Comparison of Measurement Techniques for Evaluating the Pressure Dependence of the Viscosity

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Abstract:
The different methods that can be used for measuring the effect of a hydrostatic pressure on the viscosity of polymer melts are evaluated. A linear low-density polyethylene is chosen as test material, as it can be expected to have a small pressure dependency. Special attention is given to methods employing capillary rheometry, as these methods yield a range of shear rates and pressures that are typically encountered under polymer processing conditions. The accuracy of the different techniques is evaluated considering also the complexity of the experimental devices. First it is investigated to which extent standard capillary rheometry can be used to extract information about the pressure dependency of the viscosity. Secondly, it is shown how the accuracy can be greatly increased by the simple addition of a pressure chamber below the exit of the capillary, with a needle valve to regulate the back pressure. The results from this device are compared with those from a more robust method using a pressurized double piston rheometer and with literature data. The experimental values for the pressure coefficient of the viscosity will also be compared with those predicted from PVT data using Utracki's method.

Zusammenfassung:
Es werden unterschiedliche Methoden ausgewertet, die für das Messen des Effektes eines hydrostatischen Drucks auf die Viskosität von Polymerschmelzen verwendet werden können. Als Testmaterial wurde low-density Polyäthylen gewählt, da es sich aufgrund seiner geringen Druckabhängigkeit der Viskosität besonders eignet. Besondere Aufmerksamkeit wird denjenigen Methoden gewidmet, die Kapillar-Rheometrie einsetzen, da sie eine weite Spanne – typisch für die Polymerverarbeitung – von Scherraten und Drücken realisieren lassen. Die Genauigkeit der unterschiedlichen Techniken wird ausgewertet, wobei auf die Komplexität der experimentellen Anlagen ebenfalls eingegangen wird. Zunächst wird untersucht, in welchem Masse die Standard-Kapillar-Rheometrie herhalten kann, um Information über die Druckabhängigkeit der Viskosität bereitzustellen. Anschliessend wird gezeigt, wie die Genauigkeit verbessert werden kann durch Hinzufügen eines einfachen Druckraums, mit Nadelventil zur Regulierung des Rückstaus, unter dem Ausgang der Kapillare. Die Ergebnisse, die mit diesem Instrument erhalten wurden, werden mit denjenigen einer robusteren Methode, einem unter Druck gesetzten doppelten Kolbenrheometer, sowie mit Literaturdaten verglichen. Zusätzlich werden die Daten mit denen verglichen, die sich aus PVT-Daten nach Utracki's Methode ergeben.

Résumé:
Les différentes méthodes qui peuvent être employées pour mesurer l'effet de la pression hydrostatique sur la viscosité des fondus de polymères, sont évaluées. Un polyéthylène lineaire basse densité est choisi comme matériau test, puisque l'on peut s'attendre à trouver une faible dépendance à la pression. Une attention particulière est donnée aux méthodes qui emploient les rhéomètres capillaires, car elles impliquent des grandeurs de vitesses de cisaillement et de pression qui sont typiquement rencontrées lors de la mise en œuvre d'un polymère. La précision des différentes techniques est évaluée, tout en considérant également la complexité des appareils instrumentaux. Premièrement, nous avons cherché à savoir jusqu'à quel point un rhéometre capillaire peut être employé afin d'extraire des informations sur la dépendance en pression de la viscosité. Deuxièmement, il est montré comment la précision peut être grandement accrue par la simple addition d'une chambre de pression en-dessous de la sortie du capillaire, avec une "valve aiguille" afin de réguler la pression de retour. Les résultats obtenus avec cet appareil sont comparés à ceux obtenus avec une méthode plus robuste, qui utilise un rhéometre pressurisé à deux pistons, et avec les données de la littérature. Les valeurs expérimentales pour le coefficient de pression de la viscosité seront également comparées avec celles prédites à partir des données PVT et en utilisant la méthode d'Utracki.

Key words: rheometry, pressure dependency, polymer melts

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1 INTRODUCTION

The effects of pressure on the rheological behaviour of polymer melts are often ignored. Nevertheless, typical pressures encountered during polymer processing operations can be very high and the assumption that a polymer melt can be treated as a pressure-invariant fluid is not necessarily valid. Whereas the effects on the flow rates due to changes in density with pressure can typically still be neglected [1], the effect of pressure on the viscosity is much larger and needs to be accounted for. As early as 1957, Maxwell and Jung [2] demonstrated very clearly that the viscosity of polymers can be increased by one or two orders of magnitude for a range of pressures typically encountered in injection molding (0-150 MPa). Following the work of Maxwell and Jung, various measurement techniques and devices were subsequently developed in the 1960's and 1970's [1,3-7]. As demonstrated by a number of recent papers on this subject, there is a renewed interest in pressure effects and various new devices and applications have been investigated [9-18]. This renewed attention is not surprising given the potential importance of the effect of pressure on the rheological properties, and the need to incorporate this in the increasingly sophisticated numerical simulations of polymer processing operations. Moreover, pressure can affect other important phenomena such as e.g. strain-induced crystallization [17].

To express the effect of pressure on viscosity, different methods can be used. Similar to the temperature shift factor, a pressure shift factor can be defined as:

$$a_p(p) \equiv \frac{\eta_0(p)}{\eta_0(p_0)} \quad . \tag{1}$$

This shift factor can be used to obtain a master curve by applying it to both the viscosity and shear rate (see e.g. [10,17]). Very often the shift factor varies exponentially with pressure so that it can be expressed in terms of a pressure coefficient β_0:

$$a_p(p) = exp\,[\beta_0(p-p_0)] \quad . \tag{2}$$

For polymers for which time-temperature-pressure superposition holds, β_0 should be a function of molecular structure alone. This factor can be obtained from superposition methods [16] or by using master curves to which generalized Newtonian models can be fitted [10,17]. In the present work, however, a pressure coefficient β defined as [19]:

$$\beta = \frac{1}{\eta}\left(\frac{d\eta}{dP}\right)_T \quad , \tag{3}$$

will be used. In the limit of zero shear rate, this corresponds to the definiton of β_0 given by Eq. 2. As defined by Eq. 3, β is no longer a thermodynamic property, but will generally be a function of temperature, pressure and shear rate. Nevertheless, β will be used in the present work as it can be obtained directly from the experimental data without the need for data-shifting or curve fitting which can induce additional errors. Hence the parameter β enables a more direct comparison of the various experimental techniques.

Literature data on the pressure dependency of rheological parameters remain sparse. One reason could be the intrinsic difficulty to obtain accurate data. Possibly due to the different definitions of the pressure coefficient and the different experimental methods used, the reported values of the pressure coefficients β_0 and β for a given polymer show large differences. In addition, the pressure coefficient has been observed to decrease with increasing temperature [10, 15], but temperature independent values have also been observed [6]. The same holds for the effect of shear rate; both shear rate dependent [24, 17] and essentially shear-rate independent [10, 12] pressure coefficients have been reported. The conditions under which temperature, pressure and shear rate can be treated as separable parameters are not clear but for some polymers at least a temperature and pressure invariant description of the viscosity seems possible [10].

The detailed chemical and physical characteristics of the molecules are expected to play a role in determining the importance of pressure effects. The value of the pressure coefficient for

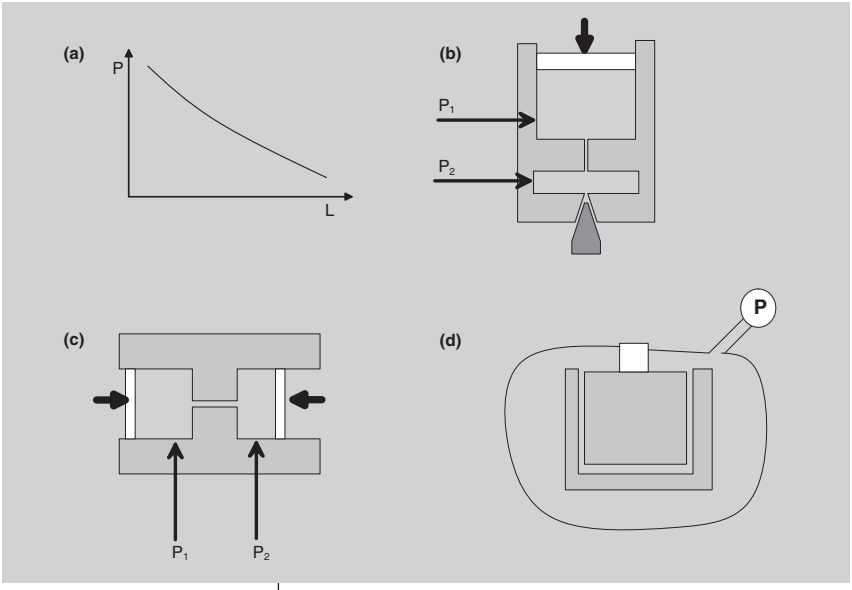


Figure 1: Schematic representation of the different methods to determine the effect of pressure on the viscosity : (a) non-linear pressure profiles : P(L), (b) enhanced exit pressure devices (c) pressurized capillaries (d) pressurized drag flow devices.

polymers with side groups or bulky backbone groups (e.g. PS or ABS) is always higher than the pressure coefficient of polymers such as PE or PP (see e. g. Kadijk and van den Brule [10]). This dependence on molecular structure is not surprising. An increase of the viscosity is related to a reduction of the free volume. The free volume approach has been used to study theoretically the effect of pressure on viscosity. Based on these ideas, Utracki [21,22] proposed a fairly simple method to estimate the pressure dependency of the viscosity from PVT data.

In the present paper, a brief review is given of the available methods for determining the effect of pressure on the rheological properties. Some of these methods will be evaluated by comparing the measured pressure coefficients (β) for a linear low density polyethylene.

2 OVERVIEW OF AVAILABLE METHODS

2.1 ANALYSIS OF NON-LINEAR PRESSURE PROFILES

The pressure dependency of the viscosity causes non-linearities in the pressure profiles observed during flow in a capillary or slit geometry (see Fig. 1a). For capillary geometries, these pressure profiles cannot be measured directly. The high curvature of the capillary wall renders it virtually impossible to mount pressure transducers. The pressure profiles can be inferred from plots of the total pressure drop over a capillary as a function of the ratio of length (L) over diameter (D). This produces the well known Bagley plots [23]. In 1967, Dudvani and Klein [20] proposed a method to use the curvature in the Bagley plots to estimate the pressure dependency of the viscosity. Assuming an exponential dependency of the viscosity on the pressure ($\eta = \eta_0 \cdot e^{\beta \cdot p}$) where β is a positive number, the momentum balance in the axial (*z*) direction,

$$\frac{\partial p}{\partial z} = \frac{1}{r}\frac{\partial(\sigma_{rz} r)}{\partial r} \quad , \tag{4}$$

can be integrated over the capillary between $z = o$ and $z = L$, assuming atmospheric pressure at $z = L$. When the entrance pressure drop is neglected this yields the following expression for the total pressure drop (Δp_{tot}) as a function of the *L/D* ratio of the capillary:

$$\Delta p_{tot} = -\frac{1}{\beta}\ln\left(1 - 4\beta\sigma_o \frac{L}{D}\right) \quad , \tag{5}$$

where σ_0 is the wall shear stress at atmospheric pressure. If the ln function is approximated by a series expansion of *(L/D)* up to the second-order term, the pressure profile can be written as [20,24]:

$$\Delta p_{tot} = b\left(\frac{L}{D}\right) + c\left(\frac{L}{D}\right)^2 \quad , \tag{6}$$

where it can be easily shown that:

$$\beta = \frac{2c}{b^2} \quad . \tag{7}$$

Hence the fit of either Eq. 5 or the quadratic approximation of Eq. 6 to an experimentally measured Bagley plot seems the most simple method to determine β. This method has been used by several authors, e.g. Dudvani and Klein [20], Penwell and Porter [1], Kamal and Nyun [8].

There are however some intrinsic problems with this technique:

- The calculation of the pressure coefficient from Bagley plots is affected by the entrance pressure drop Δp_{ent}. The latter is caused by a combination of shear and extensional flow phenomena, which also depend on pressure. In addition, these phenomena occur at the position in the capillary where the pressure is maximal. Moldenaers et al. [12] suggested the use of the same value of β to correct for the entrance

pressure drop and added a term $\Delta p_{ent} e^{\beta p}$ to Eq. 5. Work by Binding et al. [15] suggests however that the entrance pressure drop has a stronger pressure dependency than the viscous one. The pressure dependency coefficient, defined at constant deformation rates were found to differ strongly between shear and extension [15, 25]. When the pressure dependency coefficient is defined at constant stress, similar values are obtained in shear and elongation [16]. The ambiguity caused by the presence of the entrance pressure drop can be overcome by making direct measurements of the pressure profile using a slit die. Laun [24] pioneered this approach, using three pressure holes evenly spaced along the die. He also derived Eq. 6 for a slit geometry. Langelaan et al. [11] used a slit die hooked up to an extruder using 9 pressure transducers along a very long die. However, literature data using this approach remain scarce. In order to evaluate the non-linearity, detailed measurements of the pressure profile are needed. The slit die method has gained little popularity as mounting and cleaning of slit dies is rather time-consuming.

- It should be kept in mind that the pressure coefficients are typically of the order of 10^{-9} - 10^{-8} Pa^{-1}. For the pressure drops typically encountered in standard capillary rheometry, with an L/D ratio ranging from 10 to 30, the non-linearities will be small. In the following section it will be investigated whether these effects can be measured at all using standard capillary rheometry, even when it is pushed to its limits.

- Whenever the non-linearities become important, the exponential dependency can no longer be approximated by a second order equation and the use of the quadratic form (Eq. 6) will lead to an overestimation of the coefficient *c*. In addition, neglecting the pressure dependence of the entrance pressure drop in capillary rheometry will further overestimate β [12]. Indeed, Steuten et al. [26] reported that pressure coefficients calculated from Bagley plots using Eq. 6 were almost an order of magnitude higher than those obtained by more direct methods.

- Denn [27] pointed out that Eq. 5 does not fulfill the momentum balance in the radial direction. Eq. 5 also predicts that the pressure drop becomes infinite when $(4\beta\sigma_0 \frac{L}{D})$ approaches unity. For a polymer such as PS, for which $\beta \sim 10^{-8}\ Pa^{-1}$ this would occur at pressures of the order of 100 MPa. If Eq. 5 would be correct the polymer would no longer flow. Eq. 5 should be considered as an approximation, which can be used as long as $(4\beta\sigma_0 \frac{L}{D})$ is small compared to 1 and *(D/L)* is small compared to $(4\beta\sigma_0 \frac{L}{D})^{-1}$ [27].

- It should always be kept in mind that other effects can affect the non-linearity in the pressure profiles in a slit, or contribute to the non-linearity in a Bagley plot. Hay et al. [18] recently presented a detailed study of the combined effects of temperature and pressure. These authors demonstrate that the curvature of the pressure profile is affected by both temperature and pressure. Consequently, in calculating β from a non-linear pressure profile, either the viscous heating needs to be accounted for, or conditions should be such that viscous heating can be neglected. Viscous heating will typically produce a downward curvature of the pressure profile. On the other hand, wall slip with a pressure dependent slip velocity leads to upwards concave pressure profiles as nicely shown by Hatziriakos and Dealy [28].

In addition to the impact of viscous heating and wall slip, effects of not fully developed flow or flow-induced changes in the microstructure can contribute as well to observed non-linearities. For example, effects of molecular re-orientation have been shown to be responsible for strongly non-linear Bagley plots in the case of liquid crystalline polymers [29, 11, 12]. Ignoring such effects can lead to erroneous predictions for the pressure coefficient, see e.g. [30, 31], with differences of two orders of magnitude or even more when compared with results from more robust methods [11, 12].

Capillary rheometry however remains attractive because of its simplicity. In the present work it will be investigated what range of β values may be measured accurately by this technique. In addition to the above mentioned problems, we will also address the propagation of the experimental errors in the data analysis.

2.2 ENHANCING THE EXIT PRESSURE

Simple modifications of existing capillary rheometers have been proposed to study the effect of pressure on the flow behaviour in more detail [9, 15, 32]. Either a second capillary is added downstream of the first, or a conical restriction can be introduced downstream of the capillary. This method is schematically depicted in Fig. 1b. By adding a downstream pressure chamber to a piston driven device, the pressure at the exit of the die can be regulated and measured. A conical restriction as part of a needle valve can also be used to regulate the back-pressure, thus establishing a hydrostatic pressure in the capillary. The average hydrostatic pressure can be approximated by a linear average between the pressure measured at the entrance of the die and the pressure in the pressure chamber, as long as the non-linearity of the pressure profile remains small enough. Binding et al. [15, 16, 25] explored the use of the exit pressure technique, in combination with a variation of the *L/D* ratio, in order to evaluate the effect of the pressure on both the shear and elongational viscosity, the latter being inferred from the entrance pressure drop.

This method provides data of the apparent viscosity as a function of the pressure at a given shear rate. The major advantage of the exit pressure method is its increased accuracy; moreover it may be readily adapted for use with any standard capillary rheometer. The accuracy of such a device will be evaluated in some detail below.

2.3 PRESSURE DRIVEN FLOWS UNDER HYDROSTATIC PRESSURE

A more direct way to measure the pressure dependency consists of controlling the hydrostatic pressure in a capillary or slit by means of a second piston instead of a restriction, as schematically depicted in Fig. 1c.

This method was used in the early investigations by Maxwell and Jung [2], Westover [3, 33], Ito [7] and later by Karl [34]. The same method has recently been applied to slit reometers. Kadijk and van den Brule [10] designed a device that exists of two (vertical) cylindrical reservoirs separated by an horizontal slit. Each cylinder has an independently controlled piston capable of generating hydrostatic pressures up to 180 MPa via a servo-hydraulic system. Mackley et al. [13] introduced a similar device known as the „multi-pass rheometer", able to operate in both shear and oscillatory modes at elevated temperatures.

These instruments can typically generate fairly high pressures. However, their construction is not simple, nor are they easy to operate and maintain. Nevertheless, they are able to produce accurate measurements of pressure and temperature dependence of the viscosity in typical ranges of shear rates and pressure that are relevant for processing operations.

2.4 DRAG FLOWS UNDER HYDROSTATIC PRESSURE

Pressurized versions of drag flow rheometers, as depicted in fig. 1.d, have also been designed. They are especially useful to investigate the behaviour at lower shear rates or in transient flows. In 1967, Hellewege et al. [4] used a pressurized Couette cell to study the effect of pressure on the steady state and transient viscosity of polymers. A rotating cylinder viscometer was also used by Cogswell and coworkers [6] in the 70's to study the effect of pressure on the viscosity in comparison with theoretical predictions. Mattischek and Sobczak [14] designed a falling ball viscometer, using an external force field exerted by a magnet, that is suitable for measuring the low shear viscosity of polymer melts. Recently, Koran and Dealy [17] have developed a pressurized version of a sliding plate rheometer. Pressures ranging from atmospheric up to 70 MPa and shear rates between 0.3 and 300 s^{-1} can be explored. The pressurized instruments conserve all the typical advantages of drag flow experiments, but in all cases they require fairly complex mechanical constructions.

2.5 CALCULATION OF β FROM PVT DATA

Utracki [21, 22] presented a semi-empirical method to relate the zero shear viscosity of polymeric fluids to the free volume. The method is based on two assumptions. Firstly, the equilibrium free volume fraction is computed from fitting the Simha-Somcynski equations of state to the PVT data. Secondly, a semi-empirical correlation between the zero shear viscosity and the inverse of the free volume fraction is used to deduce the pressure effects on the viscosity [21, 22]. The description of the zero shear viscosity in terms of the free volume alone is however not unique [10], and the conditions under which this method is reliable are not yet clear.

In order to calculate the free volume, the Simha-Somcynsky (SS) equation of state is fitted to the experimental pressure-volume-temperature data (PVT) data. The SS equation is formulated in terms of reduced variables [36, 37]:

$$\tilde{P} = \frac{P}{P^*}; \quad \tilde{V} = \frac{V}{V^*}; \quad \tilde{T} = \frac{T}{T^*} \quad , \tag{8}$$

*P**, *V** and *T** are determined as indicated below. The SS equation of state for polymeric liquids simplifies to the following set of equations [22]:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{1}{1-2^{-1/6}\, y\Phi^{1/3}} + \left(\frac{2y}{\tilde{T}}\right)\Phi^2\left[1.011\,\Phi^2 - 1.2045\right] \quad , \tag{9}$$

$$\left[1+\frac{\ln(1-y)}{y}\right] = \frac{y}{6\tilde{T}}\Phi^2\left[2.409 - 3.033\phi^2\right] + \left[\frac{2^{-1/6}\, y\Phi^{1/3} - 1/3}{1-2^{-1/6}\, y\Phi^{1/3}}\right] \quad , \tag{10}$$

where $\Phi = 1/(y\tilde{V})$ and $y = 1 - f$ where f is the free volume fraction. The reducing parameters *P**, *V** and *T** can be found by fitting the two coupled equations to the PVT data using a multiparameter fit routine or using a simplified method by Utracki [22]. Once the reducing parameters are known, the free volume fraction can be determined for every combination of pressure and temperature.

Utracki [21,22] suggested that the Doolittle equation [35], may be used to relate the zero shear viscosity to the free volume fraction:

$$\ln \eta_o = A + \frac{B}{f + C} \quad . \tag{11}$$

C is usually small with respect to f and will be neglected here, thereby reducing the number of parameters to two. Obtaining the zero-shear viscosity as a function of temperature at atmospheric pressure is straightforward. The reducing parameters enable one to calculate f. A linear regression of the experimental zero shear viscosity data plotted as a function of the inverse free volume yields the parameters A and B. Utracki [22] noted that there is often a linear relation between $1/f$ and the reduced pressure at a given temperature:

$$\frac{1}{f} = D(\tilde{T}) + E(\tilde{T})\tilde{P} \quad . \tag{12}$$

The pressure coefficient β can then be obtained by substituting Eqs. 11 and 12 in Eq. 3 from

$$\beta_0 = \left(\frac{d\ln\eta_0}{dp}\right)_T = \frac{B \cdot E(\tilde{T})}{P^*} \tag{13}$$

However, as already noted by Utracki [21], master curves of η_0 as a function of $1/f$ are not always obtained. He suggested the use of a new rheological scaling pressure $P_r^* = n \cdot P^*$. The numerical constant, set to n=2 for some materials, however introduces some ambiguity into the calculations. Vleeshouwers [38], Kadijk and van den Brule [10] and Yahsi [39] suggested the use of a temperature dependent term into Eq. 11, for example:

$$\ln \eta_0 = A_T + \frac{B_T}{f + C_T + C_{2,T}T} \tag{14}$$

This equation, hereafter referred to as the modified Doolittle equation, renders it possible to account for molecular mobility at constant free volume fraction, hence separating temperature and pressure effects to some extent. It of course introduces the additional constant $C_{2,T}$. The methods of Utracki [21] and the modified Doolittle method [10, 38, 39] have not been systematically compared with experimental results on well characterized polymers, although Kadijk and van den Brule demonstrated that the modified method seems to work well for some polymers.

3 EXPERIMENTAL

3.1 MATERIAL

The material used in this study was a commercial linear low-density polyethylene (LLDPE) from AtoFina. The molecular weight parameters for this polymer are M_ω = 120 600 and M_ω/M_n = 5.1 as

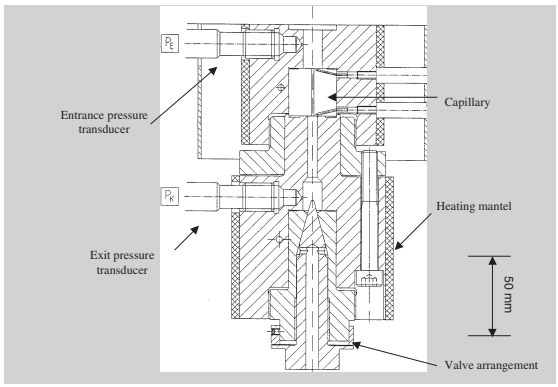


Figure 2: Schematic of the pressure tool consisting of a pressure chamber and a needle valve fitted beneath a standard capillary rheometer.

determined from GPC measurements. With this sample a critical test of the measurement techniques is possible as its pressure dependency is expected to be relatively small as compared to most other polymers.

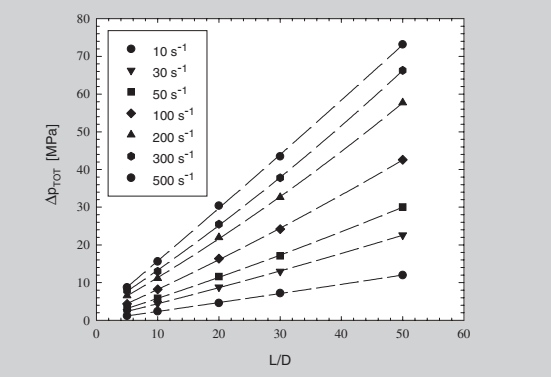
3.2 METHODS

The rheological behaviour of the LLDPE sample was first studied under standard pressure conditions using a Göttfert 2002 capillary rheometer. Capillaries with high length to diameter ratios, ranging from 5 to 50, have been used to obtain sufficiently detailed Bagley plots. For every capillary the entrance angle was 180°. The melt pressure was measured in the reservoir, 15 mm upstream from the entrance of the die. The pressure transducers were of the Dynisco class I type with nominal range of 7, 20, 50, 100, 140 and 200 MPa with an accuracy of 0.5%. The optimal transducer for the pressure range under consideration was chosen for each experiment. Each measurement point was repeated at least 3 times to check repeatability. Test temperatures of 170, 190 and 210°C were chosen and wall shear rates were between 10 and 500 s^{-1}. No measurements could be performed with sufficient accuracy at lower shear rates, even with the most sensitive pressure transducers. At higher deformation rates melt instabilities appeared. Within measurement accuracy, data obtained with capillaries of different diameters agreed, indicating the absence if significant wall slip. Some additional rheological measurements were performed using rotational rheometers, in particular to determine the zero shear viscosity. Both a stress controlled (DSR – Rheometric Scientific) and a strain controlled instrument (RMS800 – Rheometric Scientific) have been used.

A prototype of a tool to enhance the exit pressure, was designed and manufactured by Göttfert Werkstoff-Prüfmaschinen GmbH. It is shown in Fig. 2 and was used to measure directly the pressure dependence of the viscosity. This device, made from forged steel, can easily be fitted below the die. At the base of a pressure chamber a conical valve provides a constriction at the exit of the pressure tool. The valve can be moved vertically by means of a screw thread in order to vary the level of constriction, thereby changing the back pressure in the chamber. A pressure transducer, fitted upstream of the valve, records the back pressure in the chamber. In order to test its mechanical performance, the pressure chamber has been tested up to back pressure of 120 MPa. An external regulator, consisting of a heating system and temperature controller (Eurotherm regulator and Pt 100), has been used to achieve good temperature homogeneity in the pressure tool. To ensure good thermal stability the instrument was heated for at least 3 hours before starting experiments.

The experimental protocol consists of applying a constant piston speed with the constriction initially fully open. The constriction is then adjusted to the desired back pressure, resulting in elevated barrel and chamber pressures. Once steady state conditions are obtained, the pressures are measured. One should keep in mind that, with this device, the mean pressure in the die can not be controlled directly.

In order to assess the data obtained with this prototype, a pressurized slit rheometer, type c in Fig. 1 and referred to as the Philips rheometer, was used for comparison. This rheometer has been described in detail by Kadijk and van den Brule [10]. The slit has a length of 100 mm, a width of 20 mm and a depth of 1 mm. Considering the large width/height ratio, the flow can be considered to be two-dimensional. A servo-hydraulic system can generate hydrostatic pressures of up to 180 MPa on two independently controlled pistons. The pressure in the slit is measured by three Staiger-Mohilo pressure transducers (0-200 MPa). One is located at the centre of the slit and is used to determine the hydrostatic pressure in the sample. The other two are positioned at a distance of 35 mm on each side of the central transducer and measure the pressure drop over the slit. The flow rate is obtained by keeping the speed of one piston constant while the other one controls the pressure at the center of the slit. With this technique both the flow rate and the hydrostatic pressure at the center of the slit are controlled independently. Two platinum resistor



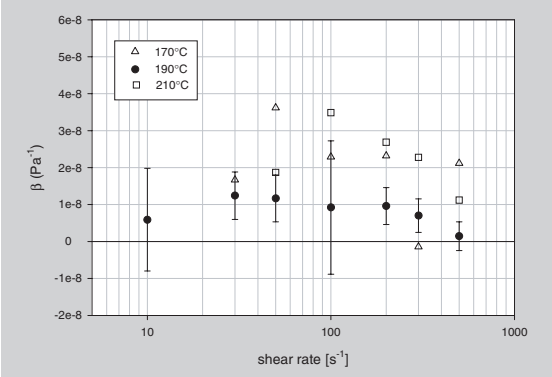


Figure 3 (left): Bagley plots for the LLDPE sample at 190° C using dies with D = 1 mm and varying L.

Figure 4 (right): Values of the pressure dependency coefficient of the viscosity as calculated from the Bagley plots for LLDPE at 170, 190 and 210° C.

temperature controllers are mounted close to the slit for temperature measurements. In order to minimize the temperature gradients the slit section is thermally insulated from the environment.

4 RESULTS AND DISCUSSION

4.1 ESTIMATION OF β FROM BAGLEY PLOTS

The Bagley plots were obtained by varying the length, *L*, while the diameter of the capillary (D) and that of the reservoir (Dr) were kept fixed in order to keep the entrance effects constant. Fig. 3 shows the Bagley plot at 190° for the LLDPE sample under investigation.

The values of the pressure coefficient were calculated by fitting Eq. 6 to the data of Fig. 3. The results are plotted in Fig. 4 together with measurements obtained from Bagley plots at 170 and 210°C. The values obtained from β scatter much and sometimes produce negative results. There is no clear relation with increasing temperature and shear rate, hence viscous heating seems not to be the main reason. To verify when viscous heating becomes important, the Nahme-Griffith number was calculated:

$$Na = \frac{\alpha\sigma\dot{\gamma}R^2}{4k} \tag{15}$$

where α is the temperature dependence of the viscosity and κ is the thermal conductivity. For the shear rate range covered in the present experiments at 190°C, the Nahme number ranged from 0.005 to 2. The Nahme number became of order 1 at shear rates above 500 s^{-1}. Viscous heating will hence only have an important effect at the highest shear rates.

In calculating β directly from the Bagley plots, one has to keep in mind that, in addition to the problems mentioned above, experimental errors propagate in the calculations and curve fittings. To evaluate the error propagation, a least squares estimation procedure combined with matrix algebra was used. Eq. 6 can be rewritten under matrix form as (see e.g. [40]):

$$\begin{pmatrix} \Delta p_{L1} \pm \varepsilon_1 \\ \Delta p_{L2} \pm \varepsilon_2 \\ \Delta p_{L3} \pm \varepsilon_3 \\ \Delta p_{L4} \pm \varepsilon_4 \\ \Delta p_{L5} \pm \varepsilon_5 \end{pmatrix} = \begin{pmatrix} 1 & L_1/D & (L_1/D)^2 \\ 1 & L_2/D & (L_2/D)^2 \\ 1 & L_3/D & (L_3/D)^2 \\ 1 & L_4/D & (L_4/D)^2 \\ 1 & L_5/D & (L_5/D)^2 \end{pmatrix} \cdot \begin{pmatrix} a \pm \Delta a \\ b \pm \Delta b \\ c \pm \Delta c \end{pmatrix} + \begin{pmatrix} \delta_{L1} \\ \delta_{L2} \\ \delta_{L3} \\ \delta_{L4} \\ \delta_{L5} \end{pmatrix} \tag{16}$$

Where Δp_{L_i} is the experimentally measured pressure drop with the capillary number i (i=1-5, L_i=5, 10, 20, 30, 50 mm) and diameter D, ε_i is the corresponding measurement error and δ_{L_i} is the error on the quadratic fitting. Starting from Eq. 16 and using a least squares minimization criterion, the parameters *a*, *b* and *c* can be computed first, together with their corresponding standard deviations Δa, Δb and Δc [40]. Using Eq. 7, it is possible to calculate the pressure coefficient with its corresponding relative error, given by:

$$\frac{\Delta\beta}{\beta} = \left(\frac{\Delta c}{c} + 2\frac{\Delta b}{b}\right) \tag{17}$$

The errors on β for the Bagley plot shown in Fig. 3 at 190° C are included in Fig. 4. Relative errors up to 250 % can be obtained. Although the data were based on a fairly large range of L/D ratios (5-50), and the measurements were repeated at least three times to reduce the variable errors on the pressure measurements. Hence the results indicate that standard capillary rheometry could not provide the required information for the sample under consideration. When considering the combined effect of the propagation of errors made by the pressure measurement and the error on the fit, the Bagley plot or non-linear pressure profile procedure will be useful only when the pressure coefficient is of the order of 10^{-7} Pa^{-1} or larger.

4.2 PRESSURE CHAMBER MEASUREMENTS

The pressure dependence of the viscosity was measured directly using the pressure cell depicted in Fig. 2. The LLDPE sample was investigated at apparent shear rates between 50 and 700 s^{-1} and

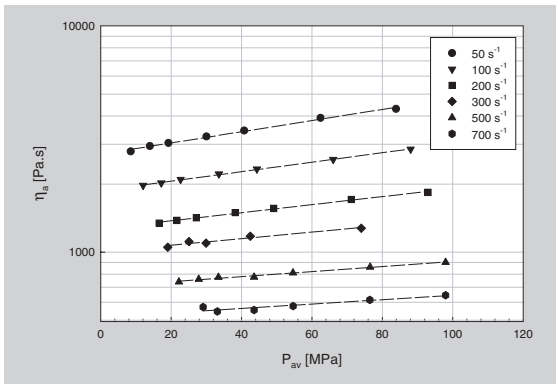


Figure 5 (left): Apparent viscosity as a function of increasing hydrostatic pressure for a LLDPE at different shear rates (190° C).

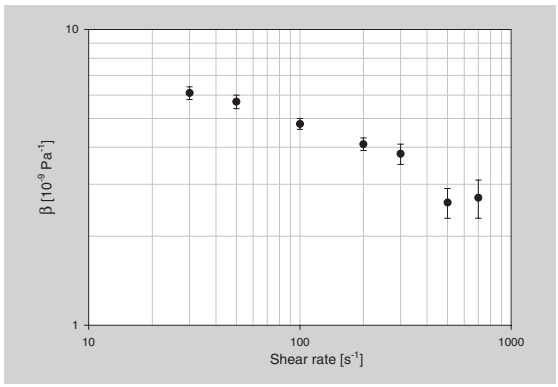


Figure 6 (right): Pressure dependency coefficient of LLDPE as a function of shear rate, using the enhanced exit pressure technique (190° C).

up to back pressures of 120 MPa. The pressure drops and flow rates through the capillary are used to determine the apparent viscosity for a given hydrostatic pressure. Values for the viscosity as a function of the mean pressure for the LLDPE sample at 190° C are given in Fig. 5. The mean pressure was calculated as a linear average between the entrance and back pressure. As long as the non-linearity in the pressure profile is small, this simple procedure should yield accurate results. This, however, does not necessarily hold for all polymers. A non-linear average can be obtained by integrating Eq. 5 between $P_{entrance}$ and P_{exit}. A pressure coefficient of 10^{-8} Pa^{-1} would lead for similar pressures to differences between the linear and non-linear average of about 4 %. For β equal to $5 \cdot 10^{-8}$ Pa^{-1}, the non-linearity in the pressure profile could no longer be neglected since the differences between the two could be up to 30 %.

Fig. 5 shows the systematic increase of viscosity with pressure at a fixed shear rate. The effect is substantial, for example an increase in viscosity of 50% is seen at 50 s^{-1} when comparing the viscosities at 70 MPa with those at atmospheric pressure. Fig. 5 shows an exponential dependence of the apparent viscosity on pressure and hence the pressure coefficient β can be evaluated directly from the slope of the curves on this semi-logarithmic plot. Fig. 6 shows the resulting β values as a function of shear rate.

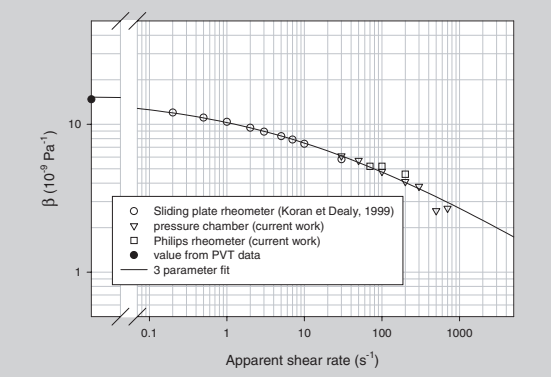
The values of β given in Fig. 6 are systematically lower than those reported in Fig. 4. Also the estimated errors on the β values are now much smaller, mainly due to the fact that β now can be obtained simply from the first order term in a linear regression rather than from a second order term. Knowing the experimental errors on the entrance and back pressures, the corresponding standard deviations of the pressure dependency of the viscosity can be easily calculated. Using a series approximation up to first order of the logarithmic function, one can compute the resulting error on the β coefficient using the matrix method presented above. Errors of the order of 10 % on the pressure coefficient are obtained. This is a major improvement as compared with methods based on the Bagley plots.

The definition of β in eq. (3) was based on the observation that the viscosity often displays an exponential dependency on pressure; experimentally, this is not always observed, sometimes a stronger dependency is is encountered at low pressures [see e.g. [14, 11]] and an exponential dependency is not sufficient. In that case, the so-called Barus (The Barus equation is named after one of the first investigators of pressure effects on the viscosity, C. Barus. He reported measurements on a „Marine Glue“ which showed this behaviour: see e. g. Am. Journ. Sci, **155** 87-96 (1893)) equation should be used to describe the results:

$$\log \eta_{o,P} = \log \eta_o + \beta p + K \cdot p^2 \quad . \qquad (18)$$

5 COMPARISON OF THE PRESSURE CHAMBER DATA WITH OTHER METHODS

The pressure dependence of the viscosity of the LLDPE was also measured directly with the Philips double piston rheometer [10] at 190° C under hydrostatic pressures of 10, 30, 50 and 70 MPa. The resulting β values are compared in Fig. 7 with the ones obtained using the pressure chamber technique. The absolute values of β obtained with different methods, agree rather well. The shear rate dependence of the β values obtained is similar to that derived with the exit pressure tool. As the geometries are quite different in the two instruments, the shear rate dependence seems not to be due to viscous heating. Following the statistical procedure outlined above, one finds a similar order of magnitude for the error of the pressure coefficient for the double piston device than with the exit pressure method. The experimentally accessible shear rate range with the double piston device is limited by two factors. At low shear rates the pressure drops cannot be measured with a sufficient accuracy. At higher shear rates, it is difficult to achieve a stationary motion of the two pistons. The typical upper limit for the present instrument and material is 300 s^{-1}.



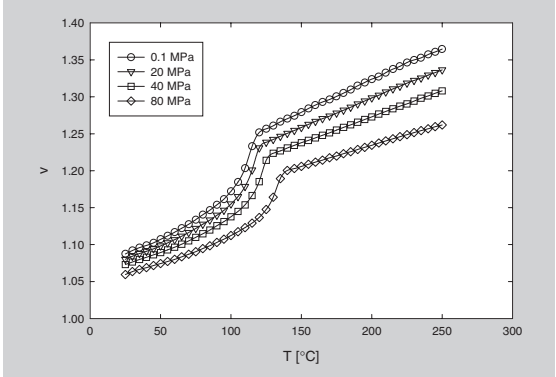


Figure 7 (left): Comparison of the pressure coefficient of the viscosity obtained by different methods.

Figure 8 (right): PVT data for the LLDPE sample used in this work.

Koran and Dealy [17] recently also studied a LLDPE sample (Dowlex 2049, M_ω = 119.000), the rheological behaviour of which was close to the one used in our study. Their data, obtained at 175° C, are included in Fig. 7 for comparison. As they use a drag flow rheometer the instrument covers lower shear rates, but the data are in line with the ones obtained with the pressure chamber data for higher shear rates. The shear rate dependence of the pressure „coefficient" β is a consequence of the way it was defined in Eq. 3. For materials for which the time-temperature superposition principle holds, a shear rate independent shift factor can be obtained by using master curves [see e.g. [10, 16, 17]]. These methods, however, require either some extent of curve fitting, an extrapolation to zero shear rates, or a shifting of the experimental curves. In each case implicit assumptions must be made about, e.g. the validity of the time-temperature superposition or the dependence of the pressure coefficient on shear rate. To compare the intrinsic differences between the various experimental techniques the definition of the pressure coefficient as given by Eq. 3 allows for a more direct comparison.

Finally, the pressure dependency coefficient was calculated from the PVT data shown in Fig. 8. Fitting the Simha-Sockynski equation of state (Eqs. 9 and 10) to the experimental data or by using the method proposed by Utracki [22], the reducing parameters were found to be P^* = 662 *MPa*, T^* = 11530 K and V^* = 1.2 ∗ 10^{-3} m^3/kg. Using these parameters, first a plot of $\tilde{P}$ versus 1/f was constructed for three measurement temperatures (170, 190 and 210° C) from which the parameters $D(\tilde{T})$ and $E(\tilde{T})$ were obtained. At 190° C, these parameters were D = 8.1 and E = 24.5. The zero shear viscosities as a function of temperature were obtained by fitting an Ellis model to the flow curves and extrapolating to zero. From the plot of η_0 versus 1/f, the parameters A and B were A= 6.28 and B= 0.390. Using Eq. 13 a value for β of 14.4 GPa^{-1} was calculated. This result for the pressure dependence of the zero shear viscosity is also included in Fig. 7. It should be noted that we used P^* as the scaling parameter. The difference between this method, the method of Utracki (with n · P^* as a scaling parameter, with n a material dependent numerical factor) [22] and the modified Doolittle method [10] has not been explored here as it lies beyond the scope of the present work.

It was not possible to measure the pressure dependence of the zero shear viscosity experimentally. Therefore the experimental data for β were fitted with a simple three-parameter model, which is given as a full line on Fig. 7:

$$\beta = \frac{\beta_0}{1 + (K\dot{\gamma})^n} \qquad (19)$$

The zero shear limit, β_0, obtained in this manner was 15.3 GPa^{-1}. Although the agreement between the extrapolated and the calculated values is good, such a comparison is not without danger. The zero shear rate pressure coefficient β_0 can also be obtained from shift factors determined by plotting the viscosity as a function of the shear stress and shifting the curves using a shift factor a_p, defined according to Eq. 1. When applying this to the data obtained with the exit pressure device, reasonable superposition of the flow curves could be obtained and a value of β_0 equal to 10.9 ± 1.2 GPa^{-1} was derived from a fit to the evolution of the shift factors with pressure according to Eq. 2. The different methods agree rather well, at least for the material under investigation. Determining which is the most reliable method to obtain β_0 from experimental data outside the Newtonian region lies beyond the scope of the present work (for a discussion we refer to [10, 16, 17]).

As an independent method, the prediction of β_0 from PVT data does not seem to produce reliable values for all polymers [22, 10]. The questions which scaling parameters should be used and whether there is a one-to-one correspondence between η_0 and f render this method less robust. However, at least for some materials this method yields a fair estimate for β_0 as was shown here.

6 CONCLUSIONS

Different methods for determining the dependence of the viscosity on pressure have been reviewed and evaluated. The use of non-linear pressure profiles obtained with standard capillary rheometry is not a viable method for many materials. The propagation of experimental and fitting errors causes the analysis of the non-linear behaviour to be an unreliable method. It is also difficult to separate temperature, pressure and slip effects with this technique. A relatively simple modification that provides accurate results is the enhanced exit pressure technique. Such a device which can be mounted on a standard capillary rheometer is described. With this set-up the pressure dependency coefficient β is obtained from a linear regression and the resulting error on β is only about 10 %. In addition β can be determined under industrially relevant kinematic conditions. The measured values agree fairly well with data obtained using more robust methods. Estimating the pressure dependency from PVT data seems to provide an alternative route to evaluate the pressure dependency of the zero shear viscosity. However, at this point, this method lacks some robustness, especially with respect to the choice of the relation between free volume and the zero-shear viscosity.

It can be concluded that reliable experimental tools are now available to investigate the effects of pressure and temperature on the viscosity of polymers. Further work should address important issues such as determining the separability of temperature and pressure effects, the uniqueness of the relation between zero shear viscosity and free volume and the pressure effect on the elongational viscosity.

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