

**NPL REPORT
DEPC MPR 019**

**Measurement of the
rheological properties of
adhesives**

**M RIDES, C ALLEN,
A DAWSON and B DUNCAN**

NOT RESTRICTED

MARCH 2005

Measurement of the rheological properties of adhesives

M Rides, C Allen, A Dawson and B Duncan
Division of Engineering and Process Control

ABSTRACT

The development of measurement methods for characterising the rheological behaviour of adhesives in conditions typical of processing is reported, focusing on the melt flow rate and capillary extrusion rheometry methods. Results are presented for a range of hot melt adhesives used for packaging and garments. The melt flow rate instrument has been modified and successfully used to measure melt volume flow rate values in excess of 1000 cm³/10 minutes. Leakage of hot melt adhesive in capillary rheometry testing was identified as a problem and methods to virtually eliminate it have been developed and implemented. However, leakage in the melt flow rate method is likely to remain a problem under certain circumstances due to the nature of the test.

Both the capillary extrusion and melt flow rate methods are capable of ranking the flow behaviour of the adhesives. Quantitative comparison of shear viscosity and entrance pressure drop results obtained from both methods indicated varying levels of agreement, it being good for shear viscosity of the higher viscosity garment adhesives. Explanations accounting for the discrepancies have been proposed.

The work was carried out as part of the “Measurements for Materials Systems” (MMS) programme funded by the Department of Trade and Industry.

© Crown copyright 2005
Reproduced with the permission of the Controller of HMSO
and Queen's Printer for Scotland

ISSN 1744-0270

National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Extracts from this report may be reproduced provided the source is acknowledged and the extract is not taken out of context.

We gratefully acknowledge the financial support of the UK Department of
Trade and Industry (National Measurement System Policy Unit)

Approved on behalf of the Managing Director, NPL,
by Dr M G Cain, Knowledge Leader, Process Materials Team
authorised by Director, Engineering and Process Control Division

CONTENTS

1	Introduction	1
2	Materials	2
3	Measurement techniques	2
3.1	Oscillatory rheometry	2
3.2	Capillary extrusion rheometry	3
3.3	Melt flow rate testing	5
4	Rheological results	8
4.1	Oscillatory rheometry results	8
4.2	Capillary extrusion rheometry results	8
4.3	Melt flow rate testing results	9
4.4	Comparison of capillary extrusion rheometry results with melt flow rate results	10
5	Discussion	11
6	Conclusions	12
7	Acknowledgement	14
8	References	14
	Figures	16
	Appendices	34
	Appendix 1: Analysis of melt flow rate testing	34
	Appendix 2: Determination of the extensional flow behaviour using the entrance pressure drop method	37
	Appendix 3: Correction of apparent shear viscosity values for entrance effects (Bagley correction)	38

1 Introduction

The application of hot melt adhesives by coating and spraying are high speed dispensing processes, yet materials characterisation is typically performed using low shear rate rheological¹ techniques, for example rotational and oscillatory 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 the 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 capillary extrusion rheometry. The melt flow rate 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. 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. 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.

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), 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 the material to changes in molecular structure.

The objective of this work was principally to investigate and develop the methods of capillary extrusion rheometry and melt flow rate for characterisation of the high rate rheological behaviour of adhesives, in particular to address some of the limitations of the melt flow rate method. Results for a range of hot melt adhesives using the improved methods are presented. Results obtained by oscillatory rheometry have also been presented.

This work was performed under Task 3 of the Measurement for Materials Systems project Efficiency improvements in rapid bonding processes (MMS9).

¹ Rheology: the study of the deformation and flow of matter.

2 Materials

This work investigated nine hot melt adhesives that were supplied by National Starch and Chemical. Four of the adhesives (Novacol 90, Ultra-Melt 201, Varni-Melt X10, and Instant-Pak 2600) are grades used in packaging applications. These are collectively referred to as packaging adhesives in this report. These were supplied in the form of solid pellets. The remaining five adhesives were different grades of Dispomelt pressure-sensitive hot melt adhesive (DM727, DM747, DM505, DM2000 and DM3000A) used in garments. These were supplied in the form of solid blocks. The Dispomelt adhesives are, under ambient conditions, viscoelastic and very tacky. The removal of small samples from the blocks was very difficult owing to the nature of these materials.

NPL materials code	Adhesive type	Adhesive grade
AQHN003	Packaging adhesive	Novocol 90, 134-823A
AQHN007	Packaging adhesive	Ultra-Melt 201, 134-265A
AQHN014	Packaging adhesive	Varni-Melt X10
AQHN016	Packaging adhesive	Instant-Pak 2600, 234-2600
AQFW P2	Dispomelt	DM727, 134-566A
AQLO001	Dispomelt	DM505
AQLO002	Dispomelt	DM747
AQLO003	Dispomelt	DM2000
AQLO004	Dispomelt	DM3000A

Table 1: NPL materials codes and NSC adhesive grades

3 Measurement techniques

3.1 Oscillatory rheometry

The viscoelastic properties of materials can be measured using oscillatory rheometry, as described in ISO 6721-10 [1]. The principle of the technique is to subject a specimen, held between two plates, to a sinusoidal torque or displacement. The response of the specimen to that input is measured. Typically, shear storage G' and shear loss G'' moduli are determined. The method is suitable for generating quantitatively accurate data for modelling as well as for quality control. The results of an international intercomparison on oscillatory rheometry indicated that the repeatability of G' and G'' values for high density polyethylene and glass-fibre filled polypropylene was up to 8%, and reproducibility up to 29%. The results are presented in detail, along with an analysis for the determination of the uncertainties of measurement, by Rides and Allen [2].

Oscillatory flow measurements of the hot melts were made using a Bohlin VORM rheometer. Strain sweep, temperature sweep and frequency sweep measurements were made on a range

of hot melt adhesives. A selection of results to illustrate specific features of the materials' behaviour are reported.

3.2 Capillary extrusion rheometry

The capillary extrusion rheometry method for thermoplastics, upon which this work was based, is described in ISO 11443 [3] – also see Figure 1. 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 values shear viscosities are calculated, equations 1 - 3.

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

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

where τ is the shear stress given by

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

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

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

where P is the extrusion pressure and P_e is the entrance pressure drop obtained at the same 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 quoted [3]. The method is suitable for generating quantitatively accurate data for modelling as well as for quality control.

The 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 [5-10] – see also Section 3.3. 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 results of an international intercomparison on capillary extrusion rheometry indicated that the repeatability of shear viscosity values for high density polyethylene and glass-fibre filled polypropylene was up to 24%, and reproducibility up to 34%. For entrance pressure drop determination the repeatability was up to 20% and the reproducibility up to 56%. The results are presented in detail, along with an analysis for the determination of the uncertainties of measurement, by Rides and Allen [4].

The instrument used was a Rosand RH7 twin barrel capillary extrusion rheometer. Early testing identified that additional precautions had to be taken when testing hot melt adhesives. These materials are lower in viscosity than most thermoplastics for which the instrument was primarily designed. The hot melt adhesives were typically in the viscosity range of 0.2 Pa.s - 5 Pa.s, the packaging adhesives being generally lower than the Dispomelts. This compares with values typically in excess of 100 Pa.s for thermoplastics.

Significant leakage of adhesive was observed to occur past the piston head of the rheometer, apparent from molten adhesive on the piston rod (behind the piston head) and also at the top of the barrel. It was also observed that some leakage had occurred around the outside of the die, evident from adhesive on the screw thread of the die support nut. However, no leakage was evident at the pressure transducer mounting. Leakage was a greater problem in testing these adhesives than polymer melts due to the use of significantly smaller diameter dies and their lower viscosities. The use of smaller diameter dies effectively makes the gaps through which leakage occurred (e.g. piston head - barrel gap) more significant in their contribution to the flow of material out of the barrel.

An O-ring on the die support nut eliminated leakage problems in the screw thread. However, the O-ring had to be replaced frequently to ensure continued adequate performance. To reduce flow past the piston head a redesign of the piston head was undertaken. A design based on the principle of the piston head in a bicycle pump was adopted, Figure 1. A PTFE piston head was made, but with the working surface recessed so that when pressurised the flange of the head would deform thereby making a seal against the barrel wall. This arrangement performed 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 in 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. Trapping of air below the PTFE piston did not allow degassing of the barrel and sample after inserting the piston into the barrel prior to testing. Without such degassing it was likely that the sample contained trapped air throughout. This problem was more severe for the Dispomelts than the packaging melts as with the latter air bubbles were observed to come to the top of the melt in the barrel before testing. As Dispomelts were more elastic in nature than the packaging adhesives, the tendency for bubbles to rise to the surface was likely to be lower. The problem of the PTFE piston head being too effective was remedied by scoring a small vent-groove along the length of the side of PTFE piston head to allow trapped air to escape from the barrel and material, whilst minimising the leakage of adhesive.

To combat the lower viscosities of the hot melt adhesives, pressure transducers with lower upper limits were used along with smaller diameter dies than would typically be used for thermoplastics melts. Two different diameter sets of dies were used, the 0.25 mm diameter ones used for the packaging adhesives and 0.5 mm diameter dies for the Dispomelt adhesives. The larger diameter dies were used for the Dispomelt adhesives as the extrusion pressures

were too high for the transducers at the higher extrusion rates using the 0.25 mm diameter dies.

The nominal 0.5 mm diameter dies used were a “long” die of 8.004 mm length by 0.500 mm diameter and a “short” die of 0.218 mm length and 0.500 mm diameter. The nominal 0.25 mm diameter dies used were a “long” die of 7.983 mm length by 0.262 mm diameter and a “short” die of 0.419 mm length and 0.258 mm diameter. The diameters of the 0.5 mm dies were checked by using a go / no-go gauge and thus were confirmed as being $0.500 \text{ mm} \pm 0.005 \text{ mm}$ in diameter. 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 fluid² (a correction for shrinkage effects was made by comparison of measurements on a larger die that had also been calibrated using a internal split ball micrometer instrument). The cast thus obtained was then measured optically using a microscope. This method 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 have been 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 to the uncertainty in the die diameter.

3.3 Melt flow rate testing

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 [11] was 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 2. The standard 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 $\text{cm}^3/10 \text{ minutes}$. 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) has been 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.

All melt flow rate measurements were made using a Ray-Ran Test Equipment Limited 5MPCA Advanced Melt Flow System instrument, Figure 2. 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. An analysis of the melt flow rate method is presented in detail in the Appendices.

² 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.

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 [12].

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 3, 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 [5 - 10]. Various models proposed for interpreting the entrance pressure drop data in terms of extensional viscosity have been reviewed by Rides and Allen [7]. However, one does not need to convert the entrance pressure drop data to extensional viscosity values for the data to be of value. A plot of entrance pressure drop versus apparent shear rate has been found useful in comparing materials [7]. 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 [7]. The approach is now applied to the controlled stress mode (i.e. applied load) as used for MVR measurements.

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). The dies used were 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. Again a go / no-go gauge with a variation of ± 0.005 mm was used to check the diameters.

Leakage of hot melt adhesive past the piston and die were not observed to be significant in the melt flow rate testing. However, the remedy adopted for the piston head modification in capillary extrusion testing would have not proved appropriate for melt flow rate testing, particularly when using the lower loads, as friction affects between the piston head and the barrel wall would have been significant.

With the melt flow rate testing, accumulation of the hot melt within the exit region of the die occurred. This could potentially provide additional back-pressure to the flow and should thus be avoided if possible. A nozzle geometry to the exit of the dies, Figure 4, was evaluated and found to work well, producing “cleaner” extrudate.

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, Figure 5. To improve on the capability of the instrument a non-contacting displacement transducer was installed on the instrument to measure independently the piston position, Figure 6. By differentiation of the output of the transducer with respect to time, determined from the gradient of the plot presented in Figure 7 (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.

As an extreme upper limit to the method, 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 piston head - barrel wall friction) is approximately 17800 cm³/10 minutes.

Oscillatory measurements at 150 °C and 110 °C						
Sample ID	Test ID	Temp, °C	Viscosity', Pa.s	G*, Pa	G', Pa	G'', Pa
AQHN 003	boh465	150	0.32	10.46	2.69	10.03
	boh465	110	0.75	23.62	1.64	23.51
AQHN 012	boh466	150	1.58	49.73	0.92	49.73
	boh466	110	4.66	146.45	3.41	146.45
AQHN 013	boh467	150	2.58	81.15	1.42	81.15
	boh467	110	9.41	296.36	21.77	295.55
AQHN 010	boh468	150	0.39	12.28	1.04	12.22
	boh468	110	1.18	37.15	1.15	37.13
AQHN 006	boh469	150	0.47	14.88	0.88	14.84
	boh469	110	1.32	41.54	1.19	41.52
AQHN 007	boh470	150	1.80	56.70	1.00	56.68
	boh470	110	6.00	188.55	5.45	188.27
AQHN 016	boh471	150	1.13	35.40	0.81	35.40
	boh471	110	3.52	110.55	1.95	110.55
AQHN 014	boh472	150	1.38	43.41	2.24	43.33
	boh472	110	4.97	156.73	10.94	156.36
AQFW	boh482	150	7.05	221.55	6.78	221.55
	boh482	110	45.84	1448.18	149.91	1440.91
AQLO 001	boh483	150	3.00	94.37	2.10	94.36
	boh483	110	36.49	1169.09	236.82	1147.27
AQLO 002	boh484	150	7.76	243.82	12.31	243.55
	boh484	110	41.62	1330.00	241.09	1306.36
AQLO 003	boh485	150	5.87	186.73	28.17	184.73
	boh485	110	21.07	693.82	209.09	661.55
AQLO 004	boh486	150	7.71	243.00	18.11	242.36
	boh486	110	25.77	820.73	134.91	809.73

Table 2: Oscillatory rheometry values for hot melt adhesives at 100 °C and 150 °C. Quoted values are averages of points over a temperature range of approx +/- 1 °C from nominal temperature, measured at 5 Hz and 0.1 strain.

4 Rheological results

4.1 Oscillatory rheometry results

Shear storage modulus G' , loss modulus G'' and complex shear viscosity η^* results are presented for a selection of packaging and Dispomelt adhesives, Figures 8-10 respectively, and a comparison of shear moduli in Figure 11. The results clearly show that the packaging adhesives have very sharp melt transitions whereas the Dispomelt AQFW has a much broader transition. The measured Dispomelt adhesive's behaviour is consistent with the observation at room temperature that the Dispomelt adhesive is a soft deformable material compared with the harder packaging adhesives. These plots highlight a particular problem with the characterisation of the rheological behaviour of such materials. The packaging adhesives exhibit in excess of four decades in variation of shear storage modulus, and the Dispomelts in excess of three decades variation over a 60 °C temperature range, with the consequence that it is not easily possible to capture the full range of behaviour with a single instrument. The Bohlin VORM, even when using the largest possible diameter plates for the instrument of 40 mm, runs out of resolving capability at the low viscosities of the molten adhesives at high temperatures, hence the large scatter observed in complex shear viscosity values at values less than approximately 10 Pa.s. At the other end of the scale the instrument was not able to measure complex shear viscosity values above 100000 Pa.s due to its upper torque limit. Shear storage moduli G' and shear loss moduli G'' values for the full range of adhesives are presented for 110 °C and 150 °C in Table 2.

From frequency sweep tests it is clear from the ratio of shear storage moduli G' to shear loss moduli G'' values that the Dispomelts are significantly more elastic than the packaging adhesives at high frequencies, Figure 11. This implies that at the high rates of processing, corresponding to high frequencies, the Dispomelts will exhibit a more elastic behaviour than the packaging adhesives.

4.2 Capillary extrusion rheometry results

Apparent shear viscosity (Bagley corrected [13]) and entrance pressure drop data (values obtained on extrapolation of extrusion pressure data to a die length of zero) for the packaging and Dispomelt adhesives are presented in Figures 12 – 15. The ranking of the materials is presented in Table 3, where materials of similar value are presented in the same box but the order of presentation within that box is indicative of their possible ranking. However, where presented in the same box the differences are not considered to be significant.

The raw experimental data for the short die on which the entrance pressure drop values were determined are presented in Figures 16 and 17. The conversion of these short die data to entrance pressure drop values is based on extrapolation of extrusion pressure drop data for the long and short dies to an effective die length of zero. It is seen that this correction (from Figure 16 to Figure 14 and Figure 17 to Figure 15) is significant. However, the entrance pressure drop values for a zero length die are considered to be more appropriate for comparison than the short die data as the latter die can have a significant shear flow component. It is this shear viscosity contribution that results in the observed changes from uncorrected to corrected data.

Ranking	Packaging adhesive		Dispomelt adhesive	
	Apparent shear viscosity*, Pa.s	Entrance pressure drop [#] , MPa	Apparent shear viscosity*, Pa.s	Entrance pressure drop [#] , MPa
Highest value	AQHN007	AQHN014	AQLO004	AQLO003
	AQHN014, AQHN016	AQHN007	AQLO002, AQFW	AQLO004
	-	AQHN016	AQLO003	AQFW, AQLO002
Lowest value	AQHN003	AQHN003	AQLO001	AQLO001

* Bagley corrected, [#]-value obtained on extrapolation to zero length die

Table 3: Ranking of capillary extrusion rheometry properties

4.3 Melt flow rate testing 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 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 18. The short die represents a lesser restriction to the flow and thus the material is extruded through it at a faster rate. Results for all the packaging and Dispomelt adhesives are presented as a function of load in Figures 19 and 20 respectively. The trends in the packaging adhesives results are clearer than the Dispomelt results, and long-die Dispomelt results clearer than the short-die results. The results all tend to exhibit a slight upturn in MVR values with increasing flow rate.

For the packaging adhesives in terms of decreasing MVR for both the short and long dies the adhesives were ranked:

AQHN003 – highest MVR
AQHN016
AQHN014
AQHN007 – lowest MVR

However, the difference between AQHN014 and AQHN016 was small.

For the Dispomelts the ranking obtained using the long die (dominated by shearing flow) was:

AQLO001 – highest MVR
AQLO003
AQFW, AQLO002, AQLO004 – lowest MVR

with the difference between the grades AQFW, AQLO002 and AQLO004 being negligible. The ranking of the Dispomelts using the short die was dependent on the load and perhaps reflects the greater difficulty experienced in obtaining reasonable results for the Dispomelts.

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 21 - 24. The apparent shear viscosity values are not Bagley [13] 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 significant.

4.4 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 [12]. Because of the use of the 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 [12] had to be developed further. The analysis is described in the Appendices. 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 were obtained over a relatively small shear rate range only 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 25 – 33.

For the packaging adhesives the level of agreement in shear viscosity between the two methods is relatively poor: the melt flow rate values are consistently lower than the corresponding capillary extrusion values by approximately a factor of two³, Figures 25 – 28. For the entrance pressure drop data the MVR values are both higher and lower than the corresponding capillary extrusion values, e.g. Figure 27 compared with Figure 28.

For the Dispomelt 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 %⁴, Figures 29 - 33. 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.

Testing of the adhesive AQHN007 using different die diameters, Figure 26, indicated that there was a possible geometry dependence of shear viscosity. The use of the larger 0.5 mm diameter dies resulted in a reduction in shear viscosity of approximately 30 % compared with data obtained using 0.25 mm diameter dies. The effect of die diameter on entrance pressure drop values is however unclear due to high variability in results, Figure 26.

³ For the packaging adhesives, 0.5 mm diameter MVR dies and 0.25 mm diameter capillary dies were used.

⁴ For the Dispomelt adhesives, 0.5 mm diameter MVR dies and 0.5 mm diameter capillary dies were used.

5 Discussion

The two types of adhesive, the packaging and the Dispomelt adhesives, differ quite significantly in their flow behaviour. The Dispomelt adhesives are soft, malleable solids at room temperature whereas the packaging adhesives are significantly less malleable. This observation is consistent with oscillatory testing which indicated that the packaging adhesives have a very sharp melting transition, compared with the Dispomelts which generally exhibit a gradual reduction in properties with increasing temperature. The packaging adhesives exhibited a 3 decade decrease in viscosity on melting (limited by the instrument to test satisfactorily at higher moduli values), and very low viscosity values at typical processing temperatures. Furthermore, frequency sweep testing demonstrated that at high rates the Dispomelts exhibited significantly greater elasticity than the packaging adhesives. These properties resulted in considerable complications in both capillary extrusion rheometry and melt flow rate testing.

As a result of the very low viscosities, small diameter dies were necessarily used, in part to ensure adequate pressures were generated but also to obtain data at the high shear rates characteristic of processing. In the initial capillary rheometry testing significant leakage of melt was observed past the piston head and around the sides of the die. This was rectified by the use of a novel PTFE piston head and O-rings on the die holders. However, because of this effective sealing, trapped air unable to escape from the barrel resulted in problems achieving stability of extrusion pressures. Trapped air is a greater problem for these materials than when testing polymer melts as the extrusion pressures are significantly lower and thus the volume occupied by the air is greater as it is not compressed so much during testing. To overcome this a fine air bleed channel was scored along the length of the piston head to permit escape of the air. These modifications resulted in improved testing performance.

As observed for the packaging adhesive AQHN007, there appeared to be a die diameter dependence of viscosity: a larger diameter resulting in a lower shear viscosity, Figure 26. This would account for some of the discrepancy between the melt flow rate and capillary rheometry shear viscosity results for the packaging adhesives as nominally 0.5 mm diameter dies were used in the melt flow rate testing and 0.26 mm diameter dies in the capillary rheometry testing. Thus, given the result observed in Figure 26, one would expect the shear viscosities derived from the melt flow rate results for the packaging adhesives to be lower by a factor of approximately 30 %. This, however, still leaves a discrepancy of approximately 30 % between values. On the issue of geometry dependence, the most obvious explanation, given the complex package that makes up these materials, would be the occurrence of slip. However, in the presence of slip a smaller diameter die would be expected to result in lower shear viscosity values and thus does not appear to be the explanation. Further work is required to elucidate the geometry dependence of results, but obviously this has significant implications for testing such materials.

Although leakage in the melt flow rate instrument was not apparent it may still have been occurring to a lesser extent than in the capillary rheometry testing. However, it was not considered appropriate to use the same piston head design for the melt flow instrument as it would have led to a significant error in the results due to friction between the piston head and the barrel wall thereby reducing the effective applied load, particularly with the lowest applied load of 0.325 kg. Leakage in the melt flow rate instrument would result in a higher melt flow rate, which is equivalent to higher shear rates and, given that it is a constant stress device, lower shear viscosities. Given the low shear rate dependence of viscosity of these

materials the overall shift would be dominated by a reduction in shear viscosity for a given shear rate. Thus the lack of agreement between melt flow rate testing and capillary rheometry could be accounted for by leakage. To account for the 30 % discrepancy discussed earlier, and given the near independence of shear viscosity of these packaging adhesives to shear rate, then a 30 % reduction in shear viscosity would be caused by a 30 % increase in melt flow rate and thus, if accounted for by leakage, a 30 % leakage factor. It was observed that the discrepancy in shear viscosity of the Dispomelts between melt flow rate testing and capillary extrusion testing was up to approximately 10 %, which may be due to leakage in the melt volume flow rate test. However, the uncertainty in the dimensions of the nominally 0.25 mm diameter Rosand dies could easily account for a significant proportion of the discrepancy in the packaging adhesive results (see Section 3.2).

The discrepancy was largest for AQHN003 as would be expected if due to leakage as its shear viscosity was the lowest. The difference in the discrepancies in shear viscosities between the Dispomelts and the packaging adhesives may possibly be explained by their different shear viscosities. The Dispomelts typically have higher shear viscosities than the packaging adhesives, particularly at lower shear rates. Thus leakage is less likely to occur resulting in a smaller error, but this does assume that the shear rates occurring in the leakage flow are lower than in the die for the difference in shear viscosities to be significant and thereby account for the observed difference between the Dispomelt and the packaging adhesives' behaviour. Further work is required to confirm this hypothesis.

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 for most adhesives was found to be excessive). In comparison, the capillary extrusion rheometry standard ISO 11443 [3] 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, but outliers from this range have been ignored. Obviously, the pressure transducers in the extrusion rheometer can normally be changed for one 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 with a lower range.

6 Conclusions

In conclusion:

- Oscillatory testing has demonstrated that the packaging adhesives have a very sharp melting transition compared with the Dispomelts which exhibit a much more gradual reduction in properties with increasing temperature. Oscillatory testing of a Dispomelt adhesive demonstrated that it had a higher degree of elasticity than the packaging adhesives at high rates.

- Testing the hot melt adhesives has highlighted one of the key problems in rheological testing, namely the ability of an instrument to easily cover a wide range of values, in this case in excess of three to four decades in viscosity.
- In using capillary extrusion rheometry for hot melt adhesives special provisions should be made to reduce leakage past the piston head and die support (no leakage past the pressure transducer was observed in this work, though it is possible leakage may also occur at this point in other instruments). 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. 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).
- Trapped air, made worse by the effective sealing described above to prevent material leakage, resulted in variability in the extrusion pressure traces, and consequently in viscosity and entrance pressure drop values derived from them. The effect of trapped air was minimised by adding a fine bleed channel along the length of the specially-made PTFE piston head, along with careful loading of the material into the barrel to minimise trapped air.
- 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 Dispomelts for shear viscosity, the level of agreement was not so good for entrance pressure drop and for the lower viscosity packaging adhesives.
- It is considered that the relatively poor agreement of results for the packaging adhesives was partly due to an apparent geometry dependence of results: shear viscosities from the same instrument were dependent on the die diameter. It is also suggested that part of the discrepancy was due to the effect of leakage in the melt flow rate testing, although this needs to be confirmed, or otherwise, by additional research. However, a remedy for leakage in the melt flow rate test is not obvious, given its mode of operation.
- The results suggest that melt flow rate testing of Dispomelts is suitable for obtaining shear viscosity data and to a slightly lesser extent entrance pressure drop data. However, melt flow rate testing of the packaging adhesives is less appropriate due to the observed discrepancies in results.

Further work is required to investigate the issue of geometry dependence of the measurement of shear viscosity of the hot melt adhesives.

7 Acknowledgement

The research reported in this report was carried out by NPL as part of project MMS9 of the “Materials for Measurement Systems” (MMS) programme, a programme of underpinning research funded by the United Kingdom Department of Trade and Industry (MMS9/T3/M3).

The authors would like to thank Dave Carter and Wei Kong of National Starch and Chemical for supplying the adhesives.

8 References

1. ISO 6721-10: Plastics - Determination of dynamic mechanical properties, Part 10: Dynamic shear viscosity using a parallel plate oscillatory rheometer.
2. Round robin for parallel plate oscillatory rheometry using polyethylene and polypropylene melts, M Rides and C.R.G. Allen, NPL report CMMT(A)11, January 1996.
3. ISO 11443: Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers.
4. Capillary extrusion rheometry intercomparison using polyethylene and glass-fibre filled polypropylene melts: measurement of shear viscosity and entrance pressure drop, M. Rides and C.R.G. Allen, NPL report CMMT(A)25, May 1996.
5. Rides, M., Allen, C.R.G. and Chakravorty, S., Intercomparison of extensional flow characterisation techniques for polymer melts: tensile stretching and converging flow methods, NPL Report CMMT(A)171, April 1999.
6. Rides, M., and Allen, C.R.G., Entrance pressure drop measurements by capillary extrusion rheometry: a measure of the extensional flow behaviour of polymers, Polymer Rheology '99 Conference: Polymer Rheology - A practical approach to quality control for the Plastics and Rubber Industries, Paper 13, Pages 1-4, RAPRA Technology Ltd, Shawbury, UK, 13-14 October 1999.
7. Rides, M. and Allen, C.R.G., Measurement Good Practice Guide No. 16, Extensional flow properties of polymer melts using converging flow methods, National Physical Laboratory, January 1999, ISSN 1368-6550.
8. Cogswell, F.N., Polym. Eng. Sci., 12 No.1 (1972) pp.64-73.
9. Gibson, A.G., Composites, 20 No.1 (1989) pp.57-64.
10. Binding, D.M., J. Non-Newtonian Fluid Mechanics, 27 (1988) pp.173-189.
11. ISO 1133: Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics.

12. Martin Rides, Crispin Allen and Angela Dawson, Measurement Good Practice Guide No. 61, Multi-rate and extensional flow measurements using the melt flow rate instrument, National Physical Laboratory.
13. Bagley, E.B., J. Applied Physics, 28 No.5 (1957) pp.624-627.

Figures

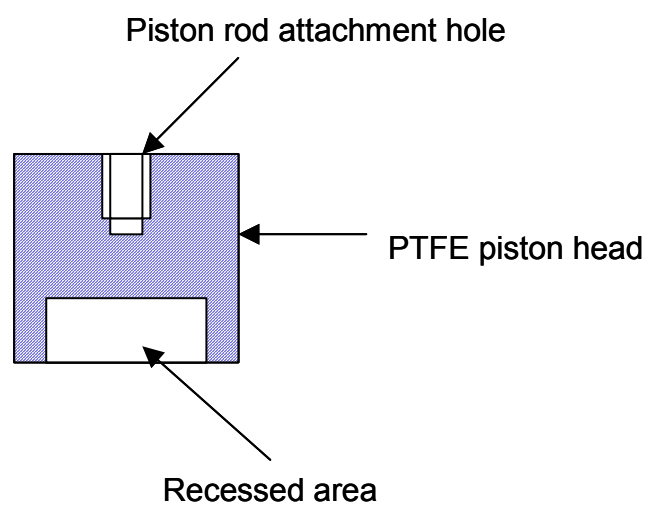
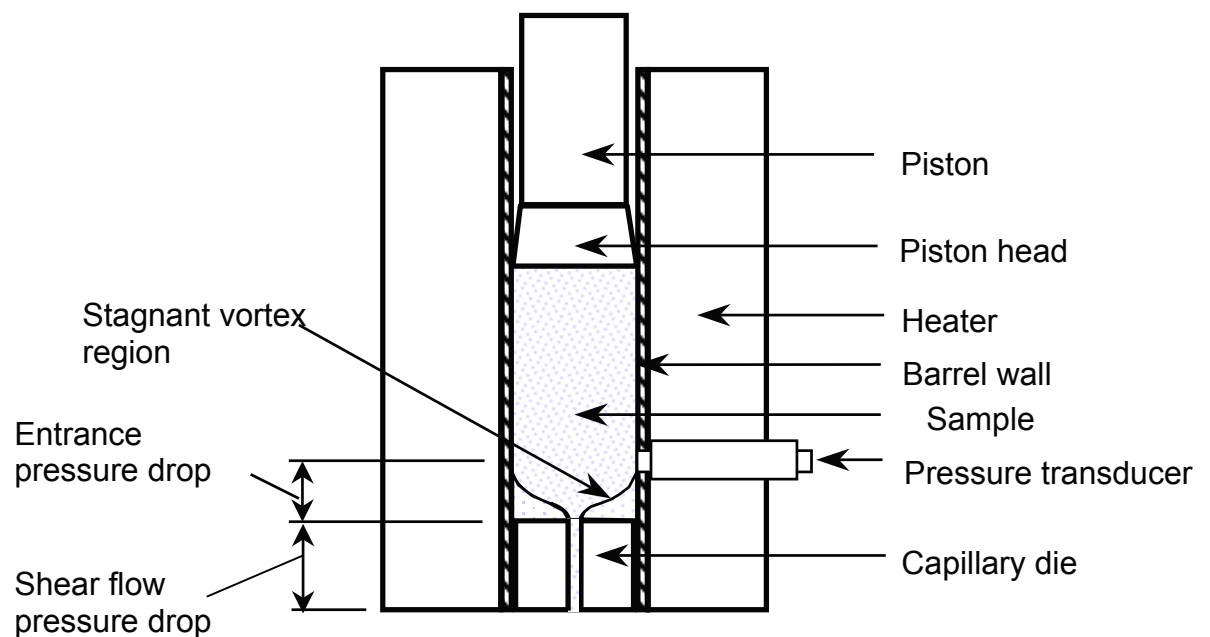


Figure 1: Schematic of capillary extrusion rheometer and PTFE piston head operating on a bicycle pump piston head principle

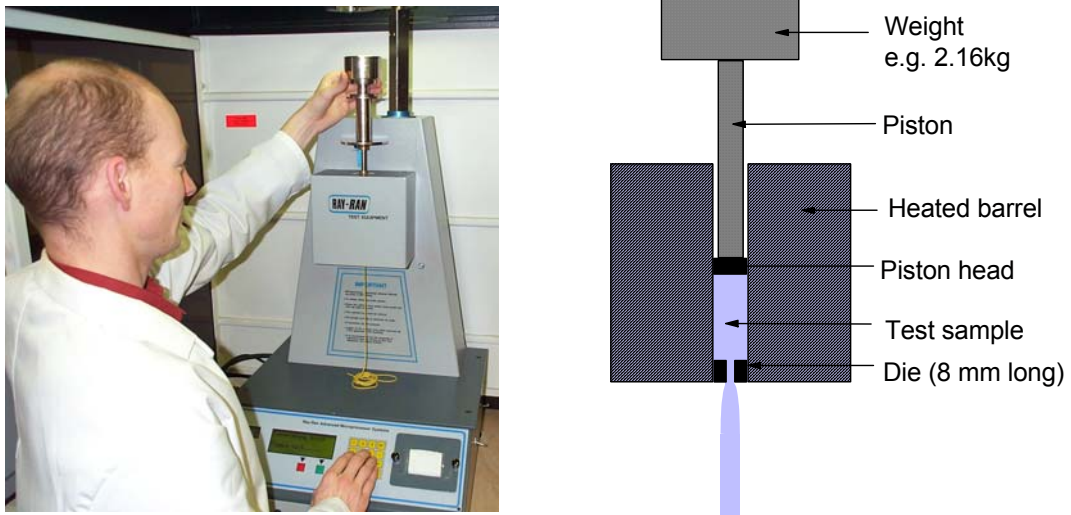


Figure 2: Standard melt flow rate instrument (ISO 1133)

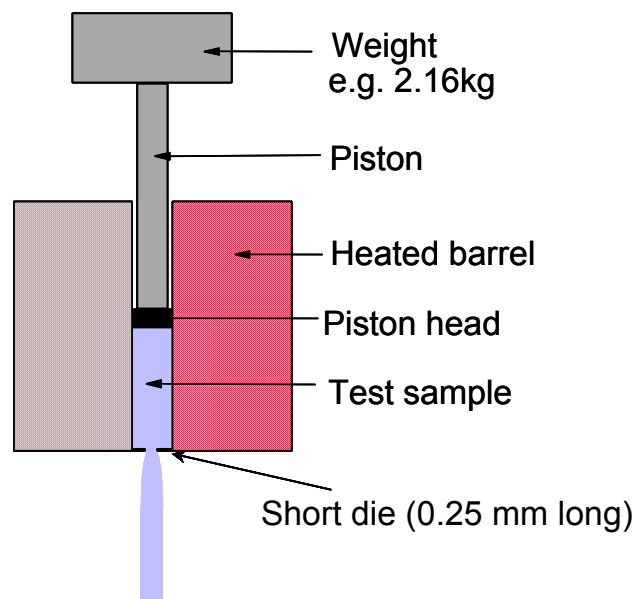


Figure 3: Modified melt flow rate instrument using a short die to determine entrance pressure behaviour

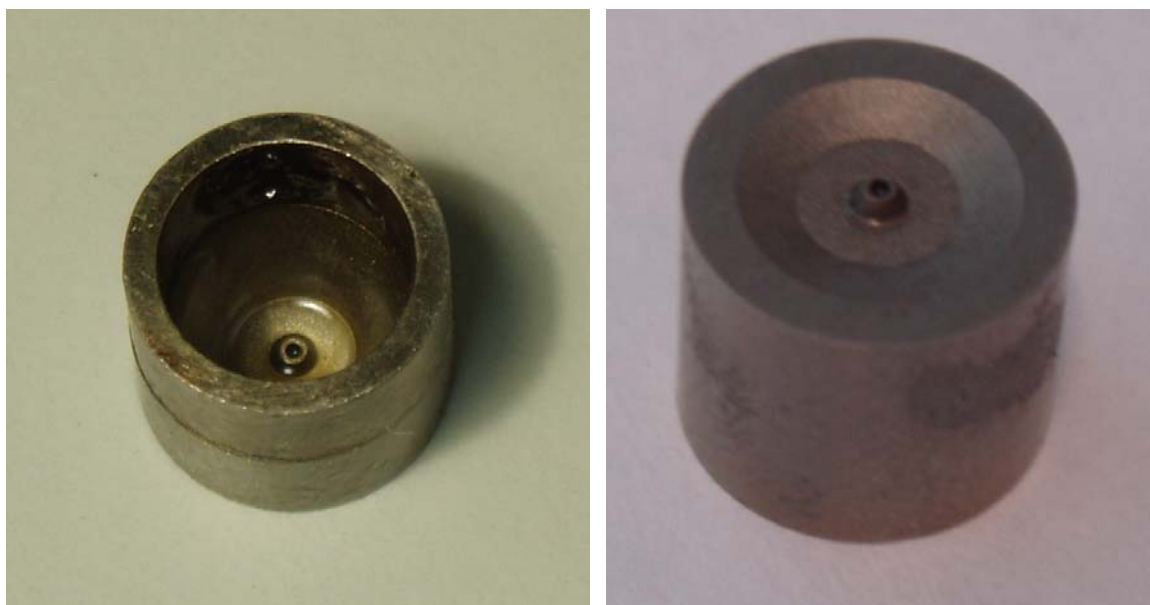


Figure 4: Short and long dies for separation of shear and extensional flow behaviours, and illustration of the nozzle geometry to avoid drooling of extrudate at the die exit.

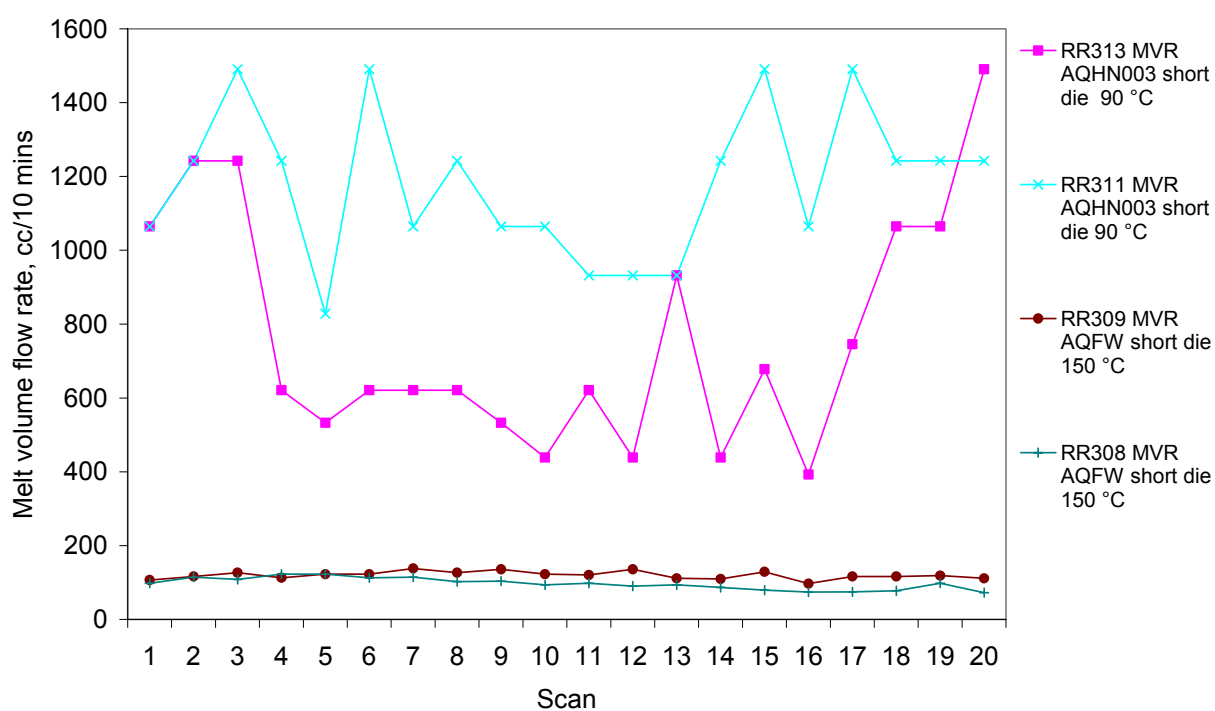


Figure 5: High rate results for a hot melt adhesive using the standard instrument set-up but with a 0.24 mm length, 1 mm diameter die.

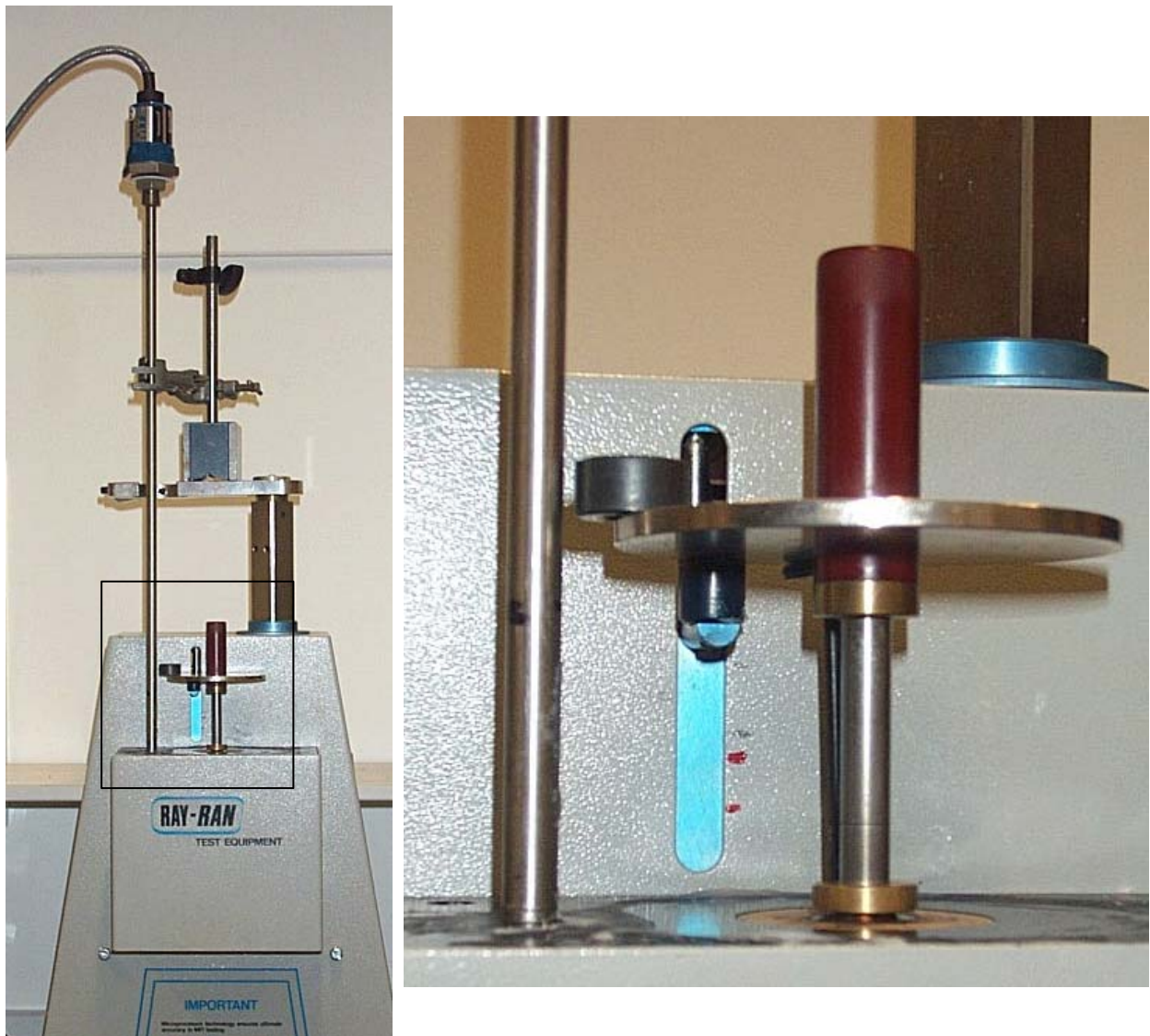


Figure 6: Modification to the melt flow rate instrument by addition of a displacement transducer to monitor the piston position and thus speed.

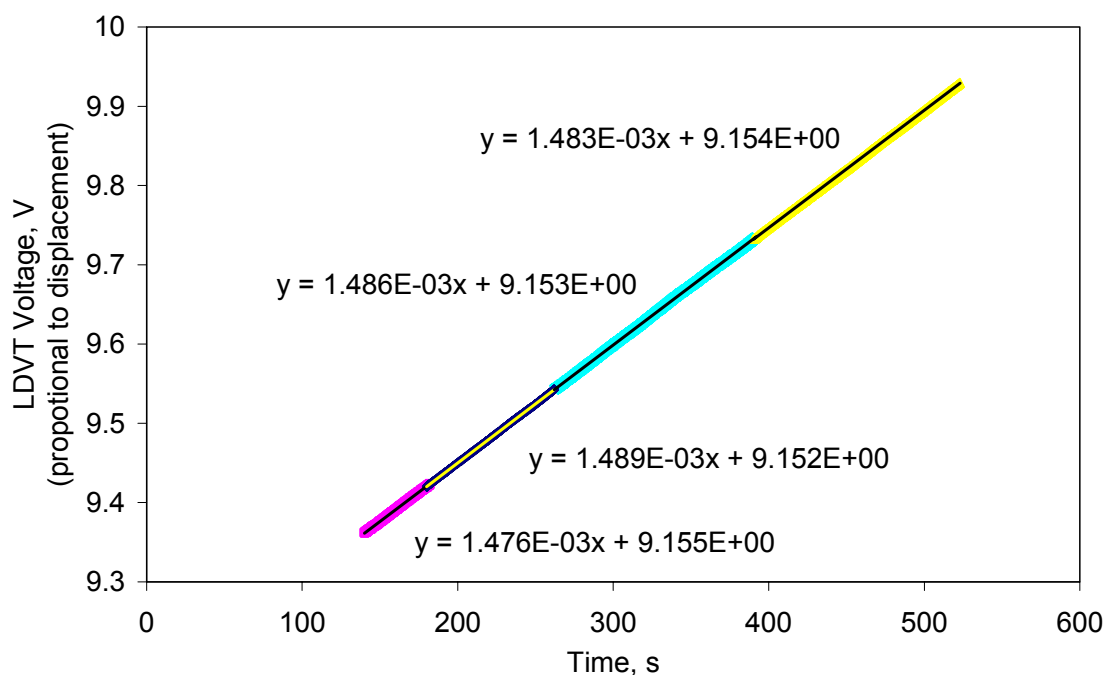


Figure 7: Output trace from the displacement transducer: gradients for various intervals illustrating the consistency of data for the Dispomelt AQFW (test ref RR343)

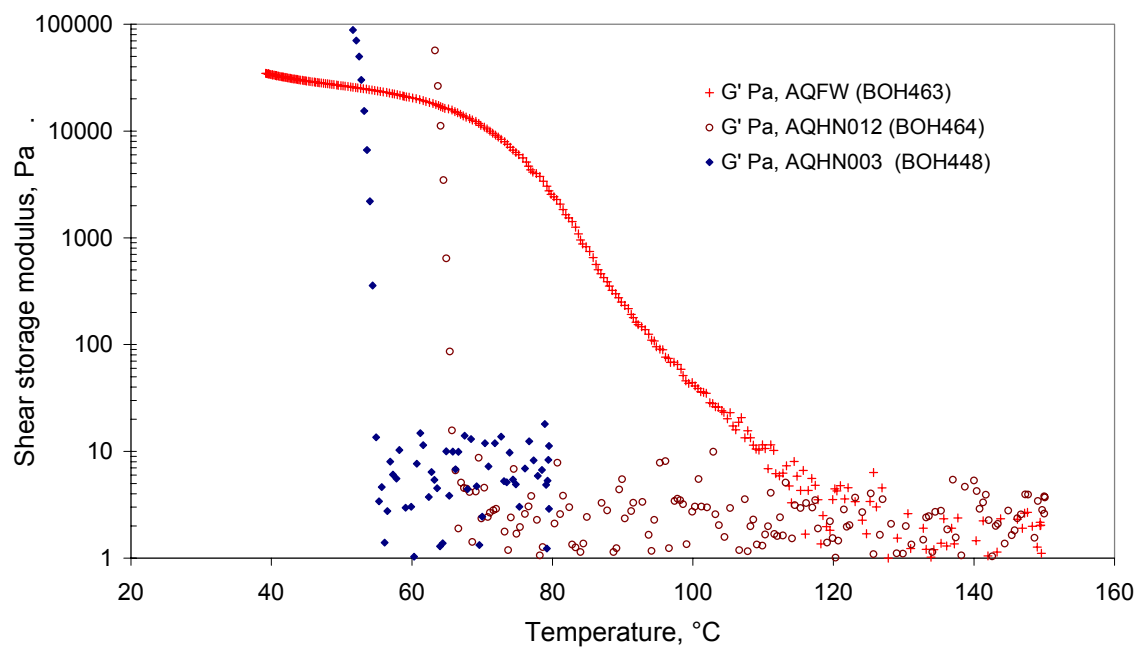


Figure 8: Shear storage modulus temperature sweep comparison of packaging adhesives, AQHN003 and AQHN012, and Dispomelt adhesive AQFW by oscillatory rheometry

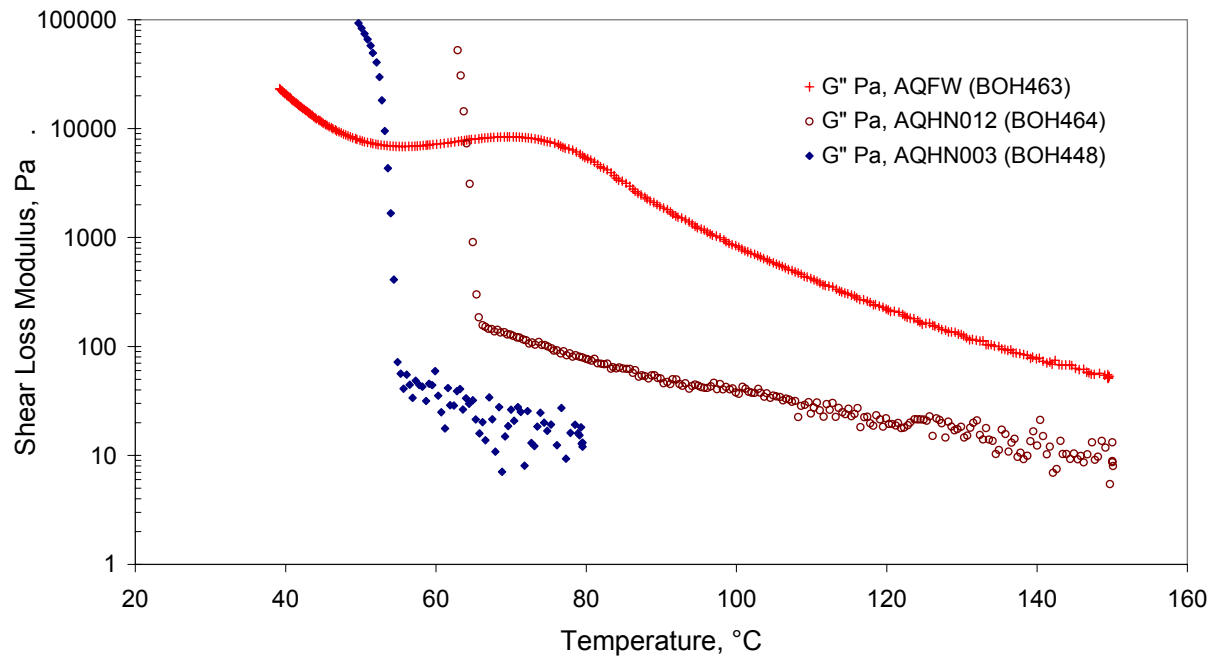


Figure 9: Shear loss modulus temperature sweep comparison of packaging adhesives, AQHN003 and AQHN012, and Dispomelt adhesive AQFW by oscillatory rheometry

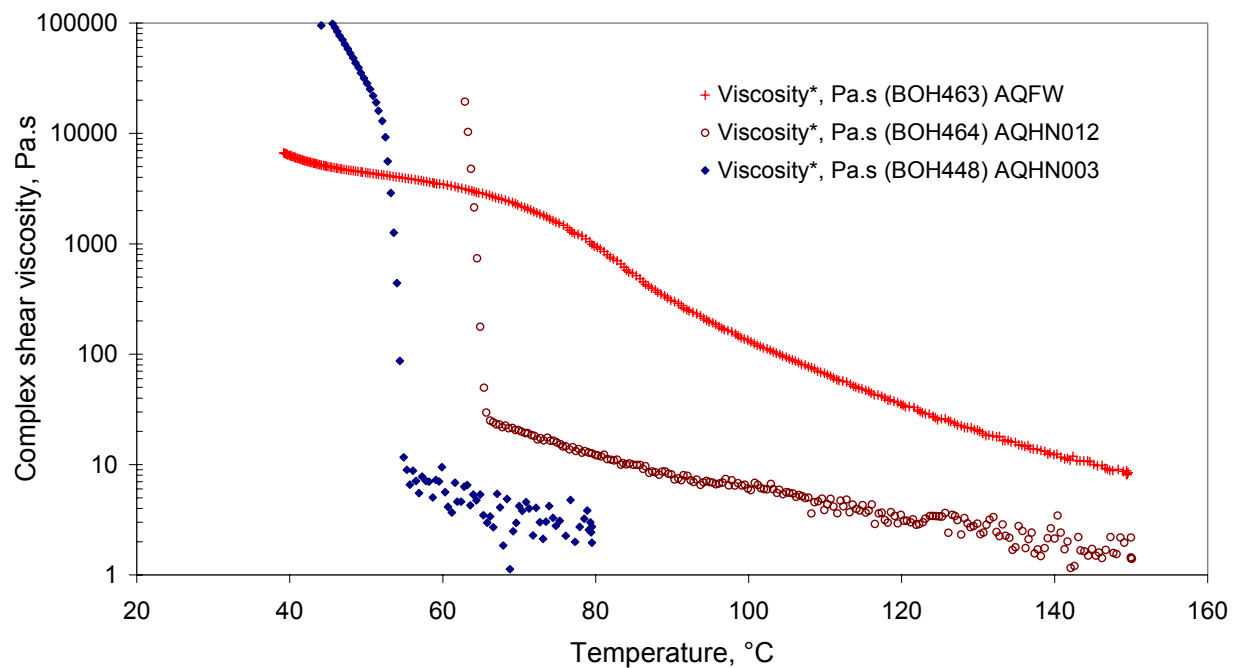


Figure 10: Complex shear viscosity temperature sweep comparison of packaging adhesives, AQHN003 and AQHN012, and Dispomelt adhesive AQFW by oscillatory rheometry

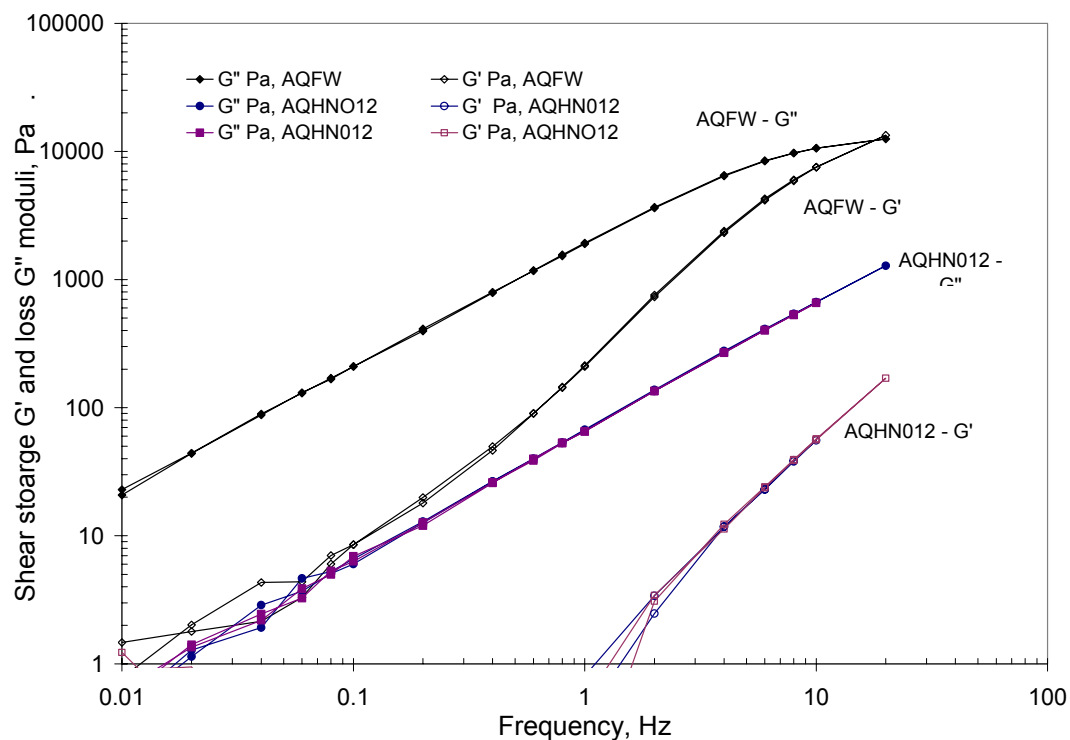


Figure 11: Shear storage and loss moduli frequency sweep comparison of packaging adhesives, AQHN003 and AQHN012, and Dispomelt adhesive AQFW by oscillatory rheometry

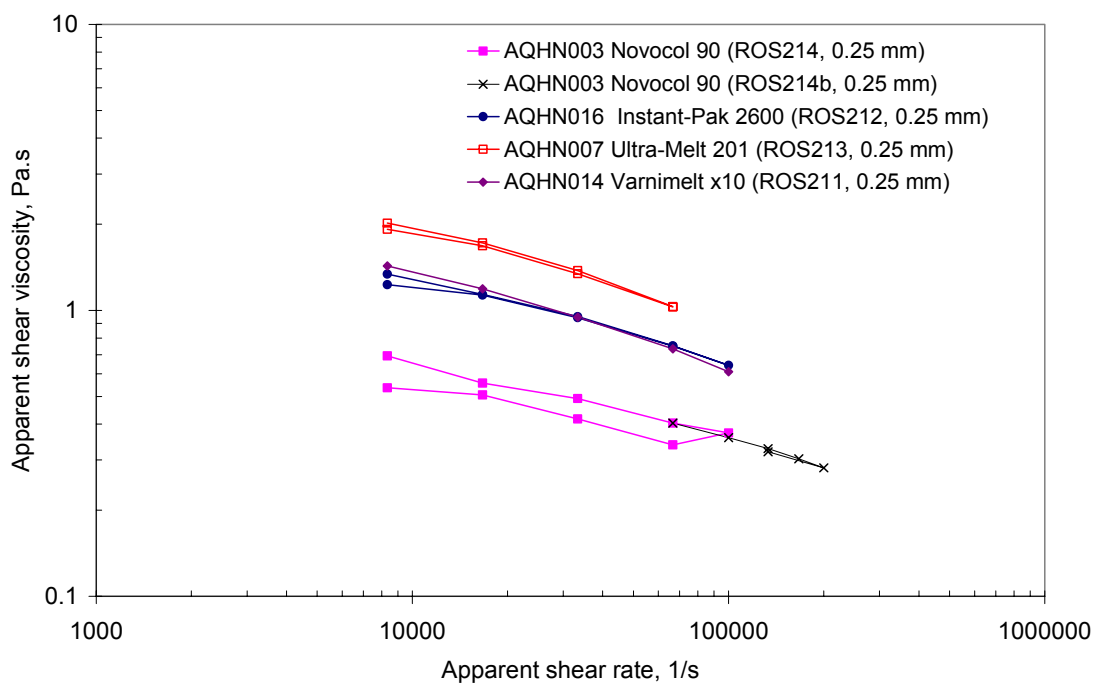


Figure 12: Apparent shear viscosity determined from capillary extrusion rheometry for the packaging adhesives at 150 °C (Bagley corrected)

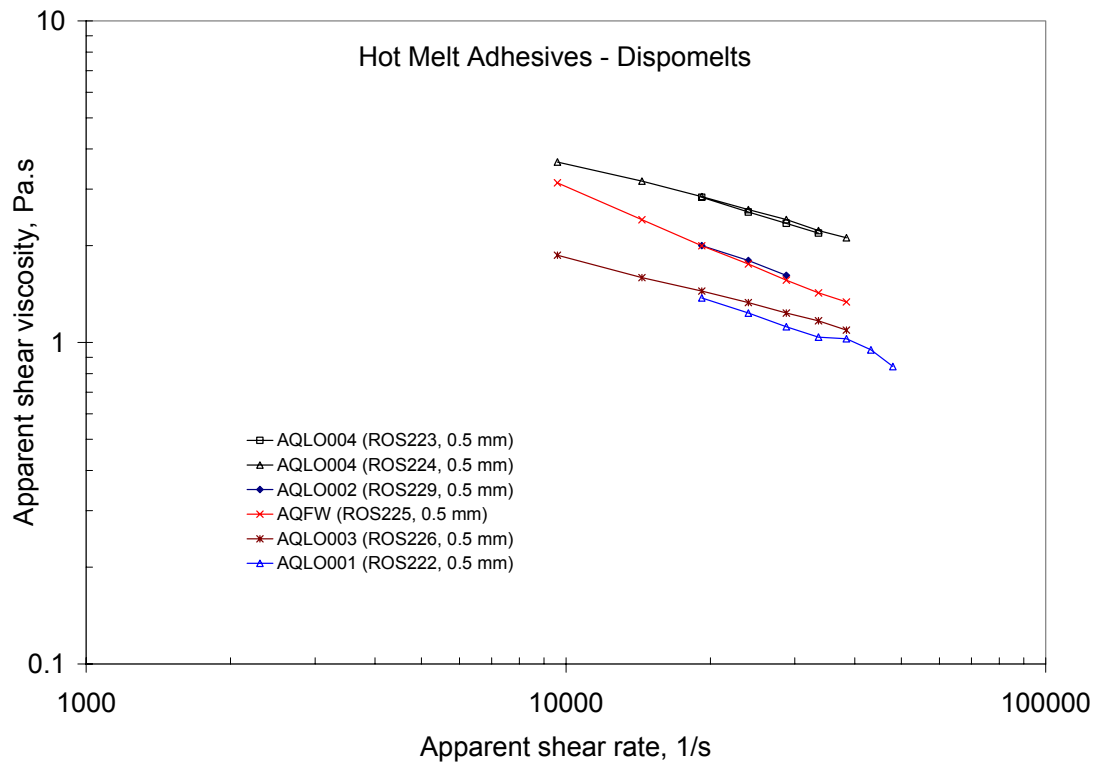


Figure 13: Apparent shear viscosity determined from capillary extrusion rheometry for the Dispomelt adhesives at 150 °C (Bagley corrected)

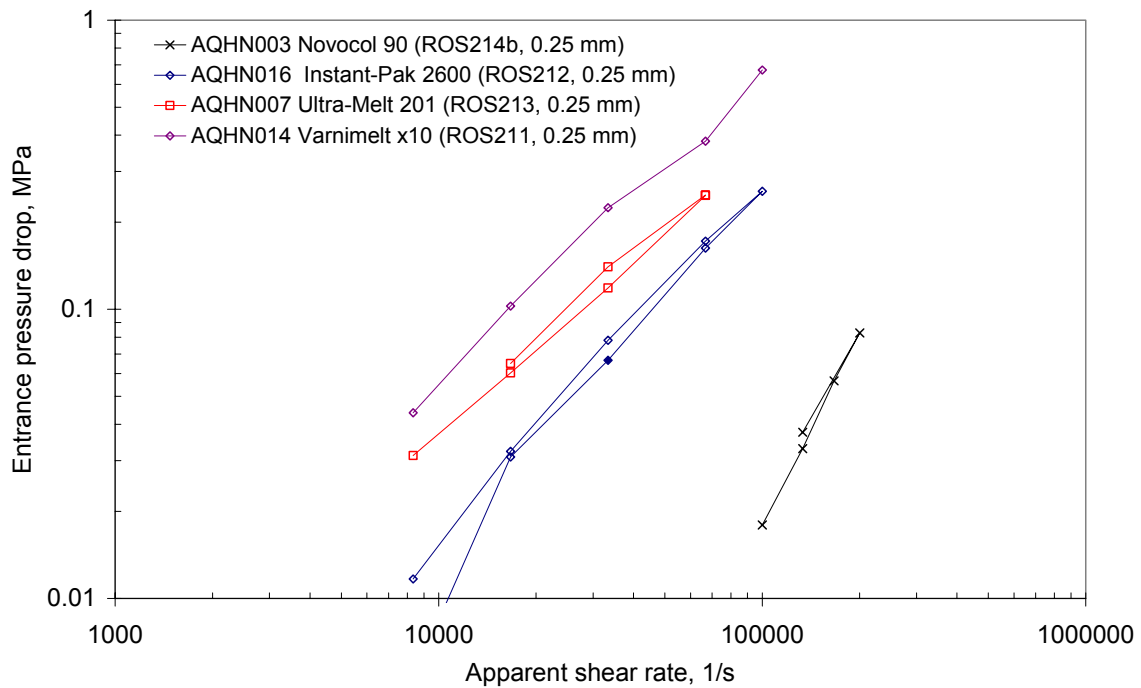


Figure 14: Entrance pressure drop data determined from capillary extrusion rheometry for the packaging adhesives at 150 °C (extrapolation to zero length die)

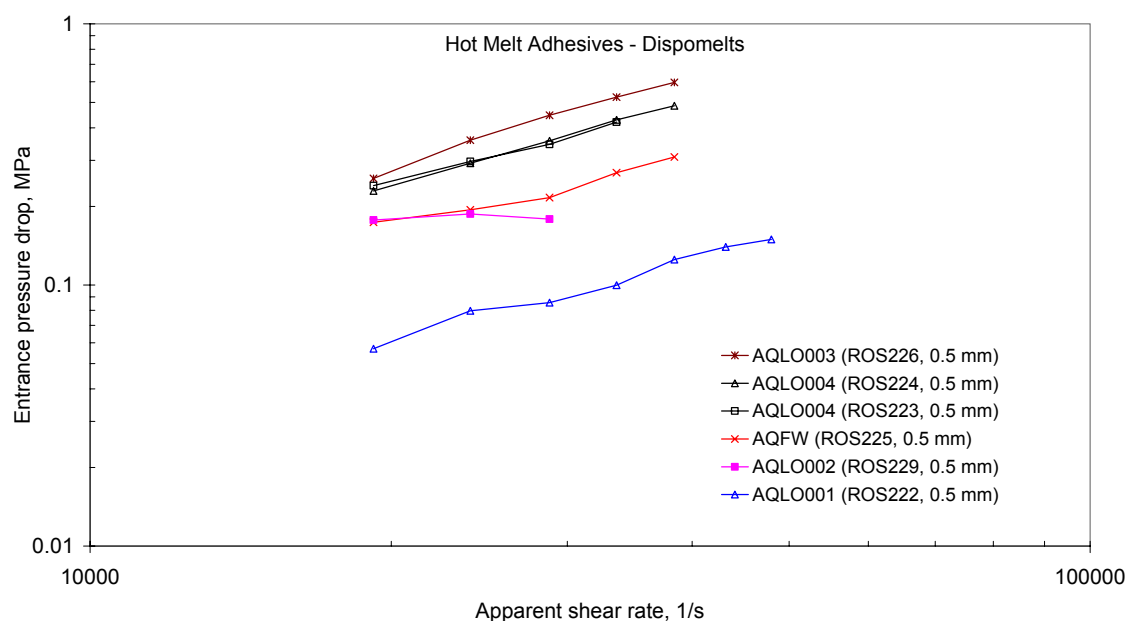


Figure 15: Entrance pressure drop data determined from capillary extrusion rheometry for the Dispomelt adhesives at 150 °C (extrapolation to zero length die)

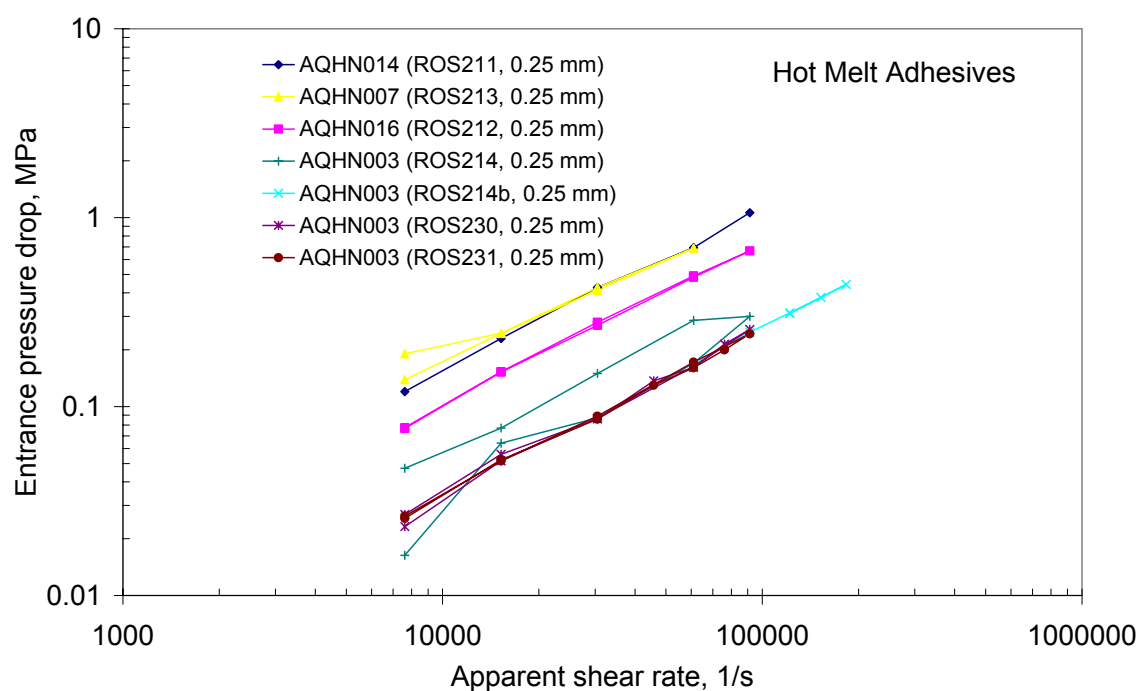


Figure 16: Entrance pressure drop data determined from capillary extrusion rheometry for the packaging adhesives at 150 °C using 0.25 mm diameter die values as entrance pressure drop values without correction for non-zero length.

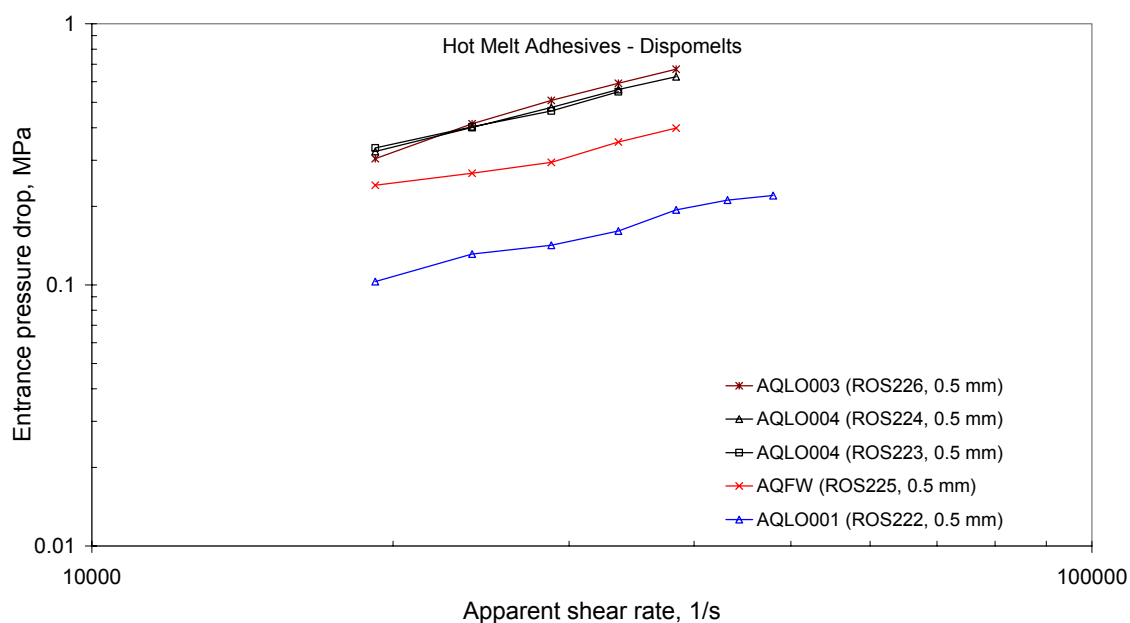


Figure 17: Entrance pressure drop data determined from capillary extrusion rheometry for the Dispomelt adhesives at 150 °C using 0.5 mm diameter die values as entrance pressure drop values without correction for non-zero length.

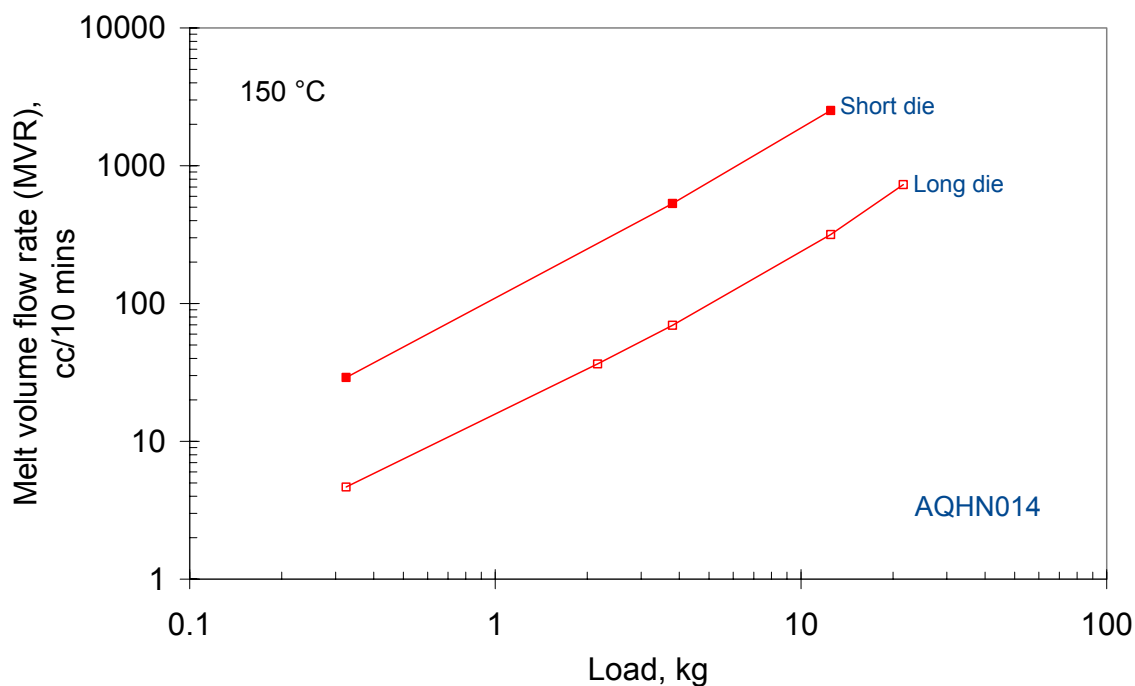


Figure 18: Typical data obtained using short (SD) and long (LD) dies for hot melt adhesive AQHN014 at 150 °C

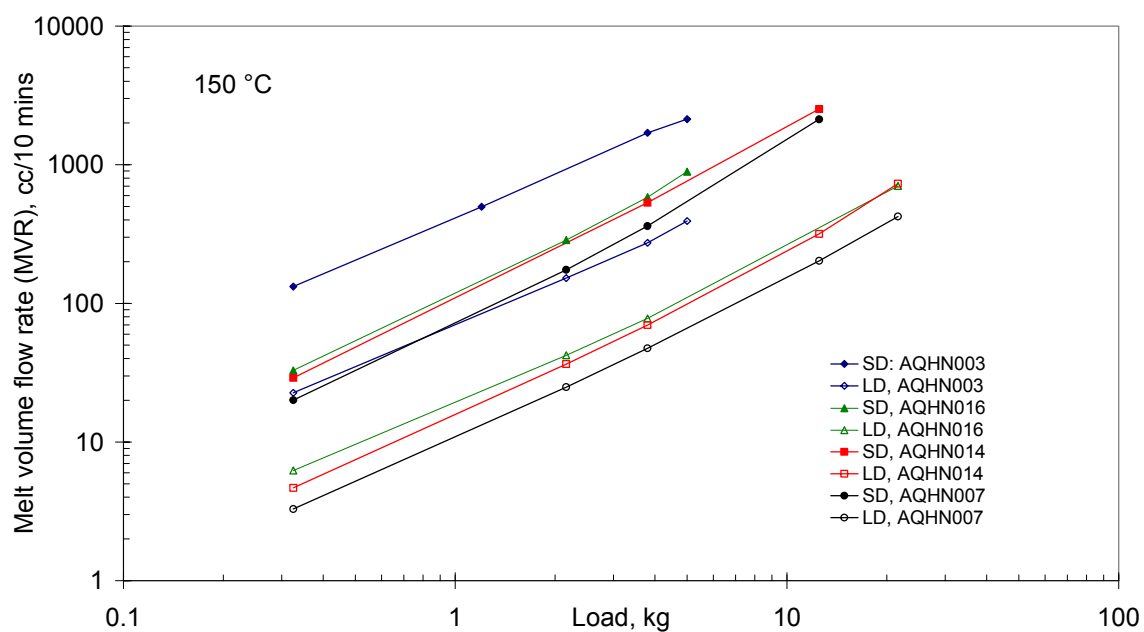


Figure 19: Melt flow rate results for packaging adhesives using short (SD) and long (LD) dies at 150 °C

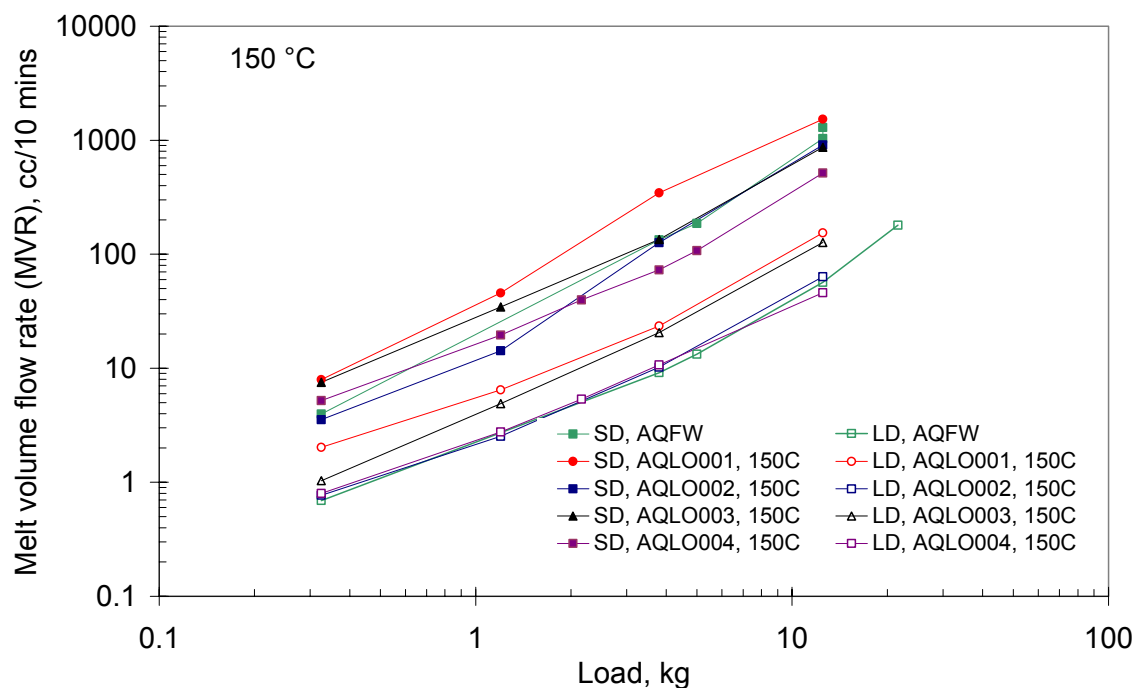


Figure 20: Melt flow rate results for Dispomelt adhesives using short (SD) and long (LD) dies at 150 °C

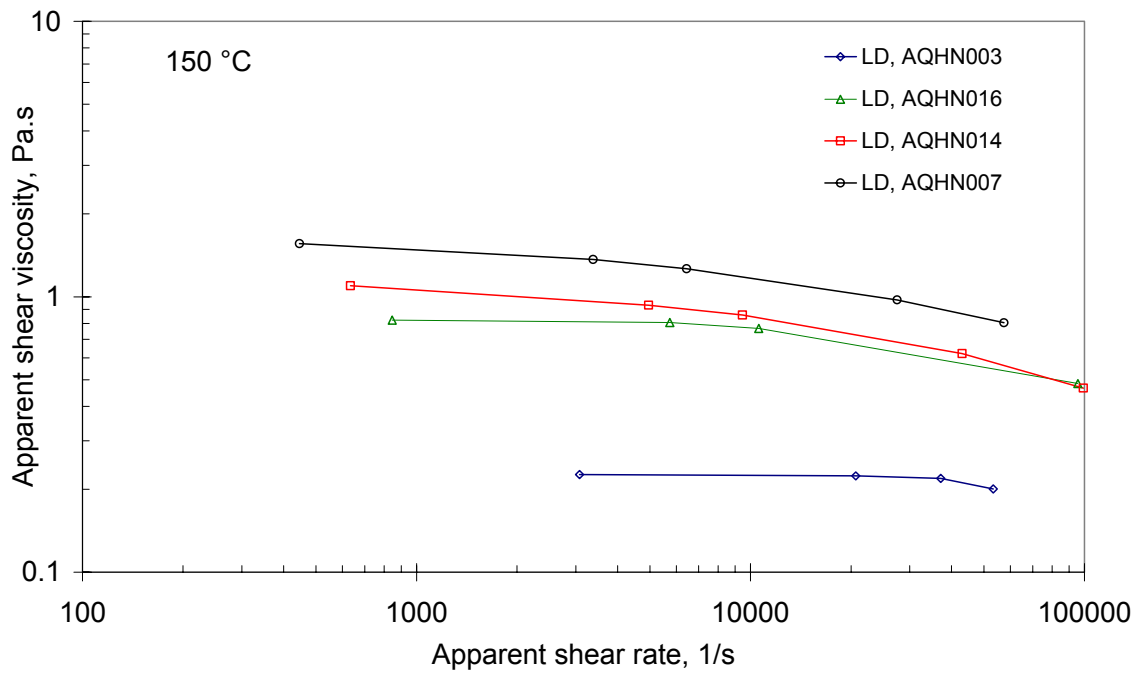


Figure 21: Apparent shear viscosity determined from the long die melt flow rate test results for the packaging adhesives at 150 °C (not Bagley corrected)

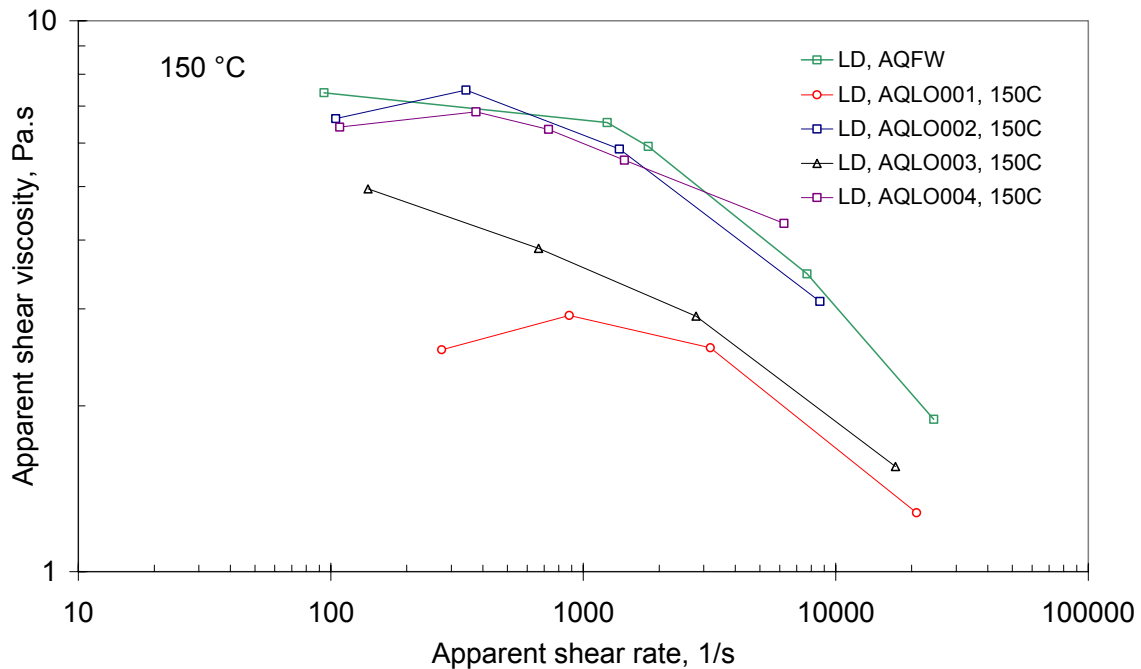


Figure 22: Apparent shear viscosity determined from the long die melt flow rate test results for the Dispomelt adhesives at 150 °C (not Bagley corrected)

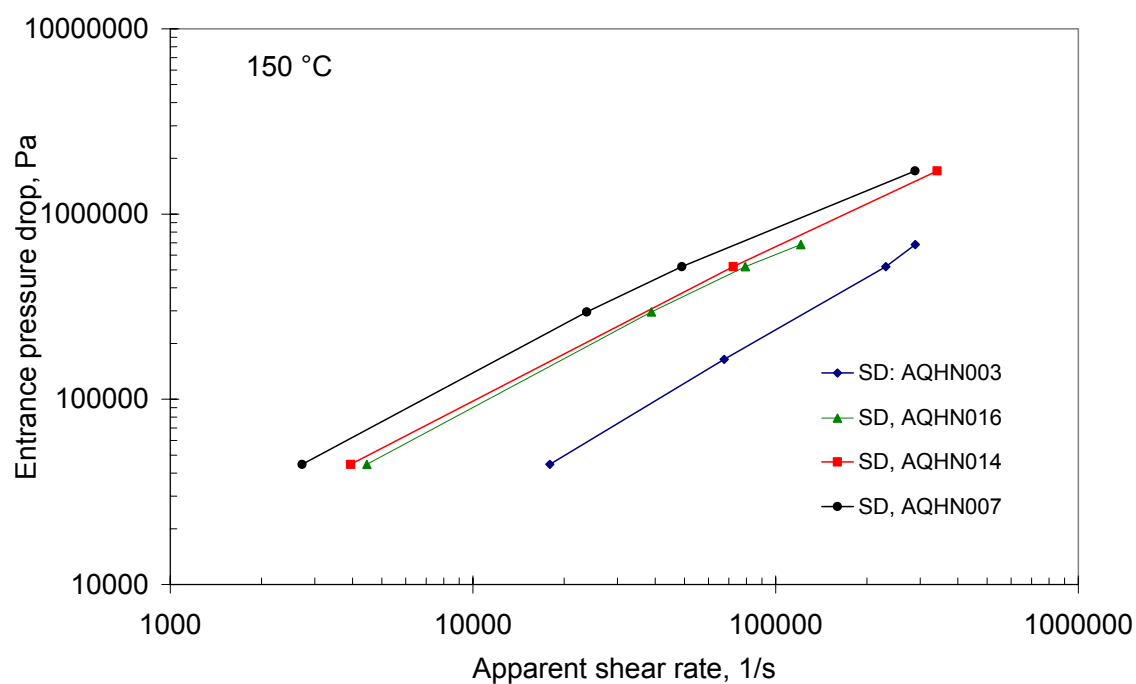


Figure 23: Entrance pressure drop determined from the short die (0.5 mm diameter, 1.029 mm length) melt flow rate test results for the packaging adhesives at 150 °C (no extrapolation to zero length)

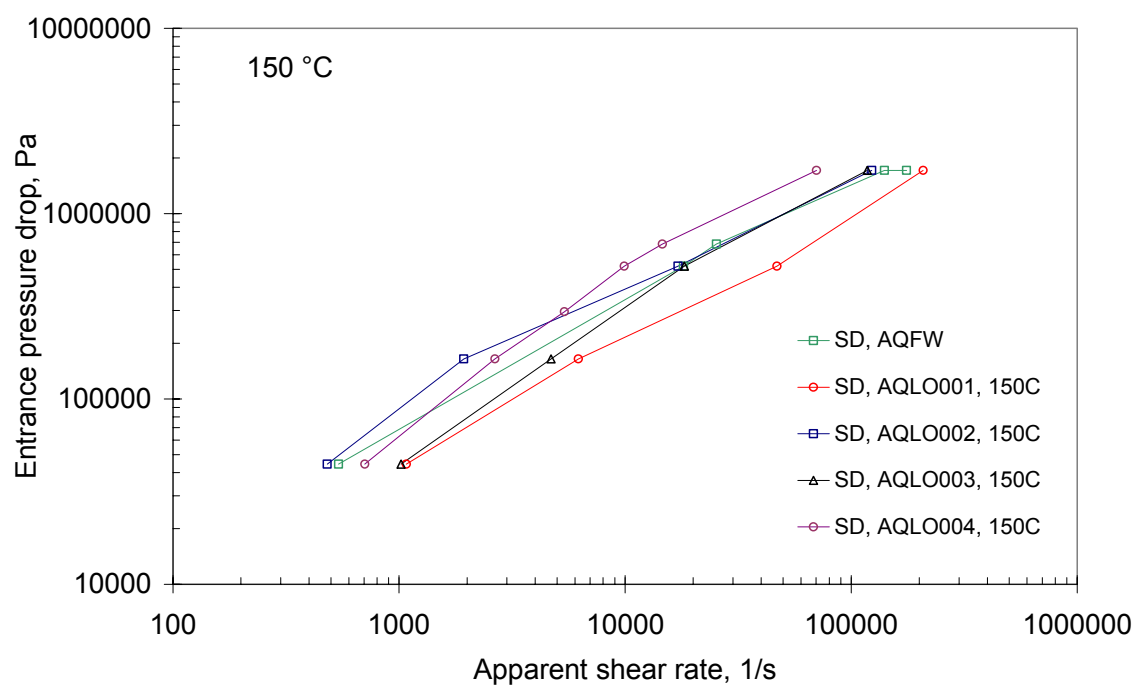


Figure 24: Entrance pressure drop determined from the short die (0.5 mm diameter, 1.029 mm length) melt flow rate test results for the Dispomelt adhesives at 150 °C (no extrapolation to zero length)

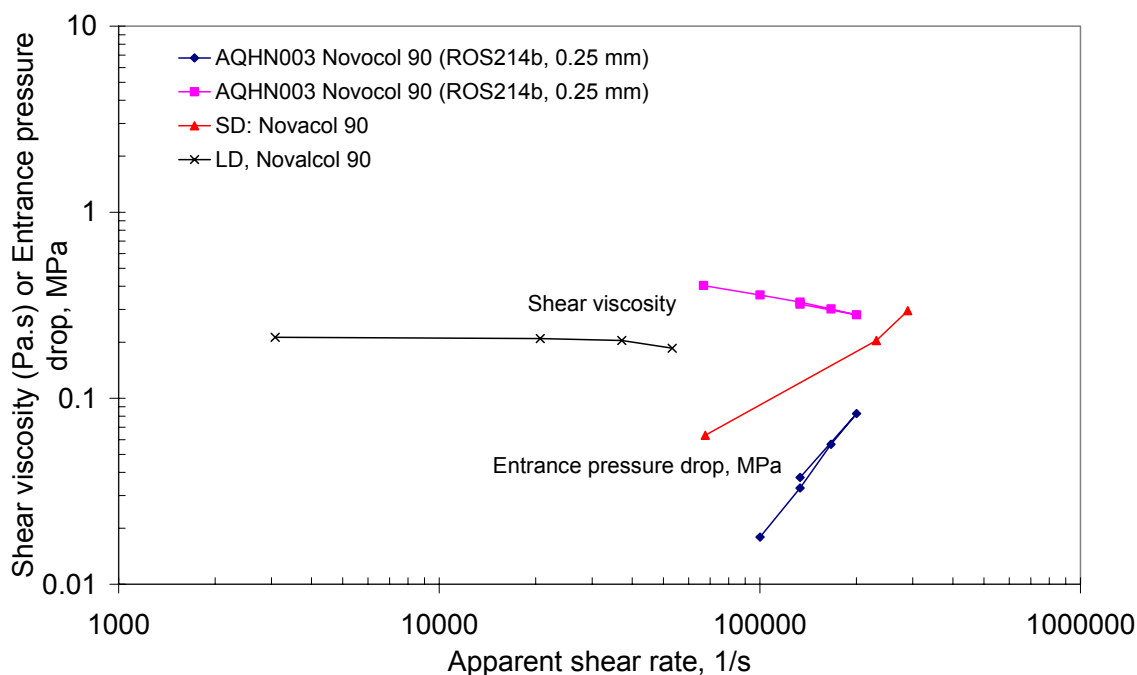


Figure 25: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for packaging adhesive AQHN003 at 150 °C.

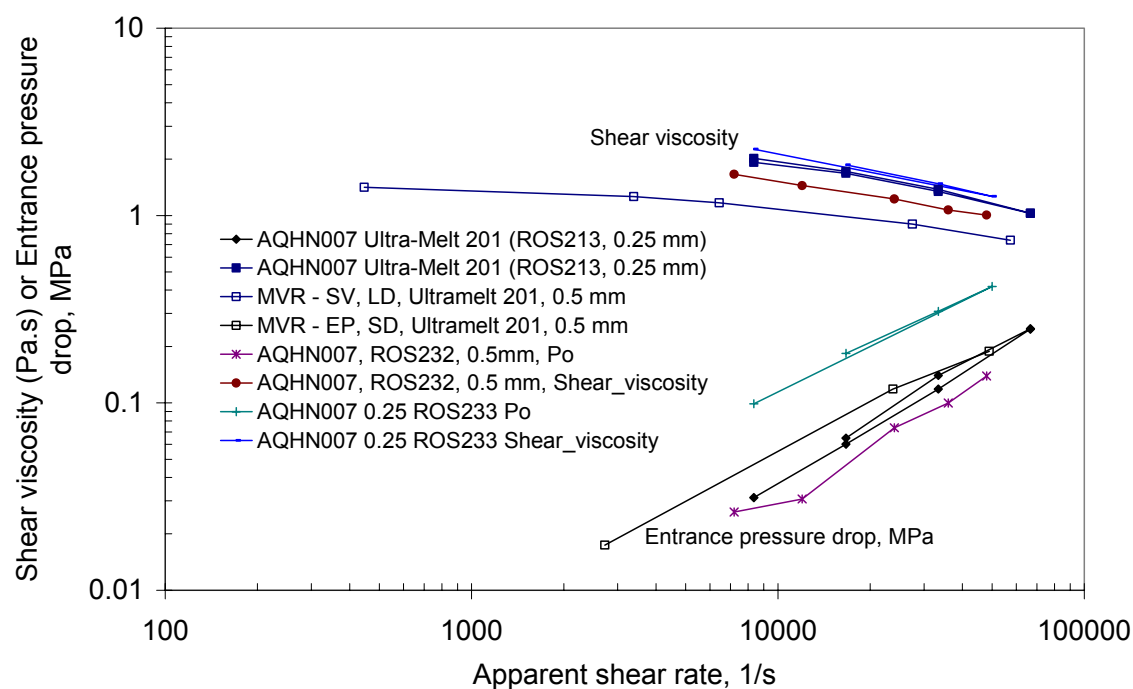


Figure 26: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for packaging adhesive AQHN007 at 150 °C.

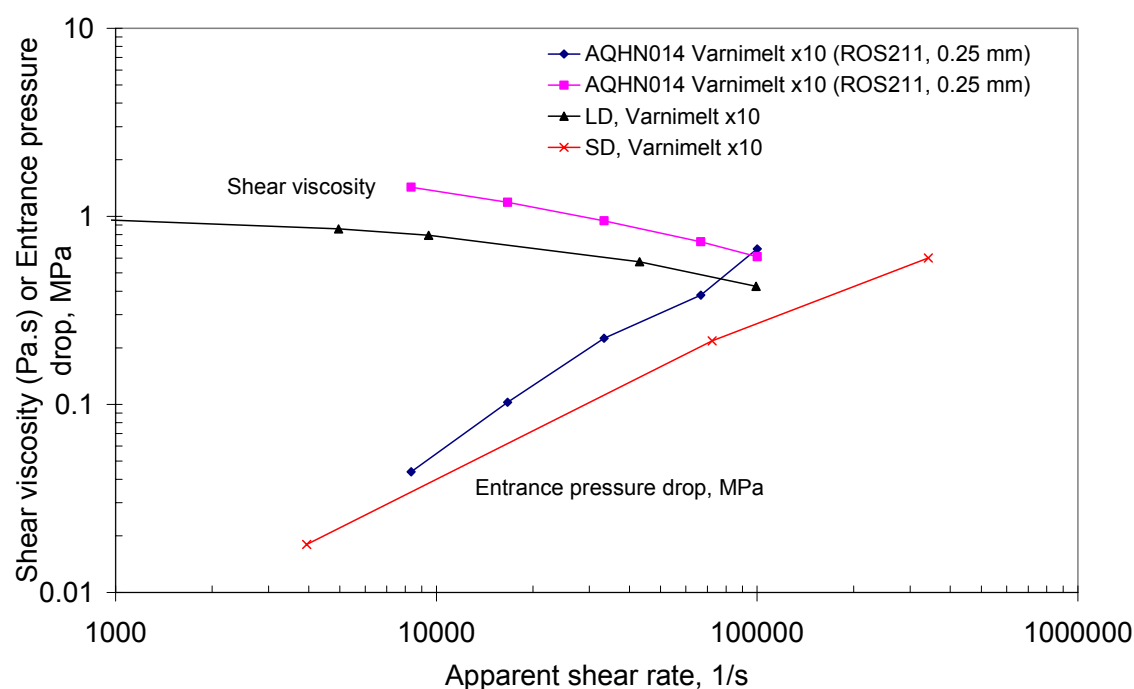


Figure 27: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for packaging adhesive AQHN014 at 150 °C.

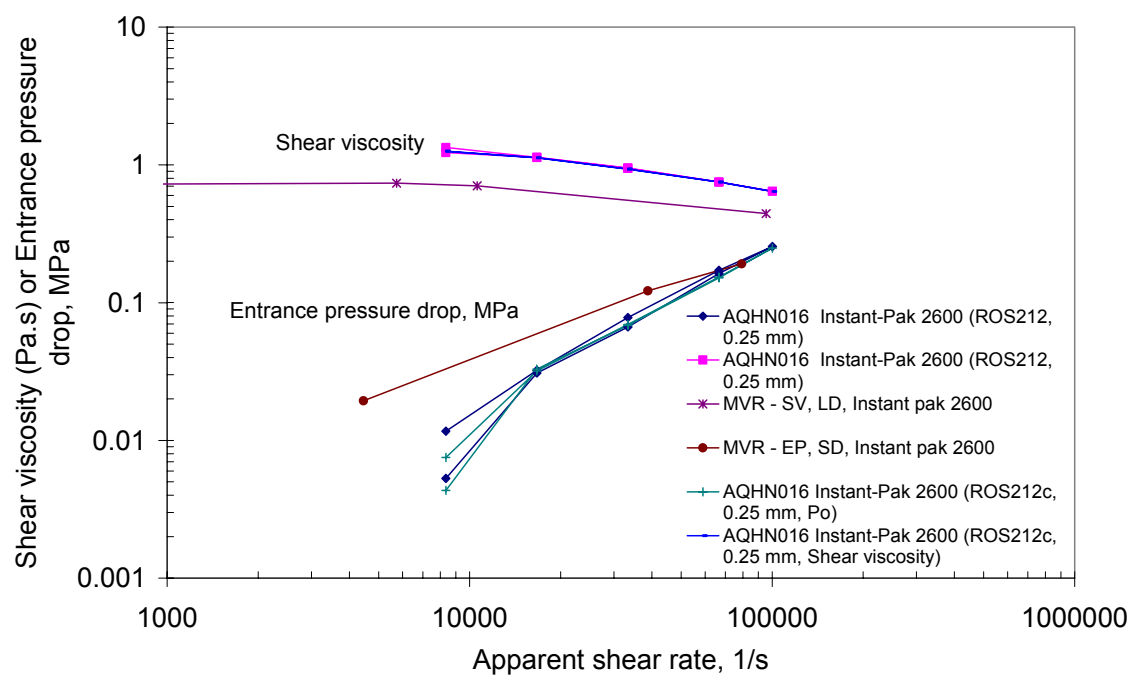


Figure 28: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for packaging adhesive AQHN016 at 150 °C.

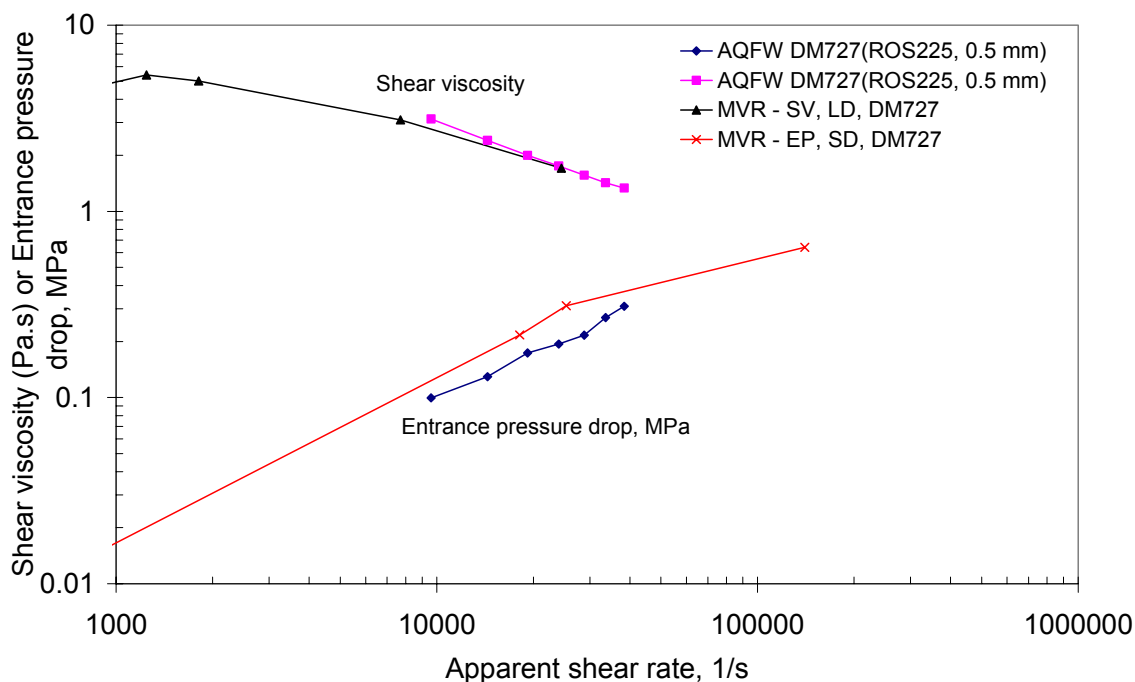


Figure 29: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for Dispomelt adhesive AQFW at 150 °C.

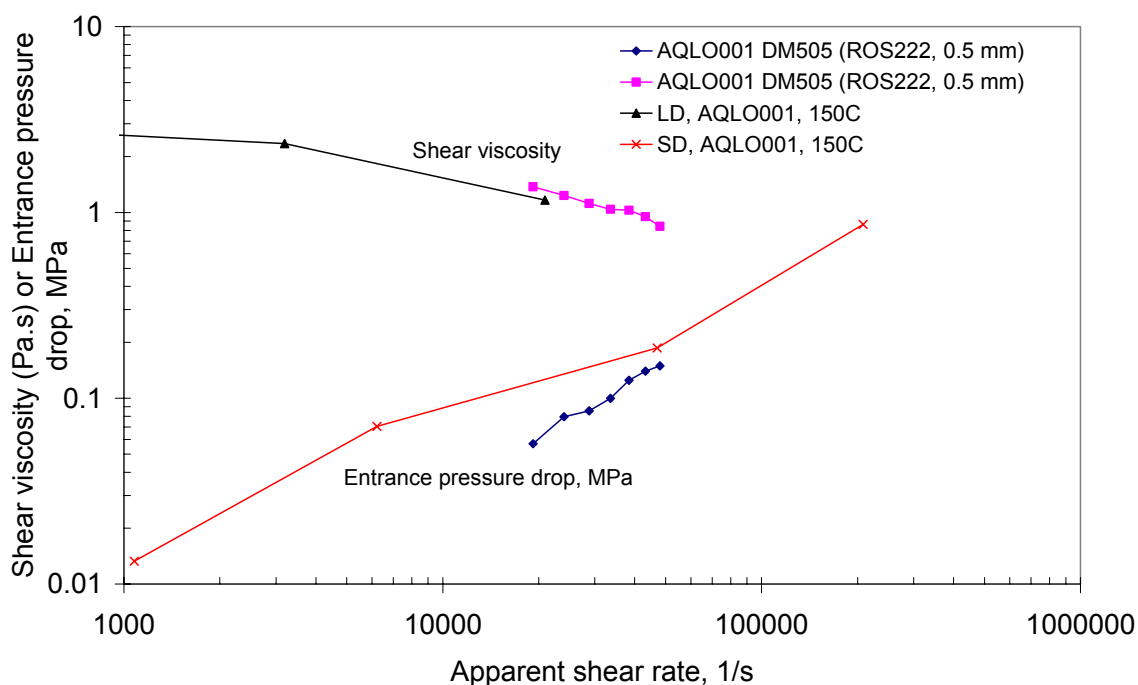


Figure 30: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for Dispomelt adhesive AQLO001 at 150 °C.

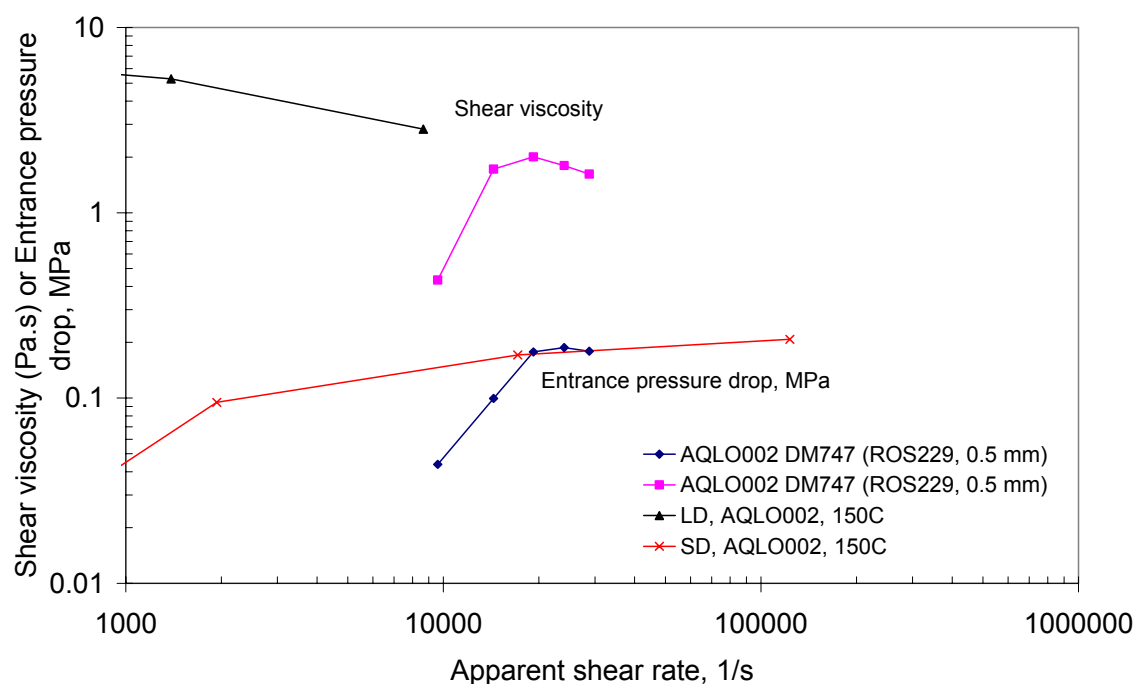


Figure 31: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for Dispmelt adhesive AQLO002 at 150 °C.

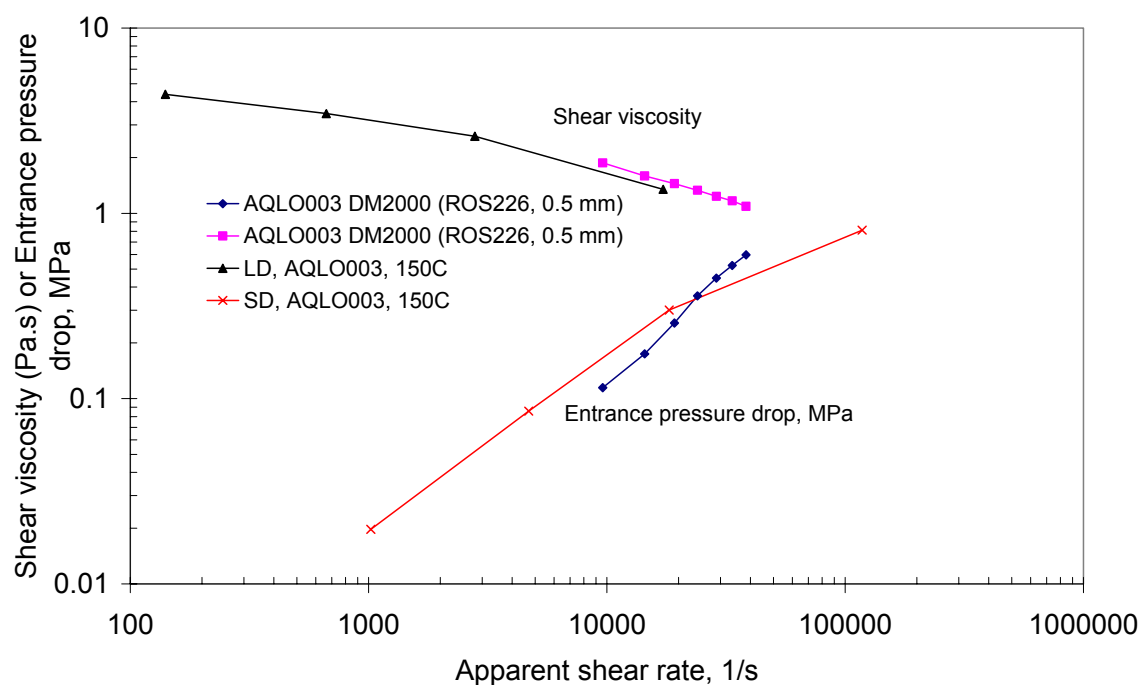


Figure 32: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for Dispmelt adhesive AQLO003 at 150 °C.

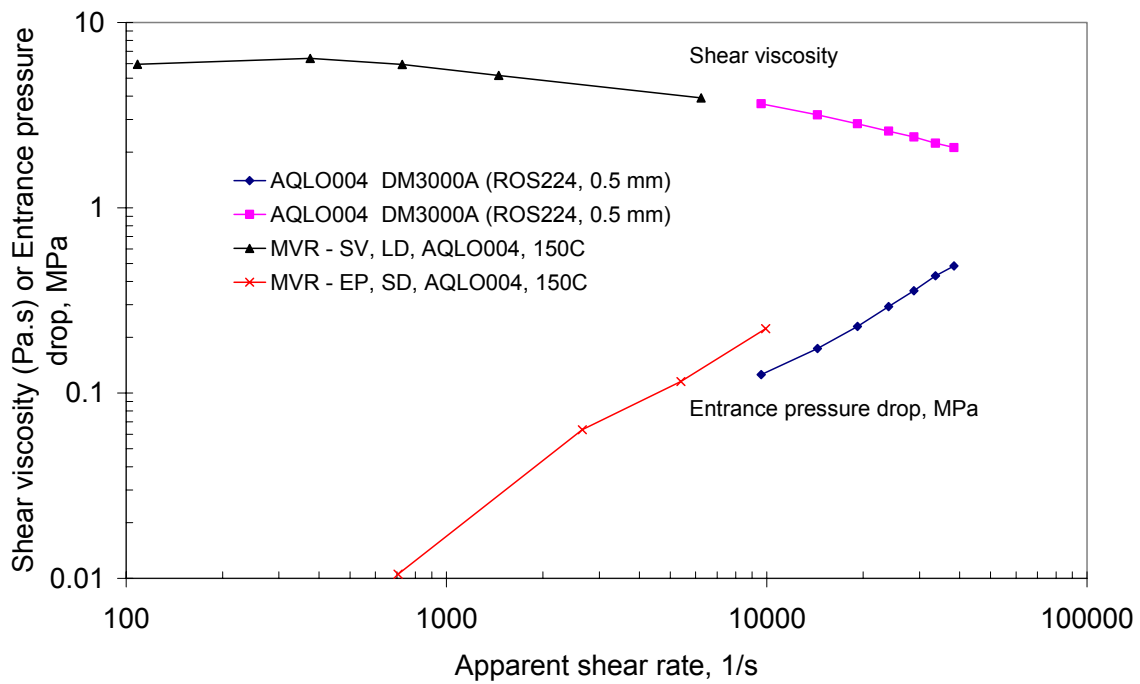


Figure 33: Comparison of shear viscosity and entrance pressure drop results obtained by melt flow rate testing and capillary extrusion rheometry for Dispomelt adhesive AQLO004 at 150 °C.

Appendices

Appendix 1: Analysis of melt flow rate testing

General

The melt volume flow rate (MVR) is given, according to ISO 1133 [11], by the expression

$$MVR = \left[\frac{t_{ref}}{t} \right] \ell \frac{\pi D^2}{4} \times 10^6 \quad (A1.1)$$

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

$$Q = \frac{MVR \times 10^{-6}}{600} \quad (A1.2)$$

or, substituting for MVR using equation A1.1, by

$$Q = \frac{\ell \pi D^2}{4t} \quad (A1.3)$$

The apparent shear rate $\dot{\gamma}_a$ in the melt at the wall of the die is given [3] by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (A1.4)$$

and thus in the melt flow rate die, substituting for Q using equation A1.3, by

$$\dot{\gamma}_a = \frac{\ell D^2}{R^3 t} \quad (A1.5)$$

where R is the radius of the die. Alternatively, the apparent shear rate is given, using equations A1.2 and A1.4, by

$$\dot{\gamma}_a = \frac{4(MVR / 600) \times 10^{-6}}{\pi R^3} \quad (A1.6)$$

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

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_a \quad (\text{A1.7})$$

or

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3} \quad (\text{A1.8})$$

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

$$Wg = \frac{P\pi D^2}{4} \quad (\text{A1.9})$$

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

$$P = \frac{4Wg}{\pi D^2} \quad (\text{A1.10})$$

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

$$P\pi R^2 = 2\pi RL\tau_a \quad (\text{A1.11})$$

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

Thus

$$\tau_a = \frac{PR}{2L} \quad (\text{A1.12})$$

or, substituting for P using equation A1.10, by

$$\tau_a = \frac{4Wg}{\pi D^2} \frac{R}{2L} \quad (\text{A1.13})$$

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 $\dot{\gamma}_a$

$$\underline{\eta}_a = \frac{\tau_a}{\dot{\gamma}_a} \quad (\text{A1.14})$$

Thus the apparent shear viscosity $\underline{\eta}_a$ is given, using equations A1.6 and A1.13, by

$$\underline{\eta}_a = \frac{300WgR^4}{D^2 L \times MVR \times 10^{-6}} \quad (\text{A1.15})$$

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.

Appendix 2: 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 [12]. 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

$$P_e = \frac{4Wg}{\pi D^2} \quad (\text{A2.1})$$

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

$$\dot{\gamma}_a = \frac{4(MVR_s / 600) \times 10^{-6}}{\pi R^3} \quad (\text{A2.2})$$

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 [12]:

$$P_e = P_o (\dot{\gamma}_a)^x \quad (\text{A2.3})$$

where P_o and x are constants.

Appendix 3: 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 as presented in Appendix 1. 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 [13]). 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

$$P = P_s + P_e \quad (\text{A3.1})$$

where P_s is the shear flow pressure drop along the length of the die and P is given by equation A1.10. Re-writing equations A1.10 and A1.15 in terms of the total pressure P yields

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

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 A3.2. Thus substituting P_s for P (using equations A1.10 and A3.1) yields

$$\eta_a = \left(\frac{4Wg}{\pi D^2} - P_e \right) \left[\frac{75\pi R^4}{L \times MVR_L \times 10^{-6}} \right] \quad (\text{A3.3})$$

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 A2.3, 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

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

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 A2.3. 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 A1.15 and **b)** the corresponding apparent shear rates using equations A1.5 or A1.6.
2. Fit a power-law model (equation A3.5) 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 .

$$\eta_a = \eta_o (\dot{\gamma}_a)^{n-1} \quad \text{A3.5}$$

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 A3.6, 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 A2.2.

$$P_e = \frac{4W_s g}{\pi D_s^2} - \frac{2L_s \eta_o (\dot{\gamma}_{a,s})^n}{R_s} \quad \text{A3.6}$$

4. Fit a power-law model (equation A2.3) 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 A3.3, where P_e is determined for the apparent shear rate occurring in the long die test (equation A1.6), and **b)** the apparent shear rates for the long die test using equation A1.6.
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.