

**Evaluation and comparison of routes to obtain pressure coefficients from high pressure capillary rheometry data**

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## Evaluation and comparison of routes to obtain pressure coefficients from high pressure capillary rheometry data

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**Abstract** A capillary rheometer, equipped with a pressure chamber is used to measure the pressure dependent viscosity of PMMA, P $\alpha$ MSAN and LDPE. Data analysis schemes are discussed to obtain pressure coefficients at constant shear rate as well as at constant shear stress. It is shown that the constant shear stress pressure coefficients have the advantage of being shear stress independent for the three polymers. The constant shear rate pressure coefficients on the other hand turn out to depend on shear rate, which makes them less suitable for use in e.g. process simulations. In addition to the commonly used superposition method, a direct calculation method for the pressure coefficients is tested. Values obtained from both methods are equivalent. However, the latter requires less experimental and calculational efforts. From the obtained pressure coefficients it is clear that PMMA and P $\alpha$ MSAN have a very similar pressure dependence, while LDPE is less sensitive to pressure.

**Keywords** Polymer rheology · Pressure coefficients · Capillary rheometry · Shear viscosity

### Introduction

The viscosity of most polymer melts is known to increase exponentially with pressure. As early as 1957, Maxwell and Jung (1957) observed that, by increasing the pressure to 168 MPa, the apparent viscosity of a branched polyethylene melt became the fourteen-fold of its value at atmospheric pressure. For polystyrene, the pressure effect was even more pronounced. This dependency has important consequences for polymer processing since, in processes like e.g. injection moulding, polymers are subjected to rather elevated pressures. The growing demands on product performance in combination with the availability of increasingly sophisticated numerical simulations require an accurate incorporation of

pressure effects into the calculations. Nevertheless, this effect is often ignored and the amount of experimental data on the pressure dependence of the viscosity is rather scarce. This is probably due to the inherent difficulty in obtaining accurate data and the fact that different methods for determining the pressure effect lead to widely varying results.

Commonly the pressure dependency of viscosity is expressed by means of a pressure coefficient  $\beta$  (Barus 1891):

$$\beta = \left( \frac{d \ln \eta}{dP} \right)_{T,i} \quad (1)$$

in which  $i$  is either the shear rate  $\dot{\gamma}$  or the shear stress  $\sigma$ . The pressure coefficient is often defined in terms of a constant shear rate (Herrmann and Knappe 1969; Steuten et al. 1994; Binding et al. 1998; Koran and Dealy 1999; Oosterlinck 2000; Goubert et al. 2001), although such a coefficient is not a real thermodynamic property of the polymer melt (Goubert et al. 2001). For molten polymers this coefficient has typically a value of the order of  $10^{-8} \text{ Pa}^{-1}$  (Couch and Binding 2000). The values of  $\beta$  in literature however show large variations, even for the same polymer. Depending on the method used or the shear rate range under investigation, shear rate dependent (Herrmann and Knappe 1969; Koran and Dealy 1999; Oosterlinck 2000; Goubert et al. 2001; Liang 2001) as well as shear rate independent (Kadijk and Van Den Brule 1994; Binding et al. 1998; Koran and Dealy 1999; Couch and Binding 2000; Sedlacek et al. 2004; Pantani and Sorrentino 2005; Carreras et al. 2006) values can be found. Also values dependent (Herrmann and Knappe 1969; Kadijk and Van Den Brule 1994; Oosterlinck 2000; Goubert et al. 2001; Liang 2001; Sedlacek et al. 2004) or independent (Ramsteiner 1970; Binding et al. 1998; Koran and Dealy 1999; Couch and Binding 2000; Sedlacek et al. 2004; Pantani and Sorrentino 2005) of temperature have been reported. As a result of a non-exponential relation between viscosity and pressure, the pressure coefficients themselves can change with pressure (Kadijk and Van Den Brule 1994).

Since the early measurements of viscosity under elevated pressure in the 1950's, a range of analysis procedures and of measurement devices have been developed for this purpose.

An overview and an evaluation of these different methods is given by Goubert et al. (2001). Basically, these methods can be subdivided into direct and indirect methods. The direct methods use either existing or ad-hoc designed instruments in order to measure the pressure dependency experimentally whereas the indirect methods determine the pressure effect from other information.

For the direct methods, two approaches exist. The first one requires no special instruments but is simply based on the non-linearities in the Bagley plots, obtained either with capillary flow (e.g. Duvdevani and Klein (1967)) or slit flow (Laun 1983). According to Goubert et al. (2001), the method is rather unreliable due to the strong propagation of measurement and fitting errors. It is also difficult to separate temperature, pressure and slip effects with this technique (Goubert et al. 2001; Laun 2003). In these studies either the logarithmic pressure profile (slit rheometers), or the logarithmic relation between pressure drop and length to diameter ratio of the die have been expanded to a quadratic function to facilitate the fitting. Recently Pantani and Sorrentino (2005) improved the accuracy of the method by performing a series expansion of the exponential of the pressure drop in the Bagley plot. This method provides a better approximation as compared to the classical analysis when the product of the pressure coefficient and the entrance pressure does not exceed 0.5, which is generally the case for capillary rheometry.

The second direct method requires special set-ups that can perform viscosity measurements under elevated pressure. The high pressure rheometer used in the fifties by Maxwell and Jung (1957) consisted of a capillary die mounted between two steel cylinders, which were adapted to accommodate a plunger. These plungers made it possible to pressurize the melt in the die. Flow was created independently by moving the cylinder assembly, containing the die, relatively with respect to the two stationary plungers. A few decades later this double piston method was applied to slit rheometers by Kadijk and Van Den Brule (1994) and Mackley and Spitteler (1996). A simpler design to measure directly under elevated pressure is the enhanced exit pressure technique, first developed by Driscoll and Bogue (1990). Here a pressure chamber has to be attached underneath the die of a capillary rheometer. This method is also used in the present work; it will be discussed in further detail in the following sections. The previous designs are all based on pressure driven flow. Such designs have the disadvantage that the flow field is not uniform, causing tedious procedures for data analysis. To overcome these difficulties, Koran and Dealy (1999) developed a high pressure sliding plate rheometer based on drag flow. The important feature of this instrument is that the pressure, shear rate and shear stress are uniform in the sample, avoiding complicated data analysis procedures.

Indirect methods have also been proposed to determine the pressure dependency of the viscosity. Utracki (1983a, 1985) developed a semi-empirical method based on the free volume principle to determine the pressure dependency of the zero shear viscosity using PVT-data and the temperature

dependency of the zero shear viscosity. Using the same information, but considering the work required for expansion of a liquid to obtain a relation between viscosity and density, Cogswell and McGowan (1972) derived an equation from which they concluded that polymers with strong pressure dependency also exhibit strong temperature dependency. This was largely supported by the experimental results of Couch and Binding (2000) and Sedlacek et al. (2004).

In this paper, different routes for the calculation of the pressure coefficient from high pressure capillary rheometry data will be explored. Both a superposition method, as well as a direct calculation based on the definition of the pressure coefficient (eq. 1) will be evaluated and their practical usefulness discussed.

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## Materials and methods

Three different polymers were used in this study. The first two are polymethylmethacrylate (PMMA, Lucryl G77, BASF) and poly- $\alpha$ -methylstyrene-co-acrylonitrile (P $\alpha$ MSAN, Luran KR 2556, BASF). Based on their chemical structure, these polymers are expected to have a large pressure dependence of the viscosity. Their weight average molecular weight is 88000 g/mole and 82000 g/mole respectively. The third polymer is a low density polyethylene of  $M_w = 110000$  g/mole (LDPE, Lacqtène, Elf Atochem), a polymer that is known to exhibit a smaller pressure dependency than the PMMA and P $\alpha$ MSAN samples. The latter samples have been dried during 8 h in a vacuum oven at 80 °C prior to the rheological measurements.

The viscosity curves were first determined with ambient exit pressures, using a classical Göttfert 2002 capillary rheometer. For the measurements under elevated pressures the enhanced exit pressure technique was used by attaching a pressure chamber, developed by Göttfert Werkstoff-Prüfmaschinen GmbH, underneath the capillary. A schematic of the experimental setup is given in Fig. 1. The needle valve of the pressure chamber can be moved vertically to vary the level of constriction, thereby changing the back pressure in the chamber. Exit pressures ranging from 5 to 70 MPa were achieved while the temperature was 210 °C in all experiments. The melting time before starting the measurements was kept at 4 minutes. Shear rates ranging from 5 s<sup>-1</sup> to 200 s<sup>-1</sup> were applied while keeping the exit pressure at a well defined setpoint. The resulting pressure drops over the capillary were measured. The pressure transducers are Dynisco class 1 transducers with a nominal range of 50, 100, 140 and 200 MPa and an accuracy of 0,5 % of full scale output. The temperature of the pressurized chamber was controlled by an external Eurotherm regulator with a Pt100 sensor. A capillary with length  $L = 30$  mm and diameter  $D = 1$  mm has been used throughout.

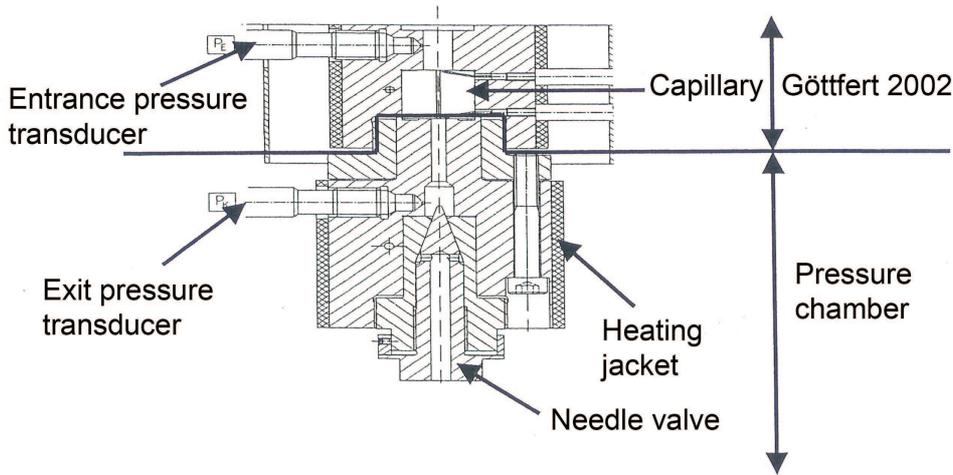


Fig. 1 Schematic of the pressure chamber attached beneath the capillary die

### Experimental results and data handling

From the pressure drops and volumetric flow rates uncorrected viscosity curves are obtained. Such a data set is shown for PMMA in Fig. 2. In order to evaluate the effect of pressure on the viscosity, the necessary corrections should first be applied to the data. In principle, the wall shear stress has to be obtained on the basis of the pressure drop over the capillary with length  $L$ , where fully developed, stationary, isotherm and laminar flow occurs. In a capillary die, the measured pressure drop will always include an exit and entrance pressure loss which has to be accounted for by means of the Bagley correction. Since the exit losses are typically much smaller than the entrance losses, the former are assumed to be negligible in this discussion.

At atmospheric pressure, the Bagley corrections for the polymers used in this work were found to be small (insignificant for PMMA and P $\alpha$ MSAN and less than 5 % for LDPE). The question remains however, how this Bagley correction changes with increasing pressure. From an equation derived by Cogswell (1972), it follows that the entrance pressure loss  $\Delta P_{entrance}^2 \sim \eta_s \cdot \eta_e$ , with  $\eta_s$  and  $\eta_e$  respectively the shear and elongational viscosity. Since the shear viscosity will have a proportional influence on the total pressure drop as on the entrance pressure loss, the importance of  $\Delta P_{entrance}$  at elevated pressure depends solely on the pressure dependence of the elongational viscosity. For most polymers the elongational pressure coefficient is different from its counterpart in shear flow (Binding et al. 1998; Couch and Binding 2000; Laun 2004; Sedlacek et al. 2004; Carreras et al. 2006). For instance, for P $\alpha$ MSAN at 210 °C, so-called throttle coefficients relating entrance and total pressure drops to exit pressure, are available (Laun 2004). Using these throttle coefficients and the measured pressures at the exit and entrance of the die, this would, for the highest exit pressures used here, result in a ratio  $\Delta P_{entrance}/\Delta P_{tot}$  that is approximately 5 times higher than at atmospheric conditions. Since the Bagley correction at atmospheric conditions was insignificant for P $\alpha$ MSAN, it is fair to assume that this is

also approximately the case at elevated pressures. Regarding the similar flow behaviour of PMMA and P $\alpha$ MSAN (Laun 1998), it seems justified to expect a comparable behaviour for PMMA.

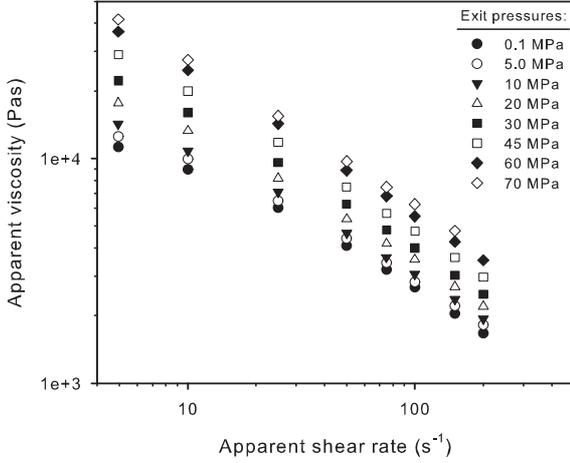
For LDPE the situation is slightly different. Carreras et al. (2006) studied 4 different grades of PE, of which two grades of LDPE, and found that for each of them the elongational pressure coefficients were equal or smaller than those in shear flow. Similar results for LDPE were obtained by other authors (Couch and Binding 2000; Laun 2004; Sedlacek et al. 2004), while one author reported slightly higher pressure coefficients for LDPE in elongational flow than in shear flow (Binding et al. 1998). Hence,  $\Delta P_{entrance}$  will, at most, increase with pressure to the same extent as  $\Delta P_{tot}$ . Since the Bagley correction at atmospheric conditions was smaller than 5 %, it can be concluded that this will also be the case at elevated pressure. Hence, Bagley corrections have been neglected throughout and all measurements are carried out using a single die with a length of 30 mm and a diameter of 1 mm. Because the polymers under investigation are not expected to experience slip under the present conditions, the diameter of the die was not varied.

The conventional Weissenberg-Rabinowitch correction was applied to deal with the non-Newtonian behaviour of the polymers by converting the measured apparent shear rate  $\dot{\gamma}_s$  to true wall shear rate  $\dot{\gamma}_w$ . The corrected data were then fitted with the Ellis model in order to be able to calculate viscosities at the same shear rates at every pressure level. The results of these calculations, together with the uncorrected viscosity data for PMMA at an exit pressure of 60 MPa, are shown in Fig. 3 (data at constant mean pressure: see further).

To judge the possible effect of viscous heating, the Nahme number was calculated (Macosko 1994):

$$Na = \frac{\varepsilon \eta_w \dot{\gamma}_w^2 R^2}{4k} \quad (2)$$

where  $k$  is the thermal conductivity of the polymer,  $\varepsilon$  the temperature coefficient of viscosity and  $R$  the radius of the capillary die. For LDPE the Nahme numbers varied between 0.00028 and 0.072 under all experimental conditions, the



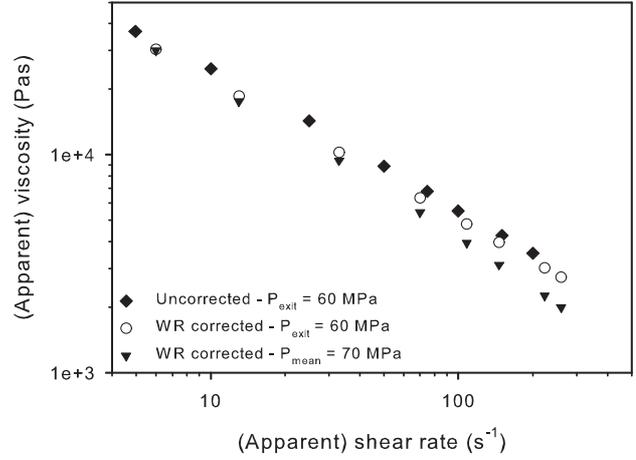
**Fig. 2** Viscosity curves for PMMA ( $T = 210\text{ }^{\circ}\text{C}$ ) at various exit pressures

highest values occurring for data with a combination of high pressure and high shear rate. For PMMA and P $\alpha$ MSAN the highest values obtained were 3.7 and 2.8. Deviations of the measured viscosities due to viscous heating can be expected for  $Na > 1$  (Macosko 1994). Therefore, all data points that gave rise to Nahme numbers above 1 have not been used in the present analysis.

As was already mentioned, the measurements were performed using a series of fixed exit pressures in the pressure chamber. Depending on the applied shear rate, the same exit pressure will lead to different mean pressures in the capillary die. Hence, since only viscosities defined at a certain mean pressure represent a real material property, a calculation of viscosity curves at constant mean pressure is needed. The resulting curves are more easily interpretable and are required to apply the superposition method on the data (see next section). Determining the mean pressure in the capillary is a nontrivial problem, since it is not possible to measure the pressure in the middle of the die directly. Other methods are necessary in order to evaluate the mean pressure. Assuming a linear pressure profile in the die, the mean pressure can simply be estimated as the arithmetic mean of the pressures at the entrance and exit of the die. In reality however, the pressure profile is non-linear as a result of the exponential pressure dependency of the viscosity. Oosterlinck (2000) slightly modified an expression derived by Denn (1981) and obtained an expression for the pressure profile over the die:

$$P(x) = \frac{-1}{\beta} \ln \left( \exp(-\beta P_{exit}) - \frac{2\beta}{R} \eta_{atm} \dot{\gamma}_w x \right) \quad (3)$$

where  $\eta_{atm}$  is the viscosity at atmospheric pressure,  $x$  is the position in the capillary die measured from the exit and  $P_{exit}$  is the exit pressure. Recently Laun (2003) showed that, for high shear rate capillary rheometry, the curvature of the pressure profile originates from the combined effect of pressure and dissipative heating. This author derived an expression

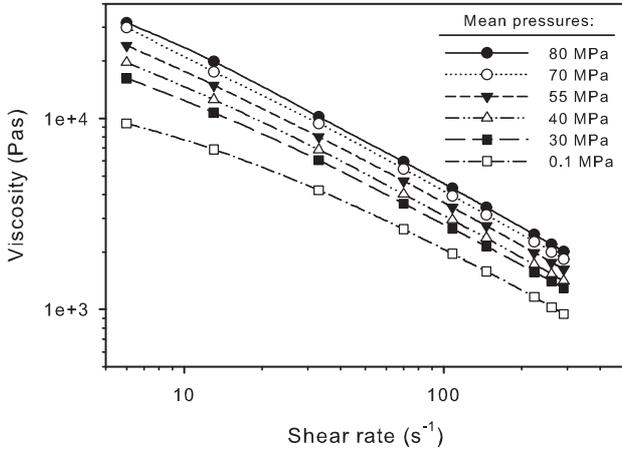


**Fig. 3** Weissenberg-Rabinowitch (WR) correction and importance of the used reference pressure for PMMA ( $T = 210\text{ }^{\circ}\text{C}$ )

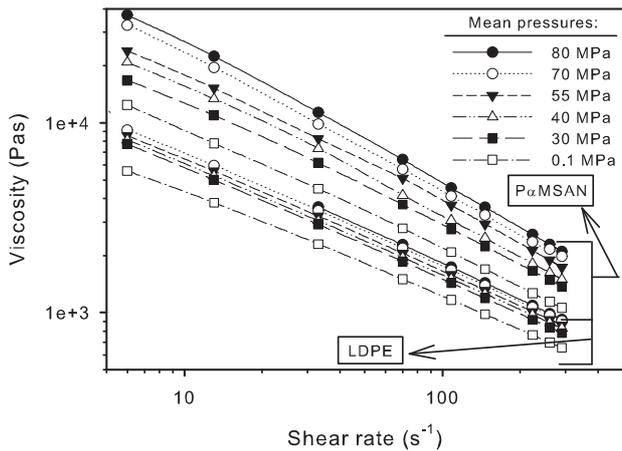
for the pressure profile which takes into account both effects. Here, the effect of viscous heating is neglected because the Nahme numbers were restricted to sufficiently low values. Eq. 3 is equivalent to the expression derived by Laun (2003) (eq. 15 in the original paper) with the dissipation heating coefficient being zero. The deviation from linearity increases with increasing pressure drops, and thus increasing exit pressures and shear rates. As an example, its importance was examined for PMMA at the rather extreme values of an exit pressure of 60 MPa and a shear rate of  $290\text{ s}^{-1}$ . By integrating eq. 3 over the length of the capillary, it is possible to determine the true pressure in the middle of the die. Here a difference of 7 % with the arithmetic mean between entrance and exit pressure of the die was obtained. Because the deviation of 7 % is an upper limit for the measurements presented here, use of the simple linear approximation is justified within engineering approximation.

By using the exponential pressure dependency of the viscosity (see eq. 1, keeping the shear rate constant), viscosities were recalculated to a series of arithmetic mean pressures (0.1, 30, 40, 55, 70 and 80 MPa) for every shear rate. As a reference pressure, the data point with mean die pressure closest to the target mean pressure was used. Several viscosity curves at a series of constant exit pressures are thus combined into one curve at constant mean pressure. This procedure clearly causes substantial data handling which is the major drawback of the enhanced exit pressure technique as compared to the double piston rheometers where the mean pressure can be controlled explicitly. The significance of the reference pressure is illustrated in Fig. 3, which shows viscosity data for PMMA at a constant exit pressure of 60 MPa as well as data at a constant mean pressure of 70 MPa. As can be seen, the slope of the curve is significantly affected.

The fully corrected viscosity curves for the three polymers are given in Figs. 4 and 5. These figures clearly show



**Fig. 4** Viscosity curves for PMMA ( $T = 210\text{ }^{\circ}\text{C}$ ) for a series of mean pressures



**Fig. 5** Viscosity curves for P $\alpha$ MSAN and LDPE ( $T = 210\text{ }^{\circ}\text{C}$ ) for a series of mean pressures

that increasing the pressure can have a substantial effect on the viscosity of polymer melts. For instance, for PMMA at high shear rates the viscosity doubles by increasing the pressure from atmospheric to 80 MPa, at low shear rates it even triples. Figs. 4 and 5 also illustrate that both PMMA and P $\alpha$ MSAN have a relatively large pressure dependency as compared to LDPE. The latter is not surprising since PMMA and P $\alpha$ MSAN have bulky sidegroups, which stiffen the polymer structure. The pressure dependence of the viscosity is associated with the presence of free volume: increasing the pressure will reduce the free volume and hereby increase the interactions occurring during flow. Less flexible chains are more susceptible to increased interactions and their viscosity will hence show a larger pressure dependency (Couch and Binding 2000).

## Determination of the pressure coefficients

In this section different methods will be used to derive the pressure coefficient  $\beta$  from the corrected data sets of the previous section. Firstly the pressure coefficient will be calculated directly (see eq. 1). These methods have the advantage that viscosity data versus shear rate or versus shear stress can be used directly without calculating viscosity curves at constant mean pressure. In addition, a superposition method will be applied to the data in Figs. 4 and 5 and its relation to the directly calculated pressure coefficients will be discussed.

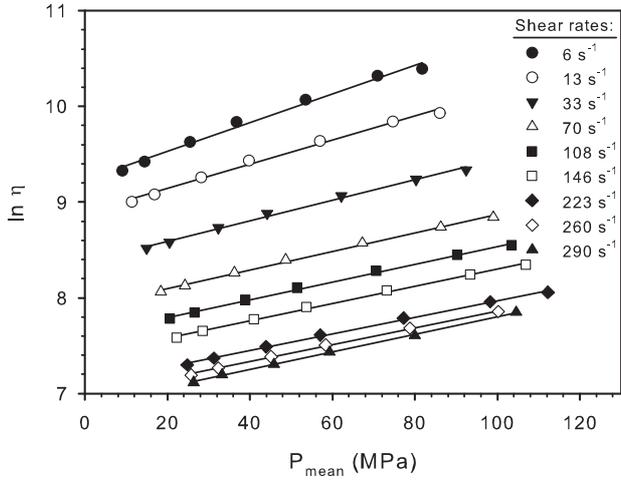
Method 1: Direct calculation of the constant shear rate pressure coefficient

By using the definition of the pressure coefficient at constant shear rate (eq. 1),

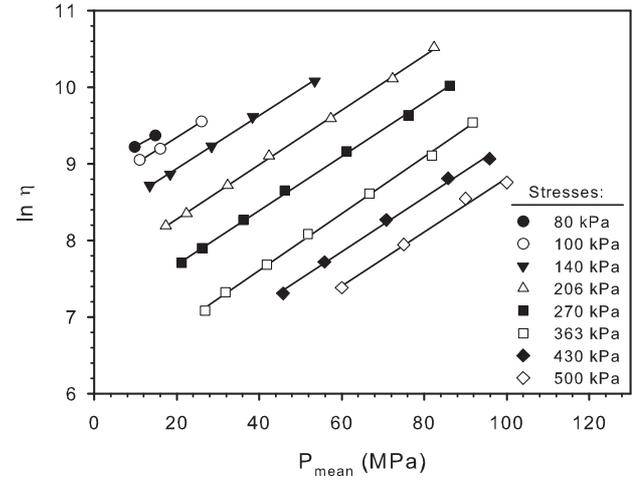
$$\beta_{\dot{\gamma}} = \left( \frac{d \ln \eta}{dP} \right)_{T, \dot{\gamma}} \quad (4)$$

it is possible to calculate  $\beta_{\dot{\gamma}}$  as the slope of the curves of the logarithm of the viscosity at a given shear rate, plotted versus the mean pressure in the die. Such an approach can lead to coefficients that depend not only on pressure and temperature but also on shear rate. Hence, such a procedure will not lead to a real thermodynamic property of the polymer melt (Goubert et al. 2001). Yet, it has been commonly used in literature (Herrmann and Knappe 1969; Steuten et al. 1994; Binding et al. 1998; Koran and Dealy 1999; Oosterlinck 2000; Goubert et al. 2001), mainly because of its ease-of-use.

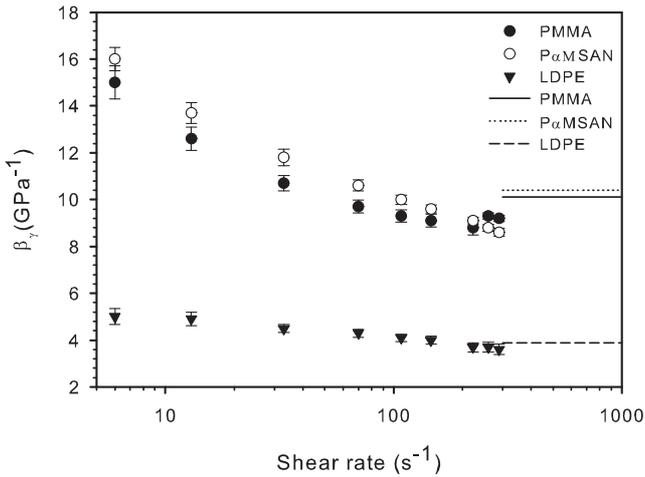
This approach is illustrated in Fig. 6 for PMMA. Viscosity values were obtained after Weissenberg-Rabinowitch correction and subsequent fitting with an Ellis model (see data handling section). From the known exit pressure and pressure drop for every data point, the corresponding arithmetic mean pressure was calculated. It can be noted that the data at the lowest shear rates show a slight downward curvature with respect to the linear regression line. This will be discussed further. The resulting values of  $\beta_{\dot{\gamma}}$  for the three polymers are summarised in Fig. 7. The error bars represent the standard deviation on  $\beta_{\dot{\gamma}}$ , estimated on the basis of a least squares fit for a linear regression through the data in Fig. 6. The pressure dependence of the viscosity for PMMA and P $\alpha$ MSAN is clearly much higher than that for the more flexible LDPE chains. Moreover, within measuring accuracy, it is hardly possible to distinguish between the pressure coefficients of PMMA and P $\alpha$ MSAN. For all three polymers, it is clear that the pressure coefficients decrease with increasing shear rate and tend to reach a constant value in the power law region of the viscosity curves. This constant value will be used in the evaluation section.



**Fig. 6** Determination of  $\beta_\gamma$  at several shear rates for PMMA ( $T = 210^\circ\text{C}$ )



**Fig. 8** Determination of  $\beta_\sigma$  at several shear stress levels for PMMA ( $T = 210^\circ\text{C}$ )



**Fig. 7** Pressure coefficients  $\beta_\gamma$  (direct method: *symbols*) versus shear rate and pressure coefficients  $n \cdot \beta_\sigma$  (superposition method: *lines*) ( $T = 210^\circ\text{C}$ )

**Method 2: Direct calculation of the constant shear stress pressure coefficient**

Secondly, an adapted version of the direct calculation method for the pressure coefficient will be discussed. It is based on the definition of the pressure coefficient at constant shear stress:

$$\beta_\sigma = \left( \frac{d \ln \eta}{dP} \right)_{T, \dot{\gamma}} \quad (5)$$

In order to calculate  $\beta_\sigma$ , the data are first converted to obtain viscosities as a function of shear stress by using the Ellis model for the data after the Weissenberg-Rabinowitch

correction. For every selected value of the shear stress, the logarithm of these viscosities is plotted versus the arithmetic mean pressure in the die, similar to Fig. 6. This is illustrated for PMMA in Fig. 8. The accuracy of the regression seems to be similar for all stress levels, in contrast with the curves in Fig. 6. It should be noted however, that less data points are available at the lowest shear stresses.

The resulting values for  $\beta_\sigma$  are shown in Fig. 9. The error bars again represent the standard deviation on  $\beta_\sigma$  estimated on the basis of the least squares fit. The most important property of this pressure coefficient is the fact that its value does not depend on shear stress, even for the shear rates below the power law region. Hence,  $\beta_\sigma$  seems to be a more appropriate indicator than  $\beta_\gamma$  to describe pressure dependence of viscosities of polymer melts e.g. in process simulations. The relation between  $\beta_\sigma$  and  $\beta_\gamma$  will be discussed in the evaluation section.

**Method 3: Calculation of the pressure coefficients by superposition**

Rather than calculating the pressure coefficient directly, its value can be extracted from the superposition method. The drawback of this method is the rather involving data handling needed to obtain the viscosity curves at constant mean pressure (see data handling section).

According to Couch and Binding (2000) the three processing parameters (shear rate, temperature and pressure) that influence viscosity can be taken into account by defining a single shift factor  $a_{TP}$ :

$$\frac{\eta(\dot{\gamma}, P, T)}{a_{TP}} = \eta(a_{TP} \cdot \dot{\gamma}, T_{ref}, P_{ref}) \quad (6)$$

Often, the effect of pressure and temperature can be separated from the effect of shear rate, resulting in a shift factor

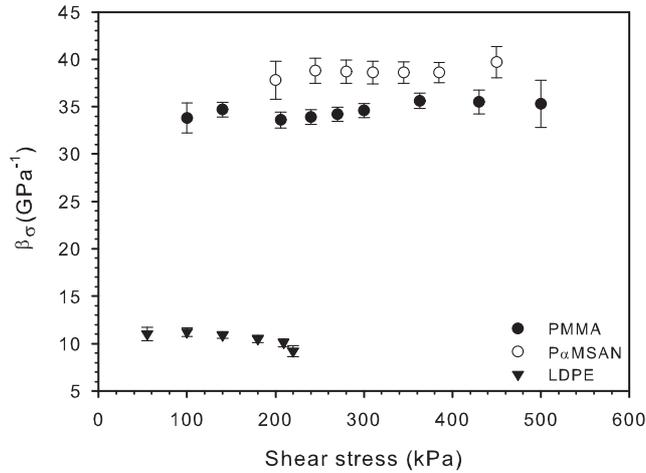


Fig. 9 Pressure coefficients  $\beta_\sigma$  versus shear stress ( $T = 210\text{ }^\circ\text{C}$ )

$a_{TP}$  which is shear rate independent. Viscosity curves at different pressures and temperatures can then be shifted onto a mastercurve by using the appropriate shift factor  $a_{TP}$  for each combination of pressure and temperature. Couch and Binding (2000) showed this to be valid in the power law region of the flow curves for most of the commonly used thermoplastic polymers, implying that the power law index is independent of pressure and temperature under the conditions investigated.

Different expressions can be used to model the pressure and temperature dependence of this shift factor. Couch and Binding (2000) proposed to describe  $a_{TP}$  by combining Barus- and Arrhenius terms in a product, which led to the following expression:

$$a_{TP} = a_P \cdot a_T = \exp(\beta_*(P - P_{ref})) \cdot \exp\left(\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \quad (7)$$

where  $E$  is the activation energy and  $R$  the universal gas constant.  $\beta_*$  defines a pressure coefficient. The Arrhenius equation usually only applies over a limited temperature range, as was the case in the measurements of Couch and Binding (2000). For wider temperature ranges other expressions are more suitable to describe the temperature dependence of the shift factors, but the temperature effect can not always be separated from the pressure effect (Kadijk and Van Den Brule 1994; Sedlacek et al. 2004). It should be mentioned that expressions are available to describe the combined effects of pressure and temperature (e.g. Utracki (1983b)). For instance, an equation proposed by Fillers and Tschoegl (1977), based on free volume arguments, has proven to be useful in this respect. However measurements at a single temperature are discussed in the present paper and consequently only the Barus term will be of relevance. Hence, an appropriate expression for the pressure coefficient  $\beta_*$  is given by:

$$\beta_* = \left(\frac{d \ln a_P}{dP}\right)_T \quad (8)$$

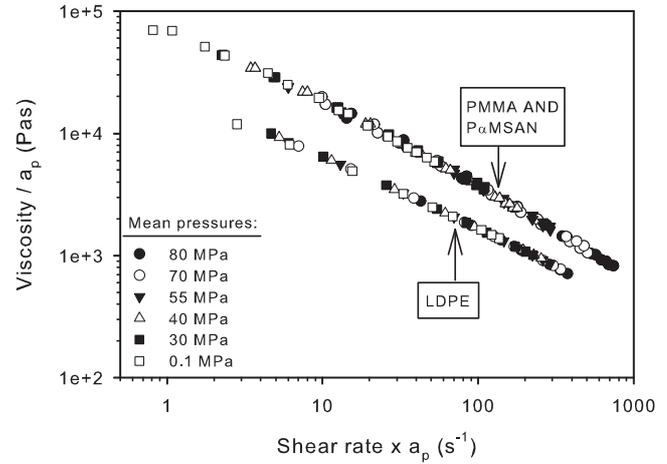


Fig. 10 Mastercurves using  $P_{mean} = 55\text{ MPa}$  as the reference state ( $T = 210\text{ }^\circ\text{C}$ )

For polymer systems that obey the time-temperature-pressure superposition principle all the relaxation times have the same dependence on either temperature or pressure. Therefore the results of Couch and Binding (2000) can be extended to the lower shear rate region where the curves no longer obey the power law. This is interesting from an application point of view because again, a single parameter will suffice to describe the pressure effect on the total viscosity curve.

Although the method should apply to the whole flow curve, the current set-up did not provide an accurate measurement of the zero-shear viscosity under pressure. Hence, in order to improve the accuracy of the superposition, only the power law parts of the curves from Figs. 4 and 5 were used in the calculation of the shift factors. The reference curve was chosen to be the viscosity curve for a mean pressure of 55 MPa. The curves were then shifted by multiplying the shear rate and dividing the viscosity by the same shift factor  $a_P$  (see eq. 6) until they superposed on this reference curve. A least squares error algorithm was used to determine these shift factors. It should be mentioned however that by using equal shift factors for viscosity and shear rate, the vertical shift factor  $\frac{T_P}{T_0 \rho_0}$  is neglected (Dealy and Wissbrun 1999). Since melts are nearly incompressible, this vertical shift factor is indeed very close to one.

The mastercurves obtained by this method are shown in Fig. 10. Data points in the transition region of the flow curves are included and the achieved superposition is good for all available data points. The mastercurves for PMMA and P $\alpha$ MSAN nearly coincide. The obtained superposition suggests that the power law exponents for the three polymers are, within experimental error, independent of pressure. This is confirmed by the values of these exponents in Table 1, which show little variation with pressure. It needs to be stressed that the superposition method is based on shift-

**Table 1** Results of the superposition method (T = 210 °C)

$P_{mean}$ (MPa)	PMMA		P $\alpha$ MSAN		LDPE	
	$\beta_*$ (GPa <sup>-1</sup> )	n	$\beta_*$ (GPa <sup>-1</sup> )	n	$\beta_*$ (GPa <sup>-1</sup> )	n
30	39.44	0.30	38.67	0.32	10.16	0.40
40	37.01	0.27	32.50	0.27	8.80	0.40
55	36.66	0.27	36.85	0.30	10.53	0.39
70	36.81	0.26	33.37	0.26	10.31	0.39
80	34.66	0.26	37.41	0.27	10.27	0.38
Mean:	37.01		36.69		10.04	

ing the viscosity versus shear rate curve over 45 °. This implies that  $\beta_*$  is a pressure coefficient for constant shear stress (Laun 2003). Hence, as will be discussed in the next section,  $\beta_*$  and  $\beta_\sigma$  are closely related to each other. An overview of the coefficients  $\beta_*$ , obtained from the shift factors by using eq. 7, for the different pressure levels is given in Table 1 (see also next section). To obtain a pressure coefficient at 55 MPa a reference pressure of 70 MPa was used. A mean value for the pressure coefficient was obtained by using eq. 8 and the shift factors for the different pressure levels.

### Evaluation of the different methods

In the previous sections, three different pressure coefficients were calculated: a pressure coefficient  $\beta_\gamma$  at constant shear rate, a pressure coefficient  $\beta_\sigma$  at constant shear stress and a pressure coefficient  $\beta_*$  derived from superposition of the viscosity curves. Their values have been summarized in Table 2.

The calculation of the pressure coefficient for a constant shear rate is somewhat hampered in the transition region. The transition from Newtonian to shear thinning shifts to lower shear rates when increasing the pressure (Ferry 1970), which causes a deviation from the exponential dependence between pressure and viscosity in this region. This can be clearly seen in Fig. 6 where, for the lowest shear rates, the points at intermediate pressures are situated above the regression line, indicating that the pressure dependence of the viscosity is slightly diminishing with increasing pressure. For practical purposes this manner of calculating  $\beta_\gamma$  can however still be used, as is confirmed by the fact that the regression coefficient for the fit at the lowest shear rate still reaches 0.989. Decreasing values of the pressure coefficient with increasing shear rate, as in Fig. 7, have been reported frequently in literature (Herrmann and Knappe 1969; Driscoll and Bogue 1990; Koran and Dealy 1999; Oosterlinck 2000; Goubert et al. 2001; Liang 2001). Pressure coefficients at high shear rates are thus the result of the combined influence of pressure and shear thinning and can not be interpreted easily (Driscoll and Bogue 1990; Liang 2001). When calculating pressure coefficients at constant shear stress, the values remain constant even in the transition region (see Fig. 9). An analogous result was presented earlier for the temperature effect around the transition to shear thinning (Lomellini

**Table 2** Overview of the different pressure coefficients (T = 210 °C)

Polymer	$\beta_\sigma$ (GPa <sup>-1</sup> )	$\beta_*$ (GPa <sup>-1</sup> )	$\beta_{HS}$ (GPa <sup>-1</sup> )	$n\beta_*$ (GPa <sup>-1</sup> )
PMMA	35	37	9.2	10.1
P $\alpha$ MSAN	39	37	8.6	10.4
LDPE	10	10	3.6	3.9

and Ferri 2000): the higher the shear rate, the lower the increase of viscosity for a decrease in temperature whereas the temperature effect remained constant when plotting the data versus shear stress. Hence, only the pressure coefficients at constant shear stress can be seen as a key thermodynamic property of the melt.

Although different data treatments lead to different values, the obtained pressure coefficients are interrelated. The superposition method is in fact equivalent to shifting the viscosity curves at a constant shear stress. Hence, the pressure coefficient at constant shear stress and the coefficient obtained from the superposition method should be equivalent. From Table 2, it can be seen that the values of  $\beta_\sigma$  and  $\beta_*$  are indeed very similar. From a practical point of view, a perfect superposition of the pressure dependent viscosity over the whole shear rate range requires accurate low shear rate data. This range of shear rates is however not accessible with the enhanced exit pressure technique used here. The direct calculation of the pressure coefficient  $\beta_\sigma$  at constant shear stress then provides a useful alternative. Furthermore,  $\beta_\sigma$  can be obtained more readily from the data since it does not require the calculation of viscosity curves at constant mean pressures.

From Table 1, it is clear that within experimental error, the power law exponent can be regarded as independent of pressure. Couch and Binding (2000) reported that in the power law regime, the constant shear rate pressure coefficient indeed became independent of shear rate. This high shear rate limit, here denoted as  $\beta_{HS}$  is hence related to either  $\beta_*$  or  $\beta_\sigma$  by the relationship  $\beta_{HS} = n \cdot \beta_*$  (Couch and Binding 2000). The values of  $n \cdot \beta_*$  are included in Fig. 7 and Table 2 for comparison with  $\beta_{HS}$ . The data indeed confirm the proposed relationship, although pressure coefficients obtained from the superposition method show somewhat higher values. Most probably, this is caused by the fact that the power-law region is not yet fully reached.

It would be interesting to compare a theoretical value for the pressure coefficient with the experimentally obtained one. In literature, a semi-empirical correlation between viscosity and free volume has been used to calculate the pressure coefficient of viscosity from PVT-data (Utracki 1983a, 1985). This method uses the Simha-Somcynski equations of state to determine the free volume in the polymer for different values of pressure and temperature. Then the Doolittle equation between zero shear viscosity and free volume (Doolittle 1951) combined with temperature dependent zero shear viscosities is used to determine the pressure dependency of the zero shear viscosity. This analysis could only be performed here for the PMMA and P $\alpha$ MSAN grades since no PVT-data for the LDPE used were available. Based on this Simha-Somcynski equation, this resulted in a value for  $\beta$  of 51 GPa<sup>-1</sup> for P $\alpha$ MSAN. For PMMA a value of 30 $\pm$ 5 GPa<sup>-1</sup> could be found in literature (Van Hemelrijck 2000). These values should be compared with the ones in Table 2 for  $\beta_{\sigma}$ , which are 39 GPa<sup>-1</sup> and 35 GPa<sup>-1</sup> for P $\alpha$ MSAN and PMMA respectively. It is intriguing to observe that it is possible to estimate the pressure dependency of the viscosity without determining any pressure dependent viscosity. However, since only two polymers (with a quite similar flow behavior) were considered here, no general conclusions can be drawn in this respect.

## Conclusions

Viscosity measurements under elevated pressure were performed on PMMA, P $\alpha$ MSAN and LDPE melts, using a capillary rheometer extended with a pressure chamber. From the results it is clear that PMMA and P $\alpha$ MSAN have a very similar pressure dependence of viscosity. The LDPE, which consists of very flexible chains, is much less sensitive to pressure.

The goal of this work was to present and compare different data analysis schemes to obtain pressure coefficients from high pressure capillary data. Both constant shear rate and constant shear stress coefficients were calculated, although the constant shear rate pressure coefficient is not a real thermodynamic property of the polymer melts. In addition to this it is very inconvenient to use in models and process simulations since its value was observed to decrease with shear rate. When calculating pressure coefficients at constant shear stress, the values remain constant, even in the transition region. Therefore, pressure coefficients at constant shear stress should preferably be used. A direct calculation procedure was proposed to obtain these pressure coefficients. This procedure leads to results equivalent with those of the superposition method, which is commonly used in literature. However it reduces experimental and calculational efforts since it becomes unnecessary to measure zero-shear or high-shear viscosities and to recalculate to viscosity curves at constant mean pressures. The measured pressure coefficients were similar to those obtained from PVT-data.

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