Characterising the rheological and thermal properties of filled thermoplastics

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Abstract

Fillers can have very significant effects on the rheological and thermal properties of polymeric materials. In very heavily filled thermoplastics slip has been observed to occur which can lead to complications in the measurement of the shear flow behaviour of materials and also in modelling their flow. For example, some researchers have reported negative or excessively high slip velocities when determined using the Mooney analysis. To understand further the strengths and limitations of the Mooney method for slip velocity determination, an intercomparison on slip flow measurements has been carried out using filled EVA and HDPE materials. Results of this intercomparison indicated that the reproducibility of slip velocity values were up to ± 40%. Recommendations for the measurement of slip flow behaviour are presented.

At the other end of the spectrum, very small concentrations of nano-fillers can, similarly, have significant affects on the processing-related properties of polymers. The addition of nano-fillers can result, for example, in significant shifts in transitions, e.g. crystallisation behaviour. The use of thermal analysis techniques to determine the "quality of mix", or dispersion, of nano-particulate filled materials is proposed.

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 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.

However, slip is a complex phenomenon. It may be due to the formation of a resin rich, low viscosity layer adjacent to the wall or loss of adhesion with the wall [1-7]. Both the wall surface texture and material of construction has been shown to influence slip behaviour [6, 8-15]. Aubry et al [8], 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. Knappe et al [9] 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. Chen et al [1] 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 [2], 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 [2] 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 measurement of slip flow behaviour using the Mooney approach is, however, not always straight-forward. Slip velocities that are negative or are higher than the mean velocity have been reported by various researchers. Negative slip velocities have been reported by Rides [16] and by Mendez-Sanchez et al [17] who suggested that it might be due to flow-induced phase separation or orientation effects. Leblanc et al [18] obtained negative slip values for filled rubber compounds but associated it with the compressibility of the material, which has the opposite effect on the measurement of viscosity to that of slip. In comparison, Hagströ̈m [19], for example, 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 mean flow velocity were obtained – obviously a nonsensical result.

This work aims to further the understanding of the strengths and limitations of the Mooney method for slip velocity determination through an assessment of the uncertainties in measurement and from the results of an intercomparison on slip flow measurements of filled EVA and HDPE materials. Implications of slip flow on flow simulation are also briefly presented.

Slip flow measurement and analysis

Slip in polymer flow has been studied by various workers, as reported by Rides [20]. It may be apparent as an obvious discontinuity in the flow curve but may also occur, without being obvious, over the entire range of the measured flow curve.

The most commonly used method for determining slip velocities is due to Mooney [21] in which different diameter dies are used in capillary extrusion rheometry. Shear viscosity is a material property and thus should be independent of the test geometry. However, if slip occurs then the measured shear viscosities are found to be dependent on the die diameter. This dependence is used to determine the slip velocities.

Following Mooney [21], and presented in detail by Rides [22], the flow of a fluid with shear and slip flow components can be described by summing the two components. Thus the total flow rate Q_T is given by

$$Q_T = Q_{shear} + Q_{slip} \tag{1}$$

where Q_{shear} and Q_{slip} are the shear and slip components of flow respectively. Assuming a power-law model for shear flow and a slip velocity V_s

$$\frac{4Q_T}{\pi R^3} = \left[\frac{4n}{3n+1}\right]\left[\frac{\tau_w}{K}\right]^{1/n} + \frac{4V_s}{R} \tag{2}$$

where K and n are the coefficients of the shear viscosity power-law model, R is the die radius and τ_w is the wall shear stress. If the wall shear stress is constant and assuming n does not vary with shear rate, then:

$$\frac{4Q_T}{\pi R^3} = \text{constant} + \frac{4V_s}{R} \tag{3}$$

This expression states 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 equal to four times the slip velocity.

The shear stress – apparent shear rate behaviour of the material is measured, following ISO 11443 [23], using at least two sets of dies of different diameter. From these data the apparent shear rates corresponding to selected shear stresses for each die diameter are determined by interpolation. From linear fits to plots of apparent shear rate against the reciprocal of the die radius for the selected shear stress values, the gradient is determined. The slip velocity is then calculated by dividing the gradient by 4, Equation 3.

Slip velocity V_s has been modelled as a function of shear stress, a commonly used form being the power-law model:

$$V_s = a\ \tau_w^{\ b} \tag{4}$$

where a and b are constants and τ_w is the wall shear stress. This form was found to fit well the slip behaviour of the material over the slip region.

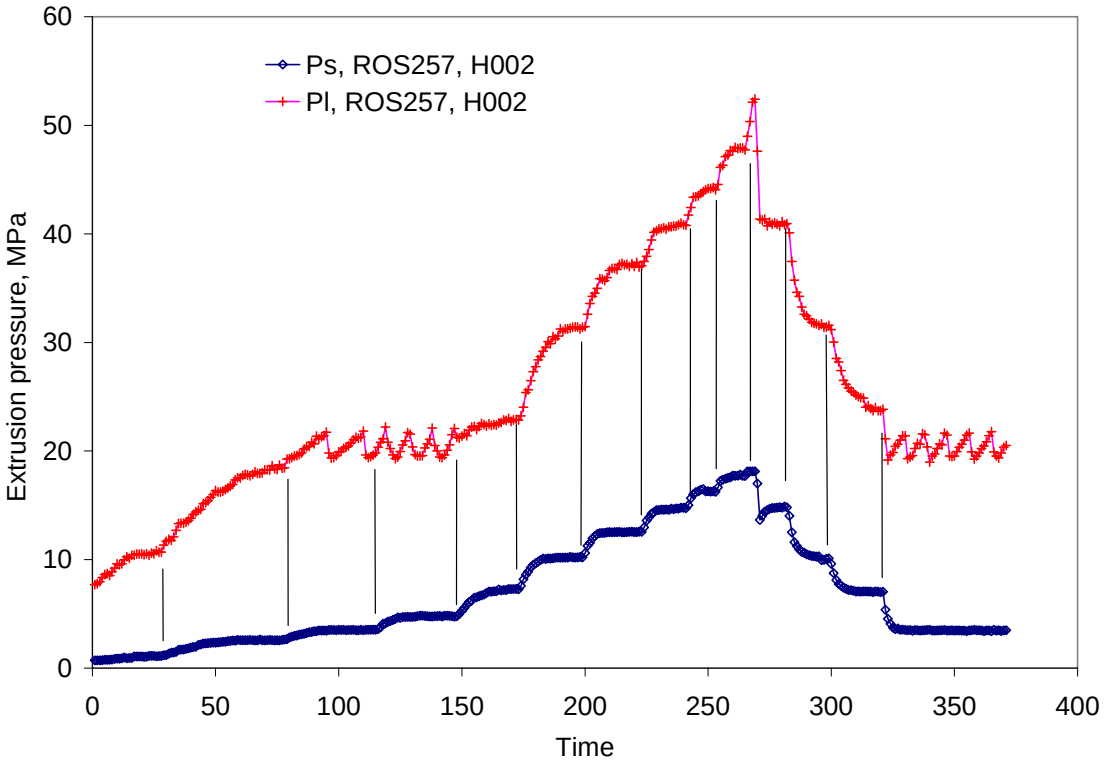

Figure 1: Extrusion pressure traces for short (Ps) and long (Pl) dies of 0.5 mm diameter for a filled HDPE at 220 °C.

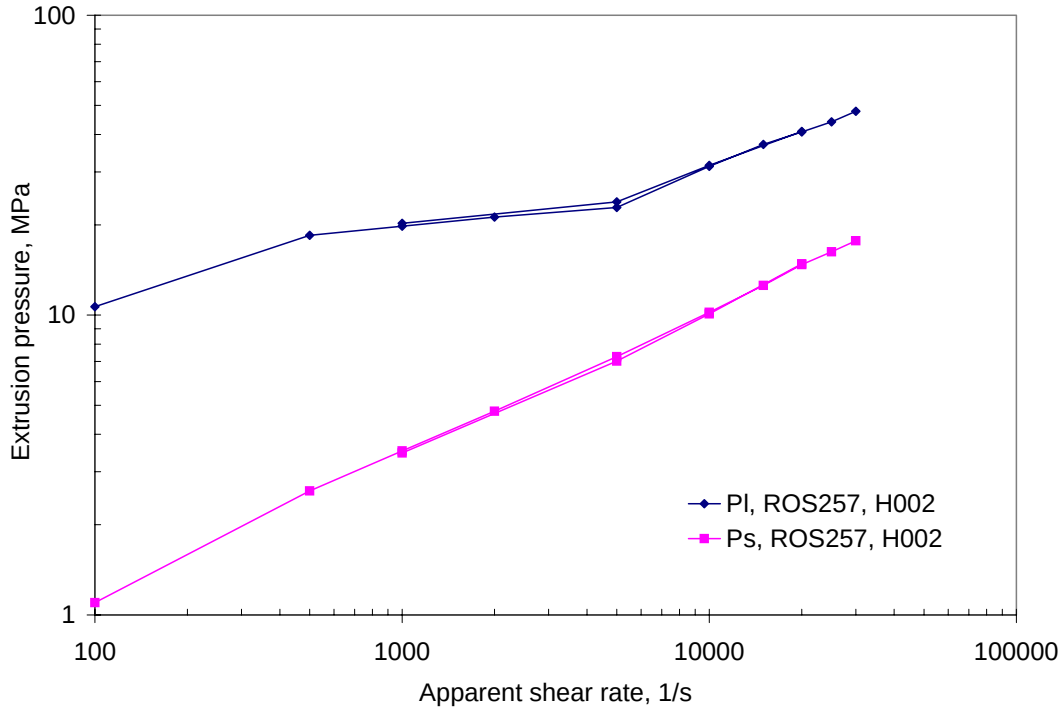

Figure 2: Extrusion pressures obtained using short and long dies of 0.5 mm diameter for a filled HDPE at 220 °C.

Slip flow results

Measurements have been carried out on two filled materials: 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. Detailed results are presented only for the filled EVA.

Typical extrusion pressure traces are shown in Figure 1 for both the long and short dies of diameter 0.5 mm and length approximately 8 mm and 0.2 mm respectively. The long die, but not the short die, trace clearly shows saw-tooth oscillations in extrusion pressure that are associated with melt distortion. At higher rates the extrusion traces become stable again. The reduction in pressure associated with the long die is clearly seen in Figure 2, where the transition initiates at approximately 500 s^{-1} up to approximately 5000 s^{-1}. No significant deviation in behaviour in the short die tests was observed thus suggesting that the phenomenon is shear flow based. Results obtained using various die diameters indicated that there was a small dependence of shear stress on die diameter below an apparent shear rate of 500 s^{-1}, but that there was a much greater dependence above an apparent shear rate of approximately 3000 s^{-1}, Figure 3. This plot indicates one of the key difficulties of slip flow measurements: being able to obtain sufficient data in the slip region with a wide range of die diameters to be able to reliably determine slip velocity values. This is, in part, because the shear rate range over which measurements can be made using each die diameter is limited, and different to that of other diameter dies, by a number of factors including piston speed and pressure transducer range.

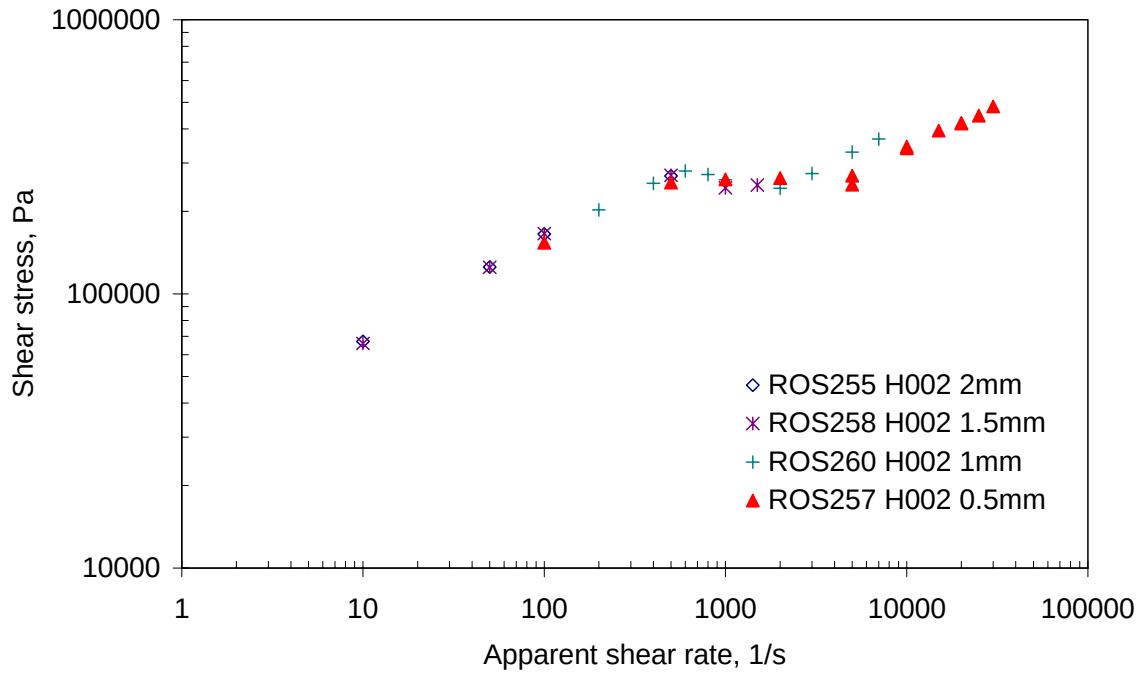

Figure 3: Shear stress results showing a transition region above an apparent shear rate of approximately 500 s^{-1} indicating slip behaviour for a filled HDPE at 220 °C.

The data in Figure 3 have been combined with data from further repeat tests, Figure 4, and best fit lines fitted to the pre-transition data and post-transition data, with individual lines fitted to the 0.5 mm and 1 mm diameter die data above the transition. These data were used to determine the data at selected shear stress values presented in Figure 5, from which slip velocities were determined, Figure 6. Figure 6 indicates that significant slip occurred above a shear stress of 250 kPa. Above this shear stress the slip velocities accounted for approximately 75% of the total flow. Below this shear stress the slip velocities accounted for typically less than 20% of the total flow.

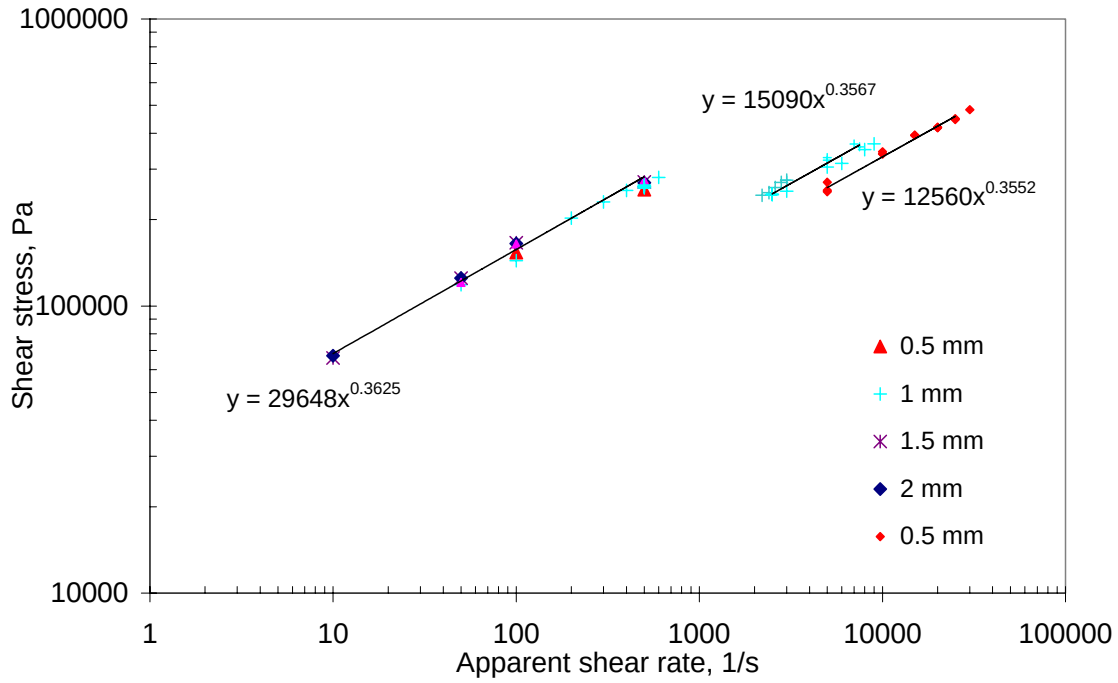

Figure 4: Shear stress results of different flow regimes and die diameters indicating a clear die dependence of results above the slip transition, with best-fit power-law lines presented to the various sets. Filled HDPE at 220 °C.

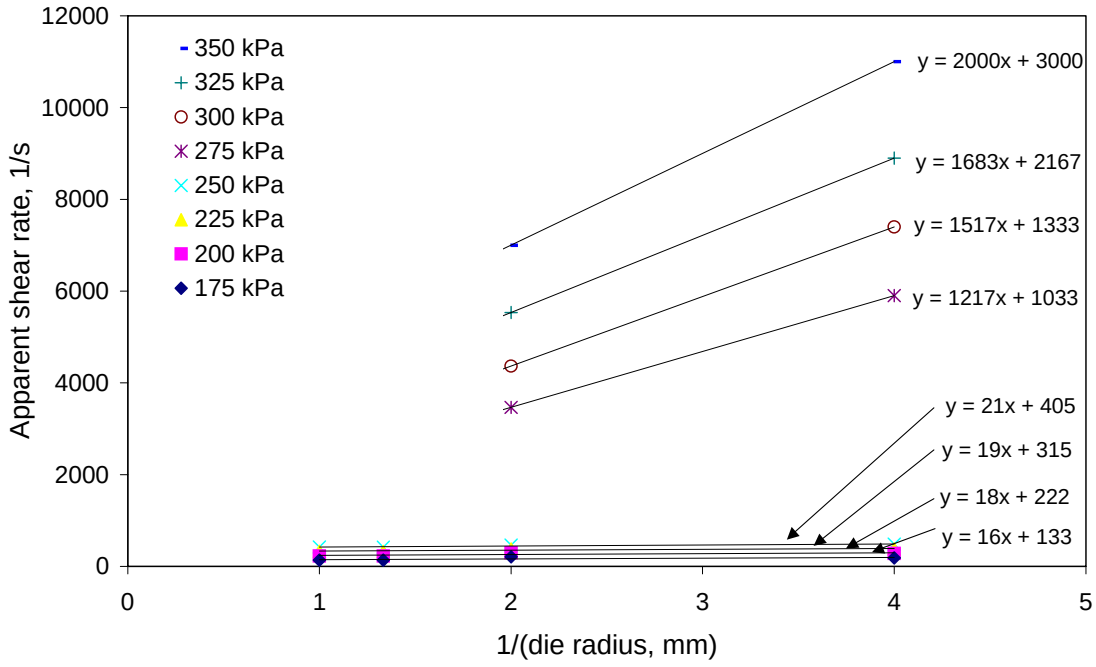

Figure 5: Constant shear stress data plots to determine the slip velocity. Filled HDPE at 220 °C.

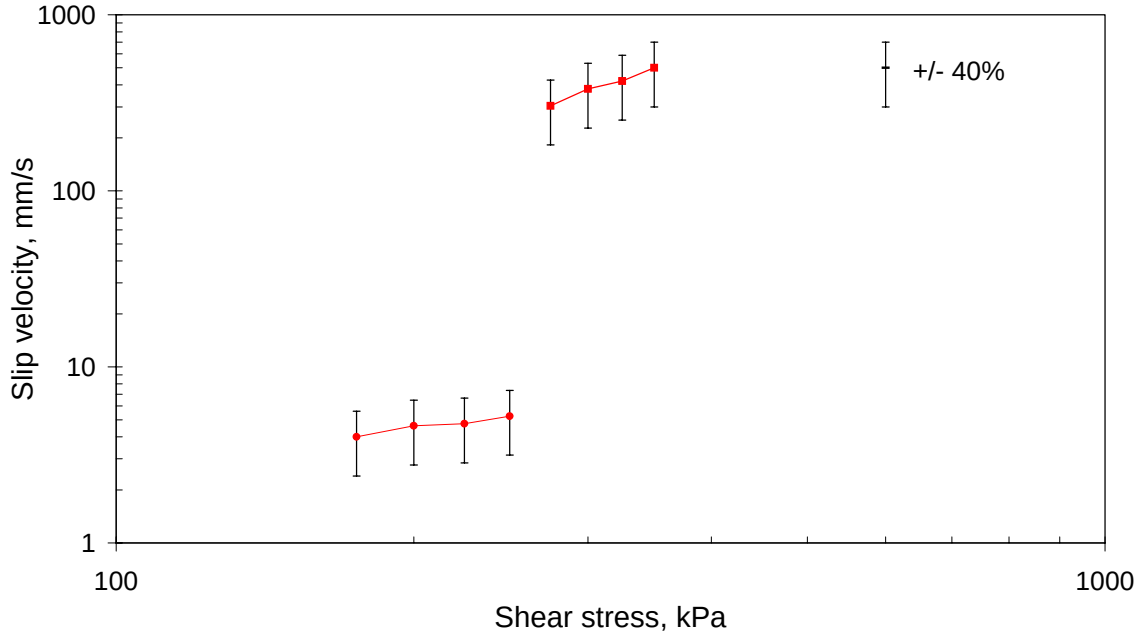

Figure 6: Slip velocity values determined from Figure 5 for the filled HDPE at 220 °C. Scatter bars give estimate of measurement uncertainties.

An intercomparison of slip velocity measurements was carried out by four laboratories on the two materials. The slip velocity results for the HDPE are summarised in Figure 7 and for the EVA in Figure 8. The level of agreement on slip velocities was considered good above the transition, with values within approximately 40% of the mean for both the filled EVA and HDPE materials. For the HDPE the level of agreement below the transition was significantly poorer. This is considered to be due to the relatively small differences in extrusion data with different die diameters in this regime.

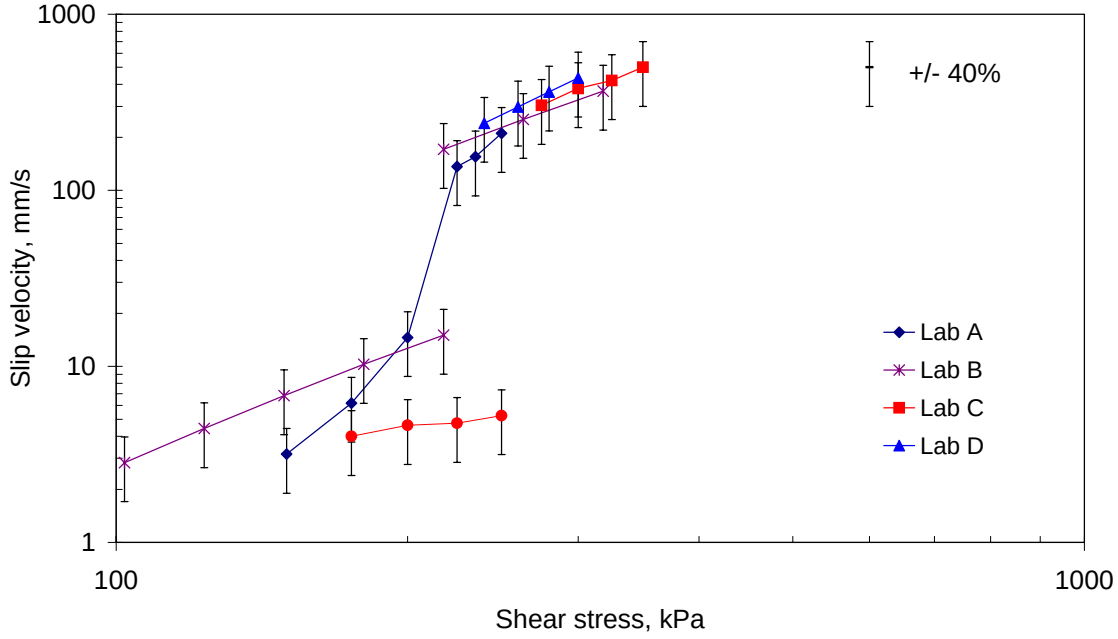

Figure 7: Results obtained from an intercomparison on slip flow velocity determination for the filled HDPE at 220 °C, with 40% tolerance bars added to indicate variation in data

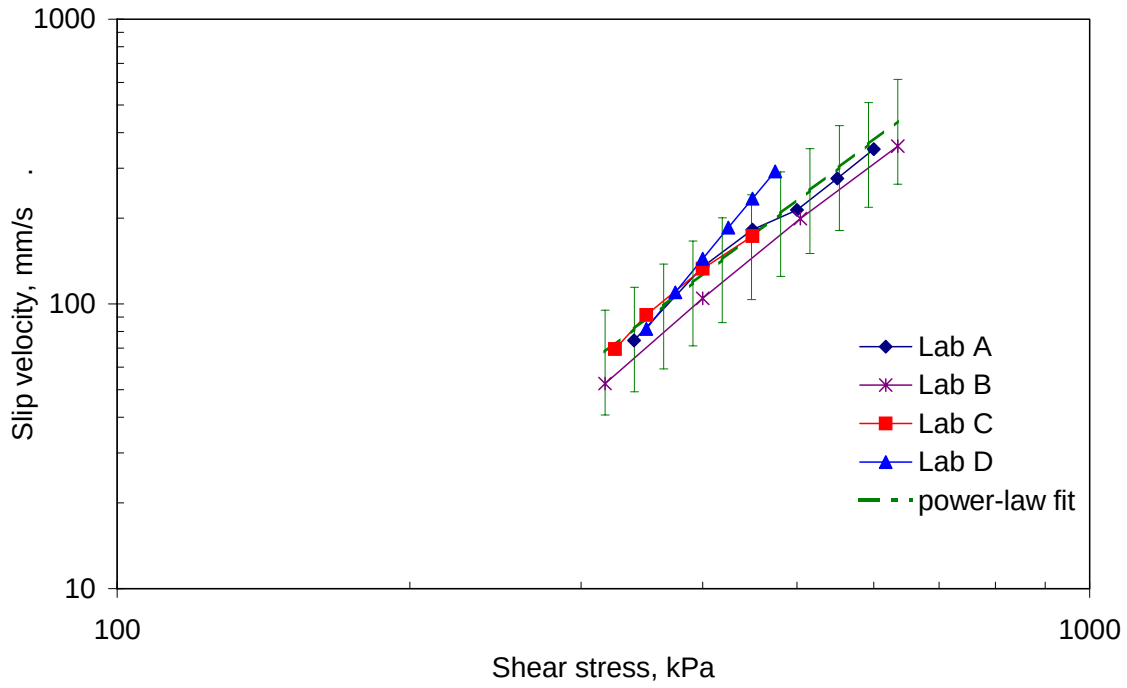

Figure 8: Results obtained from an intercomparison on slip flow velocity determination for a filled EVA at 165 °C, with 40% tolerance bars added to indicate variation in data.

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 [22]. The magnitude of the uncertainties is influenced significantly by the rate dependence of the behaviour of the material. In the cases illustrated the relative expanded uncertainties (95% confidence level) were best estimated to be of the order of 40% to 50%. Due to the potentially high sensitivity of the method to various factors it is recommended that an uncertainty analysis should be carried out in all investigations to identify the uncertainties associated with the specific experimental set-up and the material's behaviour. A key experimental factor, highlighted by the uncertainty analysis, is in the appropriate selection of the die diameters to provide a wide range in values of the reciprocal of the die radius, whilst maintaining a sufficient, common shear stress range for all dies to enable sensible Mooney analysis to be performed.

Implications for numerical modelling of flows

Numerical modelling of the flow of polymers has been carried out using Compuplast Flow2000™ Virtual Extrusion Laboratory™ simulation software for extrusion processing. A Carreau WLF model was fitted to the rheological data. Furthermore, slip flow was modelled using a power-law, Equation 4.

The effect of incorporating the slip behaviour into simulations is illustrated by the results in Table 1. Extrusion pressures, predicted with and without the slip model, are presented for the EVA at 165 °C for a 1 mm diameter die. The differences between the predicted pressure drops and the experimentally measured values are presented in brackets. These results illustrate that in the slip region when using the slip model the discrepancies were within ±5%. A similar value was obtained when modelling the no-slip region without the slip model. However, inappropriate modelling, e.g. not incorporating the slip model in the slip region, resulted in an error in pressure values of up to 43%. A 43% reduction in the pressure drop will result in a similar magnitude reduction in the heat generated by viscous dissipation. For these nominally isothermal tests the average temperature rise in the flow through the die was estimated to be ≈ 11 °C and ≈ 16 °C at 1000 s^{-1} and 3000 s^{-1} respectively.

These modelling results illustrate potential problems associated with the use of the slip function in the no-slip region, which resulted in an error of some ± 30%, indicating the need to "switch off" the slip function using, for example, a limiting shear rate value.

Table 1: Comparison of pressure drop predictions with and without slip model

	No-slip region		Slip region	
Apparent shear rate, s^{-1}	100	250	1000	3000
Measured pressure drop, MPa	18.3	24.6	22.9	31.8
Predicted pressure drop – no-slip, MPa	19.2 (5%)	24.5 (-1%)	32.2 (43%)	38.8 (22%)
Predicted pressure drop - with slip, MPa	13.1 (-28%)	16.8 (-32%)	23.6 (3%)	30.3 (-5%)

Thermal analysis of polymers – a tool for a measure of the quality of mix

The majority of this paper has considered the highly filled end of plastics market although the methodology is applicable to all plastics materials. At the other end of the spectrum, very small concentrations of nano-fillers can, similarly, have significant affects on the processing-related properties of polymers. The addition of nano-fillers can result, for example, in significant shifts in transitions, e.g. crystallisation behaviour, as demonstrated by a nylon material, Figure 9. The use of thermal analysis techniques, perhaps in combination with rheological techniques, to determine the "quality of mix", or dispersion, of nano-particulate filled materials is thus proposed.

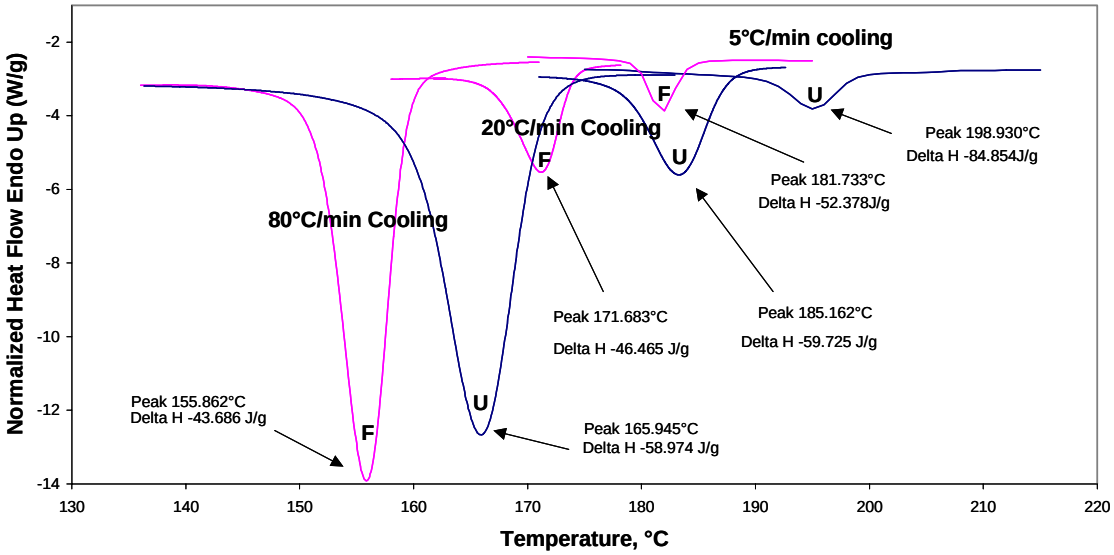

Figure 9: Differential scanning calorimetry results of nylon 6 unfilled (U - blue) and nano-clay filled (F - pink) materials at 5°C/min, 20°C/min and 80°C/min cooling rates.

Conclusions

Although the measurement and modelling of slip is often overlooked, it can have a significant effect on the flow behaviour and thus on predictions of processing. For example, for these materials the onset of slip can result in a reduction in extrusion pressure by more than 40%.

The results of the intercomparison showed reasonable agreement in slip velocity values. An analysis of the uncertainties in the measurement method indicated that the measured slip velocity values, differing by up to approximately 50%, were within the expanded uncertainty limits of the mean values.

A key, and perhaps dominant, factor in the reliable measurement of slip velocities using the Mooney method is the appropriate selection of the die diameters. It is necessary to select dies that provide a wide range in the value of 1/(die radius, R) whilst maintaining a good overlap in shear stress values for all die diameters. It is considered essential to carry out an uncertainty analysis of the experiment that includes both the experimental set-up and the material's rate dependence characteristics in order to ascertain the uncertainties and thus confidence in measured values.

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