt through the capillary. The fully constrained geometry enables the extension of the modeling approach of Molenaar and Koopmans (1994).

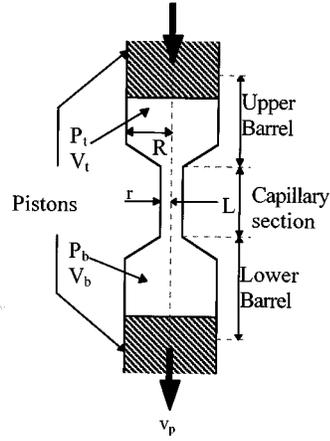


FIG. 2. Diagrammatic representation of the MPR flow geometry.

A mass balance across the top barrel and the capillary (where the volume of the capillary is negligible as compared to that of the barrel) yields

$$\rho \frac{dV_t}{dt} + V_t \frac{d\rho}{dt} + Q_c \rho = 0. \quad (2)$$

The density  $\rho$  of the polymer melt is related to the pressure  $P_t$  in the barrel by the compressibility  $\chi$  of the polymer melt given by

$$\frac{1}{\rho} \frac{d\rho}{dt} = \chi \frac{dP_t}{dt}. \quad (3)$$

Substituting Eq. (3) in Eq. (2) yields

$$\rho \frac{dV_t}{dt} + V_t \rho \chi \frac{dP_t}{dt} + Q_c \rho = 0. \quad (4)$$

In addition,

$$\frac{dV_t}{dt} = -\pi R^2 v_p = -Q_{in}. \quad (5)$$

Substituting Eq. (5) into Eq. (4) gives

$$\frac{dP_t}{dt} = \frac{1}{\chi V_t} \{ \pi R^2 v_p - Q_c \}. \quad (6)$$

Equation (6) gives the relationship between the pressure  $P_t$  and the volume  $V_t$  of the top barrel. A similar relationship can be derived for the pressure  $P_b$  and the volume  $V_b$  of the bottom barrel:

$$\frac{dP_b}{dt} = \frac{1}{\chi V_b} \{ Q_c - \pi R^2 v_p \}. \quad (7)$$

Subtracting Eq. (7) from Eq. (6) gives

$$\frac{dP_t}{dt} - \frac{dP_b}{dt} = \frac{d\Delta P}{dt} = \frac{1}{\chi} \left\{ \frac{1}{V_t} + \frac{1}{V_b} \right\} \{ \pi R^2 v_p - Q_c \}, \quad (8)$$

where  $\Delta P$  is the pressure difference across the capillary. During the course of the experiment, the melt tries to reach and maintain a capillary flow rate equal to the rate of volume displacement in the barrel because of the piston movement. The flow in the capillary takes a finite amount of time to become fully developed and this is reflected in the pressure difference buildup across the capillary. When there is a steady pressure difference across the capillary

$$\frac{d\Delta P}{dt} = 0. \quad (9)$$

Therefore, for a system at steady state, Eq. (8) can be written as

$$\pi R^2 v_p = Q_c \text{ or } Q_{in} = Q_c. \quad (10)$$

However Eq. (10) is not strictly true for the capillary flow of a compressible fluid as the density of the material in the barrels and in the capillary is not the same.

If the pressure difference across the capillary is not constant, then

$$\frac{d\Delta P}{dt} \neq 0, \quad (11)$$

which also indicates that  $Q_{in} \neq Q_c$ , and the line dependent solutions exist. The complete time-dependent behavior can be obtained by solving Eq. (8) by expressing  $Q_c$  in terms of  $\Delta P$ . To obtain a relation between  $Q_c$  and  $\Delta P$ ,  $Q_c$  is approximated to a steady-state value of  $\Delta P$  given by the flow curve shown in Fig. 1 combined with the simple coupling equation  $Q_{in} = Q_c$ . The two branches of the flow curve can be empirically expressed in terms of power-law equations of the form  $Q_c = a_i(\Delta P)^{b_i}$ , where  $a_i$  and  $b_i$  are constants which can be derived from the experimental flow curve. Hence, using the power-law relationship between  $\Delta P$  and  $Q_c$ , Eq. (8) can be written as

$$\frac{d\Delta P}{dt} = \frac{1}{\chi} \left\{ \frac{1}{V_t} + \frac{1}{V_b} \right\} \{ \pi R^2 v_p - a_i(\Delta P)^{b_i} \}. \quad (12)$$

Equation (12) is a differential equation in which  $a_i$  and  $b_i$  are determined from the experimental flow curve,  $v_p$  is the piston velocity imposed on the system and  $V_t$  and  $V_b$  are the barrel volumes which change in time depending on the value of  $v_p$  and the melt compressibility  $\chi$  has been experimentally determined. Equation (12) has been numerically solved with a numerical solver package MATLAB, using a second-order Runge Kutta method and has been used to predict the time-dependent profiles for the flow of the HDPE melt in the MPR in all four regimes (Figs. 3–6). Details of the boundary conditions for each flow regime are described in Table I, where the shear rates defined by  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_1$ , and  $\beta_2$  are all shown on the flow curve (Fig. 1).

#### IV. RESULTS

The experimental data have been compared with the time-dependent pressure traces predicted by the model for all four regimes identified on the flow curve given in Fig. 1.

In regime (1), i.e., a “stable flow” regime, the time-dependent pressure difference buildup and steady pressure value has been modeled with reasonable accuracy as shown in Fig. 3. Also, the model is capable of predicting the relaxation of the pressure difference

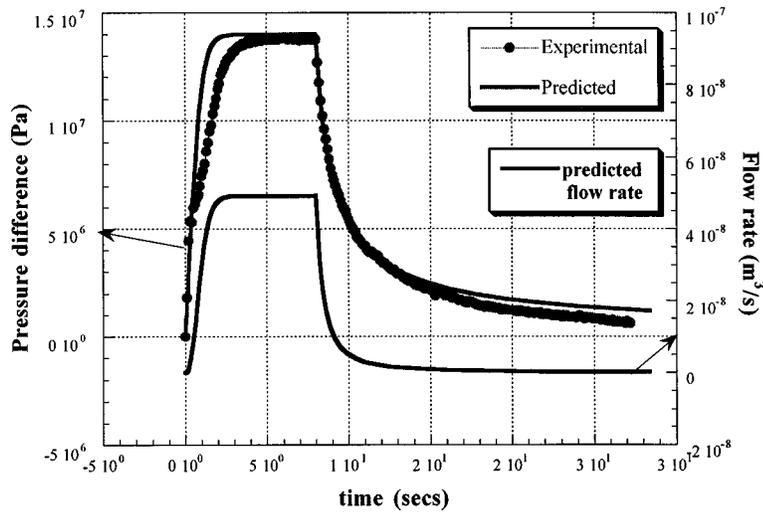


FIG. 3. Comparison of the predictions of the model with experimental data for HDPE in the stable flow regime.

across the capillary on cessation of the piston movement, where the time scale for the relaxation of pressure is of the order of 20 s.

In regime (2), a “periodic oscillations” regime, the model is able to predict with some accuracy the frequency of pressure oscillations observed as shown in Fig. 4. In this region, the discontinuity of the flow curve controls the periodic pressure oscillation and mechanisms of this phenomenon have been discussed by Pearson (1969) and Molenaar and Koopmans (1994). The model also predicts the pressure relaxation which is essentially similar to the relaxation process in Regime (1).

For regimes (3) and (4), Figs. 5 and 6 show good agreement with the experimental data and, in particular, the pressure overshoot in regime (3) is successfully predicted (Fig. 5).

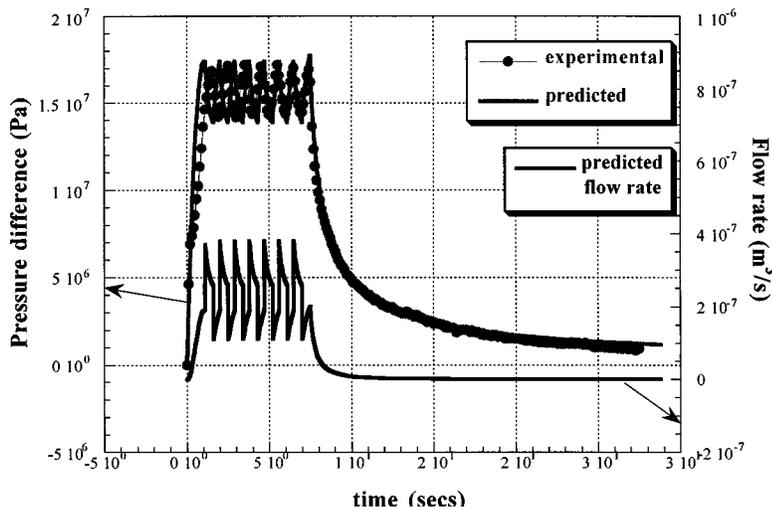


FIG. 4. Comparison of the predictions of the model with experimental data for HDPE in the periodic oscillations regime.

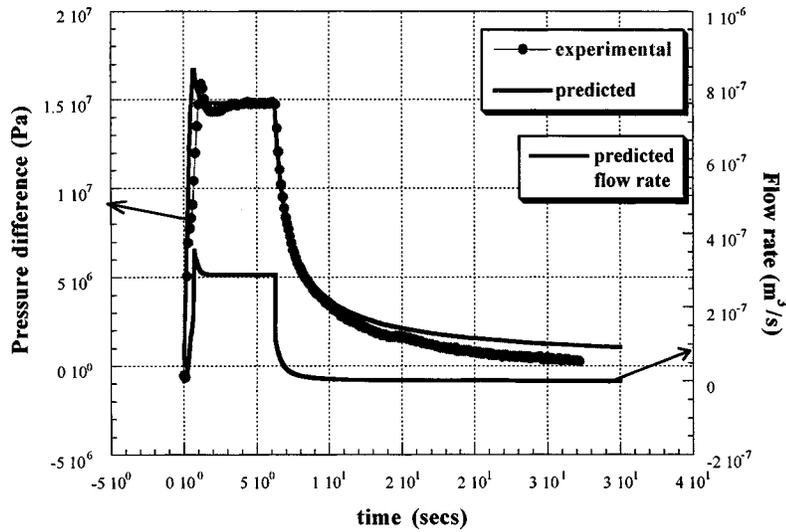


FIG. 5. Comparison of the predictions of the model with experimental data for HDPE in the overshoot regime.

Figures 3–6 also show the predicted velocity of the melt through the capillary and it can be seen that on the cessation of piston movement, it takes a finite time for the velocity in the capillary and the corresponding pressure difference across the capillary to return to zero. The fact that flow continues to occur within the capillary after cessation of the piston movement was also confirmed by direct visual observations using a slit geometry on the MPR complete with optical windows. Using similar boundary conditions to the ones described for capillary flow, it was observed that there is a steady reduction in the velocity within the slit with a time scale similar to that predicted in Figs. 3–6, thereby

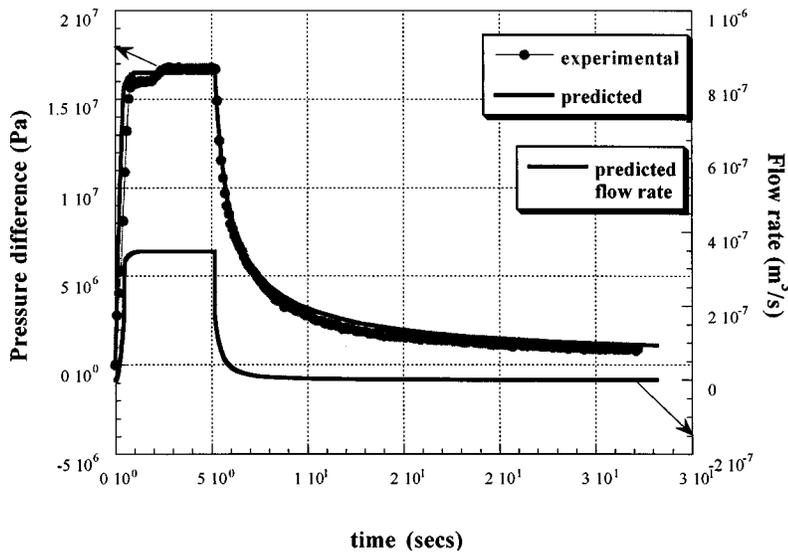


FIG. 6. Comparison of the predictions of the model with experimental data for HDPE in the high velocity regime.

TABLE I. Initial and boundary conditions used in modeling the four flow regimes.

Flow regime	During piston movement	After cessation of piston movement
1 For flow rates $0 - \alpha_1$	$t = 0, \Delta P = 0, v_p = v_p$ $Q_c = a_1^*(\Delta P)^{b_1}$	$t = t, \Delta P = \Delta P, v_p = 0$ $Q_c = a_1^*(\Delta P)^{b_1}$
2 For flow rates $\alpha_1 - \beta_2$	$t = 0, \Delta P = 0, v_p = v_p$ for $Q_c < \alpha_1, Q_c = a_1^*(\Delta P)^{b_1}$ for $Q_c < \alpha_2$ and $Q_c > \beta_2$ $Q_c = a_2^*(\Delta P)^{b_2}$ for $Q_c > \beta_1$ and $Q_c < \alpha_1$ $Q_c = a_1^*(\Delta P)^{b_1}$	$t = t, \Delta P = \Delta P, v_p = 0$ for $Q_c < \alpha_2$ and $Q_c > \beta_2$ $Q_c = a_2^*(\Delta P)^{b_2}$ for $Q_c > \beta_1$ and $Q_c < \alpha_1$ $Q_c = a_1^*(\Delta P)^{b_1}$
3 For flow rates $\beta_2 - \alpha_2$	$t = 0, \Delta P = 0, v_p = v_p$ for $Q_c < \alpha_1, Q_c = a_1^*(\Delta P)^{b_1}$ for $Q_c < \alpha_2$ and $Q_c > \beta_2$ $Q_c = a_2^*(\Delta P)^{b_2}$	$t = t, \Delta P = \Delta P, v_p = 0$ for $Q_c < \alpha_2$ and $Q_c > \beta_2$ $Q_c = a_2^*(\Delta P)^{b_2}$ for $Q_c > \beta_1$ and $Q_c < \alpha_1$ $Q_c = a_1^*(\Delta P)^{b_1}$
4 For flow rates $\alpha_2$ and onwards	$t = 0, \Delta P = 0, v_p = v_p$ for $Q_c < \alpha_1, Q_c = a_1^*(\Delta P)^{b_1}$ for $Q_c > \alpha_2, Q_c = a_2^*(\Delta P)^{b_2}$	$t = t, \Delta P = \Delta P, v_p = 0$ for $Q_c < \alpha_2$ and $Q_c > \beta_2$ $Q_c = a_2^*(\Delta P)^{b_2}$ for $Q_c > \beta_1$ and $Q_c < \alpha_1$ $Q_c = a_1^*(\Delta P)^{b_1}$

confirming that the observed pressure relaxation on cessation of flow can be directly related to flow within the capillary as opposed to the possible explanation involving viscoelastic stress relaxation.

## V. DISCUSSION AND CONCLUSIONS

This paper has shown that the MPR is capable of making precision time-dependent measurements on polyethylene for a broad range of shear rates. By virtue of the unique flow geometry of the MPR, it has been possible to modify the Molenaar and Koopmans model to describe the time-dependent capillary flow of HDPE in all four regimes using only experimentally determinable parameters. Because of the MPR's fully constrained geometry and boundary conditions, no adjustable parameters were needed in the model. The model quantitatively confirms that the kinetics of both; the pressure buildup and the relaxation process are governed by the compressibility, and that relaxation of the pressure difference across the capillary can be attributed to flow in the capillary associated with pressure equalization in both barrels. Flow visualization experiments also confirm this.

This paper, therefore, quantitatively supports the earlier work of Hatzikiriakos and Dealy (1994) and Durand *et al.* (1996) that compressibility rather than viscoelastic effects control the time dependence of capillary flow pressure measurements of the type discussed here.

## ACKNOWLEDGMENTS

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