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Improved testing using the melt flow rate instrument - multi-rate and extensional flow measurements

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ABSTRACT

The melt flow rate method is widely used in quality control within the polymer industry and is likely to remain as a dominant tool for quality control and assurance. However, it is widely accepted within the industry that the melt flow rate method has limitations. To address these limitations various developments to the melt flow rate method have been undertaken and are reported here.

These developments encompass: the use of multi-load testing to enable melt flow rate data to be extrapolated more reliably to higher shear rate, the use of alternative die geometries to separate the shear and extensional flow behaviours and the measurement of extrudate swell and draw-down.

The results presented demonstrate good agreement of shear viscosity and entrance pressure drop data measured using the multi-rate melt flow rate method with data obtained using a capillary extrusion rheometer. Furthermore, good qualitative agreement has been obtained between extensional flow behaviour measured by extrudate draw-down with that measured using a quantitative stretching technique thus demonstrating the significant value of the draw-down technique.

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MPM1.2: Viscoelastic measurement techniques for polymer melts,
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on measurements related to the processability of materials

Approved on behalf of Managing Director, NPL
by Dr C Lea, Director, NPL Materials Centre

CONTENTS

1. INTRODUCTION

The melt flow rate method, or melt flow index as it was historically known, has been in existence for several decades. It is globally used for materials specification and quality control in the plastics industry. It fulfils a requirement for rapid materials characterisation, specifically for checking the quality of the material and for assessing its processability, both of these in terms of the material's ease of flow.

The method, put simply, is to measure the quantity of material (pre-heated in the barrel) that is extruded through the die in a given time when a specified weight is applied to the piston, Figure 1. The current standard ISO 1133 [1] covers two procedures, specifically the melt mass flow rate (MFR) and the melt volume flow rate (MVR). The difference between these two measures is that in the former the mass of material extruded in a given time is measured, and in the latter the volume of material is measured. Thus a single figure is obtained for either MFR or MVR that characterises the flow behaviour of the material. MFR is expressed in g/10 minutes and MVR in cm^3/10 minutes. The MFR and MVR are thus measures of the ease of flow: the higher the number the easier the material flows. The term "melt flow rate" is used herein to indicate both MFR and MVR methods.

All testing conditions are tightly specified by the ISO standard [1]. The only parameters that are allowed to vary are the test load and the temperature. However, for any given type of material, e.g. polypropylene, there is normally only one set of test conditions permitted: that set having been selected or optimised for that class of material. As an exception, and indicative of the wider range of grades available, for polyethylene there are four permitted loads although the temperature is the same in each case. However, the criteria for selection of the loads are also tightly specified.

The tight specification of the method, its simplicity and relatively low cost are its strengths for quality control and materials specification purposes. However, it is widely accepted within the industry that the method has limitations and these have been reviewed elsewhere [2-5].

This paper presents some of the recent work carried out to address the limitations identified in the melt flow rate method by providing affordable improvements to the method. These developments are reported and entail:

- the measurement of melt flow rate at higher shear rates thus making the method more reliable in predicting the performance of materials in processing, and

- the characterisation of the extensional flow behaviour of polymer melts: a property that is important in both processing and quality control yet is normally overlooked by traditional characterisation methods.

It is emphasised that these developments are not intended to replace the current melt flow rate method but to supplement it thereby enhancing the capability and value of that method through the provision of additional, appropriate information on the flow behaviour of polymer melts.

2. DEVELOPMENTS BASED ON THE MELT FLOW RATE METHOD

2.1 GENERAL

An essential requirement for developments based on the melt flow rate method is that the current method should neither be replaced by an alternative method, nor changed to the extent that instruments would no longer comply with the melt flow rate ISO standard [1]. The melt flow rate technique is too ingrained in the global polymer industry for the successful introduction of a replacement or substantially modified method. The approach adopted has therefore been to consider improvements in the current method and the associated ISO standard, and to develop methods that can be carried out utilising the basic melt flow rate instrument. This approach is likely to maximise the uptake by industry of such measurement technology.

2.2 HIGHER FLOW RATE TESTING

The development of the method to higher flow rates, which requires greater loads, is limited by the desire to use existing melt flow rate instruments. Also, in extending testing to higher rates the divide between melt flow rate testing and capillary extrusion rheometry testing will be reduced. This divide is not sufficient to warrant the introduction of a further instrument. A principal shortcoming in the melt flow rate method, in this respect, is the inability to predict processing behaviour at higher rates. To improve on this position it is therefore considered appropriate that the extrapolation method requires improvement, rather than developing the method to test at significantly higher rates. Capillary extrusion rheometers already exist for that purpose. It is therefore proposed that the use of two or three loads is considered and a reliable procedure for extrapolating to higher flow rates is developed. For materials that exhibit rate-dependant shear thinning at low shear rates, the variable shear thinning behaviour will complicate this extrapolation with the consequence that three flow rates, and thus three loads, are likely to be required for reliable extrapolation to high shear rates.

2.3 EXTENSIONAL FLOW TESTING

The development of the melt flow rate method to enable characterisation of the extensional flow behaviour is addressed by three approaches. The intention is not necessarily to establish three separate methods from the outset but to develop the various approaches and then to identify which of those methods is most suited to testing the full range of polymers. A proliferation of test methods is not desirable to industry. It may be, however, that no single method will be suited to the whole range of polymers and that one or another of the approaches may be preferred and thus used, dependent upon the type of material and the method by which it will be processed.

The methods being developed are:

- the use of a short length die to determine entrance pressure drop data,
- the measurement of extrudate swell, and
- the measurement of extrudate draw-down (similar to parison sag).

The principle behind the use of a short length die is to obtain a measure of the resistance to flow in a converging region, which can then be related to the extensional flow behaviour of the material [6-11]. This method is simple, yields quantitative data and is potentially cheap. The measurement of extrudate swell and extrudate draw-down will correlate directly with the behaviour of melts in extrusion and blow moulding (parison sag) respectively. Whereas parison sag is predominantly governed by the extensional flow behaviour of the material, extrudate swell is a more complex phenomenon that is governed by the full rheological behaviour of the material. Nevertheless, for polymer melts the extensional flow behaviour can have a significant affect on the extrudate swell behaviour and, more importantly, extrudate swell is a measure that is of direct relevance to converters. It is thus considered a very valid approach to pursue as a quality control measure. The principal difficulties perceived with these methods are in developing the procedures to cover the range of behaviours and to obtain repeatable and reproducible results [12] thus giving the user confidence in the data generated.

An added benefit of using an additional short die is that data obtained using the standard melt flow rate die can then be corrected for entrance effects to yield reliable shear viscosity data.

2.4 EXPERIMENTAL DETAILS

All melt flow rate measurements were made using a standard Ray-Ran Test Equipment Limited 5MPCA Advanced Melt Flow System instrument. This instrument has a linear displacement transducer that allows the region over which the measurements are taken to be split into many segments. In the measurements reported herein 20 separate determinations of melt flow rate were made per barrel charge. Multi-load tests were carried out using standard loads as identified in ISO 1133 [1]. Typically, for a single barrel charge, three or four different loads could be applied. Thus for each load in a multi-load test approximately 5 separate determinations of melt flow rate were obtained. It was found preferable to apply the loads in increasing value as this allowed the operator to exert better control over the progress of the test. The short dies used were non-standard and were either 1 mm or 2.095 mm in diameter and of nominal length of 0.25 mm. Capillary extrusion rheometry measurements were made, for comparative purposes, using a Rosand twin-bore rheometer.

Automated, non-contact extrudate swell measurements were made using a Mitutoyo Laser Scanning Micrometer (LSM-3000) mounted on the melt flow rate instrument. Measurements were also made on the cooled extrudate using a hand-held digital micrometer. For comparative purposes, extensional flow measurements were made on an NPL extensional rheometer in which the specimen was stretched uniaxially [13].

2.5 DATA ANALYSIS

Theory that describes the operation of the melt flow rate instrument in its normal use is presented in detail in Appendix A2. Extension of that theory to the use of the instrument to determine entrance pressure drop data using a short die and the subsequent correction of standard melt flow rate data, using the short die data, to determine reliable shear viscosity data is presented in Appendix A3.

Theory to interpret the extrudate draw-down behaviour in terms of extensional viscosity is

presented in Appendix A4.

3. MULTI-LOAD MELT FLOW RATE DATA OBTAINED USING A STANDARD DIE

The effect of the applied load on the melt flow rate can be clearly seen for a linear low density polyethylene (LLDPE) at 190 °C, Figure 2. The test progresses from left to right, the x-axis indicating the test segment from 1 to 20. At the change-over from one load to another, spurious results may occur for that test segment: these have been discarded in the presentation of subsequent results as appropriate. As expected, a larger applied load results in a higher measured melt volume flow rate. Thus it is demonstrated that the flow behaviour over a wide range of rates can be determined by applying loads that are specified in the international standard ISO 1133 [1], i.e. 2.16 kg, 3.8 kg, 5 kg, 12.5 kg and 21.6 kg in this case. The lower load of 0.325 kg specified in ISO 1133 has not been used for this material as the MVR value would have been too small for reliable determination.

Results of 12 tests performed on a high density polyethylene (HDPE), each comprising of one or more loads from the range 2.16 kg, 5 kg, 12.5 kg and 21.6 kg, are presented in Figure 3. These results clearly show the effect of load on the measured MVR and that, within scatter, the results are independent of applying either an increasing or decreasing load. Previous oscillatory rheometry measurements [8] indicated that this material was stable for 2 hours at 150 °C. It is also noted that the first result per test, i.e. test segment 1, is often spurious due to transients at the start of the test.

4. MULTI-LOAD MELT FLOW RATE DATA OBTAINED USING SHORT AND STANDARD DIES

Multi-load results obtained using a standard die and a short die are presented for a high density polyethylene tested at 190 °C, Figure 4. The use of a standard die of length 8 mm or a short die of length 0.26 mm (same diameter as the standard die, i.e. 2.095 mm) results in different MVR values being obtained. Obviously the short die presents a lower resistance to flow and thus the MVR values are correspondingly higher, in this case by a factor of approximately x6, Figure 4.

However, by using a smaller diameter, short die (diameter 1 mm and length 0.24 mm) then MVR values of similar magnitude to those obtained using a standard die can be achieved, Figure 5. This can be of particular benefit when measuring materials that have a high MVR value using the standard die that would have MVR values that were excessively high when using the shorter die causing measurement problems and consequently large errors.

5. SHEAR VISCOSITY AND ENTRANCE PRESSURE DROP DATA DETERMINED USING THE MELT FLOW RATE INSTRUMENT

Comparison of MFR values obtained using both the standard and short dies with values calculated using capillary rheometry shear viscosity and entrance pressure drop data show very good agreement, Figure 6. The discrepancy is greatest at the lowest melt flow rate of approximately 0.1 g/10 min due to the need to extrapolate the capillary rheometry data to the low rate.

However, in this comparison differences in one parameter, e.g. shear viscosity, may effectively cancel out differences in the other, e.g. entrance pressure drop. Thus, for thoroughness, a more exacting comparison is to compare the values of shear viscosity, corrected for entrance effects, and entrance pressure drop measured using the melt flow rate instrument with values measured using a capillary extrusion rheometer. In both cases excellent agreement of results was obtained, Figures 7 and 8, thus providing confidence in the use of a melt flow rate instrument for generating quantitatively accurate rheological data.

The repeatability of measurements of entrance pressure drop is also good, Figure 8. The effect of the die diameter on the entrance pressure drop as a function of apparent shear rate is also shown to be negligible, Figure 9, thus indicating that a smaller diameter die may be used with confidence to determine entrance pressure drop data for use in correcting shear viscosity data.

It is noted that the breadth of the shear rate range that can easily be achieved by both capillary extrusion rheometers and melt flow rate instruments is similar. For the melt flow rate instrument the range of loads over which measurements can easily be made is one decade, i.e. 2.16 kg to 21.6 kg (not including the use of the lower load of 0.325 kg). Similarly, for capillary extrusion rheometry the standard ISO 11443 [14] specifies that measurements should not be made using the pressure transducer outside the range of 10% to 90% of their normal capacity. Thus the breadth of the load ranges, and hence shear rate ranges, of the two instruments are very similar. Obviously the pressure transducer in the extrusion rheometer can be changed for one of a different range thereby extending the capability of the instrument further, though this obviously results in a considerable increase in the time and hence cost of testing.

Similar multi-load results and derived entrance pressure drop and shear viscosity data are presented for four other polyethylenes, two high density polyethylenes (HGH000 – Figures 10 to 12 and HFU000 – Figures 13 to 15), a low density polyethylene (HGE000 – Figures 16 to 18) and a linear low density polyethylene (HGF000 – Figures 19 to 21). The repeatability and level of agreement with values of entrance pressure drop and shear viscosity obtained from capillary extrusion rheometry measurements is very good.

6. EXTRUDATE SWELL AND DRAW-DOWN MEASUREMENTS

Preliminary extrudate swell measurements were carried out using a laser-scanning micrometer mounted on the melt flow rate instrument. The measurement of extrudate diameter was at approximately 45 mm beneath the exit of the die. Measurements were also made using a hand-held micrometer on the cooled extrudate after completion of the test.

Typical results from laser micrometer extrudate swell measurements performed during a test in which the loads were changed in a decreasing manner are presented in Figure 22. These results clearly show, as expected, that the use of lower loads resulted in less swelling of the extrudate. Also, for a given test load, the effect of draw-down of the extrudate under its own weight resulting in a reduction in its diameter as the test progresses is apparent. Draw-down was sufficient at the lowest load to result in the diameter of the extrudate being less than that of the die.

Good agreement of hand-held and laser scanning micrometer measurements of extrudate

swell was obtained although this is considered fortuitous and a consequence of the procedure used to make the measurements, Figure 23. Of importance though is that the trend in extrudate swell with load is similar in each case.

Both the magnitude of the swelling and the draw-down are characteristic of the flow behaviour of the polymer, in particular its viscoelastic extensional behaviour. However there are many factors, both experimental and material dependant, that contribute to the extrudate swell and therefore complicate both its measurement and application to industrial practice.

The draw-down behaviour was investigated in further detail as a promising option for providing data on the response of polymer melts to stretching flows. Measurements were made with both the laser scanning micrometer positioned approximately 45 mm below the die exit and also with a hand-held micrometer on the cooled extrudate. The latter were measured in orthogonal directions (0° and 90°) on the extrudate. Measurements were taken during a standard, single-load melt flow rate test and were commenced by removing all extrudate below the die exit. The extrudate was then allowed to form until it reached the bottom of the base of the instrument: a drop of approximately 260 mm from the die. The load was selected to result in an MVR value of not more than approximately 4. As a consequence of this, when the extrudate reached the point at which the laser micrometer was scanning, its outer surface had frozen and therefore changed relatively little subsequent to that point.

Laser scanning micrometer and hand hand-held micrometer results are presented for two high density polyethylenes (HGH000 – Figures 24 and 25 and HFU000 – Figures 26 and 27), a low density polyethylene (HGE000 – Figures 28 and 29) and a linear low density polyethylene (HGF000 – Figures 30 and 31). The results demonstrate good repeatability of both methods. A comparison of the hand-held and laser micrometer results demonstrates a good level of agreement, Figure 32.

Comparison of the behaviour of these grades, which exhibit quite different extensional flow behaviours [7, 13], indicates significant differences in the extrudate swell and draw-down behaviours. These differences were exhibited in both the laser scanning micrometer and hand-held micrometer results, Figures 33 and 34. However, the loads used for these tests differed in order to obtain similar melt flow rate values: HFU000 and HGE000 were 5 kg, HGH000 was 12.5 kg and HGF000 was 2.16 kg. To reliably interpret these data a normalisation process was required. Details of the analysis, which determines an approximate extensional viscosity from this draw-down behaviour, are presented in Appendix A4.

A comparison of the derived approximate extensional viscosities of these four polyethylenes is presented in Figure 35 along with tensile stress growth coefficient[1] data presented elsewhere for the same materials [13]. The comparison of draw-down data with the maximum tensile stress growth coefficient data is not particularly valid as in the draw-down method the extrudate is stretched to a small degree whereas in determining the maximum tensile stress growth coefficient data the melt undergoes significantly higher strains. However, from those tests data have been obtained at equivalent strains as those occurring in the draw-down tests and comparison is more appropriate. For all but the LLDPE the draw-down tests underpredict the values of extensional viscosity by a factor of approximately x2 to x3. However the trend is the same which, incidentally, is different to the trend exhibited in the maximum tensile stress growth coefficient values. The reason for the good agreement of the LLDPE data is

[1] The tensile stress growth coefficient is the ratio of the tensile stress to strain rate. It is effectively a transient extensional viscosity.

considered to be due to the fact that the material is neither particularly strain hardening nor strain rate dependent and is thus affected less by the assumptions made in analysing the draw-down data. Analysis of the sensitivity of derived approximate extensional viscosity data to input values, for example for HGH000 – Figure 36, suggests that the method is not particularly sensitive to any of the input values.

Thus these draw-down measurements provide a valuable qualitative assessment of the extensional flow behaviour of polymers melts. It is perhaps important to stress that the full analysis of the draw-down in terms of an approximate extensional viscosity is not necessary for quality control purposes but that the absolute values of extrudate swell at two positions along the extrudate and their ratio are likely to suffice.

7. DISCUSSION AND CONCLUSIONS

The melt flow rate method is widely used in the polymer industry and it is likely to remain as a dominant tool for quality control and assurance for some time. However, it is generally accepted within the industry that the melt flow rate method has limitations. To address these limitations various developments have been undertaken and presented. These developments address:

- the measurement of melt flow rate at higher shear rates (multi-load testing) - thus making the method more appropriate for predicting the performance of materials in processing, and

- the characterisation of the extensional flow behaviour of polymer melts (through entrance pressure drop and extrudate swell measurements) - a property that is important in processing yet is normally overlooked by traditional characterisation methods.

It is noted that these developments are not intended to replace the melt flow rate method but to supplement it to enhance the capability and value of the method to provide additional appropriate information on the flow behaviour of polymer melts thereby addressing some of the limitations identified.

In conclusion:

- this work has demonstrated that significantly more information can be obtained from the melt flow rate instrument, with only minimal modification, than is currently the practice,

- multi-rate data can be obtained with no additional equipment beyond the standard range of melt flow rate weights,

- entrance pressure drop and shear viscosity data corrected for entrance effects can be obtained using minimal additional equipment, i.e. a short length die,

- good agreement can be obtained between melt flow rate and capillary extrusion rheometry instruments for shear viscosity and entrance pressure drop,

- entrance pressure drop values as a function of shear rate are not significantly influenced by the die diameter in the melt flow rate test, and

- valuable qualitative measures of the extensional flow behaviour of the polymer can be obtained by measurement of the extrudate draw-down behaviour during melt flow rate tests.

The value of these methods is being assessed further through ongoing industrial case studies.

8. ACKNOWLEDGEMENTS

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10. FIGURES

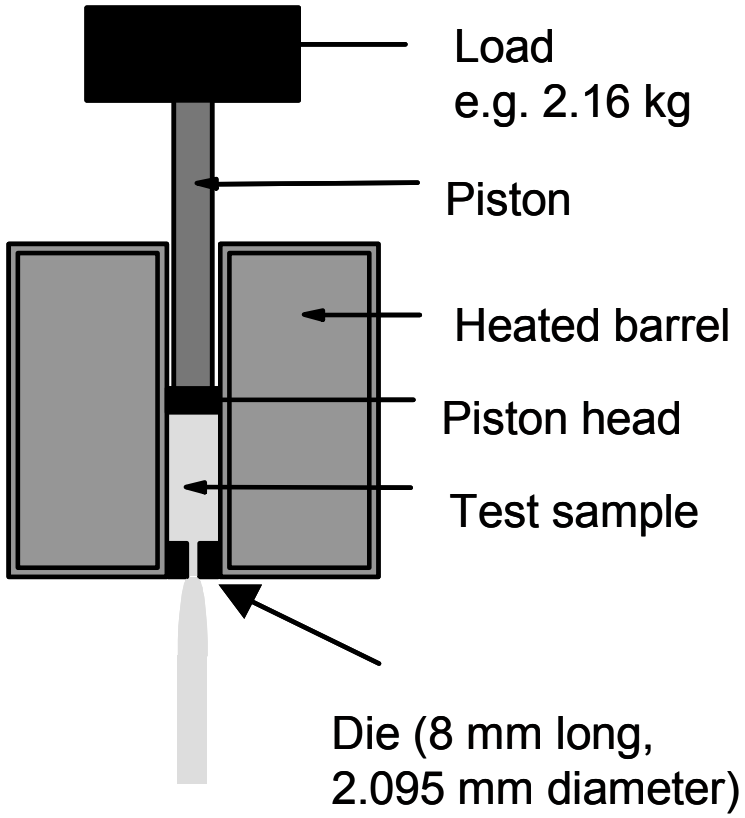

Figure 1 Schematic diagram of the melt flow rate apparatus.

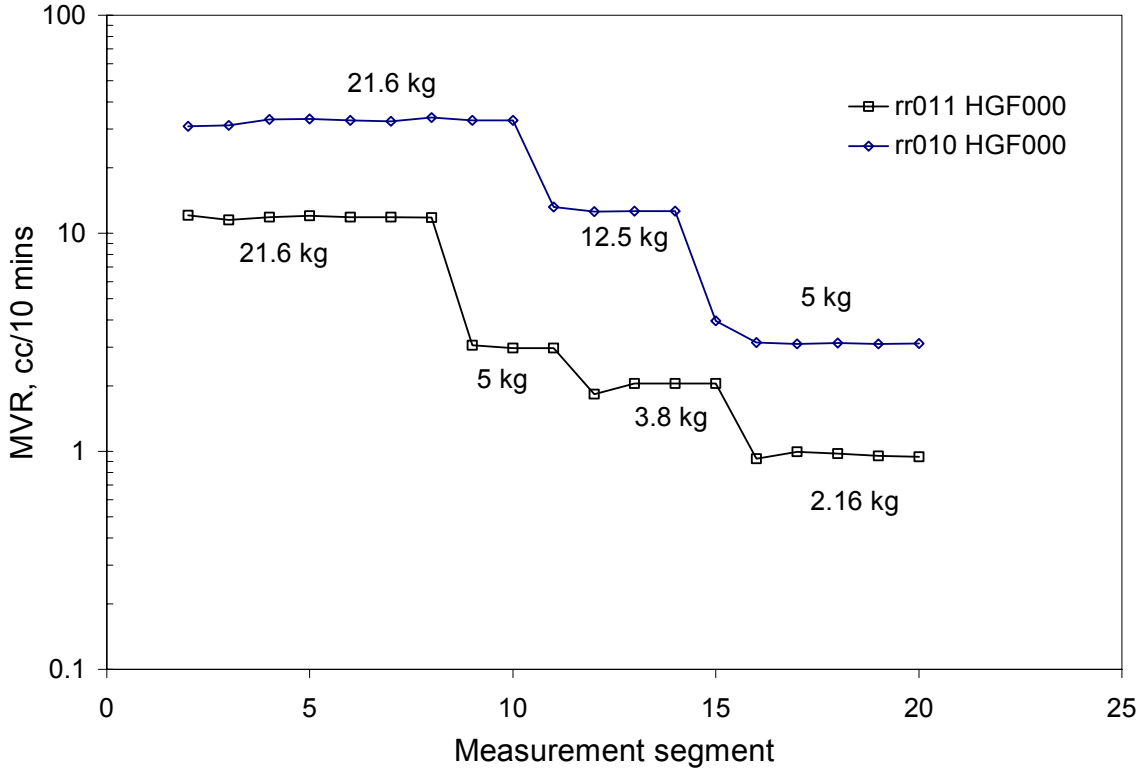

Figure 2 The effect of test load on melt volume flow rate values for a LLDPE at 190 °C.

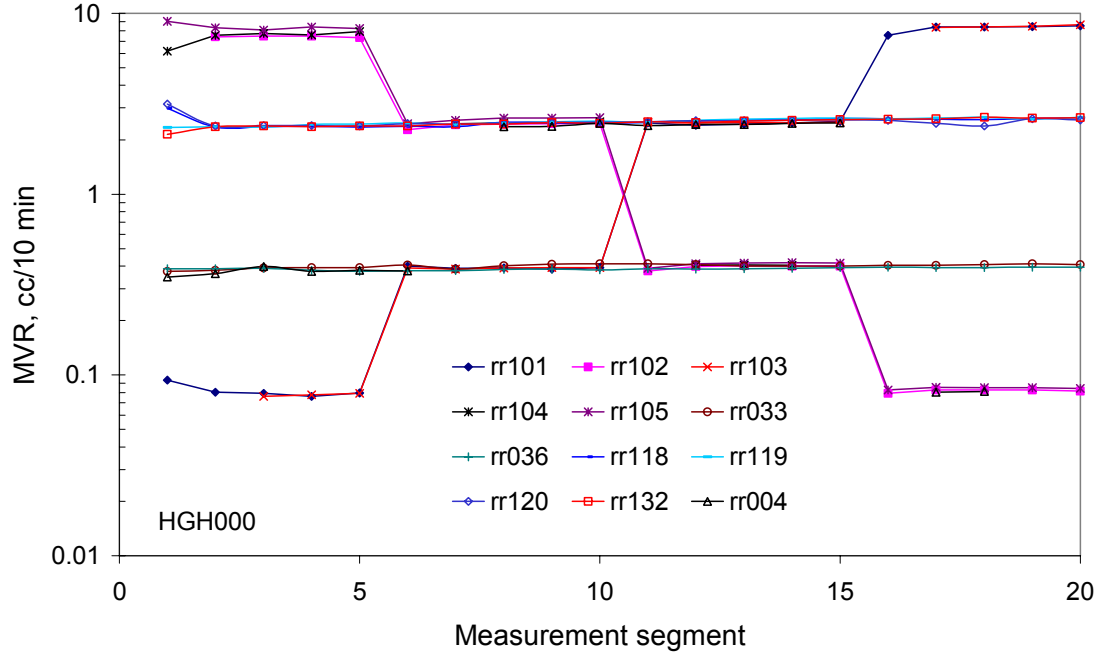

Figure 3 The effect of multi-load test order on melt volume flow rate for a HDPE (HGH000) at 190 °C.

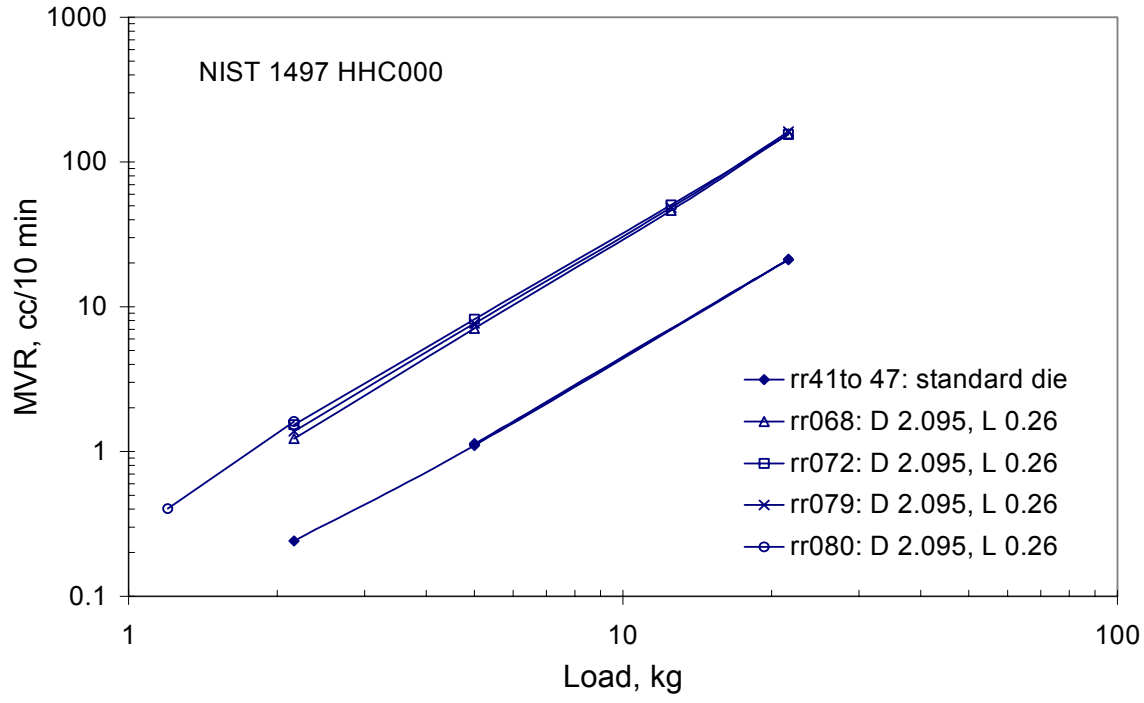

Figure 4 Comparison of melt mass flow rate values measured using a standard die with those measured using a short length die (0.26 mm) of standard diameter for a HDPE (HHC000) at 190 °C.

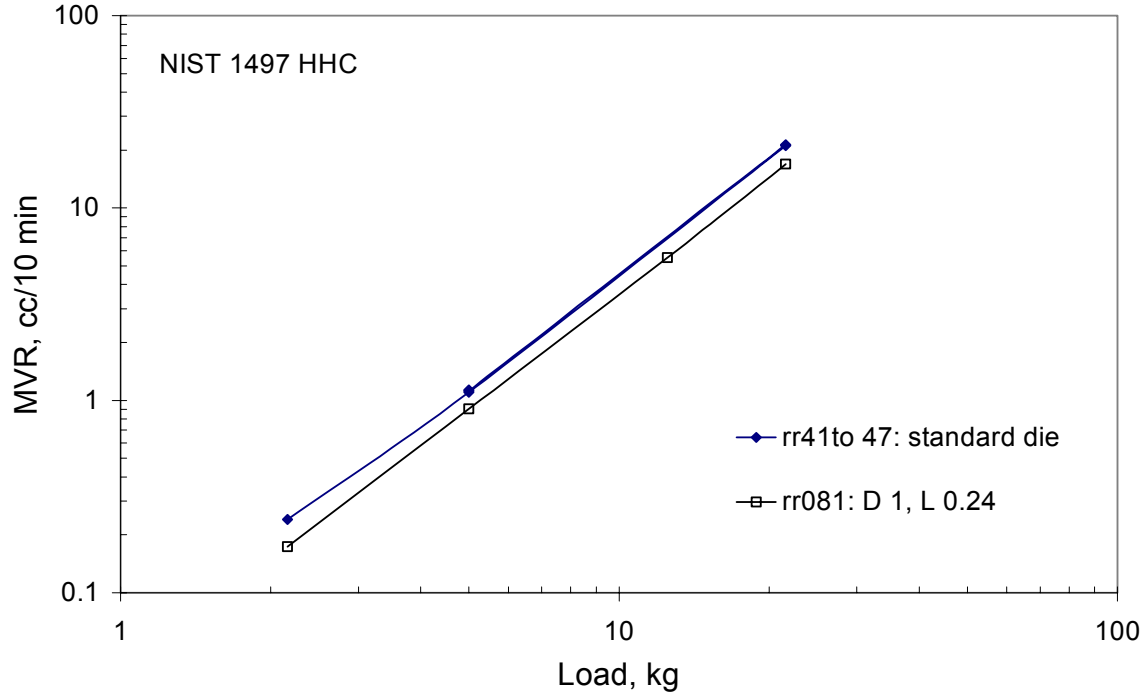

Figure 5 Comparison of melt mass flow rate values measured using a standard die with those measured using a short length die (0.24 mm) of smaller diameter (1 mm) (rr081) for a HDPE at 190 °C

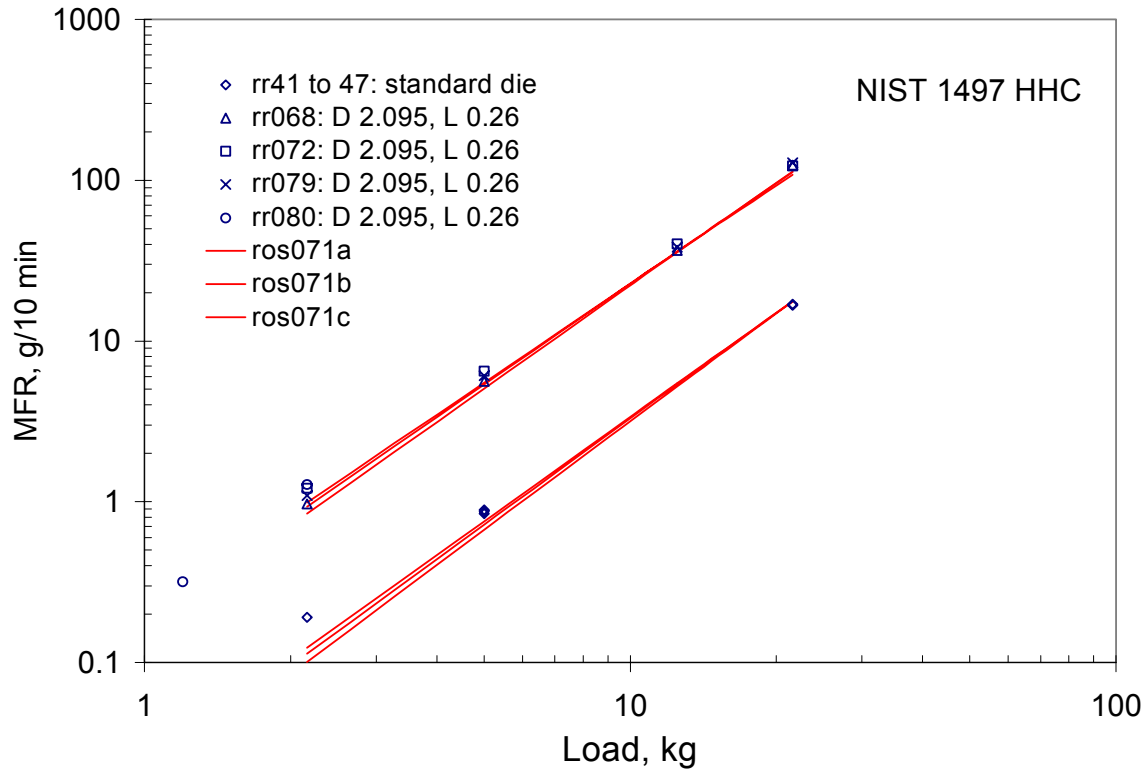

Figure 6 Comparison of predictions, using capillary rheometry data, of melt mass flow rate values measured using a standard die and using a short length die (0.26 mm) of standard diameter for a HDPE at 190 °C (lines are predicted values).

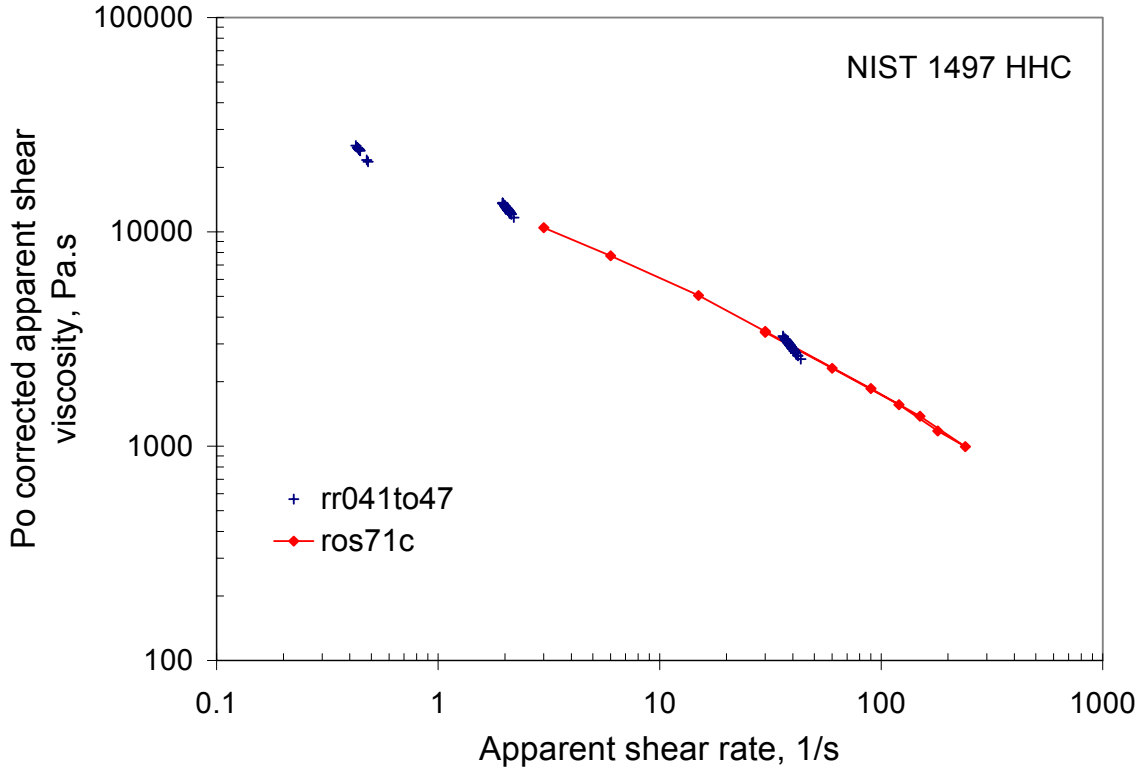

Figure 7 Comparison of shear viscosity values, corrected for entrance effects, measured using an extrusion rheometer (ros071c) with values measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) (rr041 to 47) for a HDPE at 190 °C.

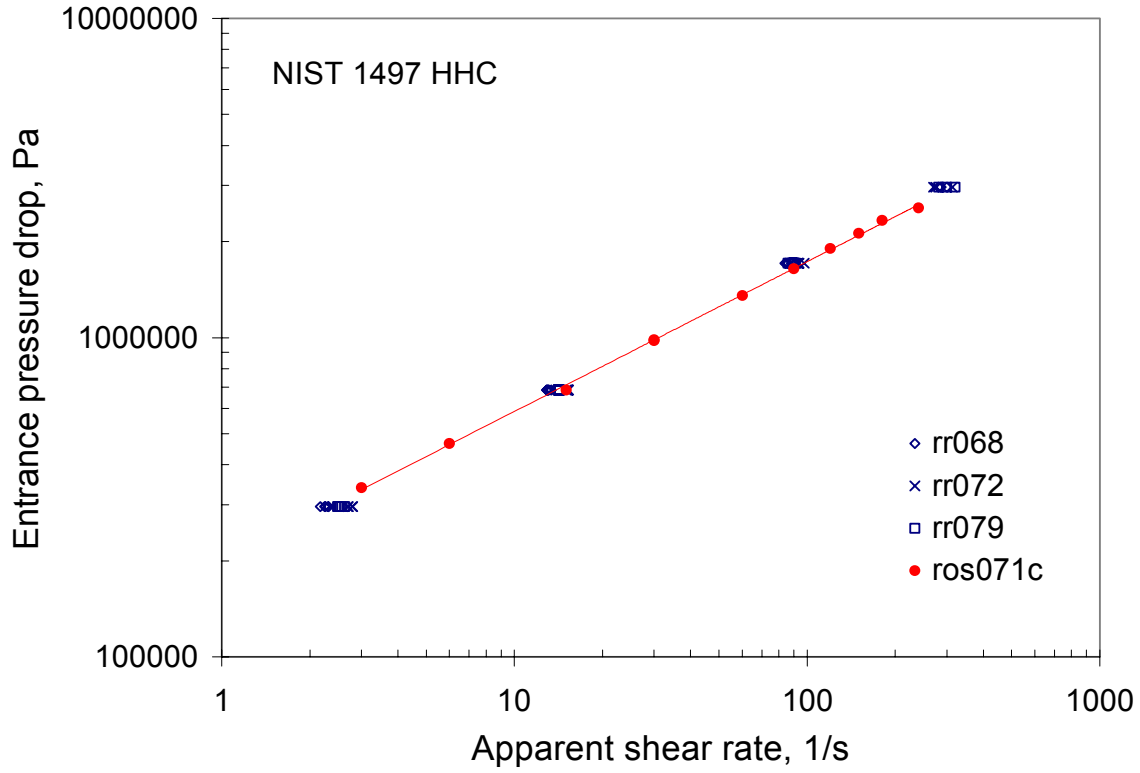

Figure 8 Repeatability of entrance pressure drop measurements using a melt flow rate instrument with a short die (0.26 mm length, diameter 2.095 mm) compared with extrusion rheometry data (ros071c) for a HDPE at 190 °C.

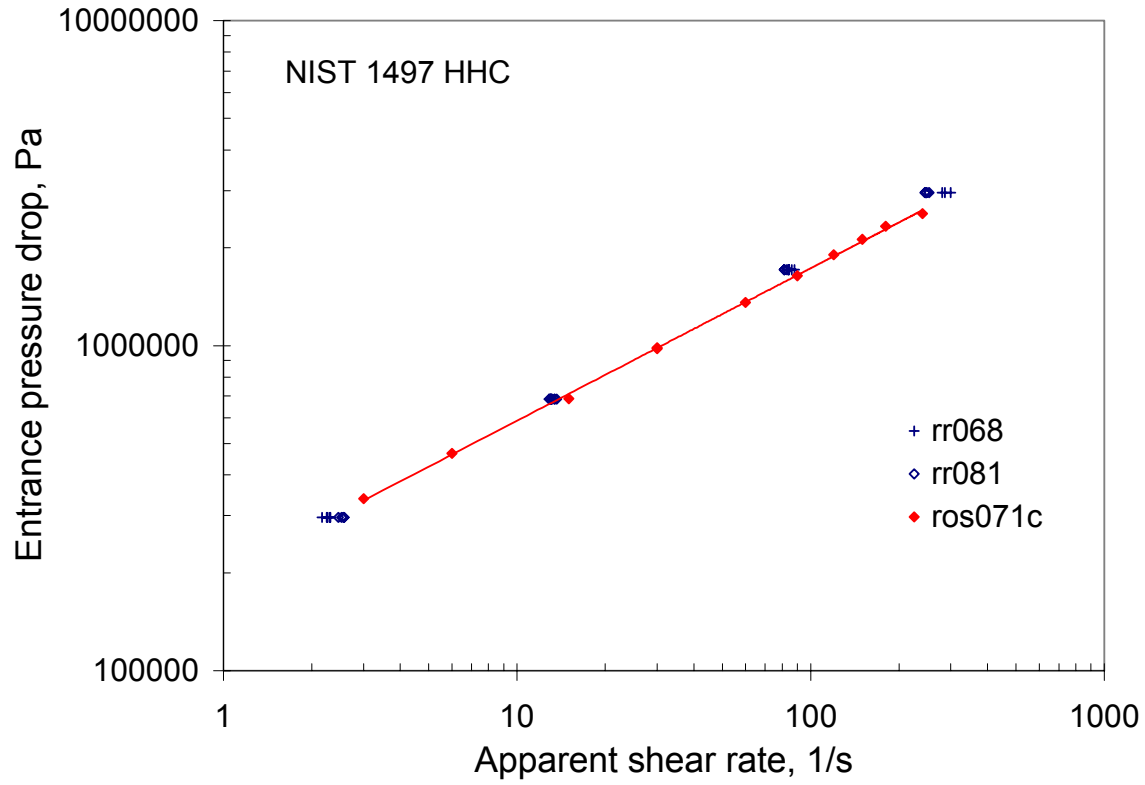

Figure 9 Comparison of entrance pressure drop values measured using an extrusion rheometer (ros071c) with values measured using a melt flow rate instrument with short dies (rr068 - 0.26 mm length, diameter 2.095 mm and rr081 - 0.24 mm length, diameter 1 mm) for a HDPE at 190 °C.

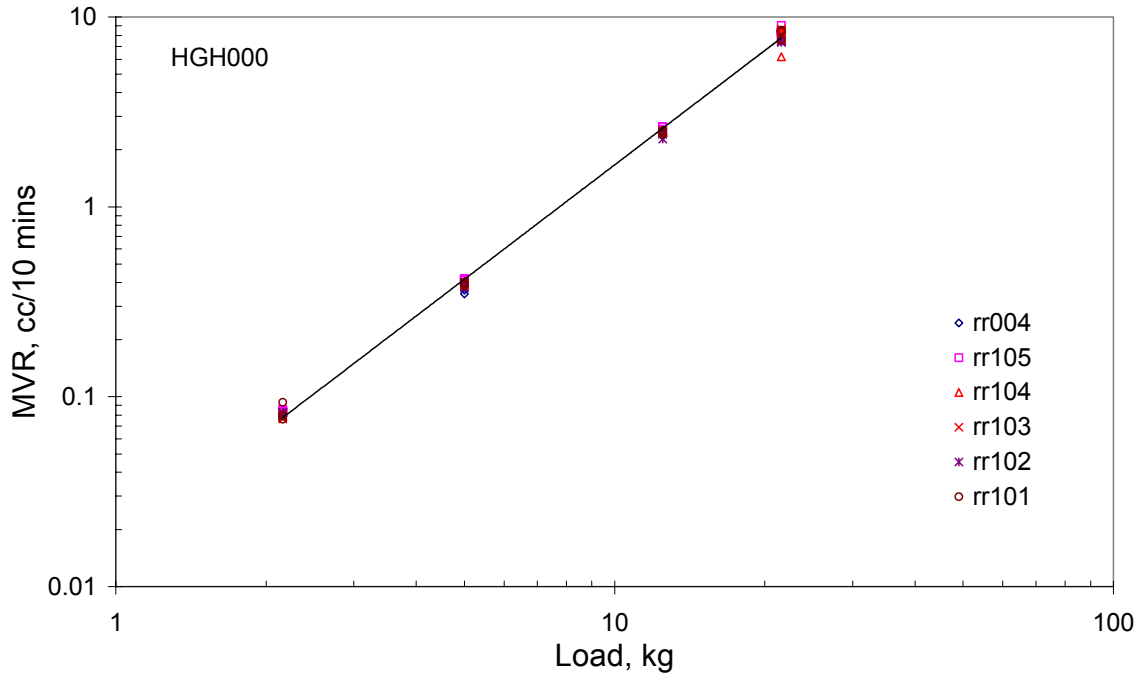

Figure 10 Effect of load on, and repeatability of melt volume flow rate measurements for a HDPE (HGH000) at 190 °C.

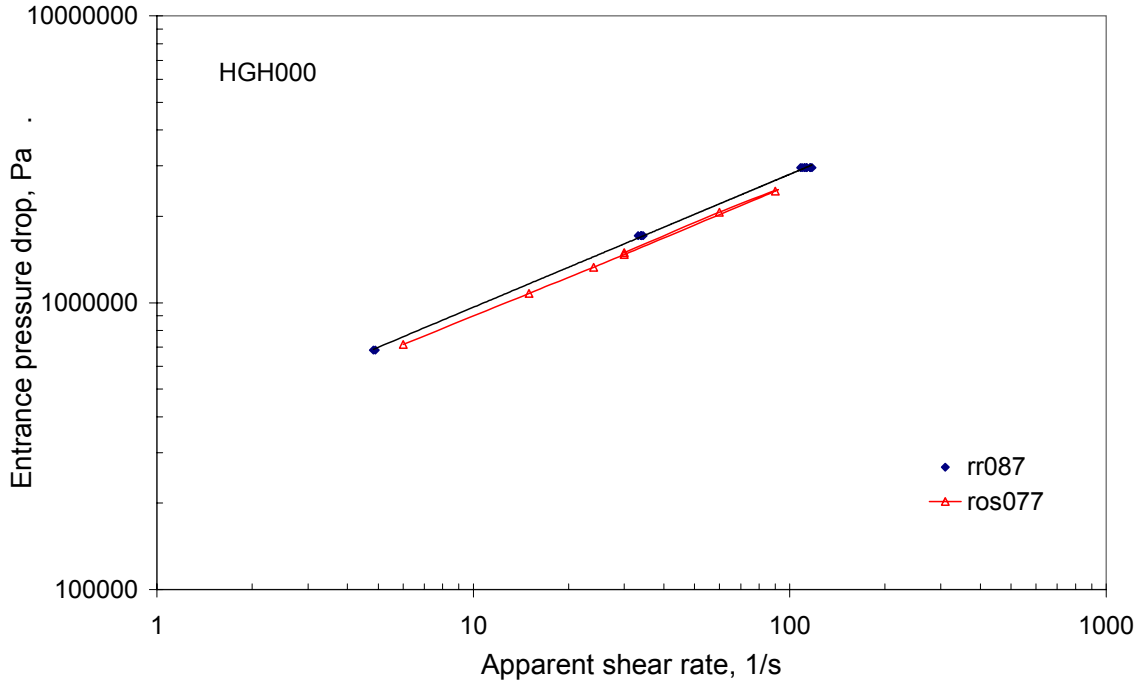

Figure 11 Entrance pressure drop measurements using a melt flow rate instrument with a short die (0.26 mm length, diameter 2.095 mm) compared with extrusion rheometry data (ros071c) for a HDPE (HGH000) at 190 °C.

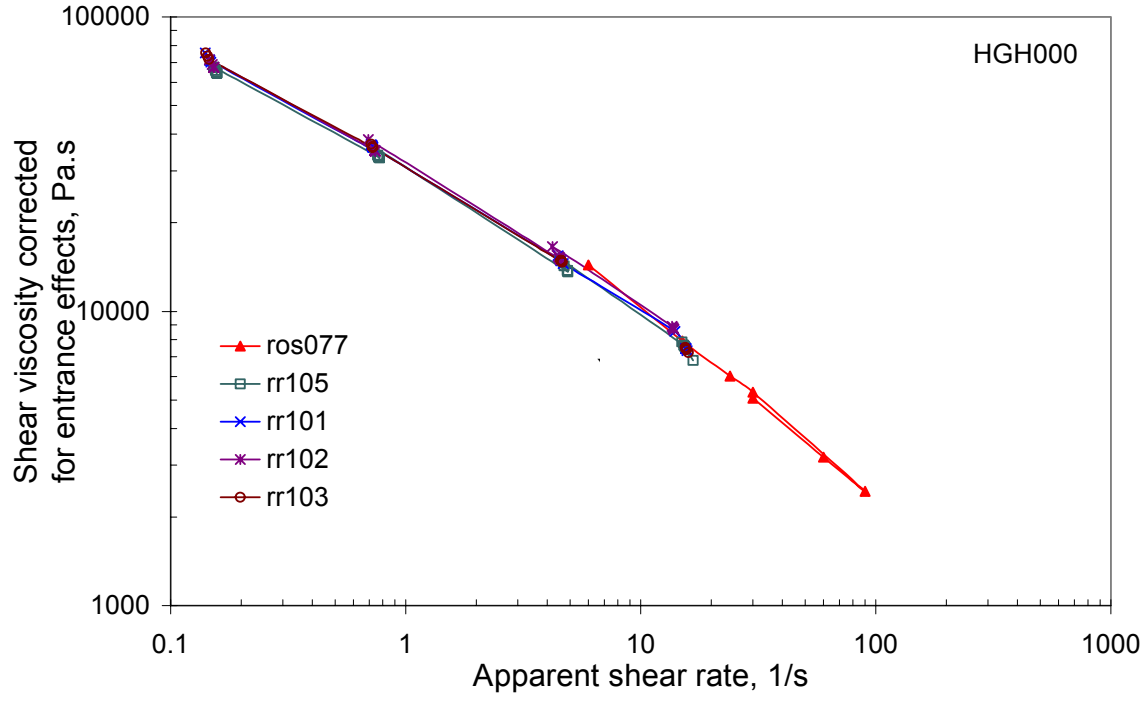

Figure 12 Shear viscosity values, corrected for entrance effects, measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) (rr041 to 47) compared with values measured using an extrusion rheometer (ros071c) for a HDPE (HGH000) at 190 °C.

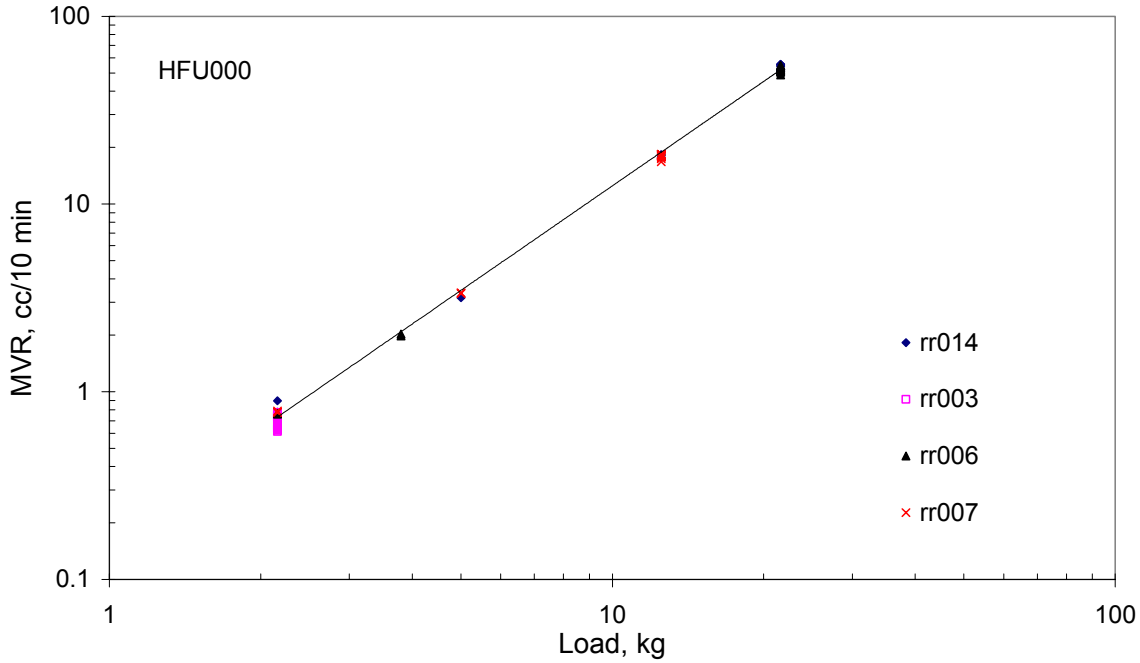

Figure 13 Effect of load on, and repeatability of melt volume flow rate measurements for a HDPE (HFU000) at 190 °C.

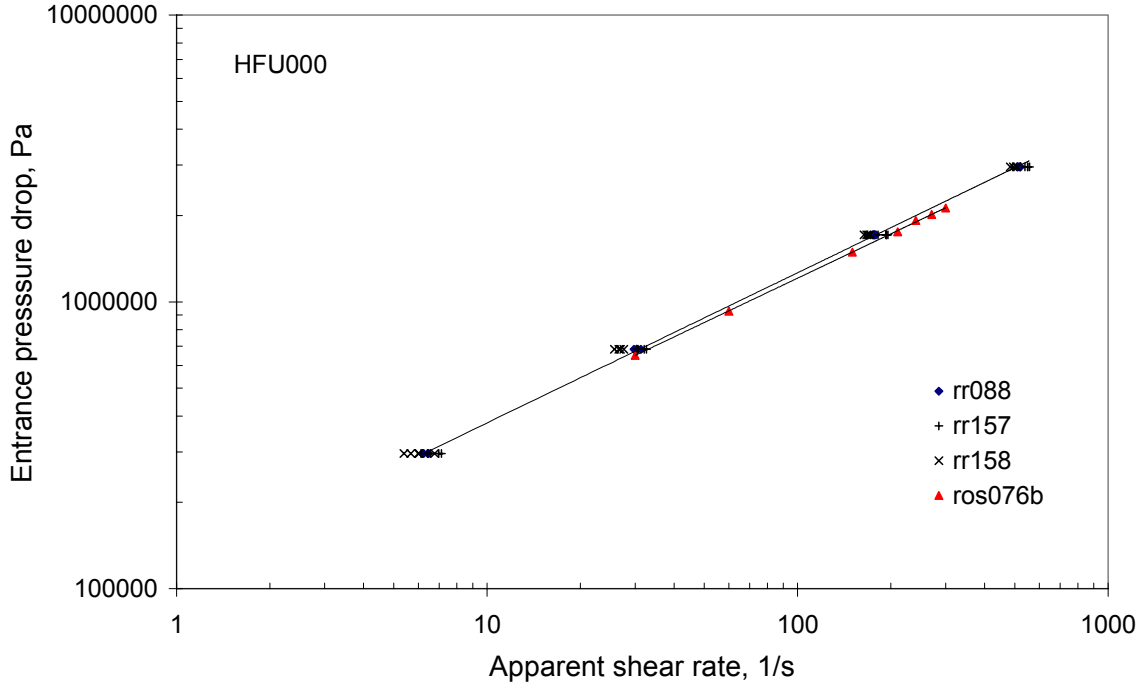

Figure 14 Entrance pressure drop measurements using a melt flow rate instrument with a short die (0.26 mm length, diameter 2.095 mm) compared with extrusion rheometry data (ros076b) for a HDPE (HFU000) at 190 °C.

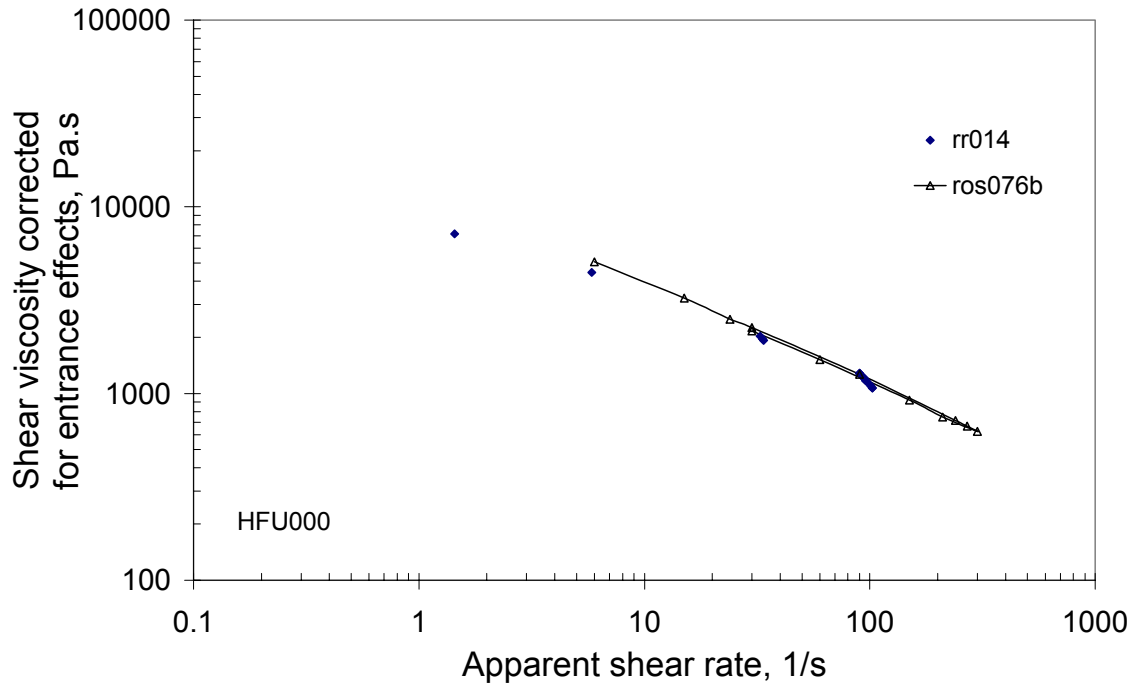

Figure 15 Shear viscosity values, corrected for entrance effects, measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) compared with values measured using an extrusion rheometer (ros076b) for a HDPE (HFU000) at 190 °C.

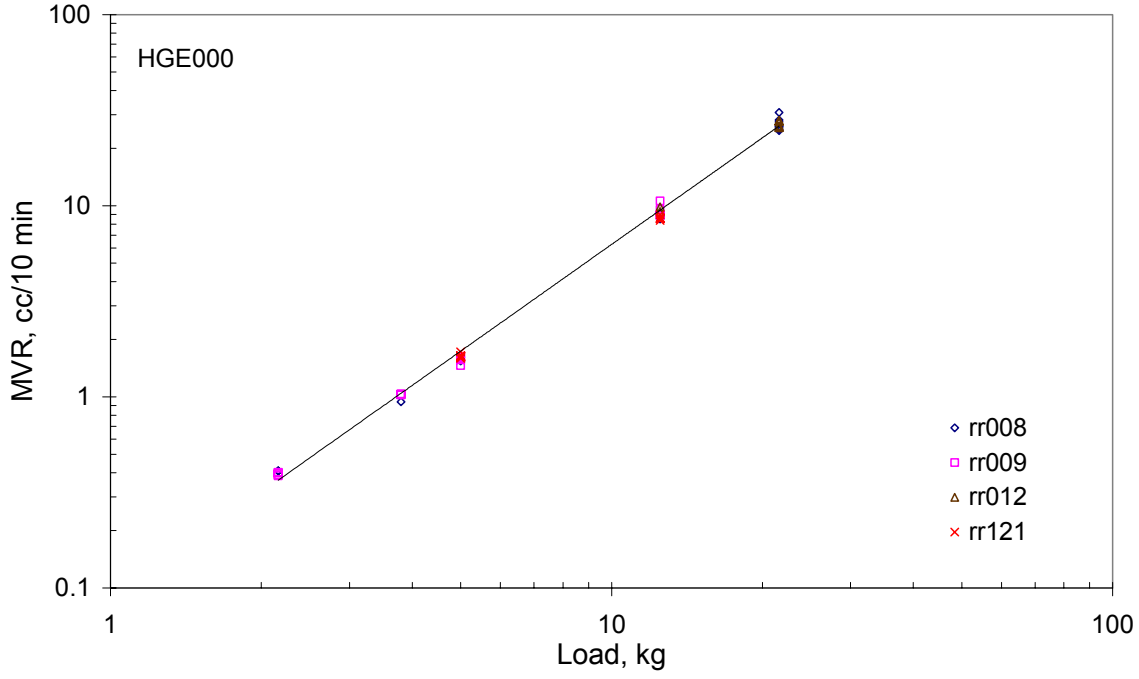

Figure 16 Effect of load on, and repeatability of melt volume flow rate measurements for a LDPE (HGE000) at 190 °C.

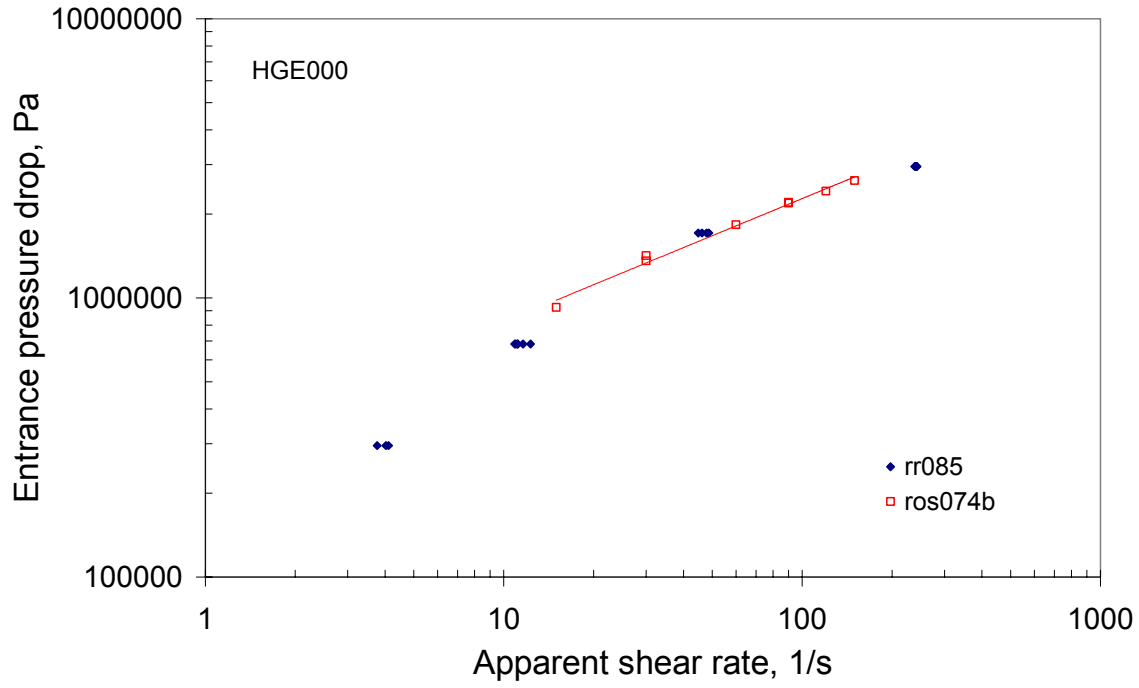

Figure 17 Entrance pressure drop measurements using a melt flow rate instrument with a short die (0.26 mm length, diameter 2.095 mm) compared with extrusion rheometry data (ros074b) for a LDPE (HGE000) at 190 °C.

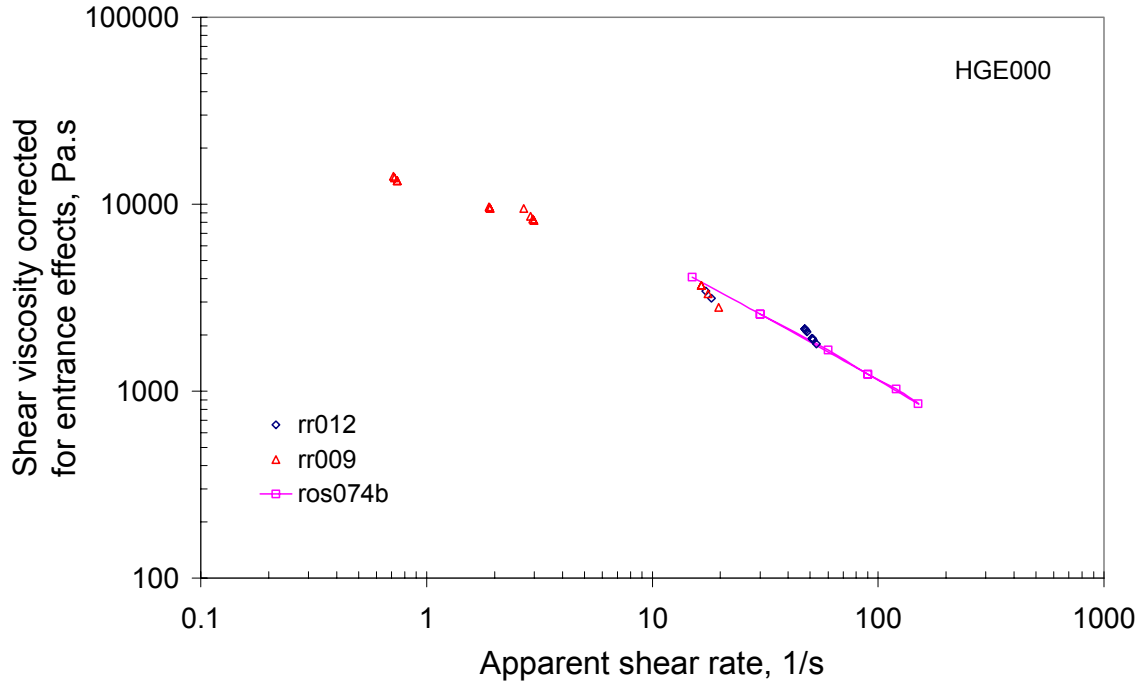

Figure 18 Shear viscosity values, corrected for entrance effects, measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) compared with values measured using an extrusion rheometer (ros074b) for a LDPE (HGE000) at 190 °C.

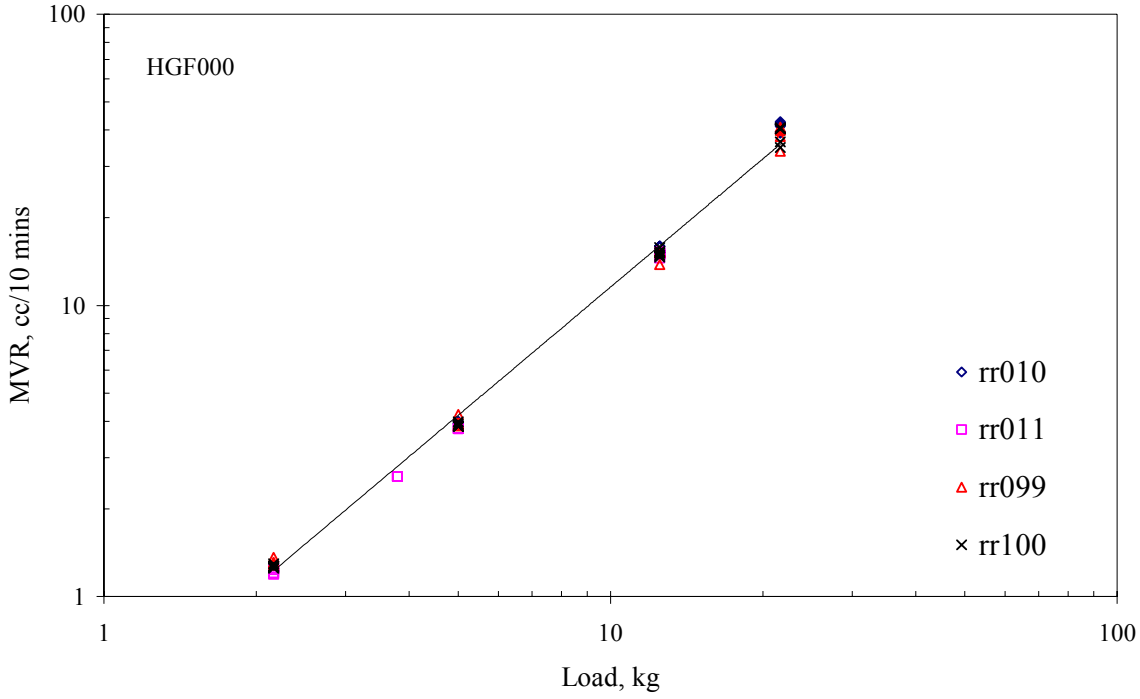

Figure 19 Effect of load on, and repeatability of melt volume flow rate measurements for a LLDPE (HGF000) at 190 °C.

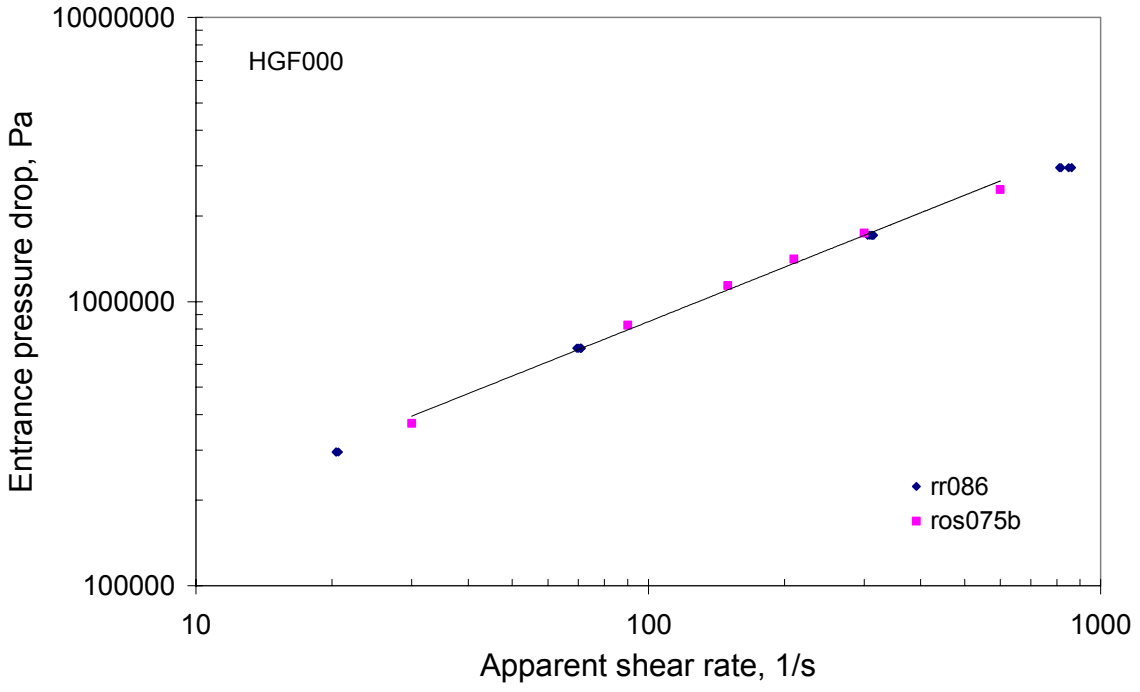

Figure 20 Entrance pressure drop measurements using a melt flow rate instrument with a short die (0.26 mm length, diameter 2.095 mm) compared with extrusion rheometry data (ros075b) for a LLDPE (HGF000) at 190 °C.

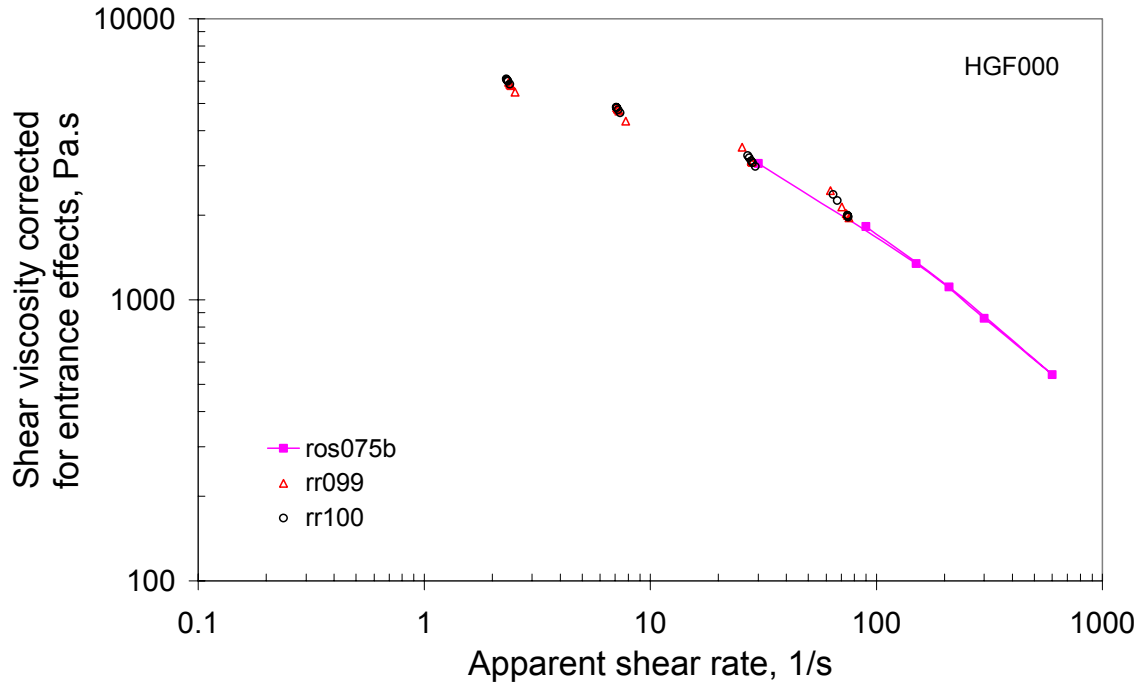

Figure 21 Shear viscosity values, corrected for entrance effects, measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) compared with values measured using an extrusion rheometer (ros075b) for a LLDPE (HGF000) at 190 °C.

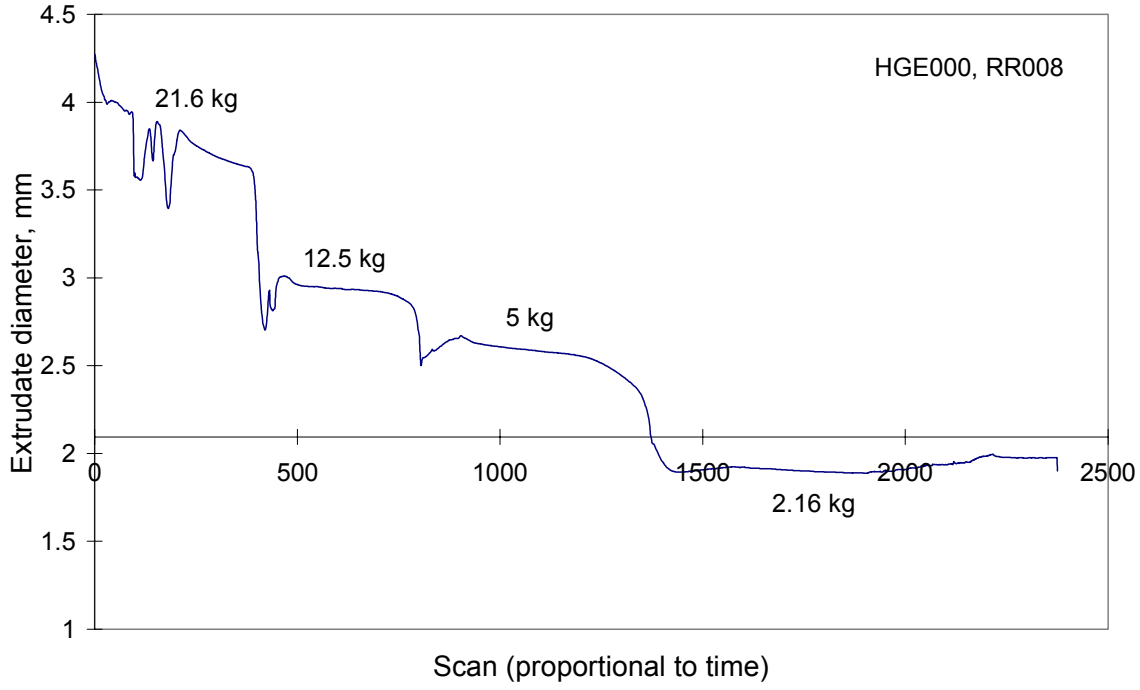

Figure 22 Extrudate diameter measured during extrusion using a laser-scanning micrometer mounted on the MVR instrument (x-axis crosses the y-axis at 2.095 mm to indicate the diameter of the die).

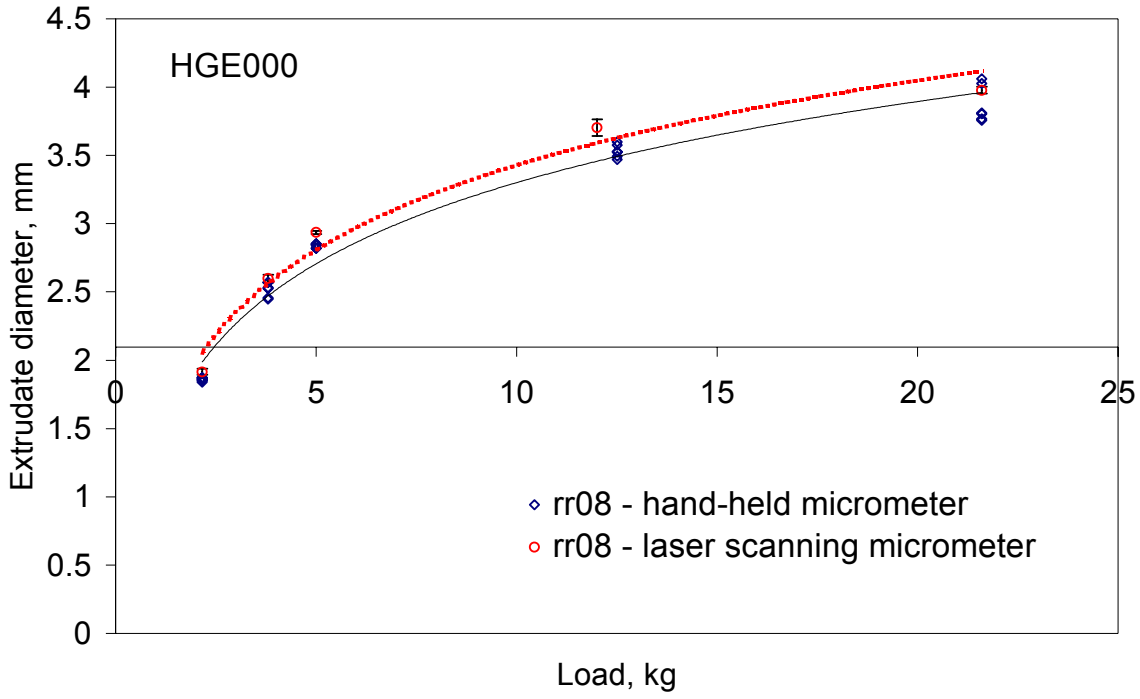

Figure 23 Comparison of laser-scanning and hand-held micrometer measurements of extrudate diameter for a LDPE (ref. rr08, HGE000).

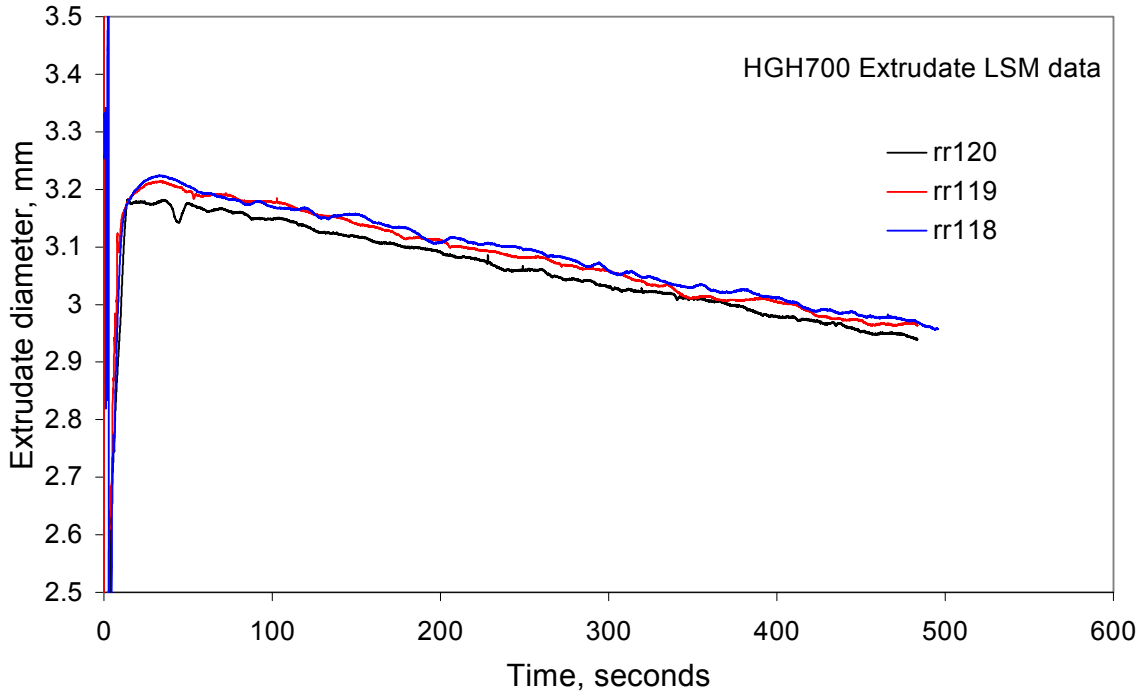

Figure 24 Repeatability of extrudate swell measurements using a laser scanning micrometer for a HDPE (HGH700) at 190 °C and a load of 12.5 kg.

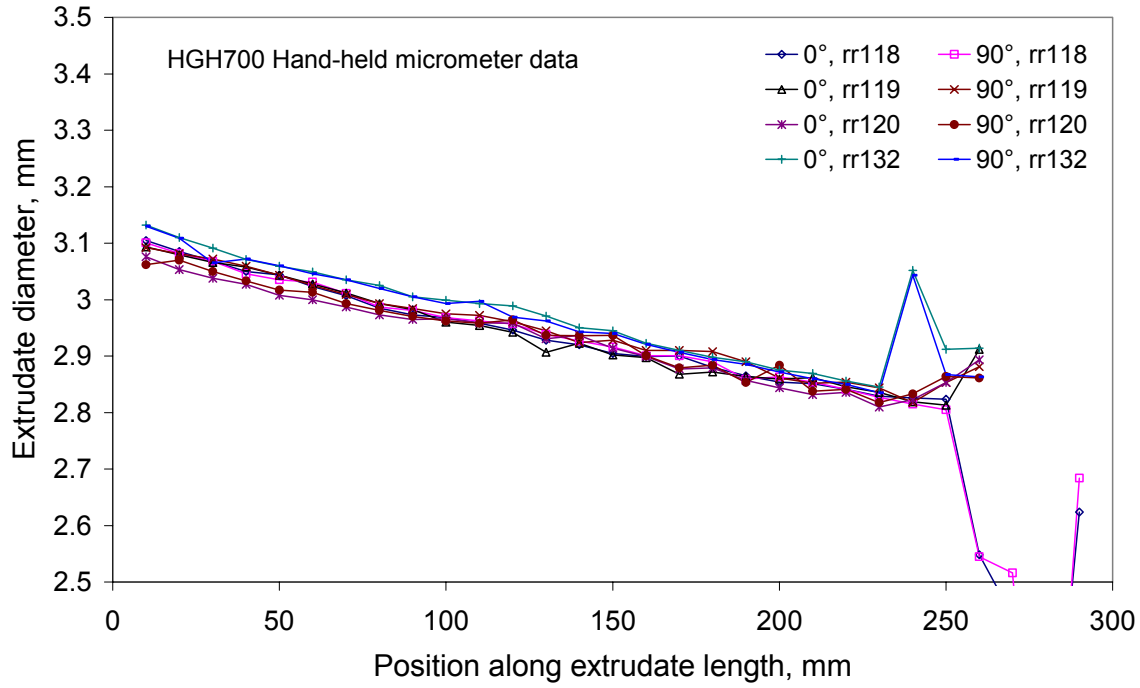

Figure 25 Repeatability of extrudate swell measurements using a hand-held micrometer for a HDPE (HGH700) at 190 °C and a load of 12.5 kg.

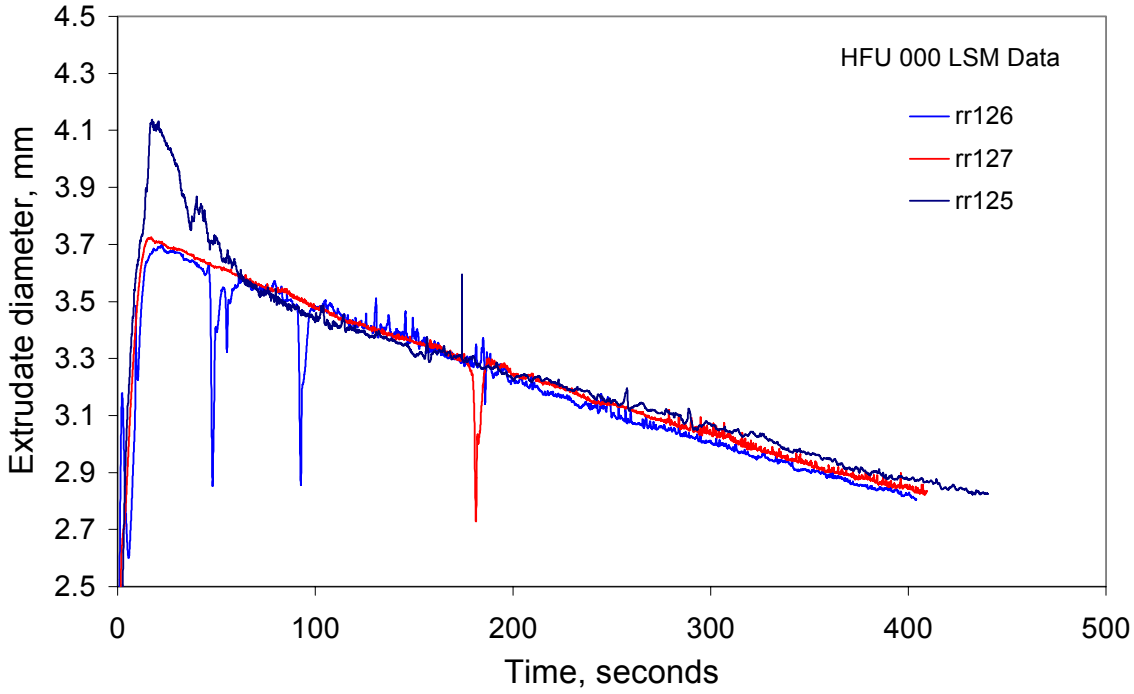

Figure 26 Repeatability of extrudate swell measurements using a laser scanning micrometer for a HDPE (HFU000) at 190 °C and a load of 5 kg.

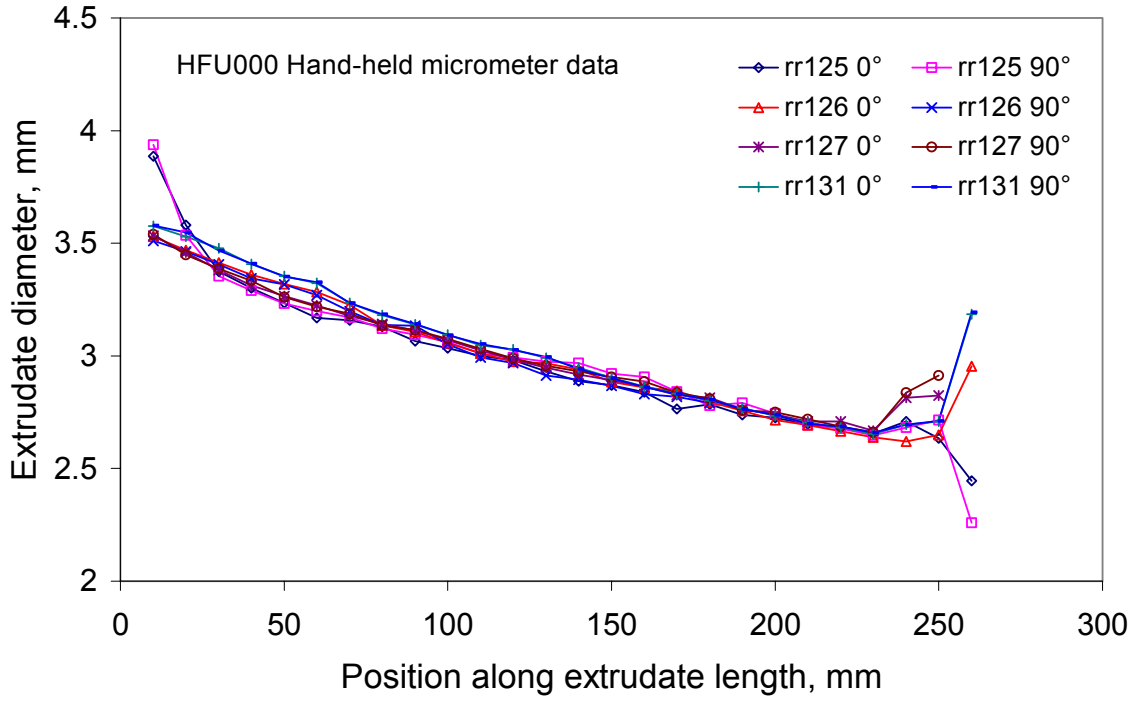

Figure 27 Repeatability of extrudate swell measurements using a hand-held micrometer for a HDPE (HFU000) at 190 °C and a load of 5 kg.

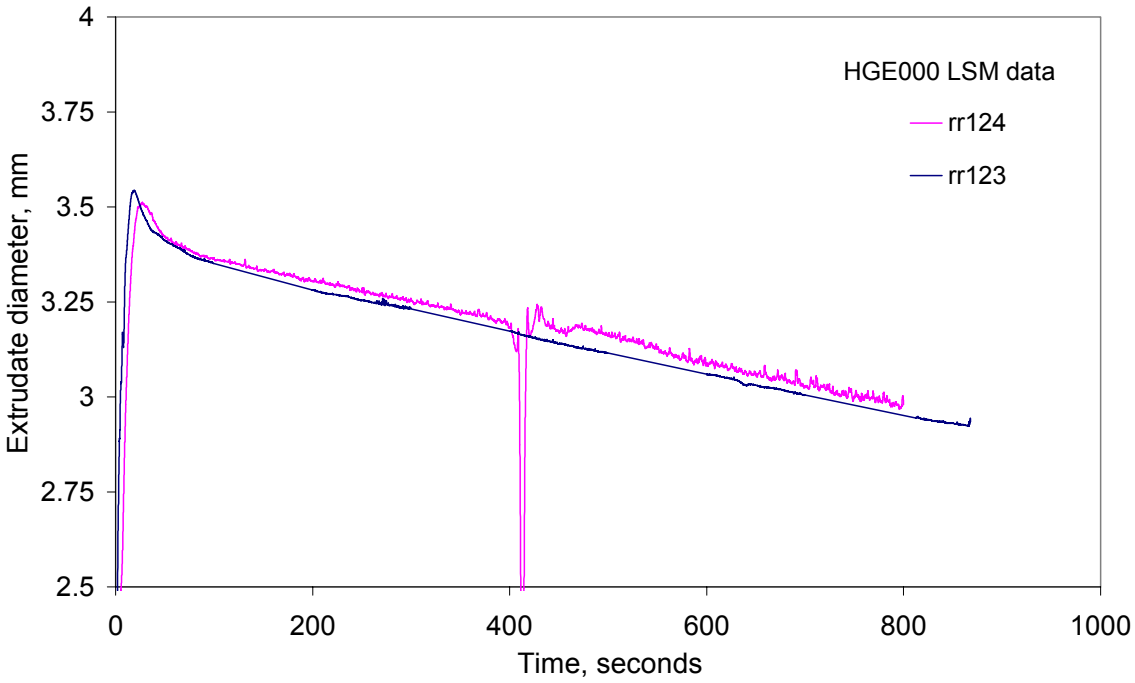

Figure 28 Repeatability of extrudate swell measurements using a laser scanning micrometer for a LDPE (HGE000) at 190 °C and a load of 5 kg.

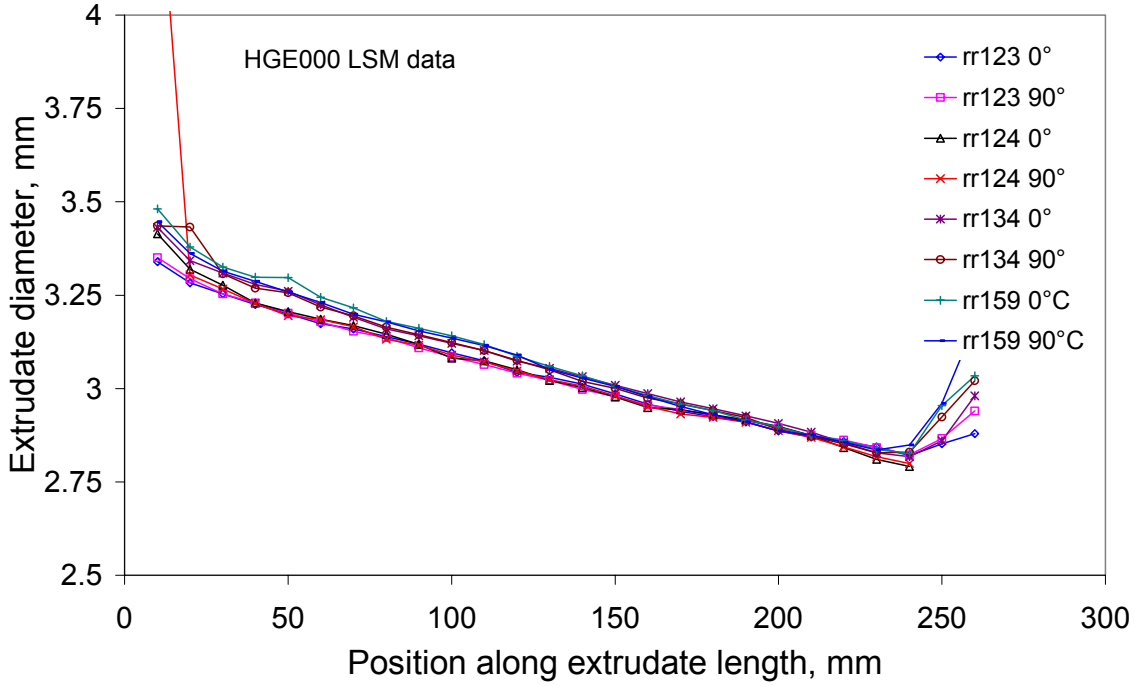

Figure 29 Repeatability of extrudate swell measurements using a hand-held micrometer for a LDPE (HGE000) at 190 °C and a load of 5 kg.

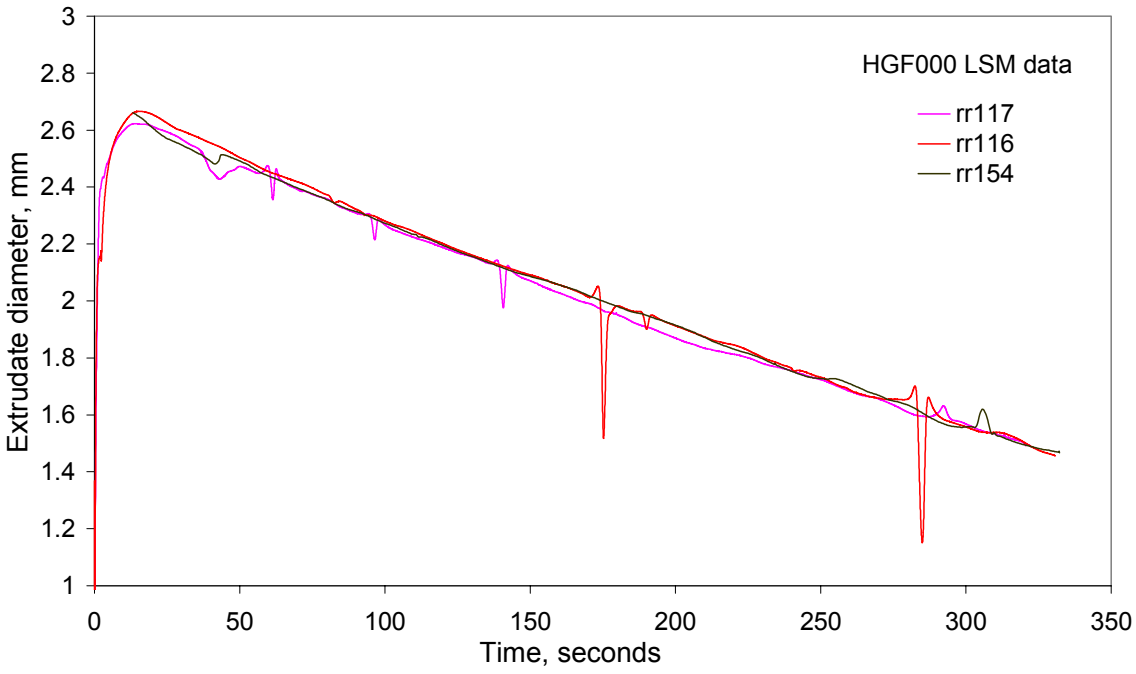

Figure 30 Repeatability of extrudate swell measurements using a laser scanning micrometer for a LLDPE (HGF000) at 190 °C and a load of 2.16 kg.

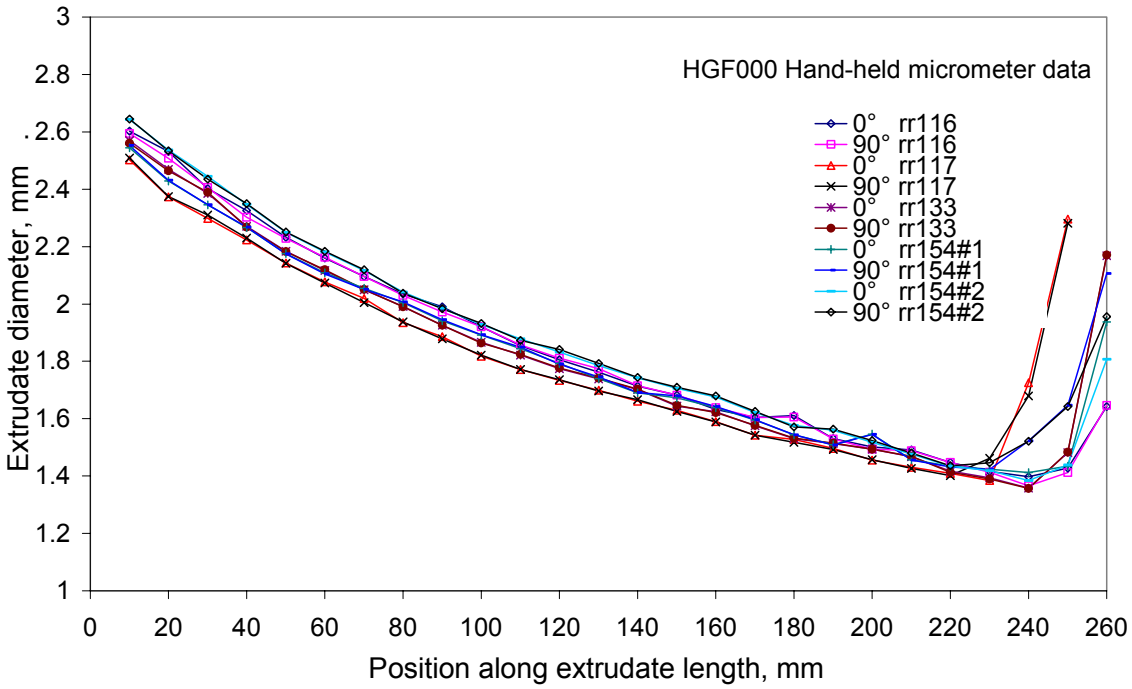

Figure 31 Repeatability of extrudate swell measurements using a hand-held micrometer for a LLDPE (HGF000) at 190 °C and a load of 2.16 kg.

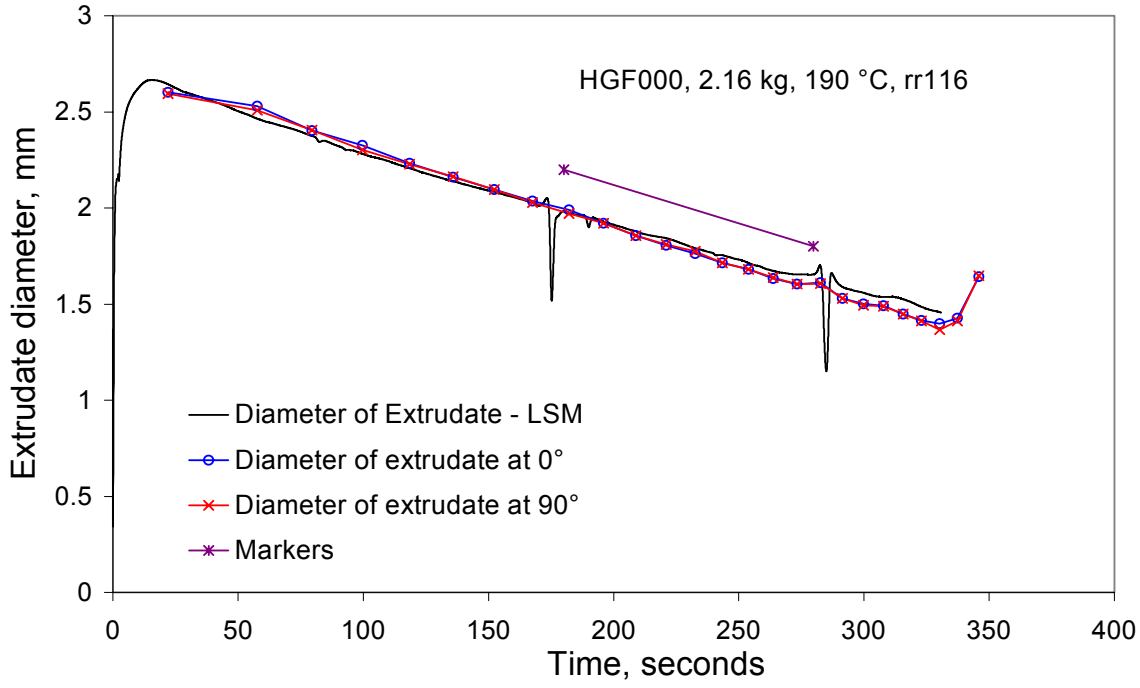

Figure 32 Comparison of laser-scanning and hand-held micrometer measurements of extrudate diameter for a LLDPE (HGF000) at 190 °C and 2.16 kg.

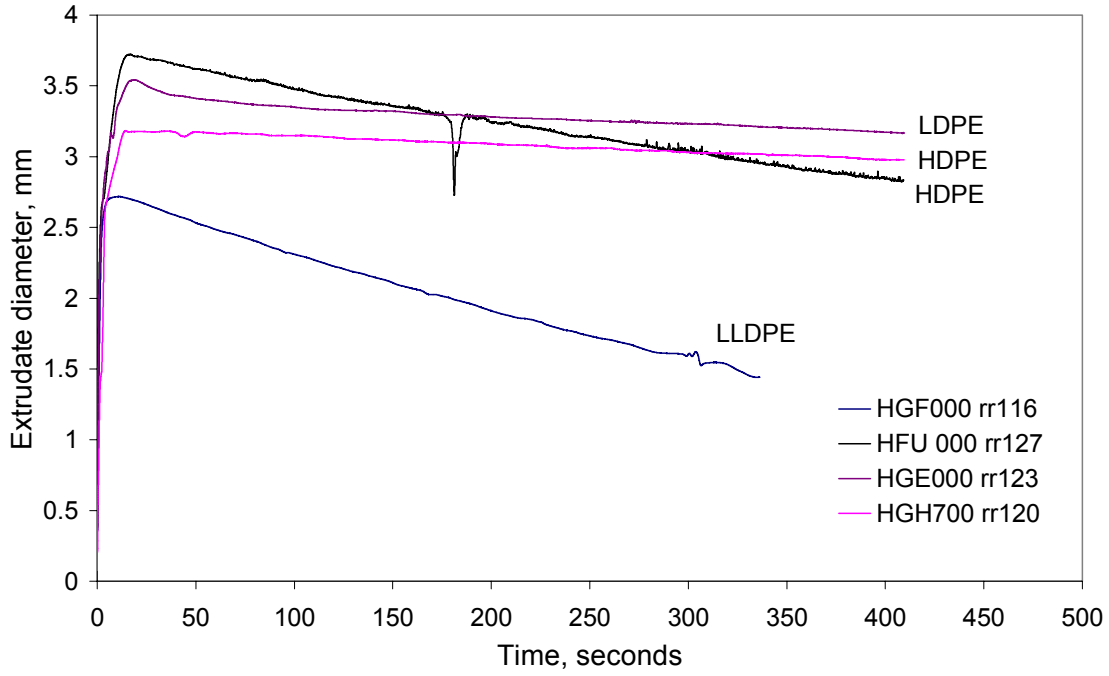

Figure 33 Comparison of laser-scanning micrometer measurements of extrudate diameter for a range of polyethylenes.

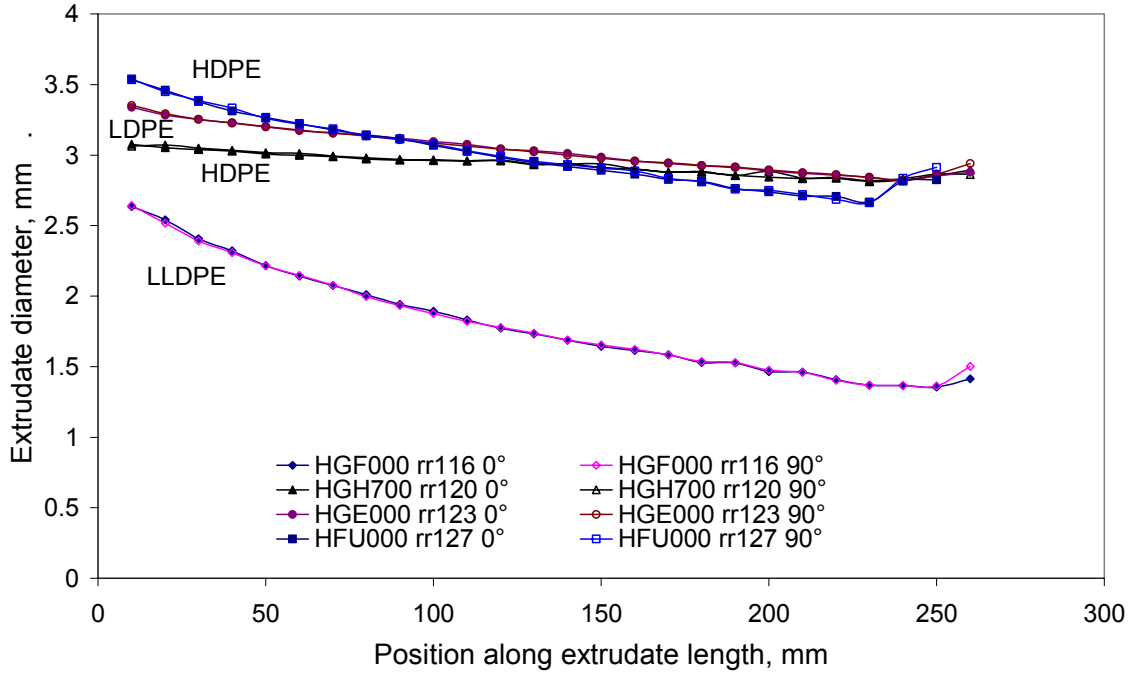

Figure 34 Comparison of hand-held micrometer measurements of extrudate diameter for a range of polyethylenes.

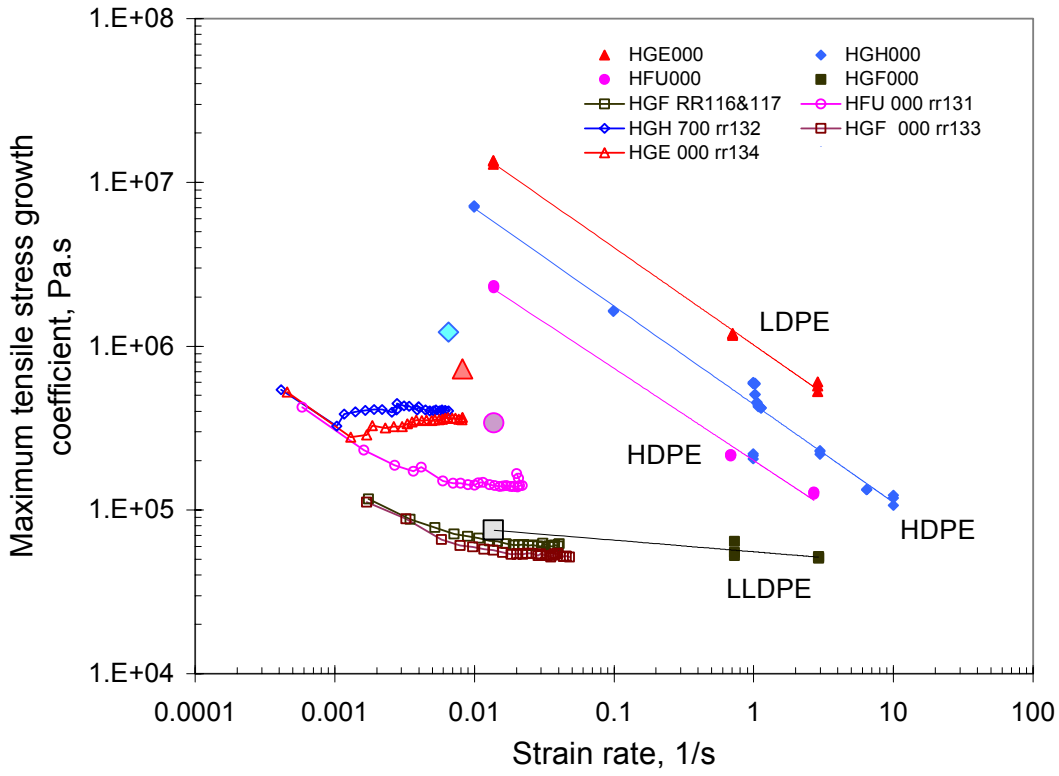

Figure 35 Interpretation of hand-held micrometer measurements of extrudate diameter as approximate extensional viscosities for a range of polyethylenes.

Solid points with lines indicate maximum tensile stress growth coefficient values. Open points with lines indicate draw-down values. Large single point symbols indicate values determined from tensile extensional testing at strains equivalent to that for the highest strain rate data points from draw-down measurements for each material. Symbols indicate materials as for other tests. Tensile extensional data obtained at 150 °C.

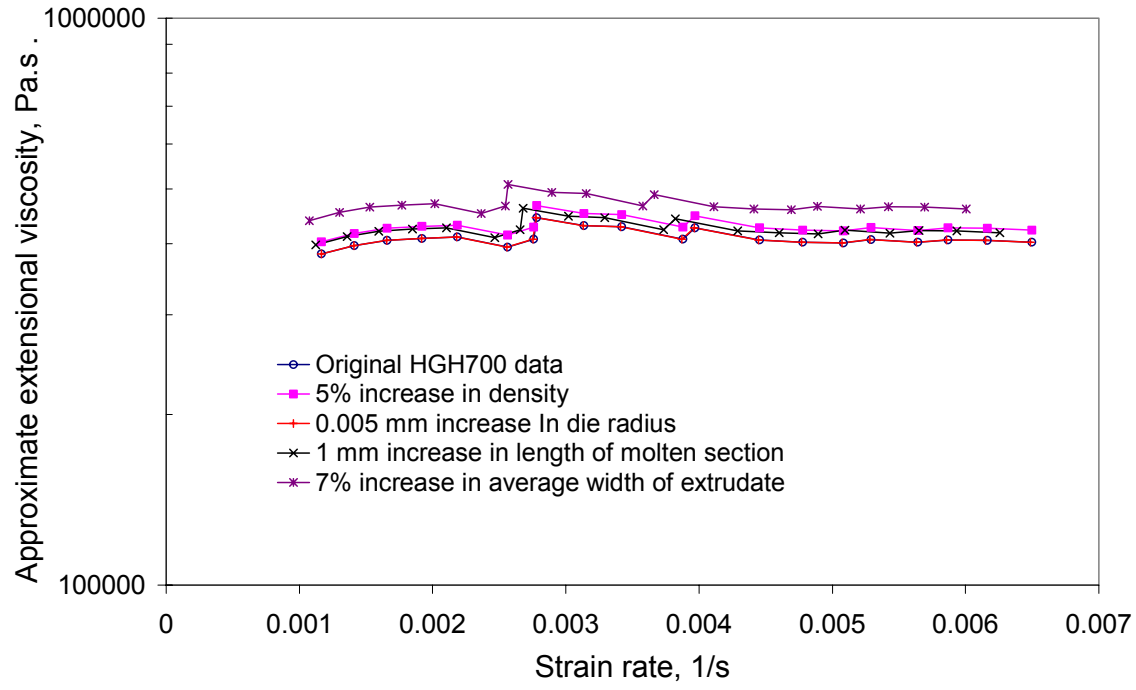

Figure 36 Sensitivity analysis of derived extensional viscosity values from draw-down data for a HDPE (HGH000).

11. APPENDICES

12. APPENDIX A1: NOMENCLATURE

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

MFR has units of grams although it is expressed as g/10 minutes indicating it is the mass extruded in 10 minutes

MVR has units of cm^3, although similarly it is expressed as cm^3/10 minutes indicating it is the volume extruded in 10 minutes

m is the mass extruded in time t, grams

t_{ref} is a reference time equal to 600 s (≡ 10 minutes)

ρ is the density of the polymer melt at the test temperature, g/cm^3

ℓ is the distance moved by the piston in time t, m

t time, s

Q volume flow rate, m^3/s

$\dot{\gamma}_a$ apparent shear rate, s^{-1}

τ_a apparent shear stress in the die (not Bagley end-corrected), Pa

τ shear stress in the die (Bagley end-corrected), Pa

$\underline{\eta}_a$ apparent shear viscosity (not Bagley end-corrected), Pa.s. It is the ratio of apparent shear stress to apparent shear rate.

η_a apparent shear viscosity (Bagley end-corrected), Pa.s. It is the ratio of shear stress to apparent shear rate.

P pressure drop, Pa

P_e entrance pressure drop, Pa

P_s shear flow pressure drop along the capillary die, Pa

D barrel diameter, m

R die radius, m

L die length, m

P_o, x constants in the entrance pressure drop power law model

Nomenclature: Draw-down analysis

R_0 radius of the extrudate at the die exit (= die radius), m

R_c radius of the extrudate at the crystallisation point, m

R_1 radius of the extrudate first extruded, m

L_1 length of extrudate from the crystallisation point to the lower end, m

L_0 length of extrudate from the die exit to the crystallisation point, m

M mass of extrudate below the crystallisation point, kg

σ tensile stress acting on the mid-point of the molten section, Pa

V_{r1} volume of extrudate below the crystallisation point, m^3

A_1 cross-sectional area of the extrudate first extruded, m^2

A_c cross-sectional area of the extrudate at the crystallisation point, m^2

V_{av} average velocity of the extrudate in the molten section, $m.s^{-1}$

t_0 time for a particle to traverse the molten section, s

$\dot{\varepsilon}_{av}$ average strain rate in the molten section, s^{-1}

ε Hencky strain, dimensionless

13. APPENDIX A2: ANALYSIS OF MELT FLOW RATE TESTING

GENERAL

The melt mass flow rate (MFR) is given, according to ISO 1133 [2], by the expression

$$MFR = \frac{m\ t_{ref}}{t} \tag{1}$$

and is determined experimentally by measuring the mass of material m extruded in a given time t and scaled appropriately using a reference time t_{ref} of 600 seconds (10 minutes). The relationship

$$MVR = \frac{MFR}{\rho} \tag{2}$$

is also given in ISO 1133 relating the melt mass flow rate (MFR) to the melt volume flow rate (MVR) where ρ is the density of the polymer melt at the test temperature. MFR has units of grams although it is expressed as g/10 minutes indicating it is the mass extruded in 10 minutes. MVR has units of cm^3, although similarly it is expressed as cm^3/10 minutes indicating it is the volume extruded in 10 minutes.

Thus the melt volume flow rate is given by the expression

$$MVR = \left[\frac{m\ t_{ref}}{t}\right] \times \frac{1}{\rho} \tag{3}$$

Alternatively this may be re-written as

$$MVR = \left[\frac{t_{ref}}{t}\right] \ell \frac{\pi D^2}{4} \times 10^6 \tag{4}$$

where ℓ is the distance moved by the piston in time t and D is the diameter of the barrel. The factor of 10^6 is introduced here and elsewhere below to account for the differences in units used for the various parameters (for units see Nomenclature Appendix A1). MVR is determined experimentally by measuring the time taken for the piston to move a given distance or vice-versa.

APPARENT SHEAR RATE

The volume flow rate Q can be determined from the MVR and is given by

$$Q = \frac{MVR \times 10^{-6}}{600} \tag{5}$$

or, substituting for MVR using equation 4, by

$$Q = \frac{\ell \pi D^2}{4t} \tag{6}$$

The apparent shear rate $\dot{\gamma}_a$ in the melt at the wall of the die is given [14, 15] by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \tag{7}$$

and thus in the melt flow rate die, substituting for Q using equation 6, by

$$\dot{\gamma}_a = \frac{\ell D^2}{R^3 t} \tag{8}$$

Alternatively, the apparent shear rate is given, using equations 5 and 7, by

$$\dot{\gamma}_a = \frac{4(MVR/600) \times 10^{-6}}{\pi R^3} \tag{9}$$

or in terms of MFR by

$$\dot{\gamma}_a = \frac{4(MFR/600\rho) \times 10^{-6}}{\pi R^3} \tag{10}$$

SHEAR STRESS AND SHEAR VISCOSITY

The pressure P above the die, assuming zero pressure loss due to fluid flow in the barrel and no frictional forces between the piston and the barrel, is determined from a balance of forces acting on the piston. Thus

$$\mathrm{Wg} = \frac{\mathrm{P}\pi\mathrm{D}^2}{4} \tag{11}$$

where W is the applied load and g is the acceleration due to gravity. Thus the pressure P above the die is given by

$$P = \frac{4Wg}{\pi D^2} \tag{12}$$

This pressure is “lost” by material flowing into and along the length of the die. Assuming no entrance pressure drop, a balance of forces along a die of length L and radius R yields

$$P\pi R^2 = 2\pi RL\tau_a \tag{13}$$

where τ_a is the apparent shear stress in the die at the wall.

Thus

$$\tau_a = \frac{PR}{2L} \tag{14}$$

or, substituting for P using equation 12, by

$$\tau_a = \frac{4Wg}{\pi D^2}\frac{R}{2L} \tag{15}$$

An apparent shear viscosity $\underline{\eta}_a$ (not Bagley end-corrected) can be simply defined for the MFR and MVR test as the ratio of the apparent shear stress to apparent shear rate

$$\underline{\eta}_a = \frac{\tau_a}{\dot{\gamma}_a} \tag{16}$$

Thus the apparent shear viscosity is given, using equations 10 and 15, by

$$\underline{\eta}_a = \frac{300Wg\rho R^4}{D^2 L \times MFR \times 10^{-6}} \tag{17}$$

or in terms of MVR by

$$\underline{\eta}_a = \frac{300WgR^4}{D^2 L \times MVR \times 10^{-6}} \tag{18}$$

Thus for each load an apparent shear viscosity (not corrected for entrance effects) and the corresponding apparent shear rate can be determined. In using several loads a flow curve can thus be determined.

However, the entrance pressure drop is not normally negligible. Assuming a non-zero entrance pressure drop P_e, the pressure drop along the die length P_s is given by

$$P_s = P - P_e \tag{19}$$

Thus replacing P_s for P in equation 14 yields the true shear stress τ in the die at the wall

$$\tau = \frac{P_s R}{2L} \tag{20}$$

Thus shear viscosities, corrected for entrance effects, can be determined given entrance pressure drop data. This is covered in detail in the following section.

14. APPENDIX A3: DETERMINATION OF THE EXTENSIONAL FLOW BEHAVIOUR USING THE ENTRANCE PRESSURE DROP METHOD AND CORRECTION OF SHEAR VISCOSITY VALUES FOR ENTRANCE EFFECTS

The extensional flow characterisation method is based on the measurement of the material's resistance to flow in a converging region. The degree of resistance to flow, characterised by the entrance pressure drop, is used as a measure of the extensional flow behaviour of the polymer. The basis for the method, when used in a controlled flow rate mode, is presented in detail by Rides and Allen [7, 16]. Briefly, by using either a short die or dies of different length but of the same diameter the magnitude of the entrance pressure drop can be determined. The approach is now applied to the controlled stress mode as used for melt flow rate measurements.

To provide the simplest experimental case a die of short length (typically 0.25 mm) is used. In using a short die it is assumed that the total pressure drop is due solely to the entrance pressure drop, i.e. there is no shear flow pressure drop along the length of the short die. Then the entrance pressure drop P_e is given by

$$P_e = \frac{4Wg}{\pi D^2} \tag{21}$$

where W is the applied load, g is the acceleration due to gravity and D is the barrel diameter.

For these tests the apparent shear rate is given by

$$\dot{\gamma}_a = \frac{4(MVR_s / 600) \times 10^{-6}}{\pi R^3} \tag{22}$$

or in terms of MFR by

$$\dot{\gamma}_a = \frac{4(MFR_s / 600\rho) \times 10^{-6}}{\pi R^3} \tag{23}$$

where the subscript s indicates the MVR or MFR values determined using the short die.

Thus in using a short die for a given load a single datum point for entrance pressure drop and the corresponding apparent shear rate can be determined.

By performing tests using different loads with the short die, the apparent shear rate dependence of the entrance pressure drop P_e can be determined. A power-law model has been found useful for fitting such data [7]:

$$P_e = P_o(\dot{\gamma}_a{}^x) \tag{24}$$

where P_o and x are constants.

These data, or more precisely the parameters of the model fitted to the data, can then be used to correct for the entrance pressure drop effect in apparent shear viscosity data obtained from

standard MFR and MVR tests, but performed using various loads, as follows.

From the apparent shear rate versus entrance pressure drop data the magnitude of the entrance pressure drop at any apparent shear rate can be derived by interpolation or extrapolation using, for example, a power-law fit, equation 24.

For the standard tests the pressure is corrected by subtracting the entrance pressure drop P_e at the corresponding apparent shear rate, using equations 9, 12, 18 and 19. Thus the corrected apparent shear viscosity is given by

$$\eta_a = \left(\frac{4Wg}{\pi D^2} - P_e \right) \frac{75\pi R^4}{L \times MVR \times 10^{-6}} \tag{25}$$

or in terms of MFR by

$$\eta_a = \left(\frac{4Wg}{\pi D^2} - P_e \right) \frac{75\rho\pi R^4}{L \times MFR \times 10^{-6}} \tag{26}$$

where P_e is calculated as the entrance pressure drop at the apparent shear rate given by

$$\dot{\gamma}_a = \frac{4(MVR/600) \times 10^{-6}}{\pi R^3} \tag{27}$$

or in terms of MFR by

$$\dot{\gamma}_a = \frac{4(MFR/600\rho) \times 10^{-6}}{\pi R^3} \tag{28}$$

These apparent shear rates are those values obtained using the standard 8 mm length die.

Thus shear viscosity data, obtained using the standard die, can be corrected for entrance pressure drop effects using short die data.

15. APPENDIX A4: EXTRUDATE DRAW DOWN ANALYSIS

This analysis is for interpreting the straining behaviour of molten extrudate immediately beneath the die exit. The straining, or draw-down, occurs due to the weight of extrudate hanging on the molten section. It is, in effect, parison sag. The assumptions are made that the geometry of the extrudate is defined by two truncated cones joined end-to-end, by their smaller ends that are of the same diameter to maintain continuity. The point at which the two cones meet is taken to be the point at which the surface of the extrudate crystallises. The upper cone is therefore of molten material whereas the lower cone is effectively of solidified material. All deformation therefore occurs in the upper cone. The distance from the die exit to the point of crystallisation is also assumed to be constant throughout the test.

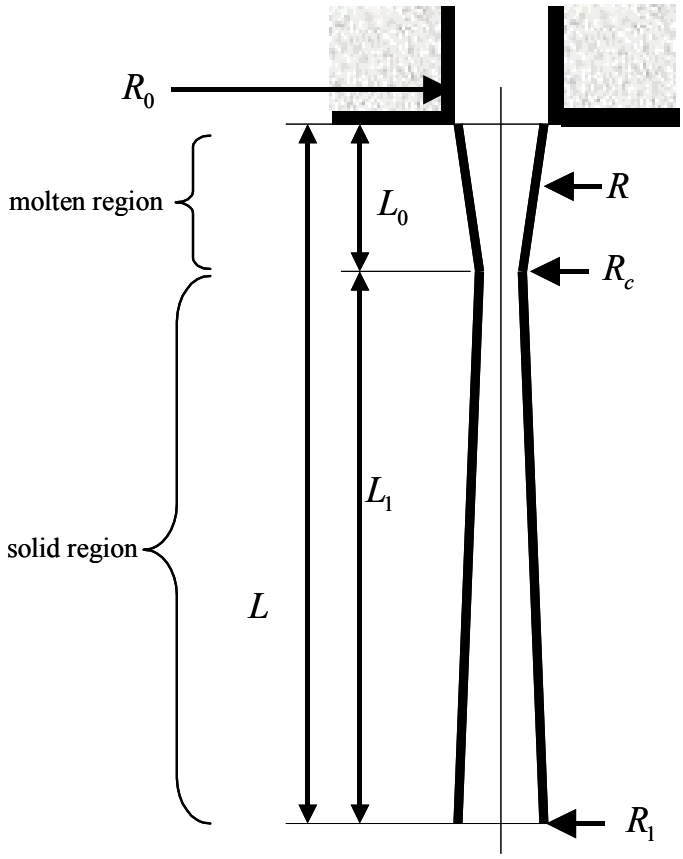

Figure A1: Schematic diagram of draw-down in melt flow rate testing

The volume of the lower truncated conical section below the crystallisation point ($r = R_c$) is given by

$$V_{R1} = \frac{1}{3}\pi L_1 \left(R_c^2 + R_1 R_c + R_1^2 \right) \tag{29}$$

Thus the mass M of extrudate suspended beneath the crystallisation point ($r = R_c$) is given by

$$M = V_{R1}\, \rho \tag{30}$$

where ρ is the density which is assumed to be constant.

The stress σ at the mid point along the length of the upper conical section (where $r = (R_o + R_c)/2$) is estimated by

$$\sigma = \frac{Mg}{\pi\left(\frac{R_c + R_0}{2}\right)^2} \tag{31}$$

[Note: As the length of the upper truncated conical section is small compared with that of the lower section then the contribution of its lower half, via its mass, to the stress at the mid-point of the upper section is assumed to be negligible. The effect of this assumption is considered later.]

The strain ε that the material undergoes due to draw down is related to the reduction in cross-sectional area of the extrudate. Assuming that the material first extruded undergoes no strain due to draw-down, as no load is suspended from it, then the strain of material at the crystallisation point is given by

$$\varepsilon = \ell n\left(\frac{A_1}{A_c}\right) \tag{32}$$

where A denotes the cross-sectional area at the positions indicated by the suffices. Thus

$$\varepsilon = \ell n\left(\frac{R_1^2}{R_c^2}\right) \tag{33}$$

The flow rate is determined from the measured melt volume flow rate by

$$Q = \frac{MVR \times 10^{-6}}{600} \tag{34}$$

Thus the average velocity V_{av} of a particle traversing from the die exit to the crystallisation point (i.e. L_0) is estimated by

$$V_{av} = \frac{Q}{\pi\left(\frac{R_0 + R_c}{2}\right)^2} \tag{35}$$

The time taken t_0 for a particle to traverse from R_0 to R_c is given by the ratio of the length traversed to the average velocity thus

$$t_0 = \frac{L_0}{V_{av}} \tag{36}$$

The average strain rate for a particle traversing from R_0 to R_c is given by the ratio of strain to time

$$\dot{\varepsilon}_{av} = \frac{\varepsilon}{t_0} \tag{37}$$

Finally an approximate extensional viscosity η_e is given by

$$\eta_e = \frac{\sigma}{\dot{\varepsilon}_{av}} \tag{38}$$

Thus by appropriate substitution of these equations an approximate extensional viscosity value can be derived from the draw-down data where the extrudate radius R_c (i.e. the radius frozen at a particular moment) is measured as a function of the length L_1 from the end that was first extruded.

Thus, by substitution

$$\eta_e = \frac{Mg}{\pi\left(\frac{R_c + R_0}{2}\right)^2} \frac{t_0}{\ell n\left(\frac{R_1^{\,2}}{R_c^{\,2}}\right)} \tag{39}$$

It is considered, given the assumptions made above, that the most reliable values for extensional viscosity will be obtained when the mass of suspended extrudate is largest and thus the stresses, strains and strain rates that the material in the molten zone is experiencing are also largest.