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**A NATIONAL MEASUREMENT
GOOD PRACTICE GUIDE**

No. 90

Slip flow measurement
by capillary extrusion
rheometry



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Measurement Good Practice Guide No. 90

Slip flow measurement by capillary extrusion rheometry

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Abstract

Reliable characterisation of the rheological behaviour of materials is important for many reasons, whether it is for developing new materials with specific flow properties, design of processes using rheological data for existing materials or for quality control of materials in production processes. The occurrence or onset of slip in flow complicates both the measurement of properties and the modelling of flow behaviour. In the measurement of shear viscosity, the occurrence of slip flow is often not considered.

This Guide presents guidance for good practice in measurement of the slip velocity of molten plastics by capillary extrusion rheometry. It:

- describes capillary extrusion rheometry testing and its application to the determination of slip velocities,
- provides guidance on the measurement of slip velocities,
- presents results of the measurement of slip velocities, including results from an intercomparison, and
- presents an uncertainty analysis of slip velocity measurement.

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Slip flow measurement by capillary extrusion rheometry

Contents

	Foreword	
1	Scope	1
2	Introduction	1
3	Capillary die extrusion rheometry and its adaptation to slip flow measurement	2
3.1	Capillary extrusion rheometry	2
3.2	Experimental method for measurement of slip velocities using a capillary extrusion rheometer	4
3.3	Analysis to determine slip velocities by capillary rheometry following the Mooney approach	4
3.4	Summary of method	6
3.5	Guidance for slip velocity determination	7
3.5.1	Guidance on experimental procedure	7
3.5.2	Guidance on analysis to determine slip velocities	9
4	Example results	11
4.1	Slip velocity results	11
4.2	Intercomparison of slip velocity measurement	15
5	Uncertainty analysis of slip velocity measurements	17
5.1	Introduction	17
5.2	Uncertainty analysis for slip velocity	18
5.3	Evaluation of uncertainties for slip velocity	20
5.4	Discussion of uncertainties analysis	25
6	Summary	26
	References	28
	Appendix A: Symbols and definitions	31
	Appendix B: Slip flow – a brief review of the literature	33
	B.1: Slip flow mechanisms	33
	B.2: Mooney method for characterising slip flow	34
	B.3: Slip flow behaviour	36

Foreword

This Guide presents guidance for good practice in measurement of the slip velocity of molten plastics by capillary extrusion rheometry.

The information presented in this Guide has been gathered under a DTI funded programme of research *Measurements for Processability and Performance of Materials*, namely project *MPP7.4 Processing Behaviour of Multi-Phase Materials Measurements*.

This Guide is one of a series of Measurement Good Practice Guides covering various areas of polymer melt rheology [1-3].

This Guide provides guidance to technologists, laboratory staff and quality assurance personnel on how to characterise the rheological properties of molten plastics. A general familiarity with rheological testing is assumed. The objective of this Guide is to familiarise the operator with good practice for characterisation of the slip flow behaviour of polymers.

1 Scope

This Guide presents guidance for good practice in measurement of the slip velocity of molten plastics by capillary extrusion rheometry. It:

- describes capillary extrusion rheometry testing and its application to the determination of slip velocities, Sections 3.1 – 3.4,
- provides guidance on the measurement and analysis of slip velocities, Section 3.4,
- presents results of the measurement of slip velocities, including results from an intercomparison, Section 4,
- presents an uncertainty analysis of slip velocity measurement, Section 5,
- presents symbols and definitions for capillary extrusion rheometry and uncertainty analysis, Appendix A, and
- presents a review of relevant literature on slip flow measurement, Appendix B.

Example results are presented to illustrate the method, including results of an intercomparison of slip velocity measurements.

2 Introduction

Reliable characterisation of the rheological behaviour of materials is important for many reasons, whether it is for developing new materials with specific flow properties, design of processes using rheological data for existing materials, or for quality control of materials in production processes. The introduction of fillers and additives can significantly affect the flow properties of the base material, e.g. lubricants can be added to improve flow properties. For fillers the effect can be very significant at high filler levels. Measurement and modelling can be complicated by the onset or occurrence of phenomena not necessarily observed in the unfilled material, for example yield behaviour and slip flow.

Slip flow, the subject of this Guide, may occur due to the formation of a lubricating layer adjacent to the wall due to migration effects or where the polymer loses adhesion with the wall, Appendix B.1, the mechanism being dependant on the material. The method presented

here for measuring slip flow does not differentiate between these two mechanisms. The occurrence and magnitude of the slip flow has been related to the surface finish and material of construction of the die, the latter suggesting an adhesion mechanism. This clearly indicates that there will potentially be a sensitivity of results to such factors.

In the method presented, Mooney [4], a dependence of shear stress (or viscosity) on the diameter of capillary extrusion dies is observed, Appendix B.2. The magnitude of this dependence is used to determine the slip velocity. Although the Mooney method [4] can be applied to slit die geometries and to rotational rheometry, this Guide focuses on the measurement of slip velocity by capillary die extrusion rheometry. However, the principles presented herein can, in principle, be applied to slip velocity measurements using other methods. Examples of the slip flow behaviour of polymers presented in the literature are described in Appendix B.3.

This Guide, presenting guidance for good practice in measurement of the slip velocity by capillary extrusion rheometry of molten plastics, compliments the standard ISO 11443 on capillary and slit die rheometry testing of polymer melts [5].

3 Capillary die extrusion rheometry and its adaptation to slip flow measurement

3.1 Capillary extrusion rheometry

The capillary die extrusion rheometry method for thermoplastics, upon which this work is based, is described in ISO 11443 [5], Figure 1. Capillary extrusion rheometry is used predominantly to determine the high rate shear viscosity of molten polymers. The pressure drops across one or more dies at various volume flow rates are measured and from these, shear viscosity values are calculated, equations 1 - 3.

An apparent shear viscosity η_a , corrected for entrance pressure effects, is defined by

$$\eta_a = \frac{\tau}{\dot{\gamma}_a} \quad (1)$$

where τ is the shear stress given by

$$\tau = \frac{(P - P_e)R}{2L} \quad (2)$$

and $\dot{\gamma}_a$ is the apparent shear rate given by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (3)$$

where P is the extrusion pressure and P_e is the entrance pressure drop obtained at the same apparent shear rate, R is the die radius, L is the die length, and Q is the volume flow rate.

Corrections can be applied to the data to take into account errors in the measurement method. Various “shear viscosities” – entrance pressure drop corrected and Rabinowitsch corrected – can be determined [5]. The method is suitable for generating quantitatively accurate data for modelling as well as for quality control.

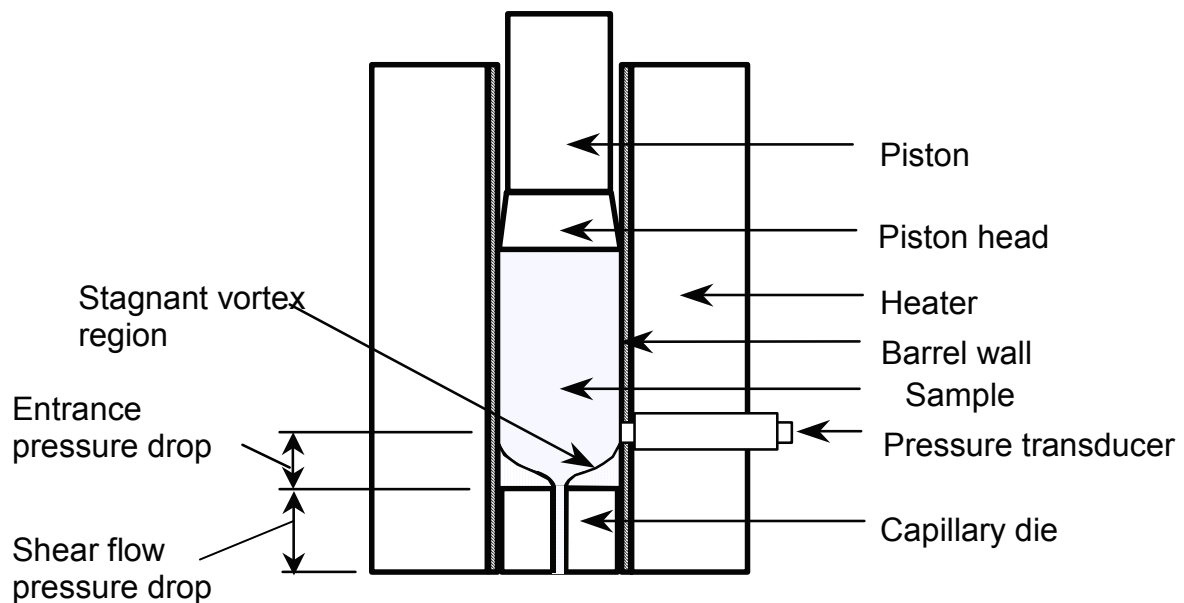


Figure 1: Schematic diagram of a capillary extrusion rheometer

The results of an international intercomparison on capillary extrusion rheometry indicated that the repeatability of shear viscosity values for a high density polyethylene and a glass-fibre filled polypropylene was up to 24%, and reproducibility up to 34%. For entrance pressure drop determination the repeatability was up to 20% and the reproducibility up to 56%. The results are presented in detail, along with an analysis for the determination of the uncertainties of measurement, by Rides and Allen [5, 6].

3.2 Experimental method for measurement of slip velocities using a capillary extrusion rheometer

The Mooney method requires the measurement by capillary extrusion rheometry of the shear stress as a function of apparent shear rate of a polymer melt using different diameter dies. The standard methodology as outlined above and detailed in the standard ISO 11443 is used without modification for the measurement of the shear stress – shear rate behaviour for each of the die diameters. Recommendations for good practice for such measurements for the determination of slip velocities are made in Section 3.4.

This Good Practice Guide focuses on the use of capillary dies only, although it is considered that the recommendations can be generally applied to the use of slit dies.

3.3 Analysis to determine slip velocities by capillary rheometry following the Mooney approach

The analysis of capillary die extrusion rheometry data for the determination of slip velocity following the approach first proposed by Mooney [4] is presented here. The term “slip” is used here to signify either a large velocity change near the wall that could be attributed to either a thin, high shearing layer with zero wall velocity, or to a non-zero wall velocity.

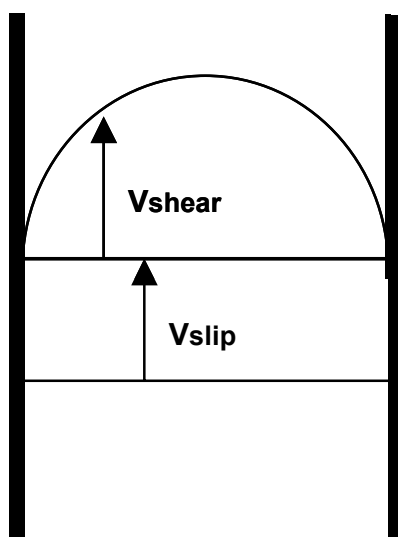


Figure 2: Schematic diagram of slip flow velocity profile

Slip flow can be modelled by the addition of a slip flow velocity to the shear flow velocity profile, Figure 2. This assumes that the slip layer can support a shear stress that is necessary for the shear flow to occur. To maintain continuity:

$$Q_T = Q_{shear} + Q_{slip} \quad (4)$$

where the subscripts T , shear and slip represent the total volume flow rate and the shear and slip volume flow rate components of the total volume flow rate respectively. The fluid is assumed to be incompressible. For flow in a capillary die of radius R the slip flow flow rate Q_{slip} is given by:

$$Q_{slip} = V_s \pi R^2 \quad (5)$$

where V_s is the slip velocity.

By definition, shear viscosity η is the ratio of shear stress τ to shear-rate $\dot{\gamma}$:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (6)$$

The shear viscosity power-law model can be written as:

$$\eta = K \dot{\gamma}^{n-1} \quad (7)$$

where K and n are constants. For a power-law fluid the true wall shear-rate $\dot{\gamma}_w$ for flow in a cylindrical die (based on the true velocity profile of a power-law fluid rather than on that of a Newtonian fluid) is given, according to Brydson [7] (based on Rabinowitsch [8]) by:

$$\dot{\gamma}_w = \left[\frac{3n+1}{4n} \right] \frac{4Q}{\pi R^3} \quad (8)$$

Using the above equations the following expression for the total flow rate in the presence of slip can be derived:

$$Q_T = \left[\frac{n\pi R^3}{3n+1} \right] \left[\frac{\tau_w}{K} \right]^{1/n} + V_s \pi R^2 \quad (9)$$

This expression predicts that a plot of $\log Q_T$ versus $\log \tau_w$ will not necessarily give a straight-line fit as would be the case for a power-law fluid with a slip velocity of zero. The dependence of the slip velocity V_s on wall shear stress will determine the shape of the plot.

Following Lupton and Regester [9] equation 9 can be re-written in the form:

$$\frac{4Q_T}{\pi R^3} = \left[\frac{4n}{3n+1} \right] \left[\frac{\tau_w}{K} \right]^{1/n} + \frac{4V_s}{R} \quad (10)$$

If the wall shear stress is constant and assuming n and K do not vary with flow rate, then:

$$\boxed{\frac{4Q_T}{\pi R^3} = \text{constant} + \frac{4V_s}{R}} \quad (11)$$

This expression predicts that, for a given wall shear stress, a plot of apparent wall shear-rate $4Q_T/\pi R^3$ versus $1/R$ will have a gradient of $4V_s$ thus enabling the slip velocity V_s to be determined.

3.4 Summary of method

In summary:

- i) Measure the shear stress – apparent shear rate behaviour of the material in accordance with ISO 11443 using at least two sets of dies of different diameter, yielding one flow curve for each diameter.
- ii) Determine, by interpolation, the apparent shear rates corresponding to selected shear stress values for each die diameter.
- iii) For each selected shear stress, plot the (interpolated) apparent shear rate values versus the reciprocal of the die radius, and determine the gradient of the linear plot to the data
- iv) Calculate the slip velocity, given by the gradient in iii) divided by 4.
- v) Evaluate the uncertainties in the results.

3.5 Guidance for slip velocity determination

3.5.1 Guidance on experimental procedure

The following issues should be considered in carrying out testing to measure slip velocities.

The dies should all be of the same material of construction, and their finish shall be the same.

There is evidence in the literature, e.g. Appendix B.1, to indicate that the slip behaviour can be significantly affected by both the material of construction and the finish of the die (in ISO 11443 [5] the surface finish is specified as having a roughness of R_a of less than $0.25\ \mu\text{m}$). Thus in using several dies to determine slip velocity it is important that these factors are the same in each. Ideally the choice of material and finish of the die should be governed by the application for the data, e.g. for flow simulation of extrusion processing the material and finish of the capillary dies should be the same as that used for the extrusion processing die.

Measurements should be performed preferably with dies of at least 3 different diameters

Although only two different diameters are necessary to determine slip velocities the use of only two dies does not provide an understanding of the confidence in the data, and whether the slip model fits the measured behaviour well. If the behaviour is in accordance with the Mooney model, the plots of constant shear stress data on apparent shear rate versus the reciprocal of the die radius axes should be linear. If only two different die diameters are used then a perfect fit straight line is always obtained, but no information on the quality of the fit of the material's data to the model is generated. Such information is invaluable for reliably determining the uncertainties in the slip velocities, as demonstrated in Section 5.

Selection of die diameters

The selection of die diameters is not straight forward as several conflicting factors influence the choice. These factors are:

The diameter affects the shear rate and shear stress ranges over which measurements can be made.

A broader range of diameters provides a greater difference in the shear stress –

shear rate curves obtained for different diameters. This reduces the uncertainties in the results of the slip velocity analysis, as the differences in behaviour are used to determine the slip velocities. The effect of the diameter range on the uncertainties can be estimated using the uncertainty analysis presented in Section 5.

A broader range of diameters reduces the overlap in shear rates and, more significantly, shear stresses over which data are obtained for all dies.

Higher shear rates and shear stresses can be achieved using a smaller diameter die for a given extrusion rheometer and pressure transducer (or pair of pressure transducers in a twin-bore instrument). Although the range of shear stresses and shear rates for a given die can potentially be extended by the use of different pressure transducers, changing pressure transducers is time consuming and potentially introduces additional uncertainties due to differences in transducer precision. Furthermore, the extrusion pressures and flow rates (which control the shear rates) are limited by the specification of the extrusion rheometer itself.

Diameters in the range 0.5 mm to 2 mm were used for the testing and intercomparison reported on in Section 4.

Die entry geometry

All the dies shall have the same die entry geometry, e.g. flat entry, to ensure consistency in measurements.

Bagley corrected shear stress data shall be used

The Mooney analysis requires the use of true shear stress data. If a Bagley end-correction for the entrance pressure drop [5] is not made, e.g. using a short or zero length die, then only apparent shear stress data can be obtained. The Bagley correction can account for a significant proportion of the total extrusion pressure drop for filled materials [10]. As the Bagley correction is likely to be a function of the contraction ratio [6, 10] then the Bagley correction shall be made using data from dies of the same diameter.

If only one short die is available then the Bagley correction could be made for all the different diameter long dies by using the short die extrusion pressure data at equivalent apparent shear rates (as opposed to flow rates). However, this procedure is not recommended in preference to using the same diameter short die(s) for Bagley correction.

Measurement procedure

It is possible that the slip behaviour may be history dependant (e.g. development of a filler-depleted zone adjacent to wall). To minimize the variation in results due to such an effect it is recommended that all tests are performed in a consistent manner, e.g. using a similar flow rate test profile.

Flow rate range

It is desirable to perform tests over as broad a flow rate range as possible to maximize the shear stress range over which slip velocity data is obtained. However, conflicting with this requirement, the accuracy of the interpolation process to determine the apparent shear rate corresponding to a given shear stress will be reduced when the interval between successive data points is increased.

3.5.2 Guidance on analysis to determine slip velocities

Selection of data

Outliers should be excluded from the data to be analysed. However, incorporation of the outliers in the analysis will give an indication as to the uncertainties in the derived values.

Where data are obtained in a region in which instabilities have occurred, observed by pressure fluctuations in the extrusion pressure traces, slip velocity determination shall not be carried out using these data.

Interpolation of shear stress - apparent shear rate data

It is necessary to interpolate the experimentally obtained shear stress – apparent shear rate data to generate apparent shear rate data at specified shear stresses in order for the analysis to be carried out. This process can be performed in a variety of ways, each of which will result in uncertainties in the derived values. The options for this include:

- curve fitting to the shear stress - apparent shear rate data and using the parameters of the best-fit curve to determine the apparent shear rates at given shear stress values, or

- interpolation between successive points

It is desirable to carry out the analysis using various methods to ascertain the sensitivity of the calculated slip velocity data to the method of analysis, thus providing greater understanding of the uncertainties in the derived data.

It is noted that the quality of the shear stress – apparent shear rate data, quantified by the fit of the curve used for interpolation of the data and the interval spacing between successive points, will have an influence on the interpolated values obtained. For comparison purposes it is important that the same method, e.g. power-law fit, is used in all cases. As rheological properties normally fit a power-law behaviour reasonably well then the use of power-law interpolation between successive points is a reasonable approach to adopt. This approach also avoids the greater smoothing of data that would occur if a fit to data over a wide shear rate range was used.

Extrapolation

Extrapolation of shear stress – apparent shear rates data for one or more dies to enable the diameter dependence of behaviour shall not be performed. If extrapolation of the slip velocity – shear stress data is required it is preferable that it is performed on the derived slip velocity – shear stress data, rather than the raw data used to obtain the slip velocities, to provide greater transparency of the scatter in data.

Mooney model

The Mooney model has been chosen in this Guide as being the approach taken. It is considered that the recommendations made here are likely to be broadly applicable to the determination of slip velocities using alternative models. However, further factors may also be critical, depending on the particular formulation of the model.

4 Example results

4.1 Slip velocity results

The shear stress - apparent shear rate data for a filled ethylene vinyl acetate (EVA) material (AAEHH005) at 165 °C are presented in Figure 3. Results are given for four different die diameters, namely 0.5 mm, 1 mm, 1.5 mm and 2 mm. These data are repeated in Figure 4, except that transition region data are removed, with best fit power-law curves fitted and thus more clearly showing the geometry dependence of data above the transition that occurs at a shear stress of approximately 400 kPa (apparent shear rate of 300 s⁻¹ at 165 °C). This geometry dependence indicates a slip regime. Below this transition value there is reasonable agreement of values obtained using different die diameters indicating a no-slip regime. In the region of 300 s⁻¹ to 600 s⁻¹ an instability (oscillations) in the extrusion pressure was observed making it impossible to determine equilibrium shear stress values. The values in this instability range determined by the instrument have been plotted and indicate an envelope of the material's behaviour.

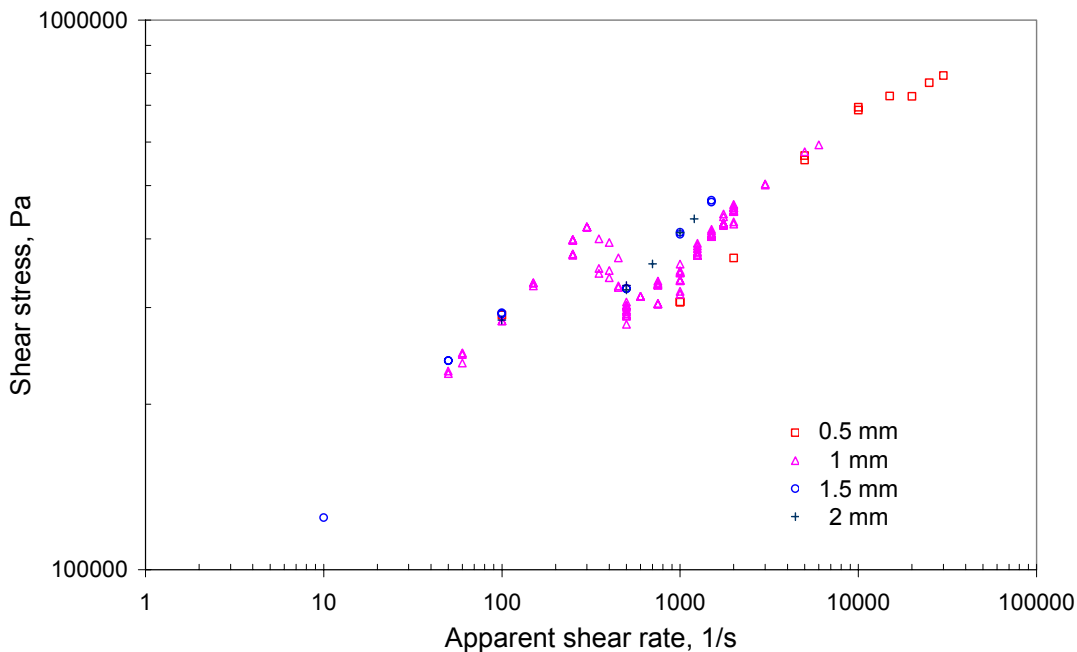


Figure 3: Shear stress data for different diameter dies indicating a die dependence above the slip transition. AAEHH005 at 165 °C.

The data in Figure 4 are then used to determine apparent shear rate values corresponding to given shear stress values for each of the dies, Figure 5. This requires interpolation of data: values obtained by linear interpolation between adjacent points are presented in Figure 5.

Analysis was also separately carried out using a power-law fit to the data and the coefficients of the fit were then used to determine the apparent shear rates at given shear stress values.

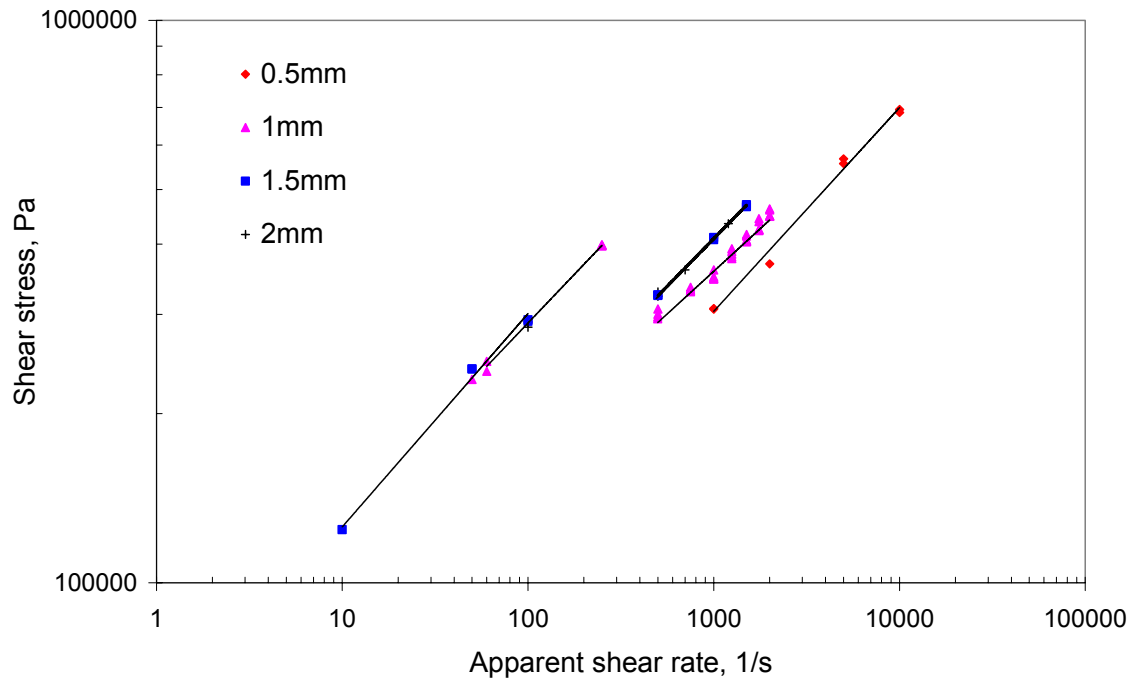


Figure 4: Repeat of Figure 3 with lines fitted to data of different flow regimes and die diameters indicating a die dependence of results above the slip transition. AAEHH005 at 165 °C.

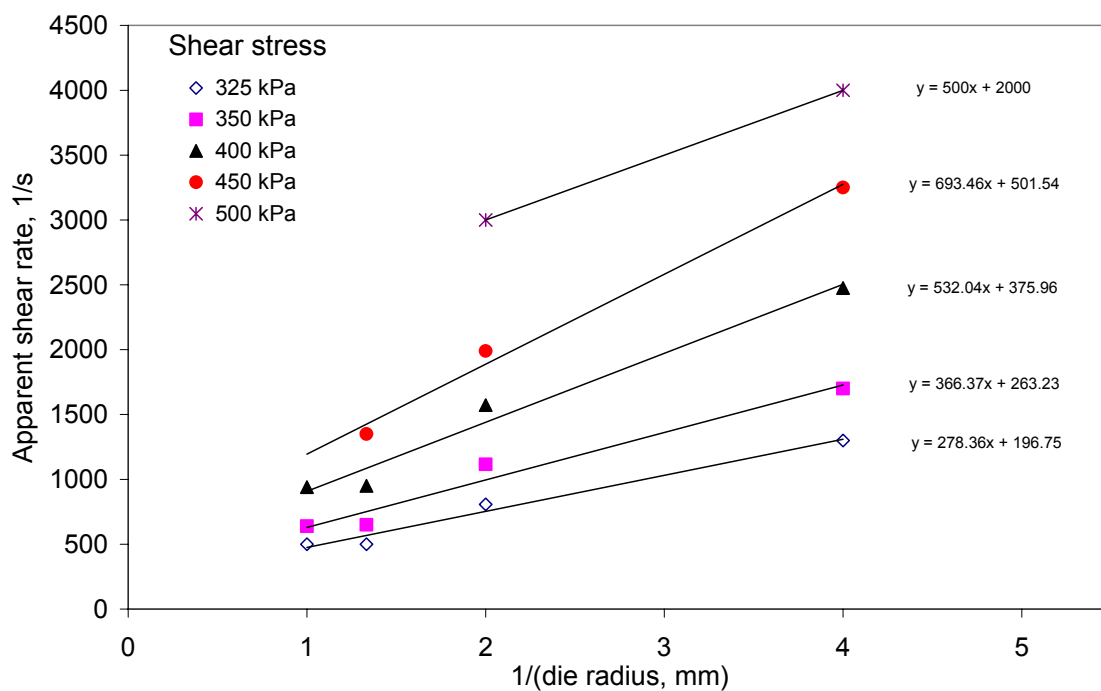


Figure 5: Constant shear stress data to determine the slip velocity. AAEHH005 at 165 °C.

A comparison of analysis methods: (a) linear interpolation between adjacent points, (b) power-law interpolation between adjacent points and (c) power-law fit to data over a range of apparent shear rates, indicated that compared with the mean values obtained from all three methods, method (a) gave slip velocity values 10% higher, method (b) 3% higher and method (c) 13% lower than the mean value – i.e. a discrepancy between methods (a) and (c) of 23%. Thus the interpolation method is critical to obtaining reliable results. Obviously these percentage values are dependant on the goodness of fit of the linear and power-law models to the data. Nevertheless, they indicate that power-law interpolation between successive points is preferred, it having yielded mid-range slip velocity values. From these observations it is clear that an important aspect of the measurements is to ensure that the data are of high quality (little scatter) with small intervals between successive points thus ensuring that the derived slip velocities are relatively independent of the method of analysis.

The assumptions in the Mooney model result in the fact that the data of apparent shear rate versus the reciprocal of the die radius will be linear. Obviously their departure from linearity provides an indication of the quality (scatter) of the data where deviations are apparently random, and possibly of deviations from the model where the deviations in the data are systematic.

Figure 5 clearly shows the importance of an appropriate selection of die radii. A halving of the smallest die diameter will extend the upper limit of the range of this plot (from a maximum for $1/R$ of 4 to 8) and be much more beneficial in terms of improving the accuracy in determining the gradient than doubling the largest diameter (from a minimum of $1/R$ from 1 to 0.5). The gradients of these lines divided by the factor of 4 (equation 11) were used to determine the slip velocities at the specified shear stress values. These slip velocity data fit well to a power-law model of shear stress, Figure 6, having a pre-exponent of 7.4×10^{-6} and an exponential of 2.78 with a regression r^2 value of 0.99.

For the 1 mm die the slip velocities determined account for some 80% of the total flow showing the significant contribution slip makes to the overall flow behaviour.

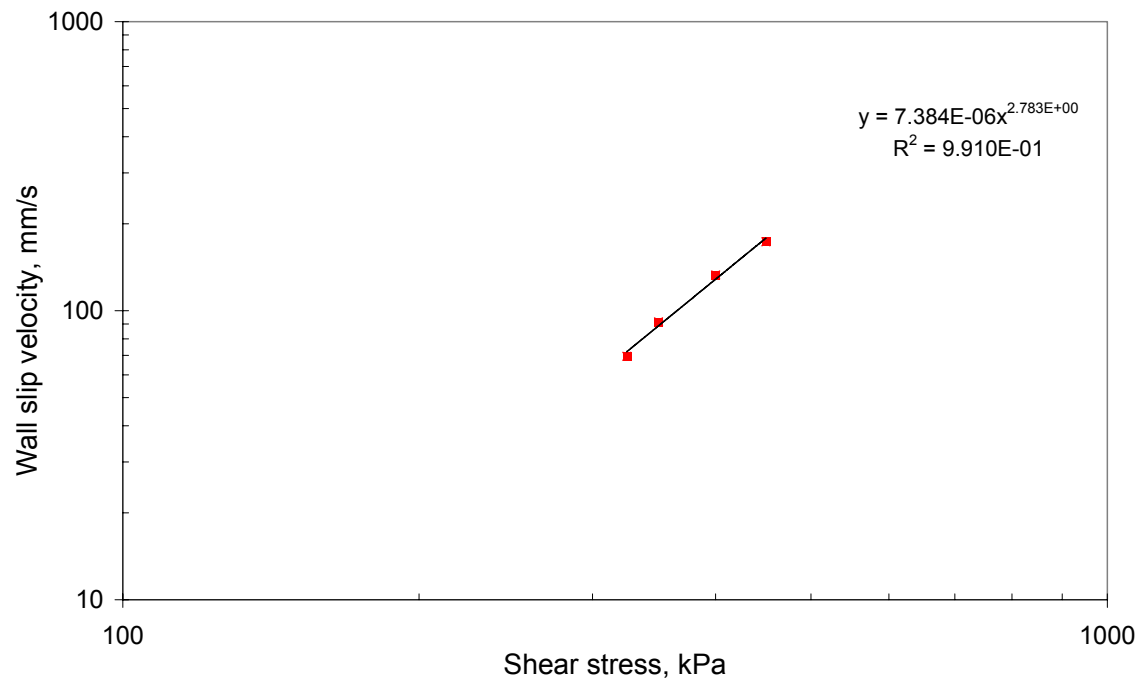


Figure 6: Slip velocity values determined for AAEHH005 at 165 °C.

4.2 Intercomparison of slip velocity measurement

An intercomparison of slip velocity measurements of two materials has been carried out by several laboratories. The two materials investigated were a carbon black filled high density polyethylene (HDPE, NPL Material identification code - AAEHH002) and a filled ethylene vinyl acetate (EVA, AAEHH005). The HDPE was tested at 220 °C and the EVA at 165 °C. The experiments and analysis to determine slip velocities were carried out by each laboratory. The results for AAEHH005 are summarised in Figures 7 to 9. The shear stress – apparent shear rate data from the laboratories for all the die diameters is presented in Figure 7, and for the 1 mm diameter die only in Figure 8. The data, Figure 8, show very good agreement of values below the transition point at approximately 300 s^{-1} . The level of agreement above the transition is slightly poorer.

Analysis of the shear stress - apparent shear rate data from the various laboratories indicates good agreement of calculated slip velocity values in the lower part of the shear stress range (approximately 10% variation), but with the discrepancy increasing up to 50% as shear stress increases up to a value of 500 kPa, Figure 9.

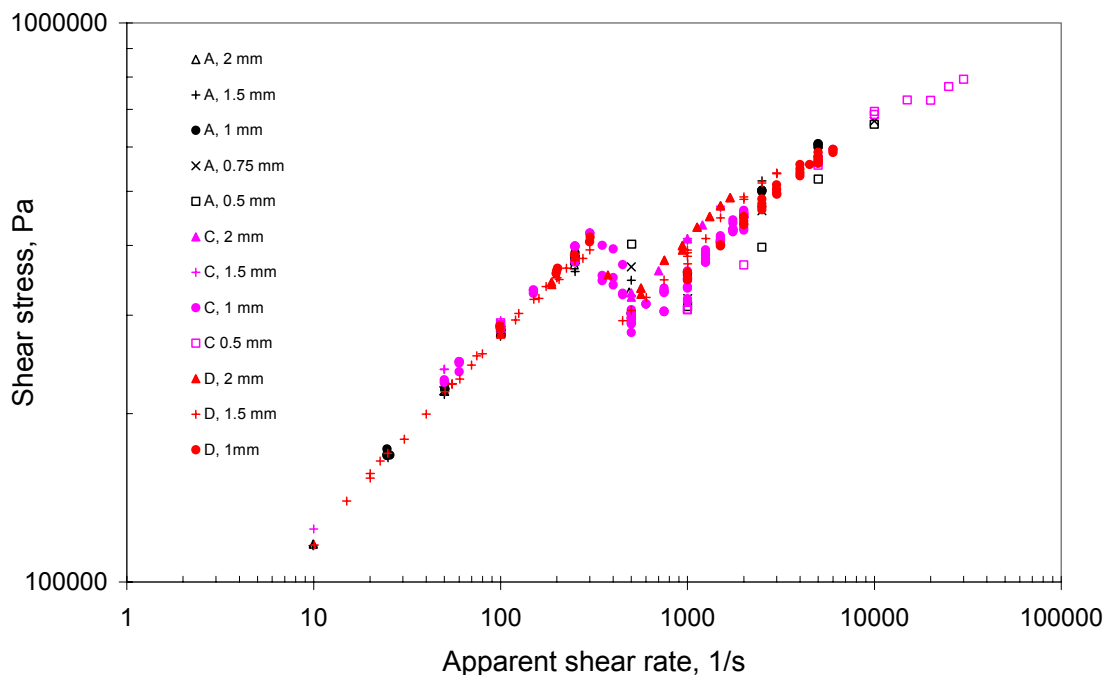


Figure 7: Shear stress plots for AAEHH005 at 165 °C from various laboratories using different die sizes.

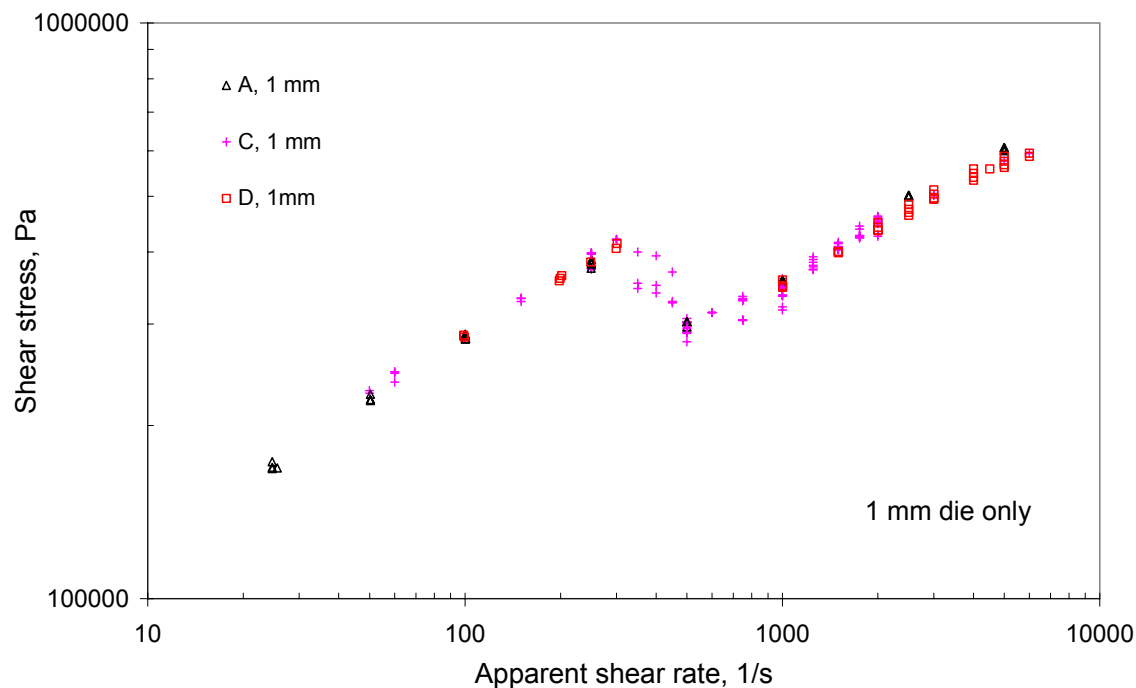


Figure 8: Shear stress data from Figure 7 for 1 mm diameter dies only indicating scatter between laboratories.

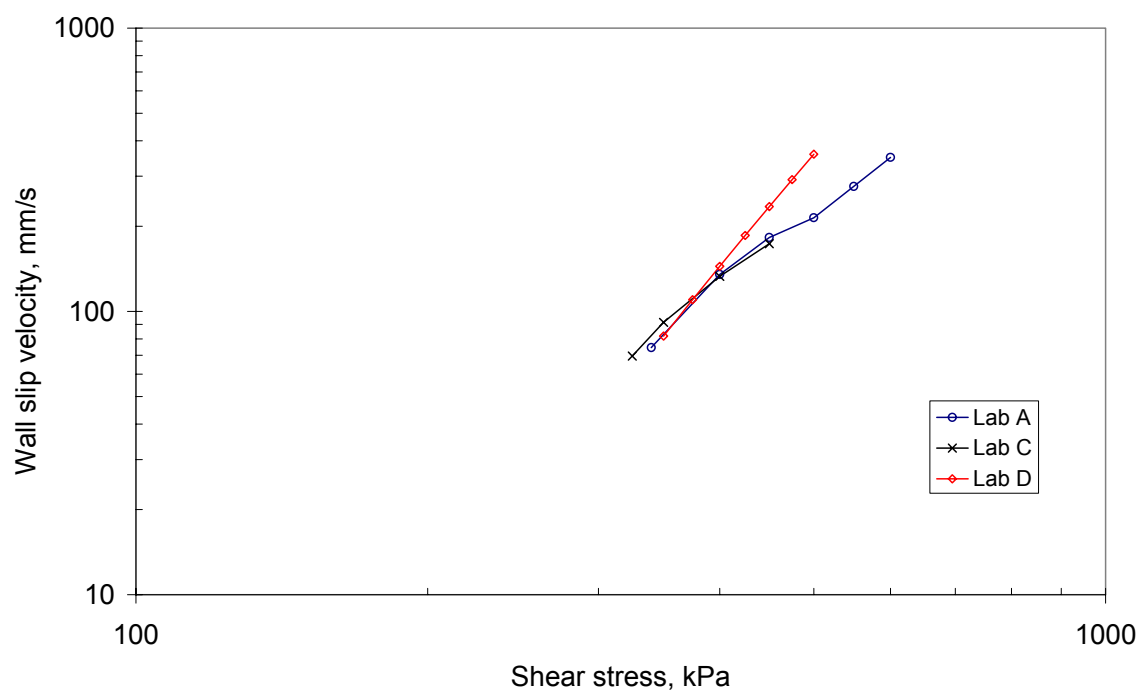


Figure 9: Wall slip velocity values determined for AAEHH005 at 165 °C by various laboratories.

5 Uncertainty analysis of slip velocity measurements

5.1 Introduction

An understanding of the uncertainties associated with the measurement is important for various reasons. In trying to improve the accuracy of the method it is essential to understand which of the experimental factors dominate the overall uncertainties, and which are relatively insignificant. By understanding this then efforts to improve the method can be best targeted to those aspects most likely to impact (reduce) the overall uncertainty. This understanding can only be achieved by carrying out an analysis of the uncertainties in the measurements. Furthermore, uncertainty analyses provide confidence levels for the data that are necessary to understand, for example, whether two materials are different to a level of statistical significance - whether tested on the same instrument or on different instruments. Also, uncertainty analyses can provide tolerances on input data to enable sensitivity analyses of predictions using simulation software to be performed. Basically, an understanding of the uncertainties in data is essential to fully understand the significance of results.

Following a rigorous approach, used for example by Kandil [11], the combined uncertainty $u_c(y)$ of the measurand y (the quantity to be measured) can be determined from the partial derivatives of the function $y = f(x_i)$ and the standard uncertainties $u(x_i)$ in the parameters of that function. Assuming that individual uncertainty sources are uncorrelated, the combined uncertainty $u_c(y)$ can be computed using the root sum squares:

$$u_c(y) = \sqrt{\sum_{i=1}^m [c_i u(x_i)]^2} \quad (12)$$

where c_i is the sensitivity coefficient (partial derivative) associated with the parameter x_i and $u(x_i)$ is the standard uncertainty in that parameter.

The combined uncertainty $u_c(y)$ corresponds to one standard deviation and therefore has an associated confidence level of approximately 68%. Assuming a normal distribution then an expanded uncertainty U , equivalent to a 95% confidence level, can be determined using a coverage factor of 2, i.e. twice the combined uncertainty value. The relative uncertainty is the ratio of the uncertainty in the parameter to the value of the parameter.

5.2 Uncertainty analysis for slip velocity

The slip velocity is written (as in equation 10) by

$$\frac{4Q_T}{\pi R^3} = \left[\frac{4n}{3n+1} \right] \left[\frac{\tau_w}{K} \right]^{1/n} + \frac{4V_s}{R} \quad (13)$$

If the wall shear stress is constant and assuming K and n do not vary, then:

$$\frac{4Q_T}{\pi R^3} = \text{constant} + \frac{4V_s}{R} \quad (14)$$

This expression predicts that, for a given wall shear stress, a plot of apparent wall shear-rate $4Q_T/\pi R^3$ versus $1/R$ will have a gradient of $4V_s$ thus enabling the slip velocity to be determined. Although the term

$$\left[\frac{4n}{3n+1} \right] \left[\frac{\sigma_w}{K} \right]^{1/n} \quad (15)$$

is taken to be constant there is still an uncertainty associated with its determination and this may need to be taken into account in the analysis if it is significant.

The following uncertainty analyses are based on the experimental approach used to determine slip velocity. However, the first analysis assumes that only two different diameter dies are used, and thus a simple relationship between the slip velocity and the experimental parameters results. Using equation 14, for two different dies of radius R_1 and R_2 :

$$\frac{4Q_{T1}}{\pi R_1^3} - \frac{4V_s}{R_1} = \frac{4Q_{T2}}{\pi R_2^3} - \frac{4V_s}{R_2} \quad (16)$$

thus

$$V_s = \frac{\left(\frac{4Q_{T1}}{\pi R_1^3} - \frac{4Q_{T2}}{\pi R_2^3} \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)} \quad (17)$$

The sensitivity coefficients c_i (partial derivatives of the slip velocity equation with respect to the parameters of flow rate and die radius) are given by:

$$\frac{\partial V_s}{\partial Q_{T1}} = \frac{\left(\frac{4}{\pi R_1^3} \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)} \quad (18)$$

$$\frac{\partial V_s}{\partial Q_{T2}} = \frac{\left(\frac{-4}{\pi R_1^3} \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)} \quad (19)$$

$$\frac{\partial V_s}{\partial R_1} = \frac{\left(\frac{-12Q_1}{\pi R_1^4} \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)} - \frac{\left(\left(\frac{4Q_1}{\pi R_1^3} - \frac{4Q_2}{\pi R_2^3} \right) \left(\frac{-4}{R_1^2} \right) \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)^2} \quad (20)$$

$$\frac{\partial V_s}{\partial R_2} = \frac{\left(\frac{12Q_2}{\pi R_2^4} \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)} - \frac{\left(\left(\frac{4Q_1}{\pi R_1^3} - \frac{4Q_2}{\pi R_2^3} \right) \left(\frac{4}{R_2^2} \right) \right)}{\left(\frac{4}{R_1} - \frac{4}{R_2} \right)^2} \quad (21)$$

The combined uncertainty in the determination of the slip velocity is given by

$$u_c(V_s) = \sqrt{\sum_{i=1}^m \left[\frac{\partial V_s}{\partial x_i} u(x_i) \right]^2} \quad (22)$$

or expanded in full

$$u_c(V_s) = \sqrt{\left[\frac{\partial V_s}{\partial Q_{T1}} u(Q_{T1}) \right]^2 + \left[\frac{\partial V_s}{\partial Q_{T2}} u(Q_{T2}) \right]^2 + \left[\frac{\partial V_s}{\partial R_1} u(R_1) \right]^2 + \left[\frac{\partial V_s}{\partial R_2} u(R_2) \right]^2} \quad (23)$$

This analysis assumes that the uncertainty in the value of the “constant” given by equation 15 is negligible. By definition the shear stress is specified and thus there should be no

uncertainty associated with it, although the absolute determination of it is subject to uncertainties and are separately taken into account in the analyses presented. Similarly, n and K are materials properties and there are uncertainties associated with their determination. Furthermore, the values of n and K are likely to be test condition dependent (e.g. shear rate) and thus will have additional uncertainties associated with their specification. Thus the analysis presented assumes that the material's behaviour is logarithmic over the shear stress range concerned (i.e. constant n and K).

The uncertainty in the shear stress values to which the slip velocities are assigned (e.g. in Figure 9) also needs to be considered. According to ISO 11443, pressure transducers shall be accurate to better than 1% of their full scale and better than 5% of the absolute (measured) value: the 5% value will only come into effect when the transducer is operating below 20% of its range. This thus limits the relative expanded uncertainty in shear stress values to better than approximately 6% (rectangular distribution assumed, and occurring when the pressure transducer is used in the lowest part of its permissible range). However, this value will be lower over most of the transducer's operating range reducing to approximately 1% (c.f. 6%) at full scale. By considering the gradient of the plot in Figure 6, a 6% uncertainty in shear stress is equivalent to an 18% uncertainty in the wall slip velocity.

In the testing reported here, however, the transducers used had a specified tolerance of $\pm 0.25\%$ of their full scale value with actual calibration errors being less than 1% absolute over their operating range. This corresponds to a relative expanded uncertainty in shear stress of approximately 2% (normal distribution assumed). Thus providing pressure transducers are used in an appropriate part of their range (above 10% of full scale, in accordance with ISO 11443) and the errors associated with the pressure measurement are small, as in the case of testing reported here, then the relative expanded uncertainties in the shear stress values to which the slip velocities are assigned can be kept to not more than a few percent. The effect of this on the slip velocity will depend on the sensitivity of the slip velocity to shear stress, as indicated by the gradient of the plot in Figure 6. For this material a 2% uncertainty in shear stress corresponds to a 6% uncertainty in slip velocity.

5.3 Evaluation of uncertainties for slip velocity

The equations given above have been used, in conjunction with the parameter values and tolerances, to calculate the sensitivity factors and uncertainties in each of the parameters Q_1 , Q_2 , R_1 and R_2 , Tables 1 and 2. The values and tolerances of each of the parameters have been estimated on the basis of experimental measurements and/or the standard ISO 11443 [5] which specifies the permitted tolerances on test parameters. ISO 11443 states that flow rates should be measured to 1% absolute and the die diameter must be known to ± 0.007 mm. However, it is most likely that the uncertainty in the determination of the apparent shear rates,

which will be similar to that for the flow rates¹, for the two dies at equivalent shear stress values will be greater, and possibly significantly greater than the 1% specified in the standard for flow rates. This is because the value for the apparent shear rate has to be determined by interpolation of experimental data (extrapolation of data is not recommended) that necessitates the selection of the interpolation method and the data on which it is carried out. These choices are many and will result in different uncertainties in the thus obtained flow rate values. It is recommended that the user of this Guide carries out their own uncertainty analysis using values for the parameters applicable to their own experimental set-up and procedures, in particular for that of the determination of the apparent shear rates at equivalent stresses.

From the data, Figure 3, the one standard deviation variation in the value of the apparent shear rate corresponding to a given shear stress was in the range approximately 4% to 15% but values up to 20% were obtained. For this material (assuming $n = 0.34$) an uncertainty in apparent shear rate of 15% corresponds to an uncertainty in shear stress of approximately 5%, given the significant non-linearity of the shear stress - shear rate behaviour, Figure 4. The standard deviation in shear stress values obtained by all the laboratories for AAEHH005 at 100 s^{-1} and 5000 s^{-1} was calculated to be 5%. A value of 20% for one standard deviation in the apparent shear rate has therefore been assumed, as a limiting value, and used in the analyses. As the uncertainty in the die diameter is small then the contribution of the diameter to the uncertainty in the apparent shear rate and shear stress is considered to be negligible. Thus the uncertainty in the flow rate can be assumed to be the same as that of the apparent shear rate, i.e. approximately 20% at a level of one standard deviation.

To further illustrate the significant effect of the material's behaviour on the uncertainties in apparent shear rate, a 5% uncertainty in shear stress corresponds to a 10% uncertainty in apparent shear rate for a material with $n = 0.5$, 17% for $n = 0.3$, 28% for $n = 0.2$, and 63% for $n = 0.1$.

The results of the uncertainty analyses presented in Tables 1 and 2 were based on the use of only two die diameters, resulting in slip velocity expanded relative uncertainty values (95% confidence level) of 66% and up.

¹ Note: As the relative uncertainty in the die diameter is small then its contribution to the relative uncertainty in the apparent shear rate is small compared with that due to the flow rate, and thus the uncertainty in the apparent shear rate is the same as that of the flow rate.

Parameter	Symbol	Units	Probability distribution	Divisor, ϕ	Parameter value, x	Parameter range, $\pm$ δ	Standard uncertainty, $u(x_i) = \delta/\phi$	δx	Sensitivity coefficient, $\partial/\partial x_i$	$[(\partial/\partial x_i) \cdot u(x_i)]^2$
Flow rate 1	Q_{T1}	m ³ /s	Normal	1	1.61E-08	3.22E-09	3.22E-09	0.2	6790611	4.77E-4
Flow rate 2	Q_{T2}	m ³ /s	Normal	1	3.73E-07	7.46E-08	7.46E-08	0.2	-106103	6.27E-05
Die radius 1	R_1	m	Rectangular	1.7321	0.00025	3.5E-06	2.02E-06	0.014	-939.043	3.6E-06
Die radius 2	R_2	m	Rectangular	1.7321	0.001	3.5E-06	2.02E-06	0.003 5	95.58083	3.73E-08
Combined standard uncertainty, m/s							0.0233			
Coverage factor							2			
Expanded uncertainty (95% confidence level), m/s							0.0466			
Slip velocity, m/s							0.0696			
Relative expanded uncertainty of slip velocity (95% confidence level), %							67%			

Notes: The divisor ϕ for determination of the standard uncertainty is based on the parameter's probability distribution. A normal distribution has been chosen for the flow rate as the value for one standard deviation was obtained from a number of determinations. For the die radius a rectangular distribution has been used, based on the fact that the actual value has an equal probability of occurring anywhere within the parameter's range (in this case the tolerance on the die radius is as specified by ISO 11443).

Table 1: Uncertainty assessment when using two dies of 0.5 mm and 2 mm diameter with a 20% standard deviation in the determination of the flow rate (or apparent shear rate) for a stress of 325 kPa for EVA H005 at 165 °C.

Parameter	Symbol	Unit s	Probability distribution	Divisor, ϕ	Parameter value, x	Parameter range, +/-, δ	Standard uncertainty, $u(x_i) = \delta\phi$	δx	Sensitivity coefficient, $\partial y / \partial x_i$	$[(\partial y / \partial x_i) \cdot u(x_i)]^2$
Flow rate 1	Q_{T1}	m^3/s	Normal	1	7.4E-08	1.48E-08	1.48E-08	0.2	2546479	0.001419
Flow rate 2	Q_{T2}	m^3/s	Normal	1	3.73E-07	7.46E-08	7.46E-08	0.2	-318310	0.000564
Die radius 1	R_1	m	Rectangular	1.7321	0.0005	3.5E-06	2.02E-06	0.007	-851.845	2.96E-06
Die radius 2	R_2	m	Rectangular	1.7321	0.001	3.5E-06	2.02E-06	0.003 5	286.7425	3.36E-07
Combined standard uncertainty, m/s									0.0446	
Coverage factor									2	
Expanded uncertainty (95% confidence level), m/s									0.0892	
Slip velocity, m/s									0.0696	
Relative expanded uncertainty of slip velocity (95% confidence level), %									128%	

Notes: See Notes to Table 2.

Table 2: Uncertainty assessment when using two dies of 1 mm and 2 mm diameter with a 20% standard deviation in the determination of the flow rate (or apparent shear rate) for a stress of 325 kPa for EVA H005 at 165 °C.

In Table 1, for 0.5 mm and 2 mm diameter dies the relative expanded uncertainties were largely insensitive to the shear stress value, with values of 67% also being obtained for both the 400 kPa and 450 kPa shear stress data. However, a reduction in the standard deviation of the apparent shear rate to 10% (from 20%) resulted in a near halving of the uncertainty from 67% to 34%, and for 15% the value obtained was 50%.

In comparison with Table 1, if 1 mm and 2 mm diameter dies were used instead, Table 2, the slip velocity relative expanded uncertainty (95%) increased to a value of 128%, and if 1.5 mm and 2 mm diameter dies were used the value increased to 320% demonstrating the clear need to ensure adequate separation of the die diameters to reduce measurement uncertainties

An uncertainty assessment was also made for testing where more than two die diameters were used. Using the experimental data set in Table 1, analyses of the uncertainty was performed using various combinations of that data. Linear regression analysis yielded the standard error of the fit of the best straight line to the apparent shear rate versus the reciprocal of the die radius data, e.g. Figure 5. The 95% confidence limits to the gradient were calculated based on the t-distribution value for 95% confidence level for the number of observations less 2, multiplied by the standard error. This approach assumes that the uncertainty is due solely to the determination of the gradient of the line, which takes into account the variation in experimental values for the apparent shear rates. As the uncertainty in the slip velocities due to the uncertainty in the die diameters is negligible, this assumption was considered reasonable. The standard errors of the best straight-line fits were determined using Microsoft Excel's regression data analysis routine.

Apparent shear rate, s^{-1}				
Radius, mm	1/R (mm^{-1})	Shear stress, kPa		
		325 kPa	400 kPa	450 kPa
1	1	500	940	-
0.75	1.333333	500	950	1350
0.5	2	806	1572	1990
0.25	4	1300	2475	3250

Table 3: Experimental values of apparent shear rates for different dies at specified shear stress values used to determine the uncertainties in slip velocity determination.

When using dies of four different diameters the relative expanded uncertainty (95% confidence level) was of the order of 40% to 50%. The uncertainty increased dramatically when only three dies were used, the increase being dependant on which die was not used and the quality of the data.

1/R	Shear stress, kPa				
	325	400	450	325	400
1	500	940	-	500	940
1.333333	500	950	1350	500	-
2	806	1572	1990	806	1572
4	1300	2475	3250	-	2475
Maximum radius ratio	4	4	3	2	4
Plot gradient	278.36	532.04	693.46	327.86	503.07
Intercept	196.75	375.96	501.54	128.4286	488.5
No. observations	4	4	3	3	3
ν	2	2	1	1	1
T distribution value	4.30	4.30	12.70	12.70	14.70
Standard error	27.33	58.92	65.95	113.57	44.66
95% confidence range on gradient value	118	254	838	1443	657
Relative expanded uncertainty of slip velocity (95% confidence level), %	42%	48%	121%	440%	131%

Table 4: Uncertainty assessment when using at least three dies with a 20% standard deviation in the determination of the flow rate (or apparent shear rate) for a stress of 350 kPa for EVA H005 at 165 °C.

5.4 Discussion of uncertainties analysis

The analysis of the uncertainties illustrates that the method is prone to very high uncertainty values if care is not taken with the selection of appropriate die diameters and testing conditions. If four dies over the diameter range 0.5 mm to 2 mm were used and assuming a standard deviation in the determination of the apparent shear rate of 20%, then the relative expanded uncertainty (95% confidence level) in slip velocity was of the order of 40% to 50%. If only two dies were used, the uncertainty was of the order of 67% when using 0.5 mm and 2 mm diameter dies, 130% when using 1 mm and 2 mm diameter dies, and 320% when using 1.5 mm and 2 mm diameter dies. This clearly shows the importance of die diameter selection

in reducing the uncertainties in the measurement. However, provided the die diameter tolerances specified in ISO 11443 [5] are adhered to, the contribution due to the uncertainty in die diameter is negligible.

Furthermore, to improve on the accuracy of slip flow determination it is also important to focus on the accurate determination of the apparent shear rates at specified shear stresses.

The high non-linearity of this material's shear stress – apparent shear rate behaviour results in the magnification of the uncertainty in determination of apparent shear rate to the order of 15% to 20% although the uncertainties in shear stresses are themselves typically less than 5%. This demonstrates that the uncertainties are sensitive to the specific case (primarily the material behaviour and die diameters) and that such analysis should be carried out for individual testing situations to obtain a fuller understanding of the slip velocity data.

Thus, considering the two approaches to determining uncertainty, and assuming reasonable quality data the relative expanded uncertainty in the determination of slip velocity for this material is estimated to be in the region of 40% to 50%, although significantly higher values could occur for some experimental conditions. In addition, the uncertainties in the shear stress to which the slip velocity is assigned is of the order of 2% in the measurements reported on here, but could be as high as 6% if pressure transducers just meeting the specification of ISO 11443 are used.

It is considered that the uncertainties could be reduced by ensuring that the quality of the raw data is high such that contributions due to the interpolation procedure are small, and that the dies cover a large diameter range.

6 Summary

A method for determining the slip velocity of flowing plastics using capillary die extrusion rheometry has been presented with recommendations for good practice both in terms of the experimental measurements and the method of analysis of the raw shear stress – apparent shear rate data.

An analysis of the uncertainties in the determination of slip velocity has clearly demonstrated that very high uncertainties can occur due to poor measurement practice, in particular in the selection of the die diameters. The magnitude of the uncertainties is influenced significantly by the rate dependence of the behaviour of the material. In the case illustrated the relative expanded uncertainties (95% confidence level) were best estimated to be of the order of 40% to 50%. Due to the sensitivity of the method to these factors it is recommended that an uncertainty analysis is carried out in all investigations to identify the uncertainties associated

with the specific experimental arrangement and the material's behaviour.

The results of the intercomparison clearly demonstrate that scatter can be significant. However, the measured slip velocity values, being up to 50% different, are within the expanded uncertainty limits of the mean values.

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Appendix A: Symbols and definitions

For the purpose of this document the following terminology is used, except where otherwise specified:

τ	shear stress (Bagley end-corrected), Pa
$\dot{\gamma}_w$	true wall shear-rate (Rabinowitsch corrected), s ⁻¹
P	extrusion pressure, Pa
P_e	entrance pressure drop, Pa
K	constant of the power-law model for shear viscosity
n	rate constant of the power-law model for shear viscosity
Q	volume flow rate, m ³ /s
$\dot{\gamma}_a$	apparent shear rate, s ⁻¹
η_a	apparent shear viscosity (Bagley end-corrected), Pa.s. It is the ratio of shear stress (Bagley end-corrected) to apparent shear rate.
R	die radius, m
L	die length, m
Q_T	volume flow rate (total), m ³ /s
Q_{slip}	slip-flow flow rate, m ³ /s
Q_{shear}	shear-flow flow rate, m ³ /s
V_s	slip velocity, mm/s

Uncertainty analysis terminology

y	measurand (the quantity to be measured)
$u(x_i)$	standard uncertainty
$u_c(y)$	combined uncertainty, corresponding to one standard deviation and therefore has an associated confidence level of approximately 68%
c_i	sensitivity coefficient (partial derivative) associated with the parameter x_i
x_i	parameter (variables of the measurand)
$u(x_i)$	standard uncertainty in the parameter
U	expanded uncertainty, equivalent to a 95% confidence level
ϕ	divisor, a scaling factor to take into account the distribution in the uncertainty of the parameter
δ	$\pm \delta$ tolerance or range in the parameter

Appendix B: Slip flow – a brief review of the literature

B.1: Slip flow mechanisms

There are two likely mechanisms for slip in polymer flow. In filled materials the development of a resin-rich layer adjacent to the wall due to particle depletion acts as a lubricating layer with the resultant apparent “slip” behaviour. Alternatively, the polymer loses adhesion with the wall and slip occurs.

Modigell et al [12] showed, using NMR imaging of suspensions of PMMA spheres in a density-matched sugar solution, that the spheres migrated from regions of high shear rate to regions of low shear rate. Macosko [13] commented that the migration is greater for higher shear rates. Yilmazer et al [14] reported that migration of filler away from the wall in capillary flow increased with increasing shear stress resulting at high flow rates with ‘effective viscosities’ of filled materials approaching those of the unfilled materials. Kalyon [15] commented that slip of 63% filled fluids was due to the formation of a fluid-rich lubricating layer at the wall. As a consequence of such particle migration, the velocity profile is significantly affected: the migration results in a steep velocity gradient near the wall with the majority of the material flowing as a plug, which can be interpreted as slip. Cohen et al [16] analysed such behaviour using thermodynamic diffusion modelling and obtained reasonable agreement with experimental data.

The wall surface texture and material of construction has been shown to influence slip behaviour [17-25]. Aubry et al [24] using steady shear rotational rheometry with smooth and textured plates, concluded that slip in polymer solutions is due to destruction of network structures in the region near the wall. However, the apparent slip was not seen when using textured plates. Chen et al [25] reported that slip behaviour of low density polyethylene was influenced by both the material of construction and by surface roughness. No-slip was observed for aluminium whereas slip was observed for glass, copper and stainless steel, and slip decreased as roughness increased. Piau et al [26], using steel and PTFE-coated dies for extruding polybutadiene, observed significant differences in the apparent slip behaviour between the dies, with significant slip and improved extrudate surface finish in the case of the PTFE coated die. Piau et al [26] commented that the slip behaviour of polymers is related to the surface energy of the die wall: PTFE has a low surface energy compared with steel and slip is enhanced by it.

The effect of texture of the wall on slip flow behaviour has been investigated by several workers, some of which is reported earlier. Knappe et al [17] reported that slip of unplasticised PVC, measured using slit dies of different thicknesses, was observed for smooth dies but was disrupted for textured dies. They suggested that this behaviour was due to the

presence of a thin lubricating layer caused by flow-induced diffusion. Malvern Instruments Application note [18] described steady shear rotational rheometry testing on low viscosity suspensions and concluded that the use of roughened (serrated) geometries appears necessary to overcome slip effects. Wear of the die surfaces in uPVC extrusion, thought to be due to the titanium dioxide filler, resulted in a reduction in the required extrusion pressure [19].

The role of slip or stick-slip in melt instabilities characterised by sharkskin or melt-fracture has been investigated by various workers over the last few decades. Slip appears to significantly modify the extrudate sharkskin and fracture behaviour, for example Piau et al [26] suggested that improved performance of extrusion processes could be achieved through modification of the die finish. However, the origins of such instabilities are still debated.

B.2: Mooney method for characterising slip flow

The onset of slip during a rheometry test should be apparent from a discontinuity in the shear stress – shear rate curve. However, if slip occurs at all the shear stress values obtained during the test then slip will not necessarily be apparent from a single die test. A second test using a different die diameter will lead to an apparent dependence of shear viscosity on the die diameter from which slip can be inferred. In the presence of slip, the use of a smaller die will produce lower apparent viscosities at equivalent apparent wall shear rates. This approach of using capillary dies of different diameter to determine the slip velocity was first developed by Mooney [4]: the analysis for capillary extrusion rheometry data is presented in Section 3.3. Mooney [4] also presented the analysis for testing using the Couette geometry in rotation following the same principles. Taking a different perspective, Macosko [13] commented that by extrapolating the viscosity as a function of die diameter to infinite diameter the “true” shear viscosity of the fluid can be determined.

Yoshimura et al [27] presented an improved method for Couette geometries utilising only two measurements, and the analysis for parallel plate geometries as well as the analysis for the Mooney method for capillary geometries. The precision of the method has not been demonstrated and under certain circumstances negative slip velocity values have been obtained which are obviously nonsensical [10]. These negative slip values could be attributed to the flow being more parabolic at higher flow rates (stresses) than at lower flow rates. At the low flow rates the stresses are insufficient to cause significant disentanglement of the fibres/filler resulting in plug-like flow behaviour. At higher flow rates, disentanglement occurs resulting in a more parabolic flow. Alternatively, at lower rates greater separation of the resin from the material occurs, as has been observed in the entry region of capillary rheometers, resulting in more efficient lubrication of the flow [10]. The consequence of this is that the flow appears more like “slip flow” at lower rates than at higher rates. When interpreted using the Mooney analysis negative slip velocities were obtained [10]. Negative

slip velocities have also been identified using capillary rheometry with the Mooney approach by Mendez-Sanchez et al [28] who suggested that it might be the result of flow-induced phase orientation effects. Similarly, Leblanc et al [29] obtained negative slip values for filled rubber compounds but associated it with the compressibility of the material. They commented that rubbers are more pressure sensitive than unfilled polymers and that compressibility has the opposite effect on the measurement of viscosity to that of slip. Thus the apparent negative slip was potentially due to the material's compressibility. Hagström [30] identified that the Mooney method failed for extrusion rheometry testing of PVC using a slit die and an oscillatory rheometer, as slip velocities greater than the average flow velocity were obtained. Fleming [31] commented that difficulties may be experienced using the Mooney approach for materials that degrade rapidly due to different residence times in the barrel, and reported that several workers have developed refinements to the Mooney approach to address the issues of too high or negative slip flow velocities [32-37].

Yeow et al [38] presented an inverse solution to the determination of shear viscosity and slip velocity from capillary rheometry data without assuming a constitutive form between relating slip velocity and shear stress to shear rate. Good agreement of derived values was obtained using data presented in the literature, but it highlighted difficulties in the determination of the critical shear stress above which slip occurred. This was reported as being an issue both for the inverse approach used and also for the Mooney approach. The approach could also be used to determine the yield stress, given appropriate data [38]. Such an approach may prove valuable in addressing the issues identified above of negative slip velocities or excessively high slip velocities due to the limitations of the Mooney approach.

Graczyk et al [18] used capillary rheometry with rough dies, flow visualisation and a twin capillary method introduced by Gleissle et al [21] to study slip of aluminium oxide-silicone oil pastes. The twin capillary method is basically the same as the standard Mooney capillary die method. However, it uses two dies of different diameter but the same L/D ratio and the extrusion pressure is controlled to obtain constant and equal stress conditions in each die. The flow rates in each die are measured. It thus avoids the need to interpolate to obtain shear rates at specified shear stress values. However, the entrance pressure losses should be negligible otherwise a Bagley correction [22, 23] for entrance effects is required [it is considered that the entrance pressure drops are not negligible]. They concluded that the Mooney and twin capillary (constant pressure) method gave unrealistically high values. They suggest that the measurements are influenced by the entry region to the dies resulting in fully developed flow being established some distance from the die entrance and that the size of the effects differs for the different diameter dies used.

Hagström [30] presented the analysis for the use of slit dies for determining slip velocity. It follows the same approach as Mooney [4] for capillary dies except that the apparent shear rate

$\dot{\gamma}_{ap}$ is plotted as a function of the reciprocal of the slit thickness ($1/H$) for constant shear stress values. The gradient of the plot is expected to be linear with a value equal to six times the slip velocity V_s .

$$6V_s = \text{gradient} [\dot{\gamma}_{ap} \text{ versus } 1/H, \text{ for constant shear stress}] \quad (\text{B1.1})$$

Kalyon et al [39] developed a variable gap in-line rheometer mounted on a screw extruder in which the gap could be adjusted using stepper motors. In theory, this provides a convenient facility for studying slip flow following the Mooney approach.

Aubry et al [24] and also Yoshimura [27] reported the method for rotational rheometry using parallel plates, plotting the apparent shear rate at the plate rim ($\dot{\gamma}_{ap}$) as a function of the reciprocal of the gap ($1/h$) for constant shear stress. The resultant plot is expected to be a straight line with a gradient equal to twice the slip velocity.

$$2V_s = \text{gradient} [\dot{\gamma}_{ap} \text{ versus } 1/h, \text{ for constant shear stress}] \quad (\text{B1.2})$$

A benefit in using rotational rheometry is that controlled stress instruments are widely available and thus there is no need to interpolate data to obtain data at constant shear stress. Collyer et al [40] commented, however, that slip in parallel plate rheometry is mathematically equivalent to setting a gap height that is too high and reported that in work by Henson et al [41] using parallel plate rheometry, the measured slip was equivalent to a 10 μm error in gap setting. Therefore, accurate gap height setting is critical for the determination of slip effects by rotational rheometry.

B.3: Slip flow behaviour

Park et al [42] used the Mooney approach for determining slip using a rotational rheometer but added that for a system in which there is a thin lubricating layer the thickness δ of that layer can be estimated by the expression:

$$\delta = \frac{V_s \eta_s}{\tau} \quad (\text{B1.3})$$

where V_s is the slip velocity, η_s is the viscosity of the lubricating layer and τ is the shear stress. The viscosity of the lubricating layer is unknown but can be assumed to be equal to the viscosity of the matrix (fluid).

Yilmazer et al [43], in testing a 60% by volume filled suspension, identified that at high flow rates the flow was dominated by slip rather than shearing flow. Similar observations were made by Jiang et al [44] for hydroxypropyl guar (HPG) gels. However, slip velocities in excess of the average velocity for the flow were calculated indicating failure of the Mooney analysis. Both reported that the slip velocity data fitted the power-law expression reasonably well over a limited range of shear stresses:

$$V_s = a \tau_w^b \quad (\text{B1.4})$$

where a and b are constants and τ_w is the wall shear stress. This expression has also been used by Yilmazer [14] and gave a good fit to data. Both parallel plate and capillary methods were used to determine the slip velocity following the Mooney approach [4]. Although there was no overlap in shear stress of data from the two methods the shear stress at the upper end of the rotational testing was similar to that at the low end of the capillary rheometry testing. Values for the slip velocity in this region were similar, although the gradients of slip velocity versus shear stress were possibly different for each of the test methods. The scatter in slip velocities was greater for those obtained by the parallel plate rotation method. Yilmazer [14] presented a further modification to the above equation of the form:

$$V_s = a (\tau_w - \tau_s)^b \quad (\text{B1.5})$$

where τ_s is the critical shear stress below which no slip occurred. However, examination of the data for a 60% filled suspension did not suggest that this latter equation gave a significantly improved fit to the data than the former. The slightly improved fit, due to the change in gradient mentioned above coinciding with the change to the other technique, may possibly be due to reasons associated with the use of different techniques rather the second equation being a more realistic model.

Haworth et al [45] showed that for $\text{Mg}(\text{OH})_2$ and talc filled PP and PE, using capillary rheometry and the Mooney approach, the slip behaviour is affected by the filler level. They proposed a model for the slip velocity of the form:

$$V_s = \left[\frac{\tau - \tau_c}{k(\phi)} \right] \quad (\text{B1.6})$$

where k is a slip coefficient that is dependant on the filler level ϕ and τ_c is a critical stress above which slip occurs. Values for τ_c typically ranged from 120 kPa to 220 kPa and the slip coefficient from 0 to 3.8.

Ahn and White [46], using the Mooney approach of different die diameters for capillary rheometry, showed that small quantities of an additive (e.g. 1% of octadecanoic acid and zinc stearate) can lead to slip in flow of polyethylene (PE) and polypropylene (PP) originating from loss of adhesion to the die wall, but that such effects were minimal with polystyrene (PS), poly methyl methacrylate (PMMA) and polyamide-12 (PA-12). It was suggested that this is due to the lower polarity of the PE and PP compared with the PS, PMMA and PA-12 and that, due to their lower polarity, the PE and PP are preferentially replaced at the wall by the lower molecular weight additives thereby creating a slip layer. Macosko [13], in summarising, commented that slip in polymer melts occurs at a wall shear stress of approximately 10^5 Pa.

