

**Surface tension and
extrusion-based
rheological
characterisation of hot
melt adhesives**

*Martin Rides, Crispin Allen,
Angela Dawson and Jaspal Nottay*

Measurement Good Practice Guide No 81

Surface tension and extrusion-based rheological characterisation of hot melt adhesives

Martin Rides, Crispin Allen, Angela Dawson and Jaspal Nottay

Division of Engineering and Process Control
National Physical Laboratory, Teddington, TW11 0LW

Abstract

This Guide presents guidance for good practice in measurement of the surface tension and the shear and extensional flow properties of hot melt adhesives. It covers:

- the measurement of surface tension of hot melt adhesives using the pendant drop method,
- the measurement of shear viscosity and entrance pressure drop by capillary extrusion rheometry,
- the measurement of melt flow rate behaviour using a simple extrusion rheometer, and
- the analysis of the melt flow rate results obtained using ‘long’ and ‘short’ dies to determine shear viscosity and entrance pressure drop data.

Example results are presented to illustrate the above methods, and to enable comparison of capillary extrusion rheometry and melt flow rate data thereby demonstrating the applicability of the melt flow rate method.

In particular, the rheological methods covered in this guide focus on high rate measurement.

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National Physical Laboratory
Teddington, Middlesex, United Kingdom, TW11 0LW

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Further Information

For further information on *Materials Measurement* contact the Materials Enquiry Point at the National Physical Laboratory:

Tel: 020 8943 6701

Fax: 020 8943 7160

E-mail: materials@npl.co.uk

Website: www.npl.co.uk

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Foreword

This Good Practice Guide describes methods for assessing the surface tension and rheological properties of hot melt adhesives under conditions typical of processing.

The information presented in this Guide has been gathered under a DTI funded programme of research *Measurements for Materials Systems*, namely project *MMS9 Measurements for Efficiency Improvements in Rapid Bonding Processes*. The project was carried out by a collaborative team consisting of NPL, Pira International, SATRA and TWI.

This Guide is one of a series of Measurement Good Practice Guides covering various areas of adhesive technology [1-8]. The outputs from this work are available through the Adhesives Design Toolkit website (www.adhesivestoolkit.com), a free information resource for adhesives.

This Guide aims to provide guidance to technologists, laboratory staff and quality assurance personnel on how to characterise the rheological and surface tension properties of hot melt adhesives in order to achieve satisfactory adhesive performance. A general familiarity with laboratory operations and mechanical testing, but not specifically adhesives testing, is assumed. The objective of this Guide is to familiarise the operator with the options available for characterisation of adhesives.

1 Scope

This Guide presents guidance for good practice in measurement of the surface tension and the shear and extensional flow properties of hot melt adhesives. It covers:

- the measurement of surface tension of hot melt adhesives using the pendant drop method,
- the measurement of shear viscosity and entrance pressure drop by capillary extrusion rheometry,
- the measurement of melt flow rate behaviour using a simple extrusion rheometer, and
- the analysis of melt flow rate results obtained using ‘long’ and ‘short’ dies to determine shear viscosity and entrance pressure drop data.

Example results are presented to illustrate the above methods, and to enable comparison of capillary extrusion rheometry and melt flow rate data thereby demonstrating the applicability of the melt flow rate method.

2 Introduction

The successful application of hot melt adhesives, whether by slot nozzle (coating), spraying, jet or daubing, is critical to the efficiency of the production process and to the performance of the bond, and is governed by the thermophysical properties of the adhesives. To remain competitive, there is increasing pressure from adhesives users to increase the speeds at which manufacturing and assembly processes operate. The drive for higher line speeds place greater demands on the performance of the adhesives, and consequently on the understanding of that process, the properties of the adhesives and how the two interact.

Poor adhesive placement and/or lack of control of spreading can result in the need to shut-down the process to enable cleaning operations to be performed. Similarly, the formation of adhesive filaments, known as “stringing”, can cause build up of adhesive on the production line, eventually requiring plant cleaning and thus production shut-down. Poor placement and lack of control of spreading of adhesive can result in poor bond performance. These issues can result in product rejection, either for cosmetic or functional performance reasons.

Both the rheological and surface tension properties control, to varying degrees, the dispensing behaviour of hot melt adhesives, the latter being more relevant to droplet formation, whether desired or undesired.

To help industry characterise and understand the performance of hot melt adhesives, this guide presents good practice for measurement of surface tension and rheological properties. In particular, the rheological methods covered are appropriate to high rate dispensing, and the issues covered in this guide focus on high rate measurement.

The methods outlined in this guide were used to evaluate a range of hot melt adhesive systems that are typically used in industry, the results of which are reported elsewhere [9, 10]. In principle, this guide could also be used to determine the surface tension and rheological properties of other types of materials that have similar properties to those discussed here.

In summary, this guide:

- describes hot melt adhesives, Section 3.
- provides guidance on surface tension measurement of hot melt adhesives using the pendant drop method, Section 4
- provides guidance on shear viscosity and entrance pressure drop measurement of hot melt adhesives using capillary extrusion rheometers, Section 5.2
- provides guidance on melt flow rate measurement of hot melt adhesives, Section 5.3
- compares shear viscosity and entrance pressure drop data obtained from capillary extrusion rheometry and melt flow rate measurements, Section 5.4
- presents guidance on density measurement of hot melt adhesives at elevated temperatures, Appendix 1,
- presents symbols and definitions for melt flow rate testing, Appendix 2, and
- presents an analysis of the melt flow rate test methods, Appendix 3.

3 Hot melt adhesives

The testing of hot melt adhesives is the focus of this good practice guide. Hot melt adhesives are thermoplastic polymer based compounds. They are applied as molten liquids, which increase in viscosity as they cool before freezing and becoming more rigid. Two common base polymers are ethylene vinyl acetate (EVA) copolymers and polyethylene (PE) homopolymers, with metallocene based hot melts now entering the market. A tackifier resin is added to achieve good hot tack, waxes to reduce viscosity (viscosity must be low at application temperature to allow good substrate wetting, but not too low to permit excessive spreading) and control setting speed, and stabilisers to prevent charring.

A typical formulation for a hot melt packaging adhesive would be:

- Tackifier resin 35% - 50%
- Polymer 25% - 35%
- Wax 20% - 30%.

Recently, pressure sensitive hot melt adhesives, which have permanent tack, have been introduced in packaging and garments. A further trend is the introduction of low process temperature (cool running) adhesives that can be dispensed around 90 °C to 100 °C, allowing more energy efficient and safer processes than traditional systems where dispensing temperatures are typically over 150 °C. Hot melt adhesives are formulated for many different purposes with properties that are specific to the market application, but there are certain adhesive attributes that are common:

- Low cost
- Clean running (absence of stringing or dripping)
- Long pot life (thermal stability – resistance to viscosity change and charring)
- Low temperature application – mainly desirable to reduce worker exposure to fumes and lessen the burn hazard
- Wide temperature application window
- Taint free – food packaging applications
- Generates substrate failure – fibre tear is a universal measure of satisfactory bond performance in the packaging industry

Several hot melt adhesive grades were supplied by National Starch and Chemical, representing the broad application categories used in industry:

- General purpose
- Deep freeze

- Heat/creep resistant
- Difficult substrates
- Low temperature application
- Pressure sensitive

The hot melt adhesives were supplied in two forms. Packaging adhesives were supplied in the form of solid pellets, provided in bags. These materials exhibited negligible tack at room temperature. In comparison, the pressure sensitive adhesives were supplied in 1 kg blocks of soft, tacky solid that presented a particular challenge for testing. In normal production use the whole block would be melted in the tank of the dispensing machine before application, but for testing smaller quantities are desired. It was extremely difficult to separate small pieces of adhesive from the block due to the high tack of the adhesive – it tends to re-bond as it is cut. Cooling in a deep freeze (to increase rigidity and reduce tack) and heating in an oven to over 100 °C (to make it more liquid) made little difference to the ease of cutting of the pressure-sensitive adhesives studied.

Details of the materials investigated are presented elsewhere [9,11].

4 Surface tension using the pendant drop method

4.1 Introduction

The surface tension, or more accurately the liquid-air interfacial tension, of a liquid adhesive is a key property for bond formation [12]. Surface tension arises from the attractive forces of molecules at the surface of a liquid. It is the force required to break the “film” formed at the surface. Surface tension is often expressed in dynes/cm (a surface tension of 1 dyne/cm is equivalent to 1×10^{-3} N/m). Surface tension is important in bonding.

- Interfacial tension of the adhesive and the surface energy of the substrate determine the wetting of the adhesive on the surface, good wetting promotes intimate contact and higher adhesion.
- The penetration of the liquid into craters and pores in rough and porous substrate, which enhances bond strength through mechanical ‘keying’, is a surface tension driven process.
- Surface tension is one of the properties controlling the stability of adhesive jets or sprays during dispensing; it may be an important parameter in effects such as stringing or drop break-up.

Surface tension depends on the interfacial intermolecular forces and can be split into contributions from non-polar (e.g. van der Waals) and polar (e.g. hydrogen bonding) components. The polar components can be further broken into electron acceptor or electron donor components (or Lewis acid/base components). Polar molecules have varying proportions of acceptor/donor components and in many cases one component will be much more dominant. Water is fairly unusual in having both strong acceptor and strong donor properties.

The surface tension of a liquid will influence how that liquid (adhesive) will wet a solid (adherend). Force balance or equilibrium at the solid-liquid boundary is given by Young’s equation (1) for contact angles greater than zero (see Figure 1):

$$\gamma_{lv} \cos \theta = \gamma_{sv} - \gamma_{sl} \quad (1)$$

where θ is the contact angle, and γ_{lv} , γ_{sv} and γ_{sl} are the surface free energies of the liquid-vapour, solid-vapour and solid-liquid interfaces, respectively. The lower the contact angle, the greater the tendency for the liquid to wet the solid, until complete wetting occurs (contact angle $\theta = 0$, $\cos \theta = 1$). For complete wetting to occur the surface tension of the liquid should be less than or equal to the critical surface tension of the substrate ($\gamma_{sv} - \gamma_{sl}$). Large contact

angles are associated with poor wettability. Thus surface tension potentially plays a significant role in the dispensing and spreading of hot melt adhesives.

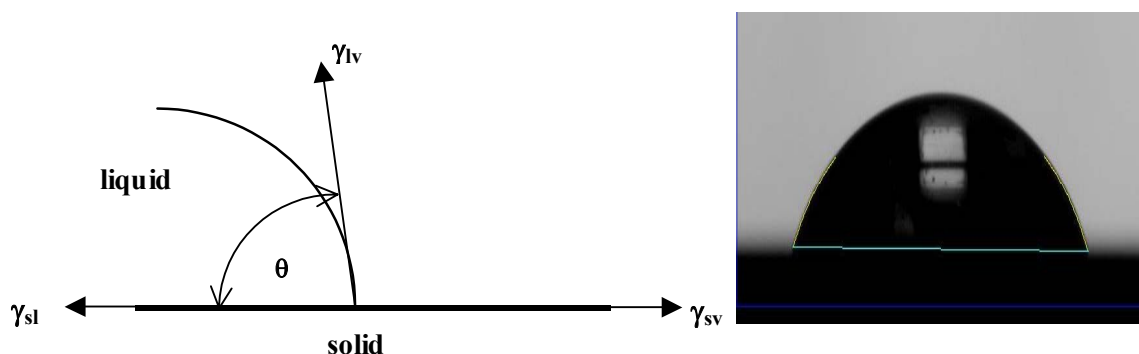


Figure 1: Contact angle of a liquid on a surface

This part of this Guide describes the pendant drop method for determining the surface tension¹ of hot melt adhesives specifically at elevated temperatures above 100 °C.

4.2 Pendant drop principles

Surface tension can be determined from the shape of a freely hanging drop of fluid under equilibrium conditions. The shape of a hanging pendant liquid drop is due to a balance between the forces acting on the drop. The principal opposing forces are:

- Gravity, which pulls the drop down, elongating the drop; and
- Surface tension, which acts to prevent the growth of surface area and tends to pull the drop into a spherical shape.

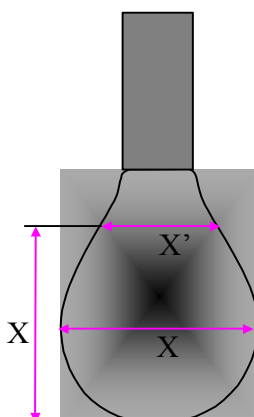


Figure 2. Pendant drop shape

¹ Interfacial tension at a liquid-vapour interface.

The shape of the drop, suspended in air, therefore contains information on both the density and surface tension of the liquid. Building on the work of Laplace, the Young-Laplace equation relates the surface tension γ_l to the density of the liquid (ρ_l), gravity and drop shape, and is used in automated drop shape analysis (ADSA) techniques [13].

$$\gamma_l = \rho_l g f(shape) \quad (2)$$

where g is the acceleration due to gravity ($g = 9.81 \text{ m s}^{-2}$). The shape factor of the drop can be calculated by automatic drop shape analysis (ADSA) software or found in look-up tables. The density of the liquid, in this case the adhesive, was unknown at the measurement temperature and needed to be determined.

4.3 Method outline

A suspended drop of the liquid sample is formed using a pipette. The pipette is held in a temperature controlled chamber. The shape of the pendant drop is projected onto a camera using back lighting and analysed using ADSA software. A schematic of the equipment used to measure surface tension is shown in Figure 3.

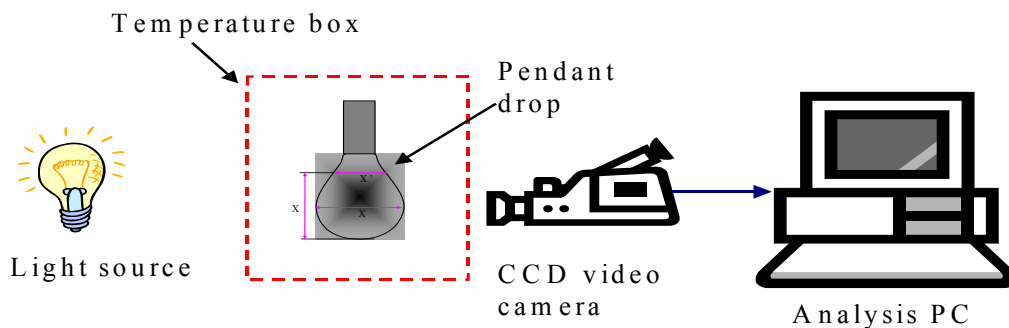


Figure 3: Axisymmetric drop shape analysis method for determining surface tension from pendant drops

4.4 Sample and dispenser preparation

A pipette dispenser can be used to form the pendant drop. Due to their tackiness and consequently contamination of tests on subsequent materials, hot melt adhesives need to be dispensed from disposable pipettes.

The tip of the pipette dispenser shall be visibly free of damage, flat and the orifice shall be circular.

The outer diameter of the tip of the pipette dispenser shall be measured carefully using a micrometer so that it can be used as a reference distance for calibration of the imaging system. The tip of the pipette was typically 1.1 mm to 1.2 mm in diameter, and measured using a digital micrometer with a resolution of 0.001 mm.

Procedures should be designed to ensure that handling and contamination of the samples and equipment should be kept to a minimum.

The disposable glass pipette dispenser then needs to be charged with the hot melt adhesive. Packing the adhesive into pipettes presents some practical difficulties. If the normal ‘draw-up’ method of loading the pipette is used the adhesive tends to cool and solidify in the narrow tip. Thus it may be more appropriate to cut the adhesive into smaller pieces that can be ‘packed’ into the pipette via the wider top opening and melted in-situ. This is a relatively simple process to perform for adhesives that display low tack at ambient temperatures. However, for adhesives that exhibit a high degree of “tackiness”, care must be taken to ensure the adhesive is not manually handled for an extended period of time as the “tackiness” tends to increase and contamination is also likely to increase. If the sample exhibits a high degree of tack, such that it is not possible to introduce the sample into the pipette dispenser, it is advisable to cool the sample to try to reduce its “tackiness” by, for example, placing in a fridge for 30 minutes, and repeat the loading procedure.

Once the pipette dispenser has been sufficiently filled, a thermocouple should be introduced into the adhesive sample in the pipette in order to measure the actual adhesive melt temperature during testing.

A rubber stopper or similar device can be used to reduce and control the rate at which the adhesive flows out of the pipette at elevated temperatures, as may be necessary when the viscosity of the sample is low.

Air bubbles may be introduced, unintentionally, to the sample during loading. Such air bubbles and any other contamination will affect the results: for example, an air bubble in the pendant drop will effectively reduce the average density of the material thus resulting in a lower measured surface tension. Air bubbles and some other types of contaminant can be clearly seen when using a glass pipette and in the pendant drop itself. Results obtained on pendant drops containing air bubbles and visible contaminants should be discarded.

An example of a syringe that is ready for testing is shown in Figure 4.

In using reference materials for checking the calibration of the instrument, the results can be very sensitive to contamination. Additional precautions not necessary for testing hot melt adhesives may need to be employed to avoid contamination.

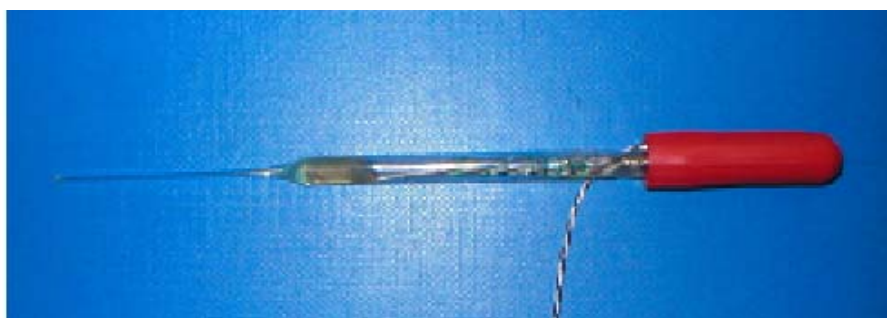


Figure 4. Glass pipette containing adhesive melt, thermocouple and control plug

4.5 Temperature and environmental control

Once the dispensing pipette has been prepared, mount it in a temperature controlled chamber.

The pipette should be mounted in such a way as to permit movement in vertical and horizontal directions and rotationally in order to correctly place the pipette tip in the field of view of the imaging system and to ensure that the pipette is vertical.

Set the temperature of the chamber to the required value.

The temperature in the chamber should be controlled and stable during measurements.

The temperature box should be designed to avoid excessive air movements, whether due to convection or fans, that could deflect and thus distort the drop shape. The temperature controlled chamber should not cause vibration of the pipette and suspended drop.

The sample should be allowed to stabilise at the measurement temperature prior to dispensing drops.

It is preferable to use the thermocouple in the pipette for measuring the sample temperature. Both the air temperature close to the syringe tip and the sample temperature within the pipette should be recorded during measurements to quantify the variations in temperature that are occurring, and in the event of high discrepancies to improve the heating procedure and equipment.

The temperature controlled chamber shall provide a ‘clean’ environment so as to not introduce contamination to the sample, e.g. through absorption.

It is important that evaporation of the drop, or of any of its components, does not occur as this is likely to affect the measured surface tension.

When testing, it is desirable to avoid temperatures near the crystallisation / solidification temperature or other transitions, as the measured behaviour will be highly sensitive to temperature and potentially to small changes in composition.

4.6 Pendant drop formation

Once the test liquid has reached the required test temperature, measured preferably using a thermocouple immersed within the test liquid, start the image capture software and dispensing of the liquid.

Measurements should preferably be of a static pendant drop that has reached a stable equilibrium shape.

A typical drop size was between 4 μl and 10 μl , corresponding to a drop diameter of approximately 2 mm to 2.7 mm.

4.7 Illumination and imaging

The drop can be imaged using a CCD camera that views the sample through a window in the temperature controlled chamber, and relays the image to the ADSA software.

The drop should be backlit, using lighting of appropriate intensity, to ensure good contrast between it and the background and thus accurate determination of its shape and size (as the software relies on the difference in contrast in order to ascertain where the drop is).

A normal lamp was used for illumination: a halogen lamp, initially tried, was found to produce too intensive a light for good image definition.

The background illumination level should be uniform in the field of view and stable during the measurement.

The camera shall be set to achieve a sharp focus on the drop.

The plane of the camera's CCD devices shall be vertical, and thus parallel to the vertical axis of the drop, and the drop centred in the picture to ensure that there is no distortion of the shape of the drop in the image, e.g. the drop should not slope from back to front in the image.

Illumination and imaging to obtain a clear outline may be more problematic owing to the presence of the temperature controlled chamber and any windows through which the drop is viewed.

- Interior surfaces may need to be masked to reduced reflections on the sample or windows.
- Window thickness should be minimised as far as possible.
- Windows should not act as a lens, distorting the magnification.
- Windows should be clean.

Variations in temperature within the temperature controlled chamber (and the resulting air density differences) may produce effects that distort the image, as occurring in a mirage. A visual check of the image may be necessary to determine if this is occurring and, if necessary, improvements should be made to ensure better uniformity of temperature in the chamber.

Once a suitable image of the pendant drop is obtained, the magnification of the optical device should be set to ensure that the observed drop occupies at least 50% of the image vertically, preferably 75%. Accuracy is dependent of how many “pixels” are available for measuring the drop size. Magnification must be accurately calibrated, which takes some time but is vital for correct results.

4.8 Drop shape measurement and analysis

Manual shape measurements can be prone to operator subjectivity but this can be removed from the process by image analysis of the drop shape using a computer programme [14,15]. There are many commercially available axisymmetric drop shape analysis (ADSA) instruments where the image of the drop is viewed using a video camera and captured on computer. An image analysis programme detects the shape of the drop. Numeric algorithms are run to define the ‘shape’ of the pendant drop from which the surface tension is determined.

In this work, the captured video image was analysed using an imaging/software system “CAMTEL, FTA 100” to determine the shape parameters [16]. The software is built around a continuous frame grabber, which is capable of digitising full RS-170 (NTSC) frames at VGA resolution. The software allows the user to run the software either in a dynamic mode, where a series of images are “grabbed” during drop formation, or in a static mode, where the user can select an individual frame. When running the camera ‘dynamically’ the frame-grabbing rate should be sufficiently high to enable adequate measurements to be made. Figure 5 shows a typical drop being analysed using this software.

When using automatic drop analysis software, identification of the edges of the drop can be critical to measurement accuracy. In using the CAMTEL FTA 100 system, construction lines are drawn on the drop (shown in light blue in Figure 5). It is important to ensure that they are exactly at the edges of the drop, as very small discrepancies will give a false measurement of surface tension.

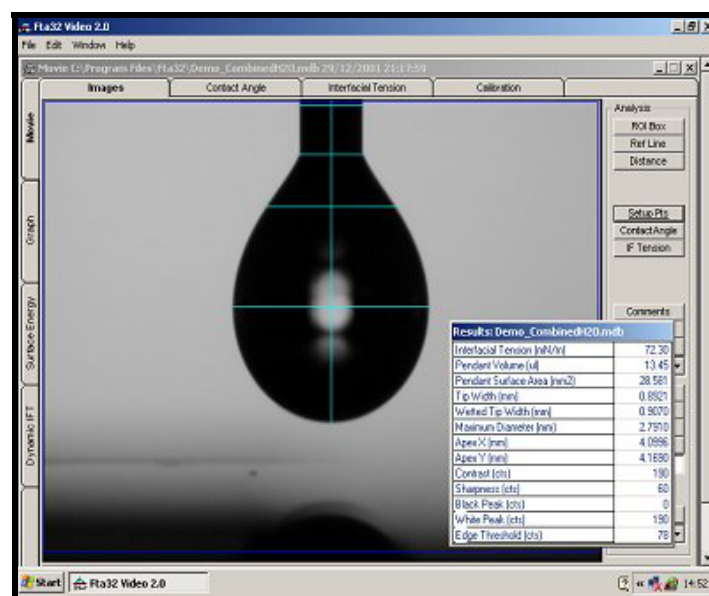


Figure 5. Screenshot of Pendant drop and software interface.

An important issue affecting the accuracy of the technique concerns the pixilation of the image. This may be a limiting factor in the uncertainty of the length measurement when defining the pendant drop using imaging systems. The effect of pixelation on the uncertainty of the length measurements should be assessed, and improved if necessary.

4.9 Density

To determine the fluid's surface tension its density at the test temperature is required (see Appendix 1). As the surface tension is proportional to the density, a 1% error in density will contribute a 1% error to surface tension.

4.10 Calibration

There are two key stages to ensuring accurate surface tension measurement by the pendant drop method. The first is to calibrate the imaging system, and the second is to run a calibration check using a reference fluid of known surface tension, for example high purity glycerol or distilled water. Both should be carried out as the first provides instrument correction factors that may need to be input into analysis software, and the second provides a check on the test procedures being used.

Additional calibration of temperature, e.g. thermocouples, and density measurement shall also be performed.

Where different software magnification factors in the x and y directions can be individually set, optical calibration of the field of view can be performed using, for example, a steel ball of uniform and known diameter. The ball shall preferably be comparable to the size of the pendant drops to be measured, and calibration shall preferably be carried out at the test temperature(s). Where different software magnifications cannot be set, a check should be made to identify whether there is a difference in x and y-direction calibration factors and to make adjustments to the equipment, e.g. to the alignment of the camera, to correct for the effect.

The dispensing pipette tip should also be used for calibrating the horizontal dimension of the imaging system. During each measurement, the pipette tip diameter (measured before the test) should be used as a reference to adjust the magnification factor.

The calibration of the system and the test procedure should be checked by performing a test using a dispensing pipette of known diameter and a fluid of known density and surface tension. It is preferable to select a test liquid for calibration that has similar chemical nature and surface tension values to the fluid to be tested. Commonly used reference liquids for measuring surface tension include distilled water and glycerol. For values of surface tensions and densities of reference materials see [17].

Table 1: Fluids used for calibration of pendant drop technique and measured values

Fluid	Interfacial tension, m/(N.m)	NPL measured value, m/(N.m)	Density, g/cm ³
Glycerol (C₃H₇O₃) at 21 °C	64	63.9	1.26
Water (distilled) at 21 °C	72.8	72.8	0.998

The surface tensions of many liquids (particularly water) can change dramatically with the absorption of small quantities of surface-active impurities (from surfaces or the atmosphere). Care must be taken with the handling and storage of samples. Water should be freshly distilled/deionised before use.

4.11 Measurement issues

The surface tension measurement may be affected by the viscoelastic behaviour of the fluid, with its associated time dependence. The time taken to reach equilibrium will depend on the viscoelasticity of the liquid and its surface tension. A fluid with little elasticity is likely to reach equilibrium quickly, but a highly elastic fluid may take considerable time to reach an equilibrium shape. It is important that sufficient time elapses prior to measurement, to allow equilibrium conditions to be established.

Longer term changes in pendant drop shape may occur due to absorption of contaminants or evaporation of components of the sample, particularly for reference fluids and at the elevated temperatures at which these samples are tested.

Capillary action has also been observed where the sample “climbs” up the outside of the pipette, and therefore changes the geometry of the drop. It is essential to ensure that the pipette, both inside and outside, is free from contamination.

4.12 Example surface tension results

Example results are presented for surface tension of a range of hot melt adhesives at 110°C, 130 °C and 150 °C. Data for three packaging adhesives are tabulated in Table 2, along with average and standard deviation values. The data for the Novocol 90 only are plotted in Figure 6. Average surface tension values are presented in Figure 7 for a range of packaging and pressure-sensitive hot melt adhesives.

It is noted that the pressure-sensitive adhesives exhibited an increasing value in surface tension with increasing temperature, whereas the packaging adhesives exhibited the opposite trend. It has been suggested that this may be a real difference, due to the complex chemistry of the materials, or may be due to experimental issues related to the significantly higher viscoelasticity of the pressure-sensitive adhesives in comparison with the packaging adhesives. The greater viscoelasticity may result in time dependant errors due to the relaxation time behaviour of the material combined with the non-equilibrium nature of the drop-forming method.

The standard deviation value of ten measurements, on each of eight materials at two or three temperatures per material, was between 1.5% and 7.1% of the mean values, with an average standard deviation of 3.0% (the exclusion of three outliers from the 180 data points reduced the upper limit of the standard deviation range to 4.4% but had little affect on the overall average).

Table 2: Pendant drop surface tension results

Adhesive	Novacol 90			Ultra-Melt 201			Varni-melt X10		
Test No.	110 °C	130 °C	150 °C	110 °C	130 °C	150 °C	110 °C	130 °C	150 °C
1	19.6	18.18	17.8	18.32	18.05	17.27	19.54	16.94	17.02
2	18.97	18.23	17.77	18.59	17.71	16.67	20.63	17.67	16.59
3	20.19	18.07	17.47	19.51	17.98	17.14	20.02	16.89	17.05
4	19.66	18.66	17.45	18.88	17.98	17.31	20.14	17.37	16.77
5	20.34	19.09	18.13	18.93	17.66	17.36	20.17	17.42	16.79
6	19.77	19.16	17.94	18.87	17.13	17.12	19.39	17.61	16.82
7	19.26	18.94	17.06	18.11	16.98	17.59	21.12	17.39	17.01
8	20.27	18.77	17.12	19.26	18.12	16.92	19.71	17.55	16.83
9	20.11	18.32	18.11	18.63	18.04	17.39	20.77	17.82	16.91
10	21.02	19.22	17.79	18.48	17.79	17.41	19.92	18.11	16.72
Average	19.92	18.66	17.66	18.76	17.74	17.22	20.14	17.48	16.85
St. Dev	0.59	0.44	0.38	0.42	0.40	0.27	0.55	0.37	0.15

4.13 Concluding remarks – surface tension

Surface tension measurements have been made on hot melt adhesives using the pendant drop method. Alternative methods for measuring surface tension exist and include:

- Wetting balance measurement.
- Maximum bubble pressure measurement.

However, the application of these measurements for accurate characterisation of high temperature, visco-elastic polymer melts was not established in this work.

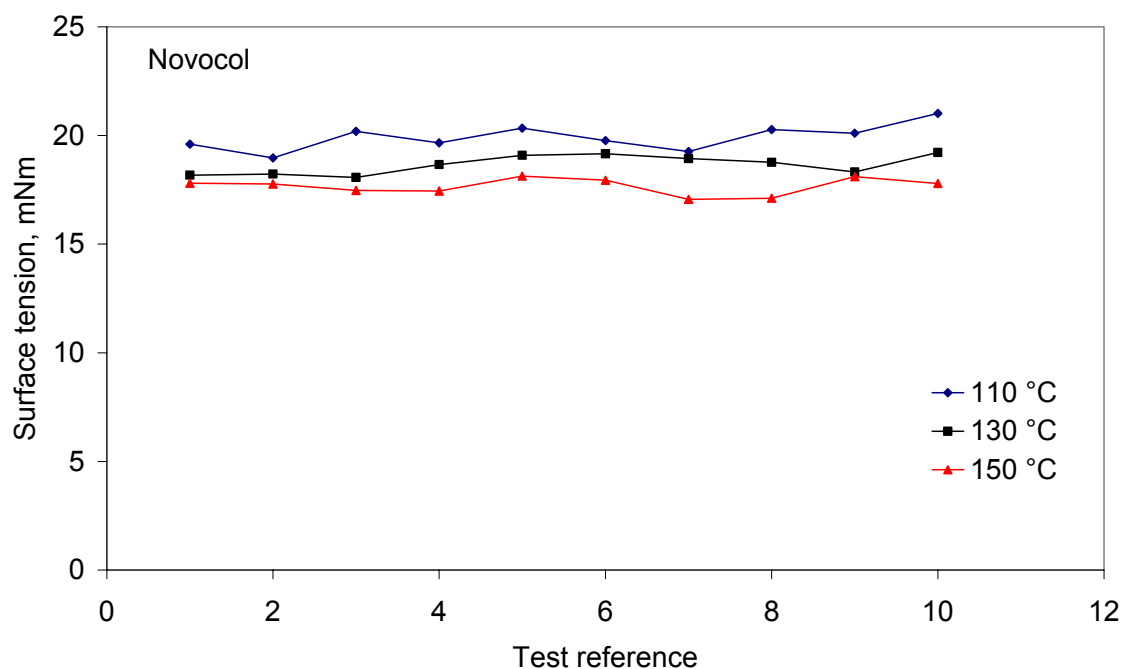


Figure 6: Successive surface tension measurements of Novacol 90 at three different temperatures

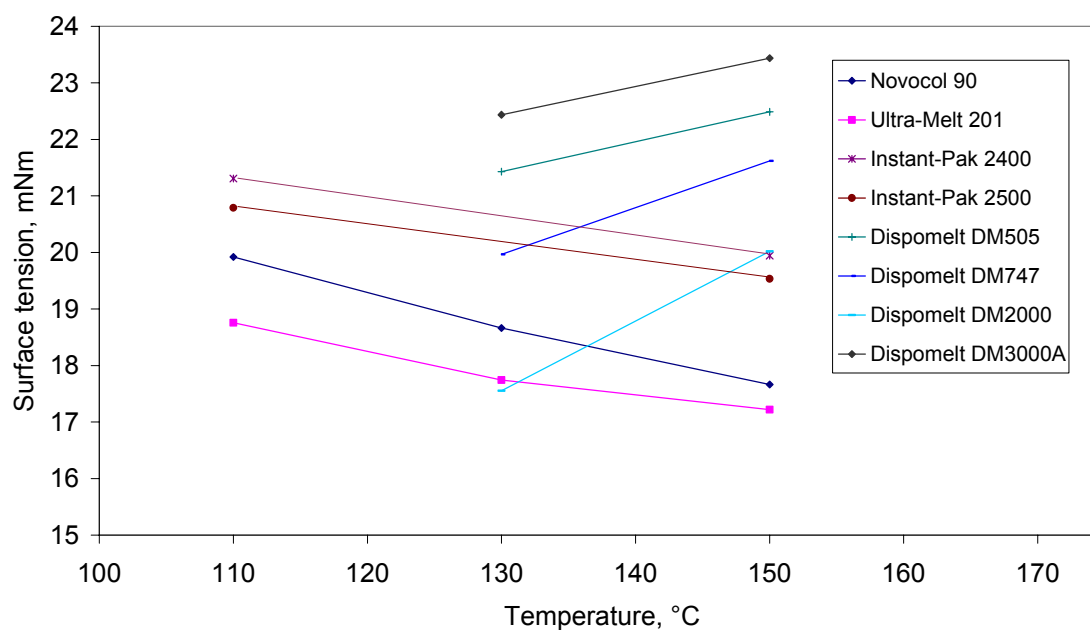


Figure 7: Surface tension measurements of a range of hot melt adhesives

5 Extrusion based rheology techniques

5.1 Introduction

The application of hot melt adhesives by coating and spraying are high speed dispensing processes, yet rheological² characterisation is typically performed using low shear rate techniques, for example rotational [18] and oscillatory [19,20] techniques. Although these methods may be informative about the adhesive, it requires considerable extrapolation of data from such low rate techniques to predict the behaviour of the adhesives in high rate applications. For example, a continuous filament of adhesive extruded onto a substrate through a 0.45 mm diameter nozzle die will experience shear rates in the die of the order of 100000 s^{-1} , compared with typically 10 s^{-1} in a cone and plate rotational rheometer.

To understand how hot melt adhesives perform under such conditions it is necessary to characterise the rheological behaviour of the melts at comparable test conditions of temperature and shear rate. As a general rule it is preferable to use test methods that mimic the process for which data are being sought.

To obtain high shear rate data, extrusion-based methods are most appropriate, in particular controlled-rate capillary extrusion rheometry³. The melt flow rate test, a simple controlled stress test, is a globally accepted plastics industry standard for determining the flow behaviour of thermoplastics. It is an inexpensive extrusion-based method but with severe limitations for achieving high shear rate data in its normal guise. Further advantages of melt flow rate testing over capillary extrusion rheometry testing - as evidenced in the plastics industry - is that it is simpler, it provides single point data (normally) and is widely used and accepted in industry. However, its disadvantages are that it provides single point data (normally), is not always able to resolve differences between materials and scatter can be high. The single point nature of the melt flow rate test, i.e. that the flow behaviour is defined by a single value, is advantageous in that it is easily understood by industry. However, it is unreasonable to expect that the complex flow behaviour of a polymeric material is adequately and accurately described by a single value.

The rheological behaviour of polymeric materials is complex and usually comprises of significant viscoelastic behaviour and differing properties in shear and extensional flow fields, characterised by the shear viscoelasticity and extensional viscoelasticity. The behaviour of polymeric materials tends to be shear thinning (i.e. dependent on the shear rate),

² Rheology: the study of the deformation and flow of matter.

³ The term “capillary extrusion rheometry” is used herein to imply extrusion rheometers that use transducers to measure the extrusion pressure. The melt flow rate method is excluded from this term, although it is an extrusion method.

temperature dependant, and may exhibit slip, yield and thixotropic phenomena.

The capillary extrusion rheometer and melt flow rate method are used primarily to characterise the shear flow behaviour of materials. However, the use of short dies to determine entrance pressure drop values in both capillary extrusion and melt flow rate testing have been evaluated in order to characterize the extensional flow behaviour of the hot melt adhesives. Extensional flow behaviour can be a more sensitive measure of, for example, changes in molecular structure of the material.

Rheological data can be used for a variety of purposes, principally materials development and selection, process (flow) simulation and design, quality control (on-line and off-line), and troubleshooting.

This guide focuses on the methods of capillary extrusion rheometry and melt flow rate for characterisation of the high rate rheological behaviour of adhesives. Example results for hot melt adhesives using the improved methods are presented. As this guide focuses on issues specifically related to testing hot melt adhesives, it is assumed that the reader is familiar with the basic methods. For details on the basic methods the reader is referred to [21-25] for capillary extrusion rheometry and [26, 27] for melt flow rate testing.

5.2 Capillary extrusion rheometry

5.2.1 Method

Principle

The capillary extrusion rheometry method for thermoplastics, upon which this work was based, is described in ISO 11443 [21], Figure 8. Capillary extrusion rheometers are used predominantly to determine the high rate shear viscosity of molten polymers. The pressure drops across one or more dies for various volume flow rates are measured and from these shear viscosity values are calculated, equations 3 - 5.

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

$$\eta_a = \frac{\tau}{\dot{\gamma}_a} \quad (3)$$

where τ is the shear stress given by

$$\tau = \frac{(P - P_e)R}{2L} \quad (4)$$

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

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (5)$$

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 procedure. Various “shear viscosities” – entrance pressure drop-corrected and Rabinowitsch corrected – can be determined [21]. The method is suitable for generating quantitatively accurate data for modelling as well as for quality control.

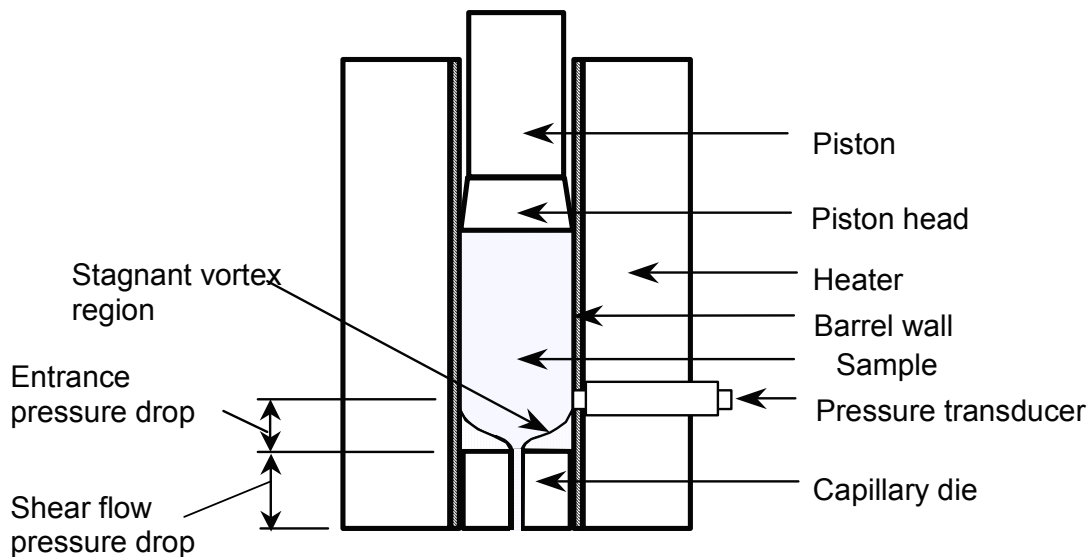


Figure 8: Schematic of capillary extrusion rheometer

Entrance pressure drop

The capillary extrusion method can be used to determine entrance pressure drop values as a function of flow rate (or apparent shear rate to normalise for different die diameters). These values can be related to the extensional viscosity of the material [24,26,27,28]. However, entrance pressure drop values are considered to be qualitatively valuable, for example when comparing similar materials. For plastics, entrance pressure drop values can provide a better capability, compared with shear viscosity, to differentiate materials with differences in molecular chain branching and fibre-filled materials.

The instrument used was a Rosand RH7 twin barrel capillary extrusion rheometer. However, when testing hot melt adhesives additional precautions need to be taken and are discussed in detail below. Hot melt adhesives are typically lower in viscosity than most thermoplastics for which the instrument was primarily designed and for which ISO 11443 [21] applies. The hot melt adhesives were typically in the shear viscosity range of 0.2 Pa.s - 5 Pa.s, the packaging adhesives being generally lower than the pressure-sensitive adhesives. This compares with values typically in excess of 100 Pa.s for thermoplastics.

Leakage flow

Due to their low viscosity, significant leakage of hot melt adhesives out of the rheometer may occur:

- a) past the piston head, which may be apparent from molten adhesive on the piston rod (on the land behind the piston head) and also on the top of the barrel,
- b) past the outside of the die, which may be evident from adhesive on the screw thread of the die support nut, and
- c) at the pressure transducer mounting, which may be evident from adhesive on the screw thread of the mounting device.

Leakage is a problem for extrusion testing as it reduces the volume flow rate passing through the die, thus resulting in a lower pressure than would be the case in the absence of leakage. Unless a correction is made for the leakage, the measured viscosity will be lower than the actual viscosity.

Leakage is a greater problem in testing hot melt adhesives than polymer melts due to their lower viscosities and the use of significantly smaller diameter dies. The use of smaller diameter dies effectively makes the gaps through which leakage occurs (e.g. piston head - barrel gap) more significant in their contribution to the flow of material out of the barrel.

Leakage can be prevented by the use of O-rings on the die support nut and pressure transducer mounting screw thread. However, the O-rings are likely to need replacing to ensure continued adequate performance, particularly where removed after testing.

To reduce flow past the piston head a design based on the principle of the piston head in a bicycle pump is recommended, Figure 9. The piston head, made of PTFE, has the working surface recessed so that when pressurised the flange of the piston head deforms thereby making a seal against the barrel wall.

The PTFE piston head has been found to perform excellently in preventing leakage. However, the PTFE piston head also prevented air from escaping from the barrel, which consequently

caused greater variability in the measured extrusion pressures. For the lower viscosity hot melt adhesives, extrusion pressures for the short die were typically less than 10 bar. The effect of trapped air in the adhesive sample was much more significant than is the case when testing thermoplastics for which pressures are typically $\times 10$ higher. The trapped air will occupy a greater volume at lower pressures than at higher pressures (in accordance with Boyle's law). Also, with the smaller diameter dies used for testing hot melt adhesives an air bubble of a certain size will have a greater effect on extrusion pressure than it would in a larger diameter die typically used for thermoplastics. The trapped air causes fluctuations in extrusion pressure as it, rather than the material being tested, passes through the die. The airtight PTFE piston traps air beneath it after the piston is inserted and prevents the barrel and sample degassing prior to testing. Without such degassing it was likely that the sample contained trapped air throughout. This problem was more severe for the pressure-sensitive adhesives than the packaging melts as, with the latter, air bubbles were observed to come to the top of the melt in the barrel during temperature stabilisation prior to testing. As pressure-sensitive adhesives are more elastic in nature than the packaging adhesives, the tendency for bubbles to rise to the surface is likely to be lower.

To avoid the trapping of air, a small vent-groove was scored along the length of the side of PTFE piston head thereby allowing air to escape from the barrel and material, whilst minimising the leakage of adhesive.

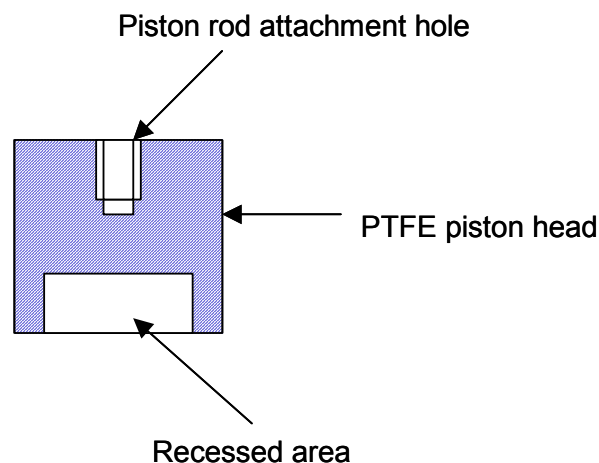


Figure 9: Schematic of capillary extrusion rheometer PTFE piston head operating on a bicycle pump piston head principle

Pressure transducers

For improved accuracy, it is important that the pressure transducers are selected such that they are operating within the 10% to 90% of their pressure range. Data obtained outside this range should be examined more closely, and rejected if considered suspect.

Die size and measurement

To cope with the lower viscosities of the hot melt adhesives, smaller diameter dies than would typically be used for thermoplastics melts are used. Two different sets of dies were used for testing hot melt adhesives, being 0.25 mm and 0.5 mm in diameter. The larger diameter dies were used for the higher viscosity pressure sensitive hot melt adhesives as the extrusion pressures were too high for the transducers at the higher extrusion rates using the 0.25 mm diameter dies.

The diameters of the 0.5 mm dies can be easily checked using a go / no-go gauge of dimensions $0.500 \text{ mm} \pm 0.005 \text{ mm}$ in diameter. For the smaller dies go / no-go gauges were not available and thus alternative methods were required. The diameters of the nominally 0.25 mm diameter dies were measured by two methods:

- a) optically, of the end of the capillary die, and
- b) by making a cast of the die using a replicating fluid⁴. A correction for shrinkage effects was made by comparison of measurements on a larger die that had also been calibrated using an internal split ball micrometer instrument. The cast thus obtained was then measured optically using a microscope.

Method b) has the advantage that the diameter along the length of the die could be determined unlike method a) in which only the end diameters could be measured.

The diameters measured by the two methods differed. The replicating cast method gave values of 0.252 mm (long die) and 0.254 mm (short die) whereas the optical method gave values of 0.272 mm (long die) and 0.262 mm (short die). In the analysis of the raw data, average values of the two methods were assumed. The uncertainty in the die diameter causes significant uncertainty in the derived shear viscosity values and shear rates, which are dependant on the die radius raised to the fourth and third powers respectively. For shear viscosity this implies an uncertainty contribution of 15% and for shear rate 12% due solely to the uncertainty in the die diameter [21]. This discrepancy and calibration of small die diameters will be investigated further.

Precision

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

⁴ Replicating fluid is available, for example, from Struers www.struers.com - “RepliSet-F5” a fast curing two-part silicon rubber compound for flexible high-resolution replicas.

presented in detail, along with an analysis for the determination of the uncertainties of measurement, by Rides and Allen [21,24].

When using smaller diameter dies whose size is of greater uncertainty the overall reproducibility is expected to increase. However, providing only one set of dies is used the repeatability of measurements is not expected to change.

5.2.2 Capillary extrusion rheometry results

Apparent shear viscosity (Bagley corrected [25]) and entrance pressure drop data (values obtained on extrapolation of extrusion pressure data to a die length of zero) for the packaging and pressure-sensitive adhesives are presented in Figures 10 and 11.

In determining entrance pressure drop data it is preferable to determine values by performing a Bagley correction, i.e. extrapolating the extrusion pressure data for the long and short dies to an effective die length of zero. It has been observed that this correction was significant for hot melt adhesives: the entrance pressure drop values for a “zero” length die are considered to be more appropriate for comparison than short die data as the latter die can have a significant shear flow component. This enables improved comparison of data with other data obtained using different length short and long dies. However, if entrance pressure drop values are assumed to be given by the extrusion pressure values obtained for a short, non-zero length die such data should only be compared with data obtained using exactly the same die geometry.

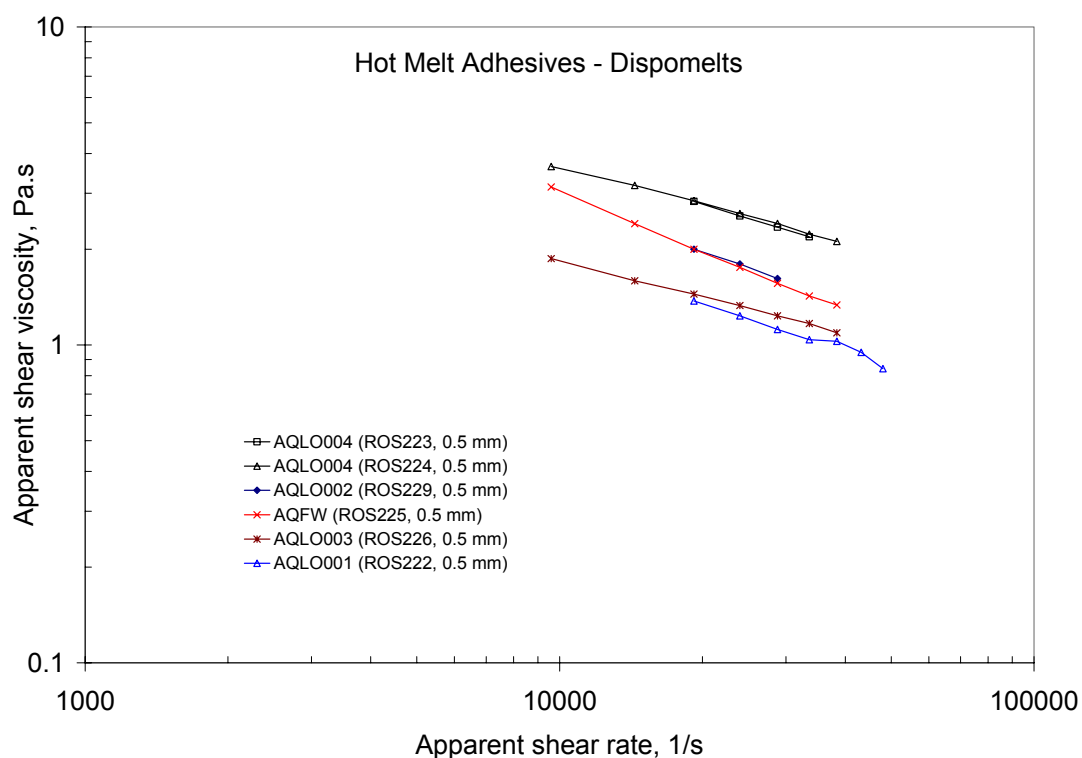


Figure 10: Apparent shear viscosity determined from capillary extrusion rheometry for the pressure-sensitive adhesives at 150 °C (Bagley corrected)

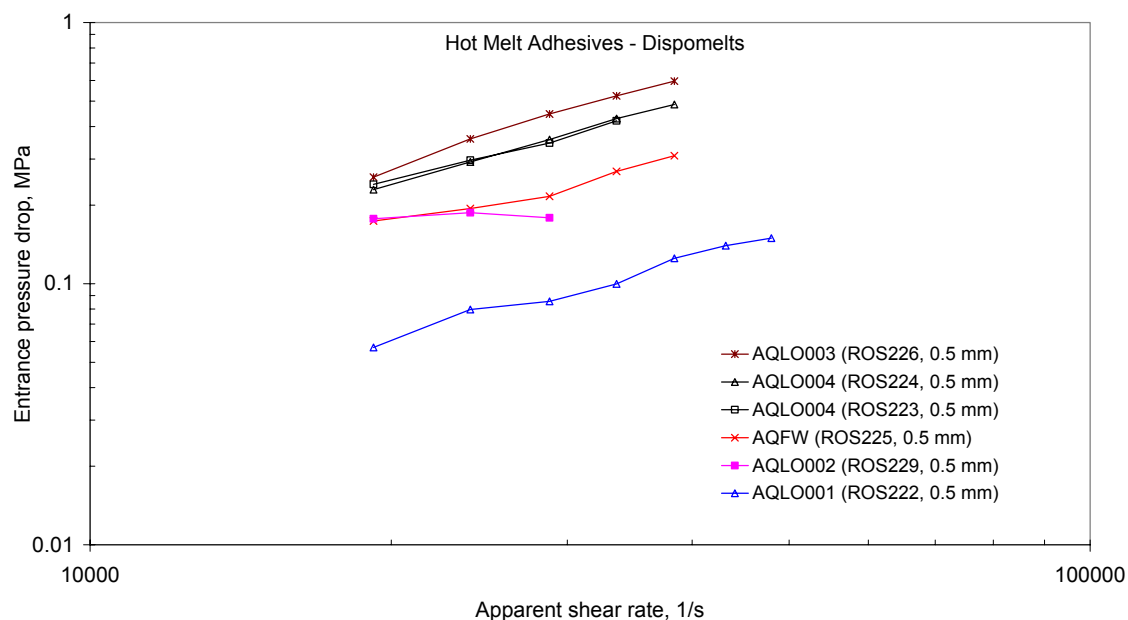


Figure 11: Entrance pressure drop data determined from capillary extrusion rheometry for the pressure-sensitive adhesives at 150 °C (extrapolation to zero length die)

5.3 Melt flow rate testing

5.3.1 Method

The standard melt flow rate method

The melt flow rate method described by ISO 1133 Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics [26] is used as the basis for testing. The melt flow rate method, put simply, is to measure the quantity of material (pre-heated in a barrel) that is extruded through a die in a given time when a specified weight is applied to the piston, Figure 12. The standard for testing thermoplastics specifies the use of a single die 8 mm in length and 2.095 mm in diameter. The standard (ISO 1133) 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 extruded 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 cm³/10 minutes. The MFR and MVR are thus measures of the ease of flow: the higher the MFR or MVR value the easier the material flows. The melt volume flow rate (MVR) is used herein in preference to the melt mass flow rate as it is more closely related to shear viscosity than melt mass flow rate, which incorporates a density term.

Shear viscosity and entrance pressure drop determination

The melt flow rate technique is appropriate for quality control purposes and provides a simple, qualitative measure of the processability of the material. The results obtained using the standard method are not fundamental rheological properties, and tend to be obtained at relatively low shear rates. However, recent work at the NPL has demonstrated that the melt flow rate instrument, with minor modifications, can be used to determine quantitatively accurate shear viscosity and entrance pressure drop data [27].

The use of a single long die in an extrusion experiment, as per ISO 1133, can only provide, at best, an approximation to shear viscosity data. To obtain accurate shear viscosity values at least one extra die has to be used. If a very short length die is used, Figure 13, then a measure of the extensional flow behaviour can be determined. The principle behind the use of a short length die is to obtain a measure of the resistance to flow in a converging region, characterised by the “entrance pressure drop”. As a converging flow is predominantly an extensional flow field, entrance pressure drop values can be related to the extensional flow behaviour of the material [24,28-30]. Various models proposed for interpreting the entrance pressure drop data in terms of extensional viscosity have been reviewed by Rides and Allen

[24]. However, one does not need to convert the entrance pressure drop data to extensional viscosity values for the data to be of use. A plot of entrance pressure drop versus apparent shear rate has been found useful in comparing materials [24]. This method is simple, yields quantitative data and is potentially cheap. The basis for the method, when used in a controlled flow rate mode, is presented in detail by Rides and Allen [24,27]. The approach is now applied to the controlled stress mode (i.e. applied load) as used for MVR measurements. An analysis of the melt flow rate method is presented in detail in the Appendix 3.

Melt flow rate instrument

All melt flow rate measurements were made using a Ray-Ran Test Equipment Limited 5MPCA Advanced Melt Flow System instrument. MVR values were obtained for a range of applied loads from the series 0.325 kg, 1.2 kg, 2.16 kg, 3.8 kg, 5 kg, and 12.5 kg at 150 °C.

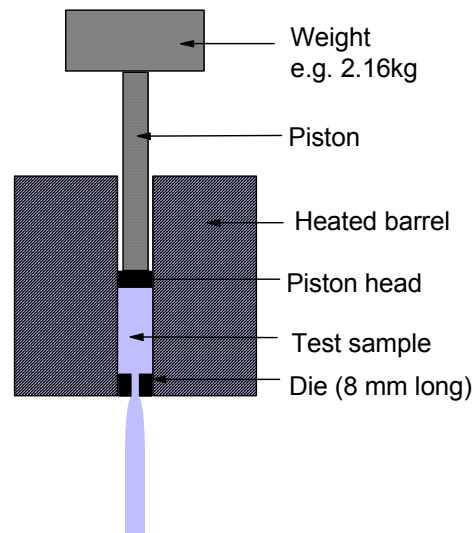


Figure 12: Schematic of standard melt flow rate instrument (ISO 1133)

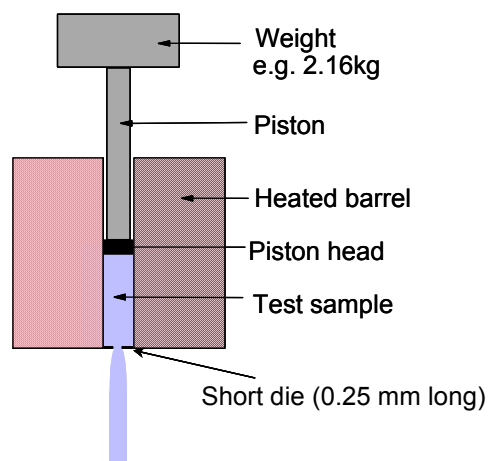


Figure 13: Modified melt flow rate instrument using a short die to determine entrance pressure behaviour



Figure 14: Short and long dies for separation of shear and extensional flow behaviours, and illustration of the nozzle geometry to avoid drooling of extrudate at the die exit.

Die selection and calibration

To provide the simplest experimental case to determine shear viscosity and entrance pressure drop data a die of short length was used in addition to the standard length MVR die (shear viscosity corrected for entrance effects), Figure 14. The dies used were nominally 0.5 mm in diameter. The “short” die had a length of 1.029 mm and the “long” die a length of 8.038 mm.

A go / no-go gauge with a variation of $0.500 \text{ mm} \pm 0.005 \text{ mm}$ was used to check the diameters.

Leakage flow

Although leakage of hot melt adhesive past the piston and die was not observed to be significant in the melt flow rate testing, it cannot be assumed that it did not occur. However, the remedy adopted for the piston head modification in capillary extrusion testing would not have proved appropriate for melt flow rate testing, particularly when using the lower loads, as friction effects between the piston head and the barrel wall would have been significant. This is thus a severe limiting factor in the use of the melt flow rate method.

Die exit design

With the melt flow rate testing, accumulation of hot melt in the exit region of the die occurred. This could potentially provide additional back-pressure to the flow thereby reducing the flow rate, and should thus be avoided. A modification to the nozzle geometry at the exit of the dies, Figure 14, was evaluated and found to work well, producing “cleaner” extrudate.

Flow rate measurement

The accuracy and range capability of flow rate measurement of standard melt flow rate instruments, designed for thermoplastics, may be insufficient for reliable testing of hot melt adhesives due to the significantly higher flow rates involved. Initial results using the standard instrument set-up but with a 0.24 mm length, 1 mm diameter die indicated that scatter was very large at high melt volume flow rate values (typically $> 200 \text{ cm}^3/10 \text{ minutes}$). To improve on the capability of the instrument a non-contacting displacement transducer was installed to independently measure the piston position, Figure 15. By differentiation of the output of the transducer with respect to time, determined from the gradient of the plot presented in Figure 16 (for example), the piston speed during testing was determined. The use of the transducer significantly reduced scatter and increased confidence in the high melt volume flow rate data.

The transducer displacement resolution and the logging rate should be chosen to ensure they do not unnecessarily limit the accuracy of the technique.

The extreme upper flow rate limit to the method, i.e. the maximum theoretical melt volume flow rate obtainable with the instrument where the piston is “free-falling” due to gravity (i.e. there is no contribution slowing the piston down due to the fluid’s viscosity, inertia effects and friction between the piston head and the barrel wall), is approximately $17800 \text{ cm}^3/10 \text{ minutes}$.

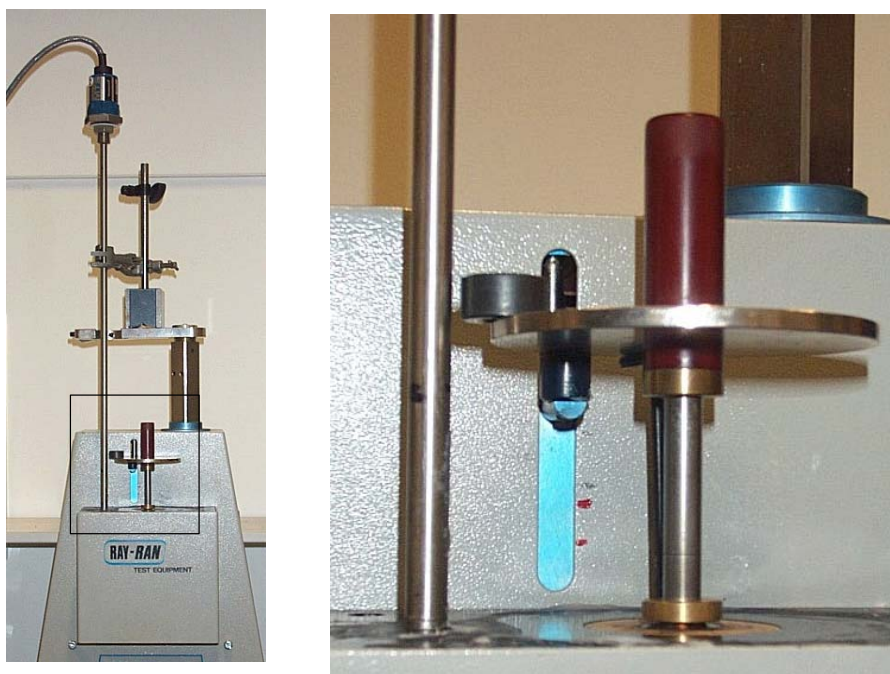


Figure 15: Modification to the melt flow rate instrument by addition of a displacement transducer to monitor the piston position and thus speed.

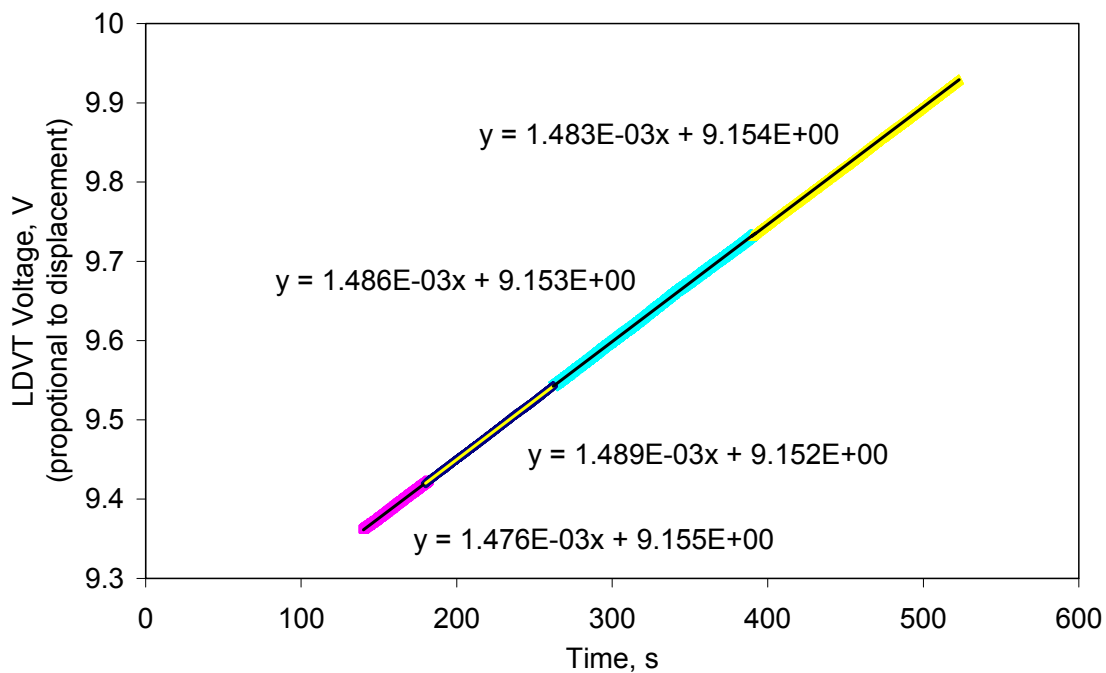


Figure 16: Output trace from the displacement transducer: gradients for various intervals illustrating the consistency of data for the pressure-sensitive adhesive AQFW (test ref RR343)

5.3.2 Melt flow rate test results

All the results presented and discussed below were obtained using the 0.5 mm nominal diameter dies: the “short” die had a length of 1.029 mm and the “long” die a length of 8.038 mm. The use of these dies combined with the displacement transducer permitted measurement of the low viscosity (i.e. high melt volume flow rate) adhesives and also materials at higher loads where previously the technique was limited by the upper limit of MVR associated with the instrument’s displacement transducer capability.

The effect of using the short die, compared with the long die of same diameter, is that a higher MVR, by a factor of $\times 6 - 7$, is obtained, for example Figure 17. The short die represents a lesser restriction to the flow and thus the material is extruded through it at a faster rate.

MVR results for the pressure-sensitive adhesives are presented as a function of load in Figure 18. The results all tend to exhibit a slight upturn in MVR values with increasing flow rate.

The long and short die MVR data have been analysed as apparent shear viscosity and entrance pressure drop data versus apparent shear rate, respectively, Figures 19 and 20. The apparent shear viscosity values are not Bagley [25] corrected, i.e. not entrance pressure drop corrected, and the entrance pressure drop data are assumed to be given by the finite length short die.

However, for the low entrance pressure drop values obtained the correction to apparent shear viscosity is relatively small and for qualitative purposes is not considered to be significant.

The results demonstrate that the method can be used for comparative, quality control measurements of hot melt adhesives.

5.4 Comparison of capillary extrusion rheometry results with melt flow rate results

Previous work on high viscosity polymer melts demonstrated good agreement of both shear viscosity and entrance pressure drop values obtained by capillary extrusion rheometry and melt flow rate testing, Figures 21 and 22 [27]. Because of the use of a nozzle type geometry on the exit of the dies, the length of the short 0.25 mm diameter die was of the order of 1 mm – a shorter length could not be used. For this die the shear flow contribution to the overall flow behaviour in this die was significant and thus the analysis previously developed [27] had to be developed further. The analysis is described in Appendix 3. An assumption of the analysis is that the rheological behaviour of the adhesives (shear viscosity versus shear rate and entrance pressure versus shear rate) can be modelled by power-laws. Although this is reasonable, this assumption introduces errors into the analysed data, particularly where the raw data are obtained over a relatively small shear rate range or where the data depart from the power-law model.

Results of the comparison of shear viscosity and entrance pressure drop data for capillary extrusion rheometry and melt flow rate testing are presented in Figures 23 and 24.

For the pressure-sensitive adhesives there was good agreement of shear viscosity data between melt flow rate testing and capillary extrusion testing, with values from the two methods differing by no more than approximately 10%, Figures 23 - 24. Also, the level of agreement in entrance pressures was, in general, reasonable although values differed by up to 40%. The entrance pressure drop values determined by melt flow rate testing were usually higher than the capillary extruder values.

For lower viscosity hot melt adhesives, having shear viscosities typically less than approximately 3 Pa.s, the level of agreement was comparatively poor.

Testing of one of the packaging adhesive using different die diameters indicated that there might be a geometry dependence (die diameter) of shear viscosity. Hot melt adhesives are complex materials, as discussed in Section 3, containing many ingredients. Waxes, used to reduce the viscosity of the hot melts, will potentially complicate the flow behaviour and may account for the die diameter dependence of results. Users of these methods should be aware of such potential complicating factors, particularly when comparing results obtained using

different size dies.

5.5 Discussion of rheometry techniques

It is noted that the breadth of the shear rate range that can easily be achieved is typically greater for the melt flow rate instrument than the capillary extrusion rheometer.

For the melt flow rate instrument the range of loads over which measurements can easily be made is approximately $\times 40$, i.e. 0.325 kg to 12.5 kg (not including the use of the higher load of 21.6 kg which was found to be excessive for most adhesives).

In comparison, the capillary extrusion rheometry standard ISO 11443 [21] specifies that measurements should not be made using pressure transducers outside the range of 10% to 90% of their normal capacity. Results have been reported here where pressures were below the 10% range, otherwise data would be even more limited – however, outliers outside this range have been discarded. Obviously, the pressure transducers in the extrusion rheometer can normally be changed for ones of a different range thereby extending the capability of the instrument further, though this obviously results in an increase in the time and hence cost of testing. However, in this case the lowest available pressure transducer range was being used and thus could not be substituted for one of a lower range.

In using capillary extrusion rheometry for hot melt adhesives, special provisions may be needed to reduce leakage past the piston head, pressure transducer and die support. O-rings and a PTFE piston head, operating on the principle of a bicycle piston, were successfully used to prevent leakage in the capillary extrusion rheometer. Providing such precautions are taken, the capillary extrusion rheometry method is suitable for testing low viscosity hot melt adhesives. The use of such a piston head in melt flow rate testing was considered unsuitable due to the error that would have been introduced by the friction between the piston head and the barrel wall, particularly for the lower load tests (e.g. 0.325 kg). Leakage flow in the melt flow rate instrument was therefore considered to prohibit its use for the lower viscosity hot melt adhesives, and would potentially account for discrepancies in results between the two methods.

Both the melt flow rate instrument and capillary extrusion rheometer provided a means for ranking the hot melt adhesives in terms of their rheological behaviour. However, comparison of the two methods indicated that although good quantitative agreement was obtained for the higher viscosity pressure-sensitive adhesives for shear viscosity, the level of agreement was not so good for entrance pressure drop and for the lower viscosity packaging adhesives. This suggests that the melt flow rate method is suitable for obtaining shear viscosity data of (higher viscosity) pressure-sensitive adhesives, and to a lesser degree for entrance pressure drop data. However, the melt flow rate method is not suitable for testing lower viscosity adhesives.

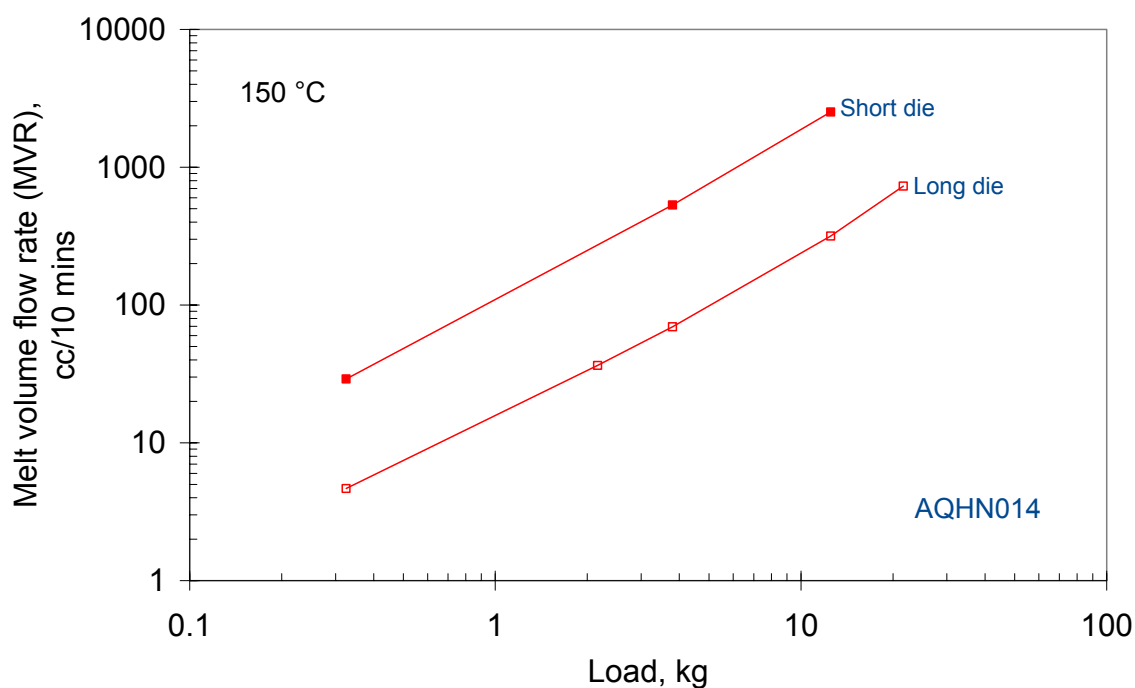


Figure 17: Typical data obtained using short and long dies for hot melt adhesive AQHN014 at 150 °C

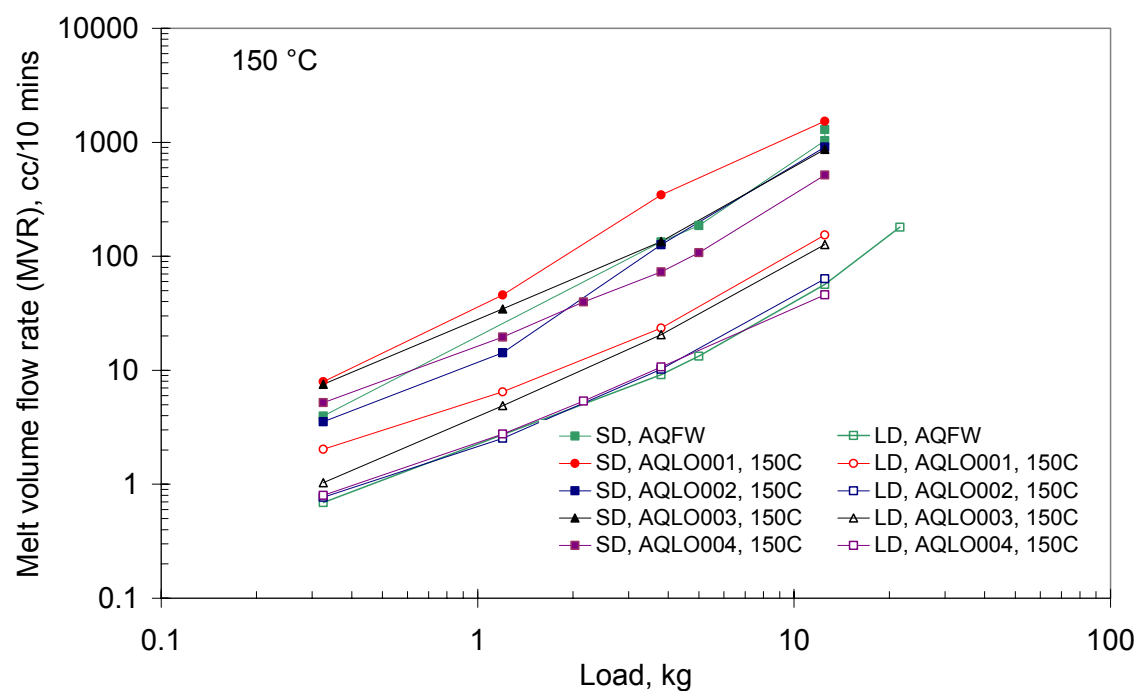


Figure 18: Melt flow rate results for pressure-sensitive adhesives using short (SD) and long (LD) dies at 150 °C

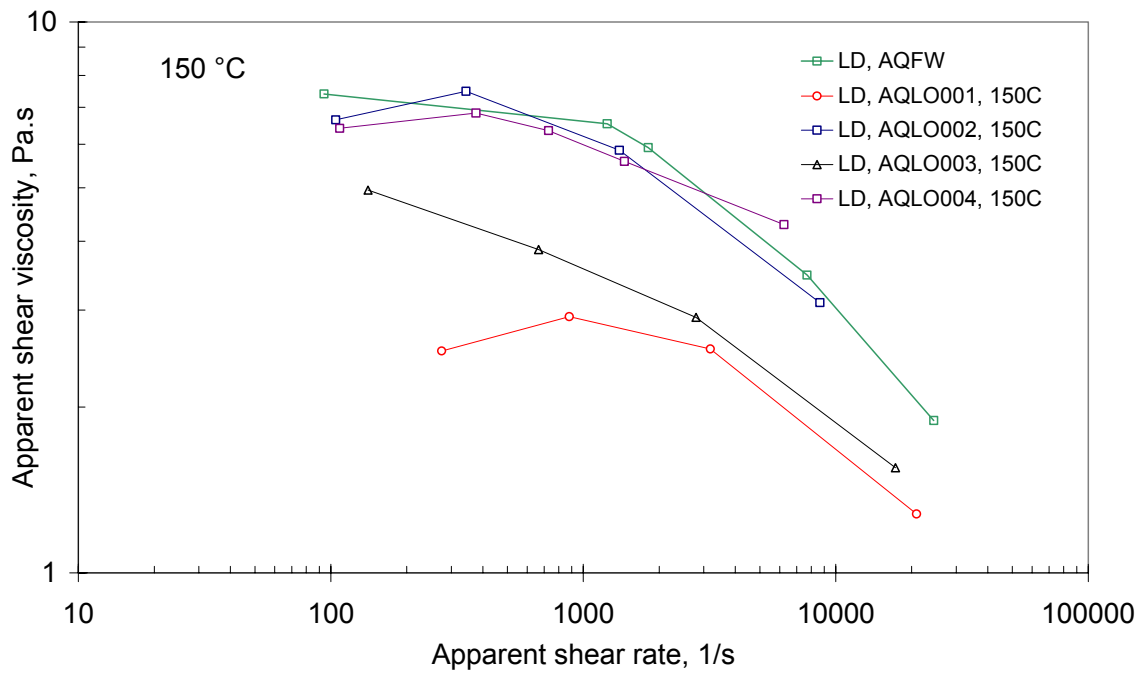


Figure 19: Apparent shear viscosity determined from the long die melt flow rate test results for the pressure-sensitive adhesives at 150 °C (not Bagley corrected)

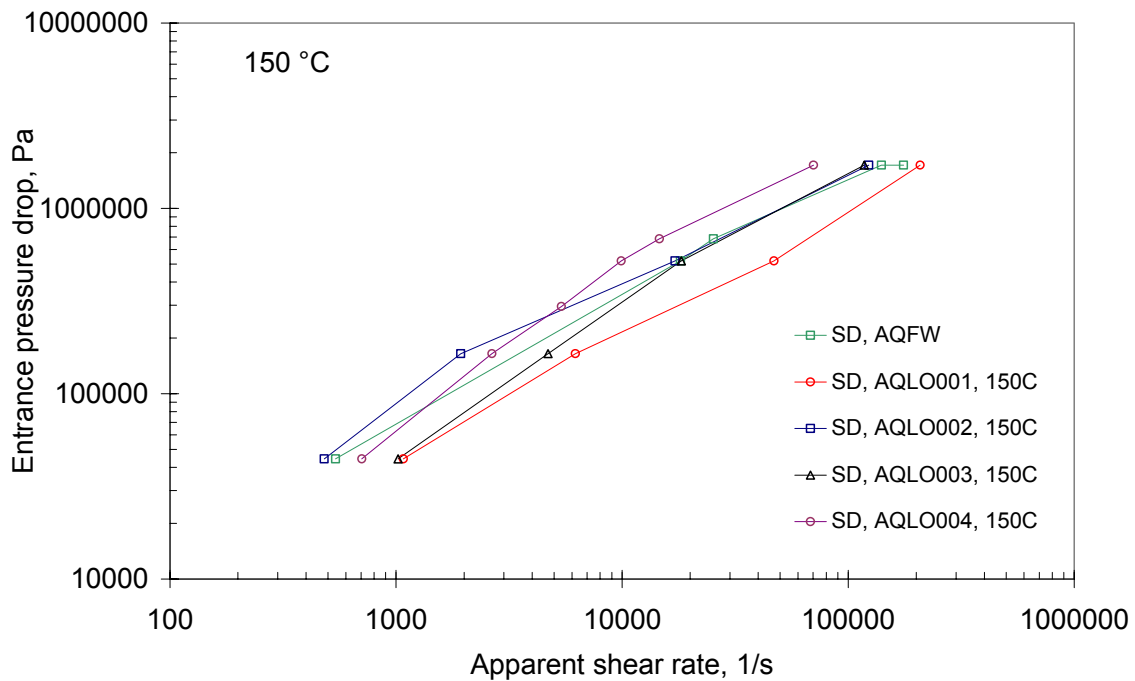


Figure 20: Entrance pressure drop determined from the short die (0.5 mm diameter, 1.029 mm length) melt flow rate test results for the pressure-sensitive adhesives at 150 °C (no extrapolation to zero length)

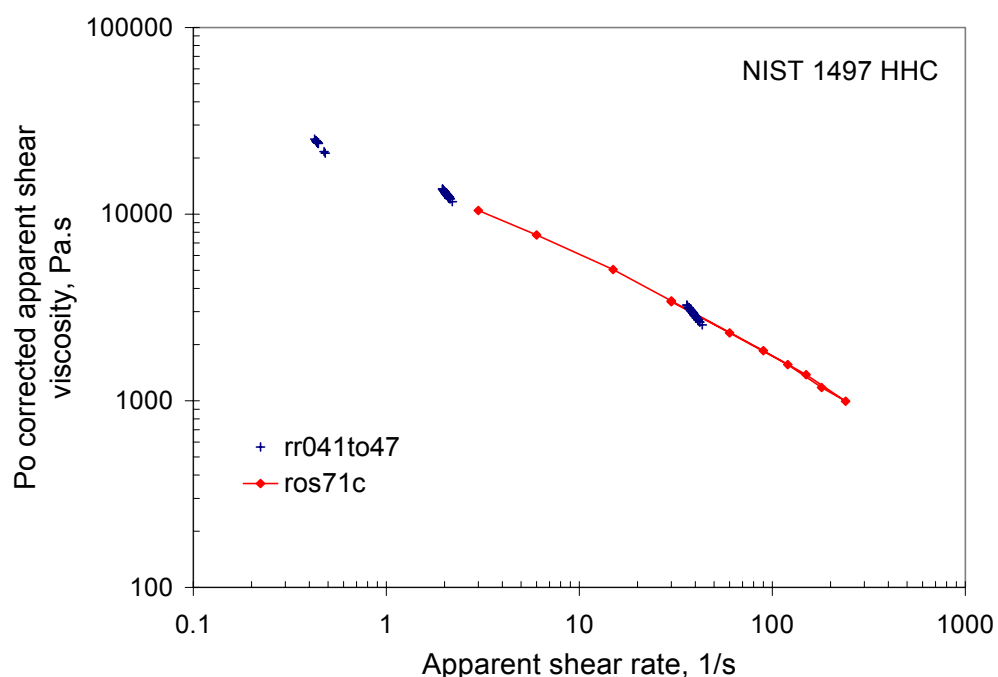


Figure 21: Comparison of shear viscosity values, corrected for entrance effects, measured using an extrusion rheometer (ros071c) with values measured using a melt flow rate instrument with a normal and a short die (0.26 mm length, 2.095 mm diameter) (rr041 to 47) for a HDPE at 190 °C.

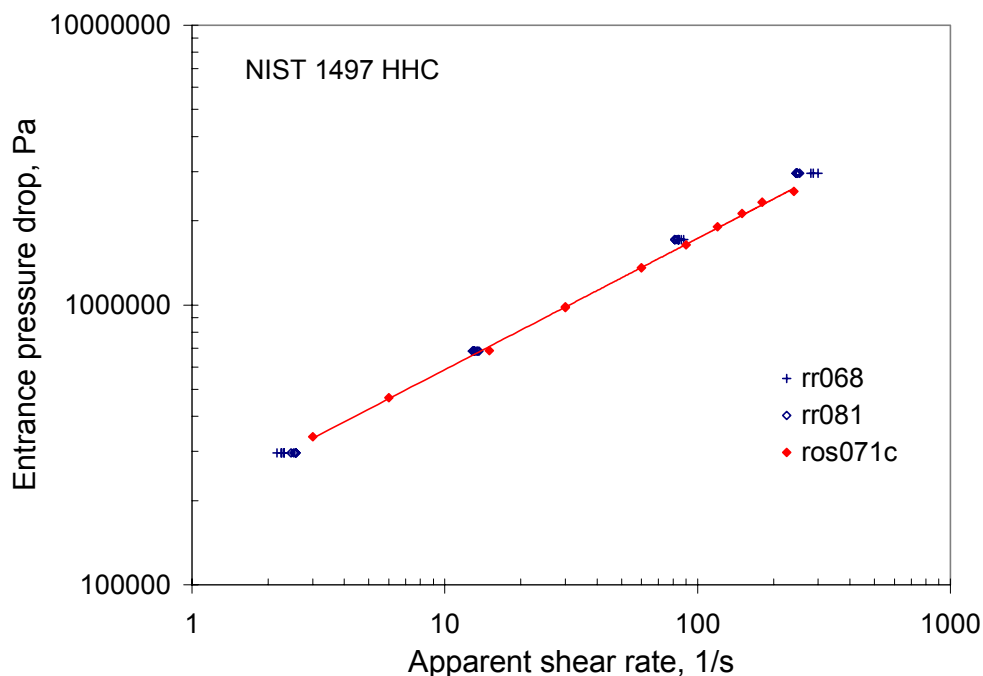


Figure 22: Comparison of entrance pressure drop values measured using an extrusion rheometer (ros071c) with values measured using a melt flow rate instrument with short dies (rr068 - 0.26 mm length, diameter 2.095 mm and rr081 - 0.24 mm length, diameter 1 mm) for a HDPE at 190 °C.

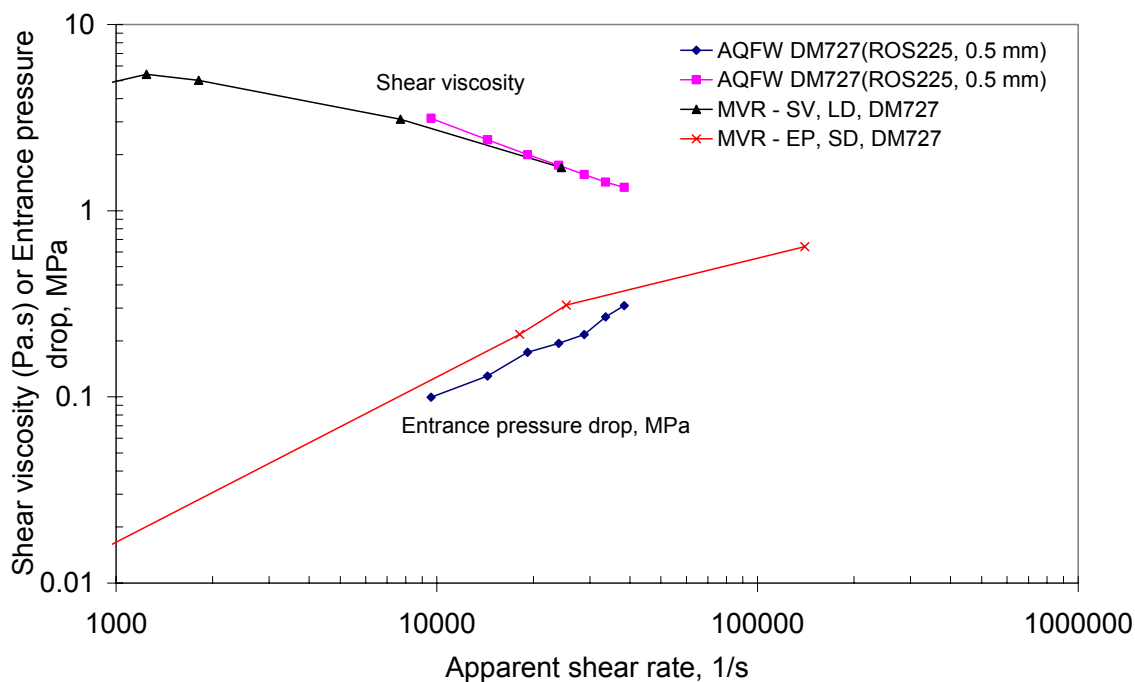


Figure 23: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing (MVR) and capillary extrusion rheometry (ROS225) for pressure-sensitive adhesive AQFW at 150 °C.

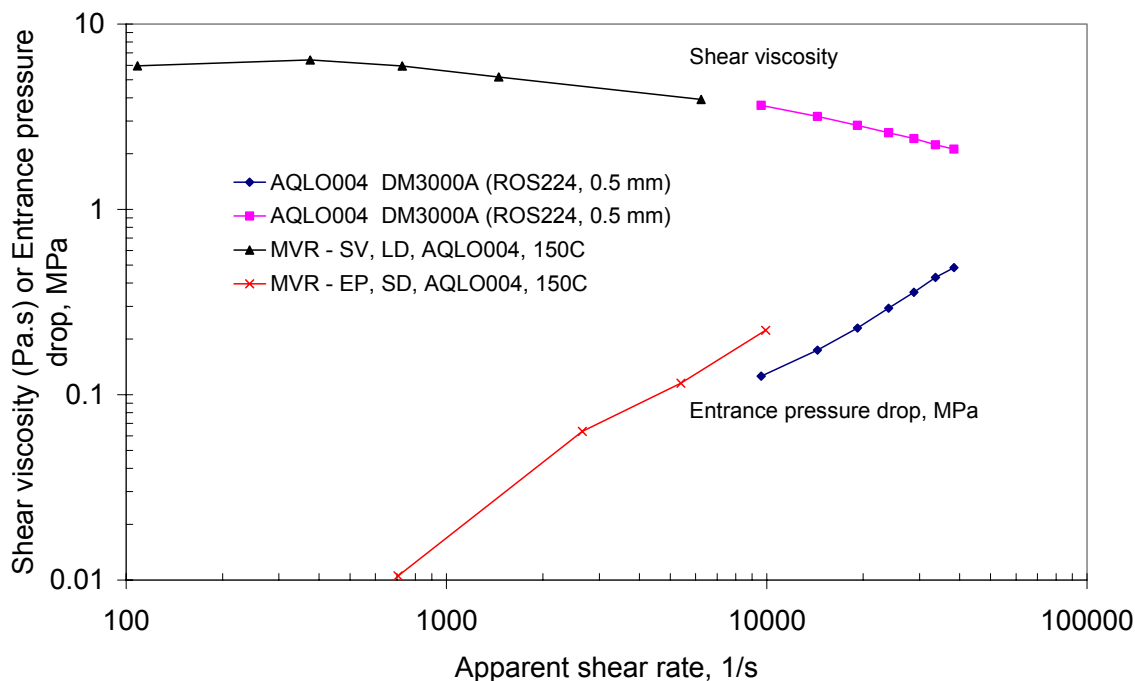


Figure 24: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing (MVR) and capillary extrusion rheometry (ROS224) for pressure-sensitive adhesive AQLO004 at 150 °C.

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Appendix 1: Density measurement

A1.1 Principle

The density of a liquid can be measured using Archimedes' principle which states that the apparent weight of an object on immersion in a liquid decreases by an amount equal to the weight of the volume of the liquid that it displaces. The decrease in weight of an object of known volume on immersion can be used to calculate the density of the fluid, ρ_l .

Using this principle a stainless steel ball, suspended from a balance using a fine Nichrome wire (welded to the ball) is lowered into a liquid (such as molten adhesive) at various temperatures within an oven (see Figure A1.1).

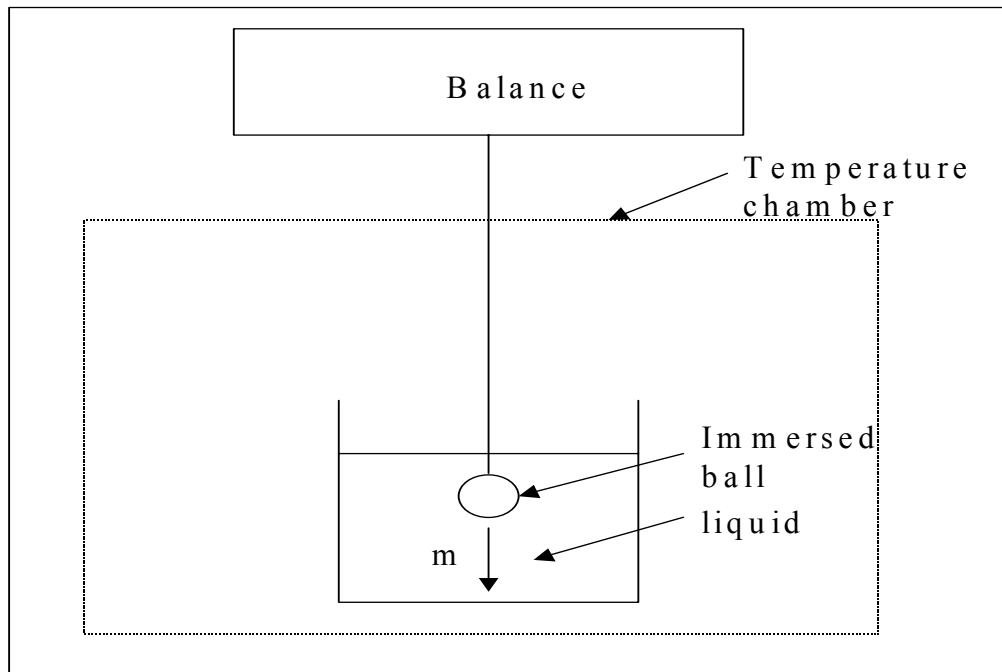


Figure A1.1. Density measurement by Archimedes' principle.

For a sphere the density of the liquid ρ_l is determined by:

$$\rho_l = \frac{m_a - m_i}{\frac{4}{3}\pi r_T^3} \quad (\text{A1.1})$$

where m_a is the mass of the steel ball in air, m_i is the mass of the ball when immersed and r_T is

the radius of the ball at the test temperature. The diameter of the ball (twice the radius) is measured using a set of digital callipers.

A1.2 Measurement Uncertainties

A1.1.2 Radius measurement

Since density depends on $1/r_T^3$, accuracy of the diameter measurement and the uniformity of the ball are important. To minimise uncertainties in the ball volume contribution in equation A1.1, the diameter should be determined with an uncertainty of better than 0.1% (0.3% total uncertainty contribution) and preferably better than 0.01% (0.03% total uncertainty contribution). Callipers having a resolution of 0.001 mm will give insignificant uncertainty in diameter measurements with a 10 mm diameter ball.

A1.2.1 Uniformity of ball shape

The ball should be spherical for accurate calculation of volume. The diameter of the ball should be determined at different locations. Any ball where the diameter differs by a predetermined value, for example the last digit of the calliper used, should be discarded and replaced by a ball that meets the acceptance criterion.

A1.2.3 Attachment wire mass and volume

The effect of the volume of wire immersed in the liquid is not included in equation A1.1. This introduces inaccuracy in the measurement. In principle, a correction can be made by calibrating using a fluid of known density. However, there will still be a small uncertainty due to the length of wire immersed during the measurement. It is recommended that the diameter and mass of the attachment wire should be as small as possible to minimise uncertainties.

A1.2.4 Thermal expansion of the ball

A correction is needed to account for the thermal expansion of the steel ball at elevated test temperatures. The elevated temperature radius, r_T , can be calculated using the room temperature radius, r_0 , and the coefficient of linear thermal expansion of steel, α , in order to compensate for the thermal expansion of the steel occurring due to a change in temperature, ΔT .

$$r_T = \alpha r_0 \Delta T \quad (\text{A1.2})$$

Equation A1.2 predicts an approximate 0.5% increase in the volume of a steel ball for a temperature rise of 100 °C.

A1.2.5 Calibration

To check the calibration of the equipment, distilled water can be used (density at 21 °C = 0.9877 g/cc). In the system used the measured value was within 0.1% of the reference value. The difference was likely to be due to the attachment wire.

A1.3 Measurement of melts

A1.3.1 Sample preparation

The ball should be cleaned of any adhering materials before making measurements. The diameter, and hence the radius, of the ball should be measured before testing.

The sample should be added to a transparent container, such as a Pyrex beaker, that will not melt or degrade at the measurement temperatures. The container should be of sufficient dimensions that the suspended/immersed ball is clear (by at least one diameter) of the sides and base. Sufficient sample must be added so that the ball is fully immersed. Care should be taken to avoid including air when adding sample to the container. Solids (powders or pellets) should be packed as densely as possible. Liquids and pastes should be poured carefully to avoid “folding” air into the sample. Adding the sample in stages, melting after each addition, is one method of preparing difficult samples. However, care must be taken not to degrade the sample by exceeding recommended periods at elevated temperatures.

Once added to the container, the liquid should be heated to the test temperature. The temperature should be checked using a calibrated thermocouple inserted in the sample. The liquid should be allowed to settle for approximately 1 hour at the test temperature to eliminate any air bubbles and confirm a stable temperature throughout the liquid. The stabilisation period may need to be reduced for samples likely to degrade at the test temperature.

A1.3.2 Immersing the ball

Once all visible air bubbles have been eliminated, the temperature should be rechecked and the suspended ball weighed in air and the value of m_a recorded. The ball is then immersed carefully in the sample. This can be done by raising the sample container on a laboratory jack until the ball is fully immersed (but not touching the sides or base of the container). The attachment wire should be taut and vertical.

A1.3.3 Measuring the immersed mass

The system should be allowed to stabilise at the test temperature for an appropriate period to allow any air introduced during immersion to escape, any viscoelastic effects to diminish and for the temperature to stabilise (temperature gradients could lead to convection currents within the liquid). There should not be any visible air bubbles attached to the ball as these will lead to inaccurate density determinations. A stabilisation period of approximately one hour is recommended for stable materials.

Once the stabilisation period is complete, the balance is activated and the mass reading monitored. The mass reading should be stable before readings can be made. The value for the immersed mass, m_i , is recorded. If density values at further temperatures are required then the oven temperature should be changed, and mass readings taken after the system has stabilised again. However, the time that the sample is at elevated temperature may be an issue if the material is likely to degrade. It may be preferable, although more time consuming, to use fresh samples for each measurement temperature (or sub-set of temperatures) and repeat from A1.3.1.

There are some concerns that the balance calibration may drift during elevated temperature tests. To check the stability of the balance, it is recommended that, before testing, the weight of the suspended ball in air is measured at test temperatures for the likely duration of the test. Drift can also be checked by removing the ball from the liquid after the density measurement and re-determining the mass in air. However, for this to be valid, none of the sample should adhere to the ball.

A1.3.4 Data analysis

At each test temperature, r_T should be determined using equation A1.2. Equation A1.1 is then used to calculate density values from the measured masses. The results should be tabulated and plotted as density against temperature. The plot should be examined to identify any possible outliers.

The thermal expansivity of the liquid, α_L , can be calculated from the slope of the density temperature curve.

$$\alpha_L = -\frac{1}{\rho_L} \frac{\partial \rho_L}{\partial T} \quad (\text{A1.3})$$

where ρ_L is the density and T is temperature. However, uncertainties in α_L can be large where a small temperature range is used and the resulting changes in density are small.

Appendix 2: Symbols and definitions for melt flow rate testing

For the purpose of this document, in particular Appendix 3, the following terminology is used for melt flow rate testing, except where otherwise specified:

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

MVR melt volume flow rate has units of cm³ although it is expressed as cm³/10 minutes indicating it is the volume extruded in cm³ 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/cm³

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

t time, s

Q volume flow rate, m³/s

γ_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

η_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

Appendix 3: Melt flow rate testing analysis

General

The melt volume flow rate (MVR) is given, according to ISO 1133 [26], by the expression

$$MVR = \left[\frac{t_{ref}}{t} \right] \ell \frac{\pi D^2}{4} \times 10^6 \quad (A3.1)$$

where ℓ (m) is the distance moved by the piston in time t (s) and D (m) 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. MVR is determined experimentally by measuring the time t taken for the piston to move a given distance ℓ or vice-versa, and scaled appropriately using a reference time t_{ref} of 600 seconds (or 10 minutes) thereby determining the volume of material that would have been extruded in 10 minutes. MVR is expressed as $\text{cm}^3/10$ minutes indicating it is the volume extruded in 10 minutes.

Apparent shear rate

The volume flow rate Q (m^3/s) can be determined from the MVR and is given by

$$Q = \frac{MVR \times 10^{-6}}{600} \quad (A3.2)$$

or, substituting for MVR using equation A3.1, by

$$Q = \frac{\ell \pi D^2}{4t} \quad (A3.3)$$

The apparent shear rate $\dot{\gamma}_a$ in the melt at the wall of the die is given [21] by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (A3.4)$$

and thus in the melt flow rate die, substituting for Q using equation A3.3, by

$$\dot{\gamma}_a = \frac{\ell D^2}{R^3 t} \quad (A3.5)$$

where R is the radius of the die. Alternatively, the apparent shear rate is given, using equations A3.2 and A3.4, by

$$\dot{\gamma}_a = \frac{4(MVR / 600) \times 10^{-6}}{\pi R^3} \quad (\text{A3.6})$$

The apparent shear rate is the shear rate that would have occurred if the material exhibited a Newtonian behaviour, i.e. the viscosity is independent of shear rate, and is a convenient measure for describing the flow. In practice, polymeric materials are non-Newtonian, i.e. they are shear rate thinning. The true shear rate $\dot{\gamma}$, Rabinowitsch corrected for the non-Newtonian velocity profile resulting from the shear thinning behaviour, is given by

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_a \quad (\text{A3.7})$$

or

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3} \quad (\text{A3.8})$$

where n is a power law index. The value of $n-1$ is equivalent to the gradient of the plot of $\log(\text{apparent shear viscosity})$ versus $\log(\text{apparent shear rate})$. The Rabinowitsch correction has not been applied in the analysis of the results presented in this report. It is considered important for quantitative determination of accurate shear viscosity data but for qualitative determination it is not considered so necessary.

Apparent shear stress and apparent shear viscosity (not entrance pressure drop corrected)

When using a long die, for which the relative contribution to resistance to flow due to the entrance flow is small, the apparent shear stress and apparent shear viscosity (without entrance pressure drop correction) can be determined.

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

$$W_g = \frac{P\pi D^2}{4} \quad (\text{A3.9})$$

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

$$P = \frac{4Wg}{\pi D^2} \quad (\text{A3.10})$$

This pressure is “lost” through viscous resistance 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

$$P\pi R^2 = 2\pi RL\tau_a \quad (\text{A3.11})$$

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

$$\tau_a = \frac{PR}{2L} \quad (\text{A3.12})$$

or, substituting for P using equation A3.10, by

$$\tau_a = \frac{4Wg}{\pi D^2} \frac{R}{2L} \quad (\text{A3.13})$$

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

$$\underline{\eta}_a = \frac{\tau_a}{\dot{\gamma}_a} \quad (\text{A3.14})$$

Thus the apparent shear viscosity $\underline{\eta}_a$ is given, using equations A3.6 and A3.13, by

$$\underline{\eta}_a = \frac{300WgR^4}{D^2 L \times MVR \times 10^{-6}} \quad (\text{A3.15})$$

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.

Determination of the extensional flow behaviour using the entrance pressure drop method

The extensional flow characterisation method is based on the measurement of the material's resistance to flow in a converging, or entry flow, 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 et al [27]. 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, and thus the die is effectively of zero length. Then the entrance pressure drop P_e is given by

$$P_e = \frac{4Wg}{\pi D^2} \quad (\text{A3.16})$$

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

$$\dot{\gamma}_a = \frac{4(MVR_s / 600) \times 10^{-6}}{\pi R^3} \quad (\text{A3.17})$$

where the subscript 'S' indicates the MVR value 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 [27]:

$$P_e = P_o(\dot{\gamma}_a^x) \quad (\text{A3.18})$$

where P_o and x are constants.

Correction of apparent shear viscosity values for entrance effects (Bagley correction)

The entrance pressure drop is not normally negligible for polymeric melts and consequently there is an error in the apparent shear viscosity values determined when using only one long die. For this reason those values are referred to as apparent shear viscosity values that are not corrected for entrance pressure drop effects (the Bagley correction [25]). For these hot melt adhesives this can result in an error of the order of approximately 10%. To correct for this the following approach is used.

Assuming a non-zero entrance pressure drop P_e , the total pressure drop P along the long die length is given by

$$P = P_s + P_e \quad (\text{A3.19})$$

where P_s is the shear flow pressure drop along the length of the die and P is given by equation A3.10. Re-writing equations A3.10 and A3.15 in terms of the total pressure P yields

$$\eta_a = P \left[\frac{75\pi R^4}{L \times MVR_L \times 10^{-6}} \right] \quad (\text{A3.20})$$

where MVR_L refers to the MVR value obtained for the long die test. To determine shear viscosity corrected for entrance effects η_a only the pressure drop due to resistance to shear flow must be used in equation A3.20. Thus substituting P_s for P (using equations A3.10 and A3.19) yields

$$\eta_a = \left(\frac{4Wg}{\pi D^2} - P_e \right) \left[\frac{75\pi R^4}{L \times MVR_L \times 10^{-6}} \right] \quad (\text{A3.21})$$

where P_e is the entrance pressure drop calculated at the apparent shear rate occurring for the long die test. P_e is calculated using equation A3.18, the coefficients of which have been determined by analysis of multiple-load short die tests. The apparent shear rates used for the determination of P_e are given by

$$\dot{\gamma}_a = \frac{4(MVR_s / 600) \times 10^{-6}}{\pi R^3} \quad (\text{A3.22})$$

where the subscript “S” indicates values for the short die MVR test. Thus from the apparent shear rate versus entrance pressure drop data determined using the short die with various loads, 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 A3.18. This is then used to correct the long die melt flow rate test data to determine apparent shear viscosities corrected for entrance pressure effects.

However, examination of capillary extrusion pressure drop data for short and long dies identified that for the nominally 1 mm length die used as the short die in the melt flow rate testing the shear flow component was not negligible. It could thus not be assumed that the short die gave reliable entrance pressure drop values. Thus an iterative procedure to solving the above equations had to be developed to correct for the shear flow component of the short die test as follows.

1. Using the long die data for all loads, calculate **a)** apparent shear viscosity data (not corrected for entrance effects) using equation A3.15 and **b)** the corresponding apparent shear rates using equations A3.5 or A3.6.
2. Fit a power-law model (equation A3.23) to the apparent shear viscosity versus apparent shear rate data obtained from step 1 to yield the coefficients of the shear viscosity power-law model η_o and n .

$$\eta_a = \eta_o (\dot{\gamma}_a)^{n-1} \quad (\text{A3.23})$$

3. Using the apparent shear viscosity power-law model (from step 2) calculate **a)** the entrance pressure drop values corrected for shear flow in the short die tests using equation A3.24, where the subscript “S” indicates that property for the short die test, and **b)** the corresponding apparent shear rates $\dot{\gamma}_{a,s}$ using equation A3.17.

$$P_e = \frac{4W_s g}{\pi D_s^2} - \frac{2L_s \eta_o (\dot{\gamma}_{a,s})^n}{R_s} \quad (\text{A3.24})$$

4. Fit a power-law model (equation A3.17) to the corrected entrance pressure drop versus apparent shear rate data obtained from step 3 to yield the coefficients of the entrance pressure drop power-law model P_o and x .
5. Using the entrance pressure drop power-law model from step 4 calculate **a)** the apparent shear viscosity values corrected for entrance pressure effects using equation A3.21, where P_e is determined for the apparent shear rate occurring in the long die test

(equation A3.6), and **b)** the apparent shear rates for the long die test using equation A3.6.

6. Repeat steps 2 to 5 until iterative convergence has been obtained.

It is noted that it may be necessary to extrapolate short die MVR data to carry out the correction to some of the long die MVR data. Such extrapolations should be carried out with care as the accuracy of extrapolated values can be poor, and is dependant on the quality and quantity of the data used to extrapolate. Statistical and uncertainty analyses can provide further information on the confidence that one can place on such extrapolated values.