

NPL REPORT MAT 3

**The use of the melt flow rate
method for moisture
sensitive materials and an
evaluation of the
uncertainties in melt flow
rate measurement**

**Martin Rides and
Crispin Allen**

NOT RESTRICTED

SEPTEMBER 2007

The use of the melt flow rate method for moisture sensitive materials and an evaluation of the uncertainties in melt flow rate measurement

Martin Rides and Crispin Allen
Industry & Innovation Division

ABSTRACT

The current melt flow rate method (ISO 1133) does not adequately cover the measurement of materials that degrade or further polymerise at the melt flow rate test conditions. Materials such as PET, PBT and PA containing absorbed water tend to degrade, sometimes rapidly, at processing temperatures. This will result in poor repeatability and reproducibility of melt flow rate results. The ISO Plastics Melt Rheology committee (TC61/SC5/WG 9) is currently developing a modified melt flow rate method for reliable measurement of moisture sensitive materials, e.g. PBT and PET, thereby providing an alternative to intrinsic viscosity measurements. The modified method controls more tightly the time-temperature history experienced by the material and thus the resultant variability in measured properties due to degradation. Results on a range of moisture sensitive materials are presented, demonstrating the effect of moisture content on measurements. Repeatability of measurements of melt flow rate were up to 10% (1 standard deviation). The need to tightly control the sample preparation (e.g. drying) and sample handling procedures is considered critical to reliable measurements of such materials. Furthermore, an evaluation of the uncertainties in the measurement using the current ISO 1133 is reported and recommendations for improved measurements are made.

© Crown copyright 2007
Reproduced with the permission of the Controller of HMSO
and Queen's Printer for Scotland

ISSN 1754-2979

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.

Approved on behalf of the Managing Director, NPL
by Susan Evans, Director, Industry and Innovation Division

CONTENTS

1.	Introduction.....	1
2.	The melt flow rate method.....	2
3.	Development of the melt flow rate method for materials that are sensitive to their time-temperature history	3
4.	Uncertainties in melt flow rate testing.....	4
5.	Materials and sample preparation	9
6.	Effect of moisture on the rheological behaviour of polymers	9
6.1	Preparation and testing regimes	9
6.2	Test results	10
6.2.1	Polypropylene	10
6.2.2	Poly(butylene terephthalate).....	15
6.2.3	Poly(ethylene terephthalate).....	21
6.2.4	Polyamides.....	27
7.	Discussion and conclusions	30
8.	Acknowledgements.....	31
9.	References.....	32
	Appendices.....	33
	Appendix 1: Nomenclature.....	33
	Appendix 2: Analysis of melt flow rate testing.....	34
	Appendix 3: Summary of constraints on melt flow rate testing for ISO 1133	38
	Appendix 4: Analysis of viscous heating in the flow	40
	Appendix 5: Comments on melt flow rate testing.....	42

1. Introduction

The melt flow rate method is widely used in the polymer industry and is likely to remain as a dominant tool for quality control and assurance. It is globally used for materials specification. The melt flow rate method, or melt flow index as it was historically known, has been in existence for several decades. It fulfils a requirement for rapid materials characterisation, specifically for checking the quality of the material and for assessing its processability, both of these in terms of the material's ease of flow. However, the melt flow rate also has its critics. The relevance of the low flow rate, shear flow dominated data obtained in melt flow rate testing to high rate moulding processes is questionable, and is discussed further in Appendix 5. Nevertheless, the method is widely used.

One of the limitations of the melt flow rate method is in the testing of materials that are unstable at their test temperature. The current melt flow rate standard ISO 1133 [1] does not adequately cover the measurement of materials that degrade at the test temperature resulting in poor repeatability and reproducibility of results. This is quite clearly stated in its scope. Examples of such materials are poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), polyamide 6 (PA6) and polyamide 66 (PA66). When these materials contain absorbed water and are heated to the temperatures used for their melt processing they will degrade, potentially very rapidly, due to the presence of the water. Thus test results for such materials will be very sensitive to their moisture content and the time-temperature history experienced during the test. Variations in, for example, the residence time are likely to affect results. Such materials need appropriate drying regimes to reduce their water content and handling regimes to reduce water absorption after drying to minimise degradation effects during testing.

Materials sensitive to moisture, e.g. PET, PBT, PA 6 and PA 66, are often characterised by their intrinsic viscosity; a technique in which the polymer is dissolved in a solvent e.g. 96% (m/m) formic acid, 90% (m/m) sulphuric acid, and m-cresol. The use of such solvents makes these intrinsic viscosity measurements potentially hazardous and costly, and thus undesirable. An alternative characterisation technique is required for these materials, but it needs to overcome the issue of the sensitivity of the material to moisture content.

To address this issue the ISO TC61/SC5/WG 9 Plastics Rheology Working Group is currently developing a method for reliable measurement of materials sensitive to their time-temperature history thereby providing an alternative to intrinsic viscosity measurements. The proposed method is based on the melt flow rate method but controls more tightly the time-temperature history experienced by the material and thus the resultant variability in the measured properties due to degradation. Standardized sample drying and testing conditions for such materials also need to be established. The method is described in more detail and results demonstrating the effect of moisture content on measurements are reported.

Furthermore, an evaluation of the uncertainties in the measurement using the current standard ISO 1133 is reported and recommendations for improved measurements are made.

2. The melt flow rate method

The melt flow rate method, put simply, is a measure of the quantity of material (pre-heated in a barrel) that is extruded through a die of a given length and diameter in a given time when a specified load is applied to the piston, Figure 1. The current standard ISO 1133 [1] covers two principal 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 in a given time is measured. Thus a single value is obtained, for either MFR or MVR, that characterises the flow behaviour of the material¹. 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 melt flow rate number the easier the material flows (i.e. lower viscosity). The term “melt flow rate” is used herein to indicate both MFR and MVR methods, with “mass” or “volume” used to differentiate between the two. An analysis of the melt flow rate method in its normal use is presented in detail in Appendix 2.

The MVR is preferred as a measure of the flow behaviour of a material as it is independent of its density and is thus a true measure of its flow properties. To illustrate this point, when comparing materials of different densities, e.g. two materials having different filler levels, the filler content will also affect the MFR value through its contribution to the density (the density of the filler usually being significantly greater than that of the polymer). Furthermore, to illustrate its perceived relative importance, MVR is specified by CAMPUS [2], a widely used database for plastics properties data, rather than MFR.

All MFR and MVR test conditions are tightly specified by the ISO standard on melt flow rate [1]. Some of the key specifications that influence the uncertainties in testing are presented in Appendix 3. The test parameters that can be varied by the operator are the load and temperature although for any given type of material, e.g. polypropylene, there is normally only one set of test conditions permitted: that set having been selected or optimised for that class of material and specified in the relevant materials specification standard (see clause 2 of [1]). As an exception, and indicative of the wider range of grades available, for polyethylene there are four permitted loads although the temperature is the same in each case. A table of test conditions is presented in ISO 1133 [1]. However, the criteria for selection of the loads are also tightly specified leaving the operator no choice.

The tight specification of the method, its simplicity and relatively low cost are its strengths for quality control and materials specification purposes. However, it is widely accepted within the industry that the method has limitations and these have been reviewed elsewhere [3-6] and discussed in Appendix 5.

The ISO standard for melt flow rate testing is ISO 1133: Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics [1]. The BS standard BSI 2782 - 720A is dual numbered with the ISO standard and is

¹ The MFR and MVR values are related by the density of the material, i.e. $MFR = \text{density} \times MVR$

identical. The other significant standard that specifies the procedure for melt flow rate testing is ASTM D1238 'Standard test method for flow rates of thermoplastics by extrusion plastometer' [7].

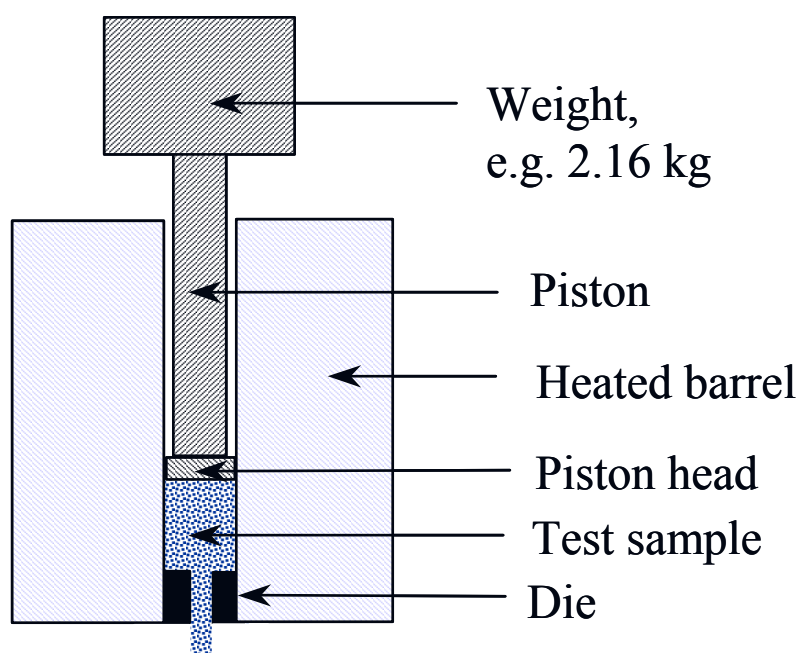


Figure 1: Schematic of a melt flow rate instrument.

3. Development of the melt flow rate method for materials that are sensitive to their time-temperature history

The proposed development of the melt flow rate method for testing materials that are sensitive to their time-temperature history, i.e. materials that either further polymerise, cross-link or degrade when exposed to the high temperatures at which they are tested, is based on controlling the time-temperature history of the test more tightly. This involves tighter specifications, primarily of the time permitted for charging the barrel and the time permitted for extruding the material during the test. The latter restriction is achieved by constraining the melt flow rate range that can be tested by the method to values greater than $10 \text{ cm}^3/10 \text{ minutes}$ (or $\text{MFR} > 10 \text{ g}/10 \text{ minutes}$) and preferably less than $40 \text{ cm}^3/10 \text{ minutes}$ (or $\text{MFR} < 40 \text{ g}/10 \text{ minutes}$). The lower constraint ($10 \text{ cm}^3/10 \text{ minutes}$) results in an extrusion time of not more than ≈ 130 seconds and the upper constraint ($40 \text{ cm}^3/10 \text{ minutes}$) of not less than ≈ 30 seconds. Measurements of high MVR materials would reduce the extrusion time which perhaps would not be a significant issue in terms of the effect on the “degraded” state of the material but the errors due to the high rate, short time of testing would increase. Testing of materials with MVR values lower than $10 \text{ cm}^3/10 \text{ minutes}$ (or $\text{MFR} < 10 \text{ g}/10 \text{ minutes}$) would result in longer extrusion times that could result in degradation of the material during the test. Thus, due to acceptable differences in procedures used from one laboratory to another, poorer reproducibility would almost certainly result.

In addition to controlling the time-history of the test more tightly, the proposed development also controls the test temperatures more tightly by specification of tighter tolerances on temperature variations in the barrel with respect to both position and time. By more tightly specifying these tolerances the rate of cross-linking or degradation will be more consistent between instruments and the effect on uncertainties due the temperature sensitivity of the material will be reduced thereby decreasing the overall uncertainty.

The intention of the proposed development is to produce a method for MVR/MFR testing of materials that are time-temperature history sensitive that has comparable repeatability and reproducibility to the existing method (ISO 1133 [1]) for stable materials.

4. Uncertainties in melt flow rate testing

Following a rigorous approach, used for example by Kandil [8], the combined uncertainty $u_c(y)$ of the measurand y (the quantity to be measured) can be determined from the partial derivatives of the function and the uncertainties in the parameters. Assuming that the individual uncertainty sources are uncorrelated, the combined uncertainty $u_c(y)$ can be computed using the root sum squares:

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

where c_i is the sensitivity coefficient (partial derivative) associated with an input quantity x_i and $u(x_i)$ is the standard uncertainty in that quantity. The standard uncertainty is obtained by dividing the quantity range, defined by a standard deviation value or limits, by a divisor where the value of the divisor is dependant on the distribution of that quantity (e.g. normal or rectangular distribution).

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

An assessment of the uncertainties for measurement of MFR and MVR is presented. Only the uncertainties due to the parameters of time and distance travelled by the piston have been taken into account as these are considered to contribute most significantly to the rapid growth in the uncertainties under certain testing conditions. A melt density of 1 g/cm^3 is assumed in the calculation of the uncertainties in MFR.

The melt flow rate method is complicated by the various criteria used in ISO 1133 [1] to specify the measurement envelope. These criteria comprise of specifications of permitted parameter ranges or are effectively imposed by specification of the resolution to which the various parameters are measured. These criteria are summarised in Appendix 3. The constraints on the operating envelope of the melt flow rate method are presented in diagrammatic form in Figures 2 and 3 for MVR and MFR respectively, following Fahrenholz [9]. The figures present lines of constant MVR or MFR that, due to the proportionality of piston displacement and time, have a gradient of 1. Constraints

imposed by the instrument's resolutions are given by thick blue lines, constraints imposed by the specification are given by thick red lines and constraints imposed by the requirement for three measurements per barrel charge are given by thick pink lines. These constraints, when plotted on a piston displacement versus times plot, provide a pictorial representation of the operating envelope for melt flow rate testing, Figures 2 and 3. The "Recommended test criteria, ISO 1133" plotted in each of Figures 2 and 3 gives the recommended operating conditions, in accordance with ISO 1133.

These figures when examined in conjunction with Figures 4 – 7, which present MVR and MFR values and their relative uncertainties as functions of piston displacement and time, can be used to optimise the test conditions by minimising the uncertainties in measurements. For MVR measurements performed in accordance with ISO 1133 [1] the maximum relative uncertainty (1 standard deviation) was estimated to be of the order of 13%, Figure 5, and for MFR it was 19%, Figure 7. These uncertainties are based solely on the contributions due to the uncertainties in the displacement and time components of the measurement and thus assume that the uncertainties in temperature, linear dimension and load and the effect of friction between the barrel and piston are negligible. These diagrams indicate that it is important to operate in the top-right hand corner of the envelope of testing conditions to minimise the uncertainties in measurement. By operating in this region the repeatability and reproducibility of results are likely to be improved.

It is noted that there is an inconsistency between the Method A requirement (MFR) which stipulates that the extrudate cut-off length should preferably be between 10 mm and 20mm (equivalent to piston displacements of between 0.48 mm and 0.96 mm) whilst simultaneously presenting contrary recommended cut-off time intervals. Furthermore, neither the recommended cut-off intervals nor the recommended extrudate lengths minimise the uncertainties in the measurement as neither occupy the top right hand corner of the test envelope. Similarly, it is noted that the recommended operating conditions (specified by the cut-off intervals) in MVR testing do not permit three measurements to be made using a single barrel charge, although the uncertainties are minimised due to operation in the top right hand corner.

These diagrams can be used to optimise the testing conditions to minimise the uncertainties in testing. However, due to the complexity of the specification of the testing conditions, the different resolutions with which each parameter has to be measured depending on its magnitude, and the different temperature sensitivities of various polymers, it is recommended that an uncertainty analysis should be carried out for each material to identify the uncertainties associated with the results.

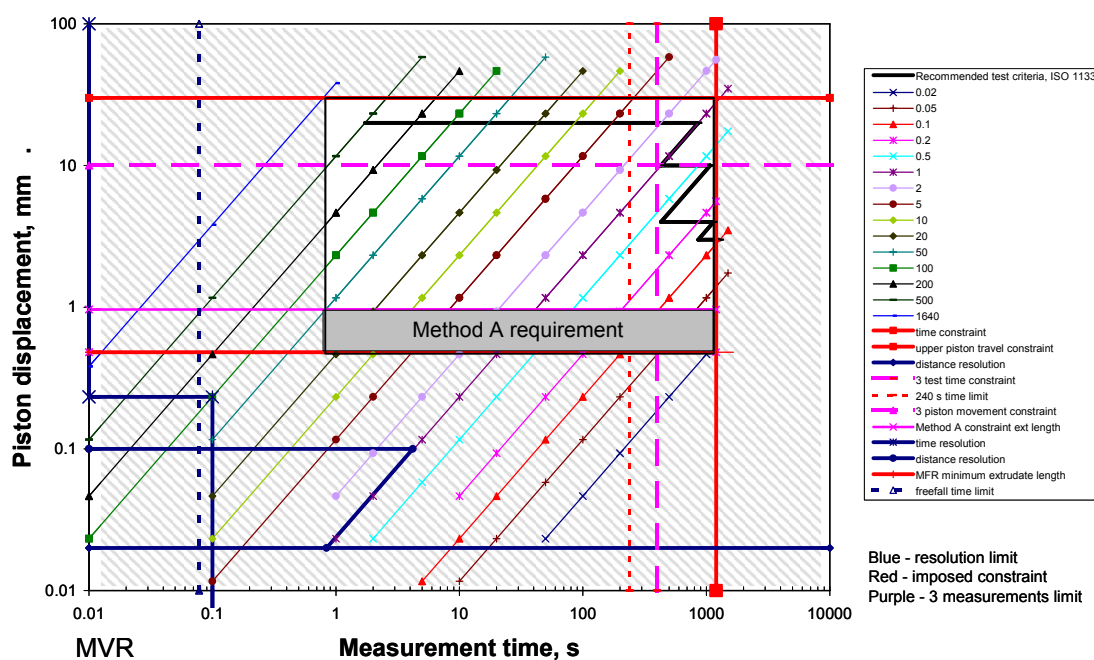


Figure 2: MVR constraints diagram (light-grey outer shaded area indicates region outside measurement range).

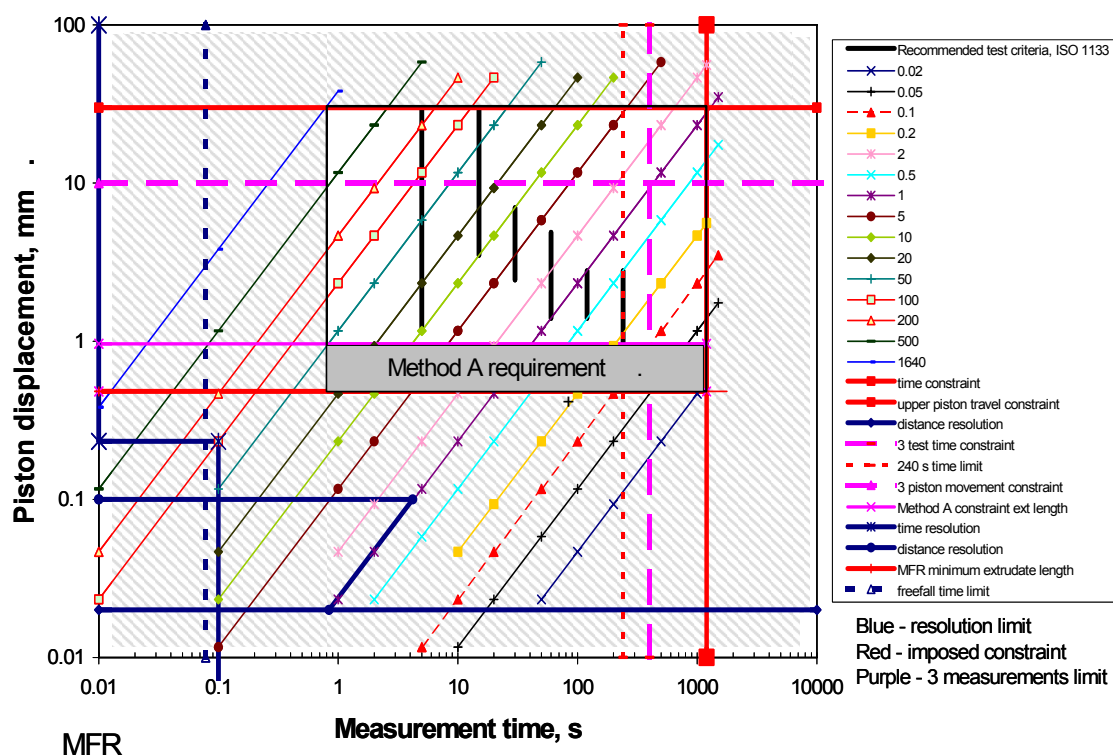


Figure 3: MFR constraints diagram (light-grey outer shaded area indicates region outside measurement range).

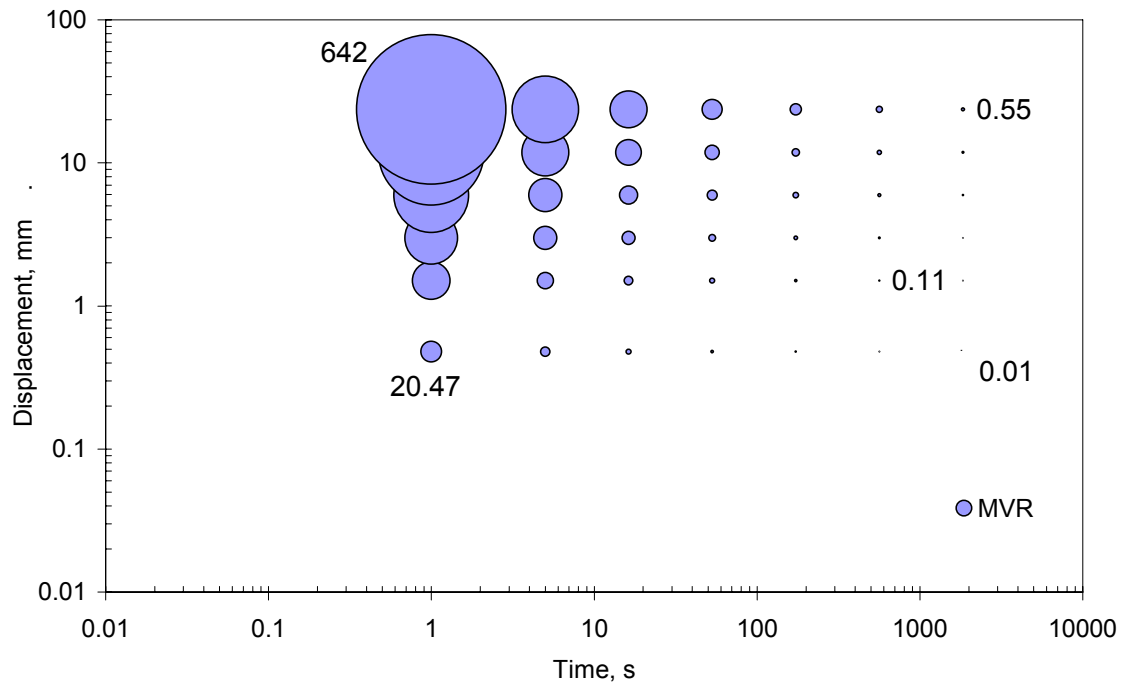


Figure 4: MVR values as a function of piston displacement and time.

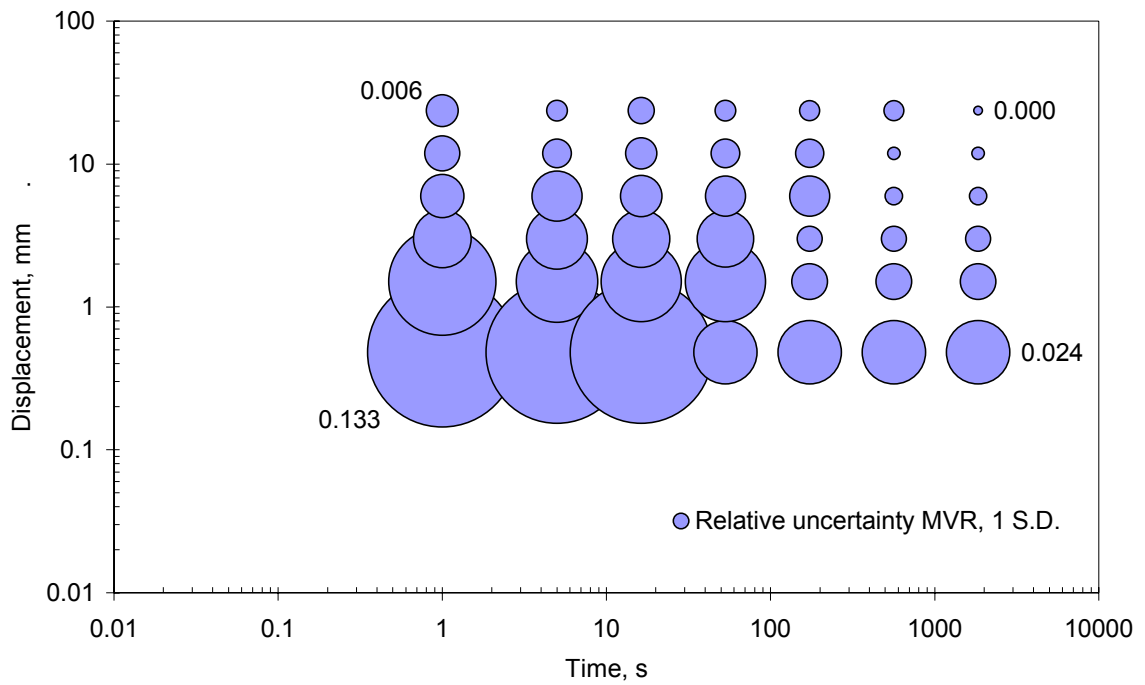


Figure 5: MVR relative uncertainties as a function of piston displacement and time (1 standard deviation values presented).

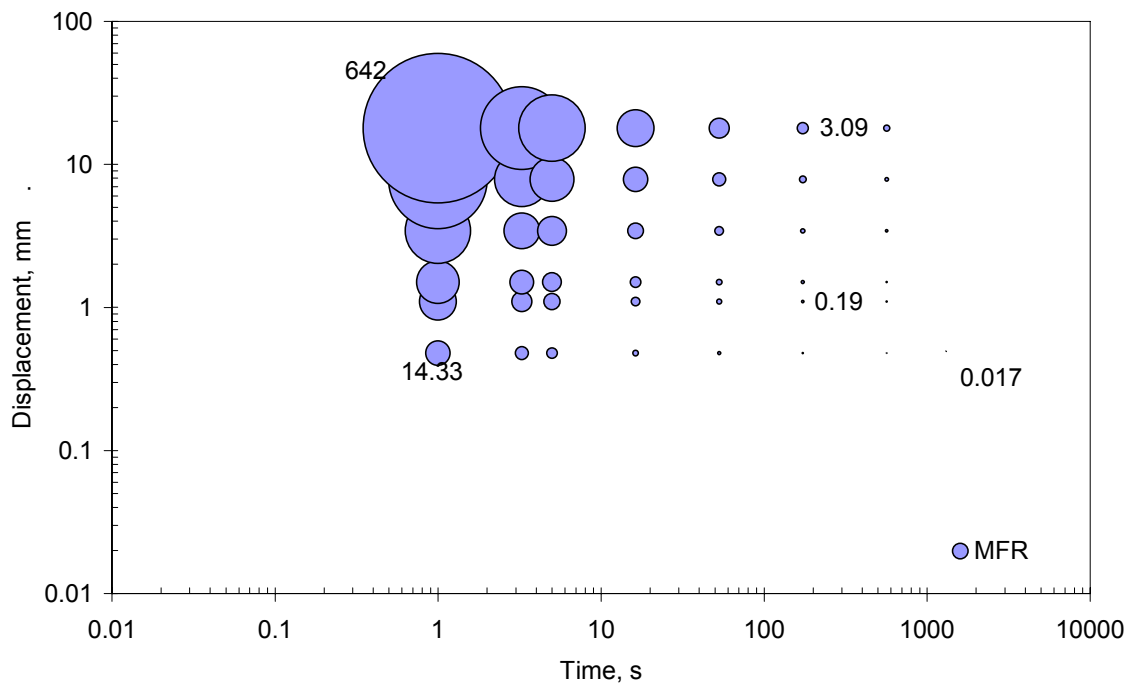


Figure 6: MFR values as a function of piston displacement and time.

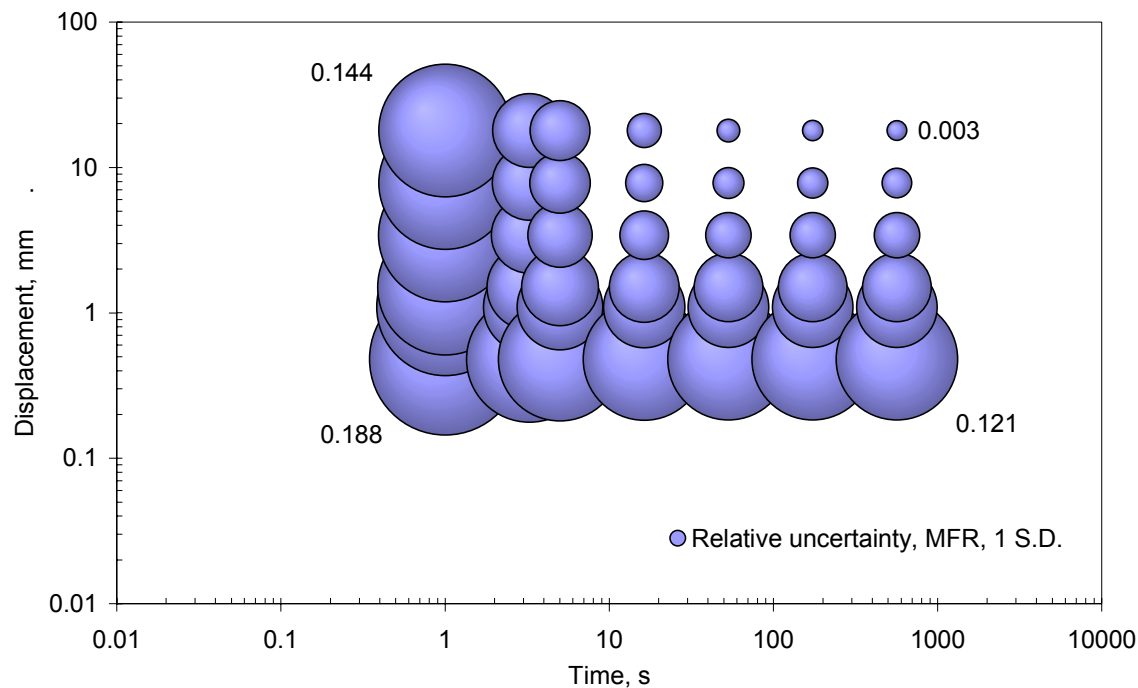


Figure 7: MFR relative uncertainties as a function of piston displacement and time (1 standard deviation values presented).

5. Materials and sample preparation

In this study of melt flow rate testing of time-temperature history sensitive materials, three materials have been investigated in detail: a poly(ethylene terephthalate) (PET), a fibre-filled poly(butylene terephthalate) (PBT) and a polypropylene (PP). The first two are materials that typically are moisture sensitive, i.e. they are likely to degrade at the high temperature typical of processing (and thus melt flow rate test temperatures) when they contain absorbed moisture. The third material, PP, was selected as a relatively stable material that is not moisture sensitive and thus would provide a baseline against which comparisons for the other moisture sensitive materials could be made. A further three moisture sensitive materials (two polyamide 6 materials and a polyamide 66 material) were tested in addition to the above materials to help determine the repeatability of melt flow rate measurements. Details of these materials and their normal melt flow rate test conditions are given in Table 1. These materials have also been used in an international intercomparison, led by NPL and in support of the development of ISO 1133 for time-temperature history sensitive materials, the results of which will be presented in a later publication.

Material	Grade	Normal test conditions	Drying conditions
PP	Polypropylene	2.16 kg, 230 °C	Samples not dried
PBT	Fibre-filled poly(butylene terephthalate)	2.16 kg, 250 °C	Vacuum oven 90 °C
PET	Poly(ethylene terephthalate)	5 kg, 280 °C	Vacuum oven 130 °C
PA66	Polyamide 66	2.16 kg, 275 °C	Vacuum oven 80 °C
PA6(1)	Polyamide 6	1.2 kg, 250 °C	Vacuum oven 90 °C
PA6(2)	Filled polyamide 6	5 kg, 275 °C	Vacuum oven 90 °C

Table 1: Materials, sample preparation and testing conditions.

6. Effect of moisture on the rheological behaviour of polymers

6.1 Preparation and testing regimes

Samples of the materials were dried in a vacuum oven using the drying temperatures specified in Table 1 but using various drying times to obtain samples of varying moisture content. Weighing of samples was performed to estimate the moisture content of the materials as a function of the drying regime. After drying, the samples were immediately stored in sealed glass bottles and were normally tested as soon as possible to limit their moisture uptake after drying.

The PP, PBT and PET samples were subjected to melt volume flow rate and oscillatory rheometry testing at the conditions specified in Table 1. The samples were also tested at a temperature that was 5 °C higher in order to evaluate the temperature sensitivity of their behaviour. The PA6 and PA66 samples were subjected to melt flow rate tests only.

Melt flow rate testing was performed broadly in accordance with ISO 1133 [1] using a Ray-Ran Advanced Microprocessor Systems 5MPCA melt flow rate instrument. The

instrument uses a displacement transducer to measure the piston travel from which melt volume flow rate results are derived. Using this transducer, each test run was divided into 20 separate test intervals. Results are presented for each of these test intervals, and are also averaged over the 20 test intervals. The standard die of nominally 8 mm length and 2.095 mm diameter was used in all tests.

The oscillatory rheometry measurements were performed broadly in accordance with ISO 6721-10 [10] using a TA Instruments AR-G2 rheometer with 20 mm diameter parallel plates using a strain amplitude of 1% and a plate gap of approximately 0.5 mm.

6.2 Test results

6.2.1 Polypropylene

Results for the PP are summarised in Figures 8-12 and Tables 2-4. Occasional spurious results primarily but not entirely associated with initial transient results covering the first few intervals were observed, Figure 8. The transients at the beginning of the test are considered to be more apparent due to the low viscosity / high melt flow rates of the materials, and are probably due to trapped air at the die entry causing rapid acceleration of the piston. Such data have been omitted from the remaining results presented, this being identifiable from an absence of the data points in the plots. Such data have also not been included in calculating average values. From the results it is quite apparent that the PP behaviour is relatively independent of the drying process, Figure 9, as expected. The variation in the average MVR values was up to $\pm 2\%$ with a standard deviation of 1.3%, which is considered reasonable for such a high MVR material. The results, Figure 9 and presented in Figure 11 with best-fit straight lines, suggest that there is possibly a slight decrease in melt flow rate as the test progresses, but this effect may be due to initial experimental transients rather than a real variation in material behaviour. The effect of temperature on melt flow rate is shown in Figure 10 and Table 3 which indicates a sensitivity of between 1 %/°C and 2 %/°C.

The effect of temperature on degradation is clearly seen in the oscillatory rheometry results, Figure 12, where there is approximately a 20% decrease in viscosity (proportional to the shear loss modulus G'') over a period of 30 minutes (1800 seconds). This is significantly longer than the melt flow rate test duration for a material of MVR of approximately 60 cm³/10 minutes, which would be of the order of 5 minutes equilibrating time plus the actual extrusion time of 25 seconds, and thus a total test time of 325 seconds. The initial transient behaviour observed in Figure 12 for times less than approximately 500 s is due to heating of the sample and thus the thermal effects on viscosity – it was chosen to log the data as soon as possible after loading the sample rather than wait for thermal equilibrium to be achieved. The time interval from the start of loading the sample between the plates of the rheometer and the start of data logging was up to ≈ 60 seconds (broadly equivalent to that in melt flow rate testing). The oscillations in the temperature due to control of the heater are clearly apparent in the plot. The absolute values of the shear loss modulus G'' curves are considered unreliable due to the need to load the sample quickly into the instrument so that the specimen was not subjected to a significant time-temperature history before data could be logged. This resulted in a specimen geometry that was not as well controlled as is normally the case, with possible under filling or over filling with poor trimming off of

the specimen occurring. This was particularly the case for the filled materials (PBT and PA6(2)) where the specimen geometry was affected by the filler resulting in possible non-repeatable filling between tests. Nevertheless, the curves clearly show that at the test temperature at 235 °C the material degraded more rapidly than at 230 °C. The amount of variation that occurred during the extrusion part of the test of 25 seconds was of the order of 1%, Figure 12, and thus represented a relatively small variation. The reduction in G'' values would correspond to an increase in MVR, which was not observed in the MVR testing.

These results set limits on the repeatability that one might expect from the method when testing high melt flow rate materials.

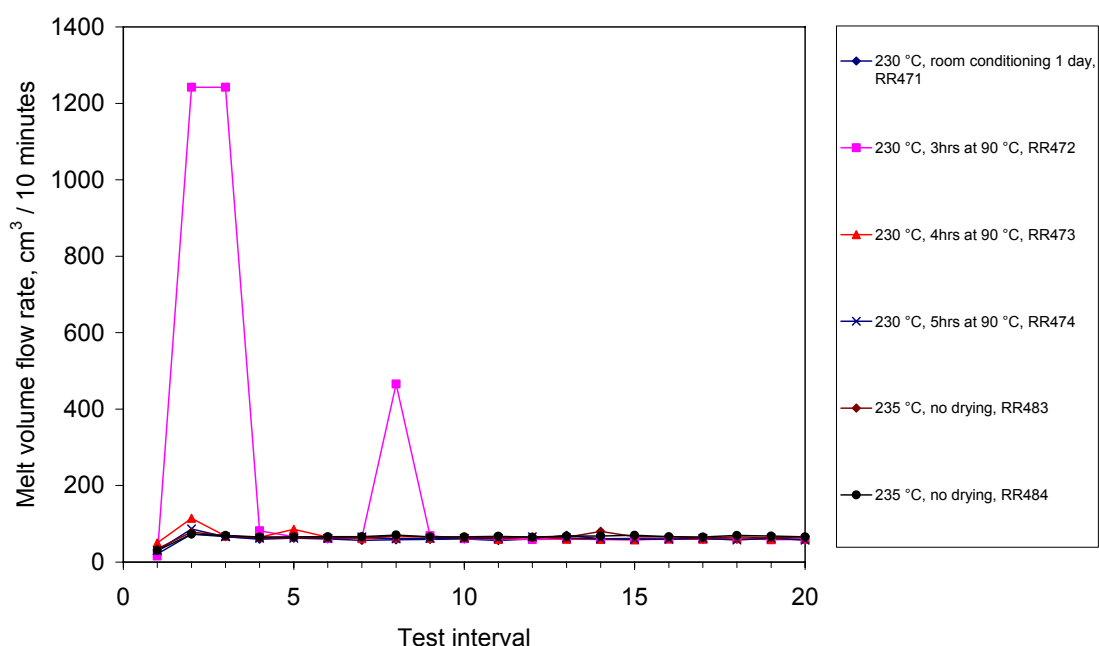


Figure 8: Initial transient results observed in melt volume flow rate testing of PP. 2.16 kg load.

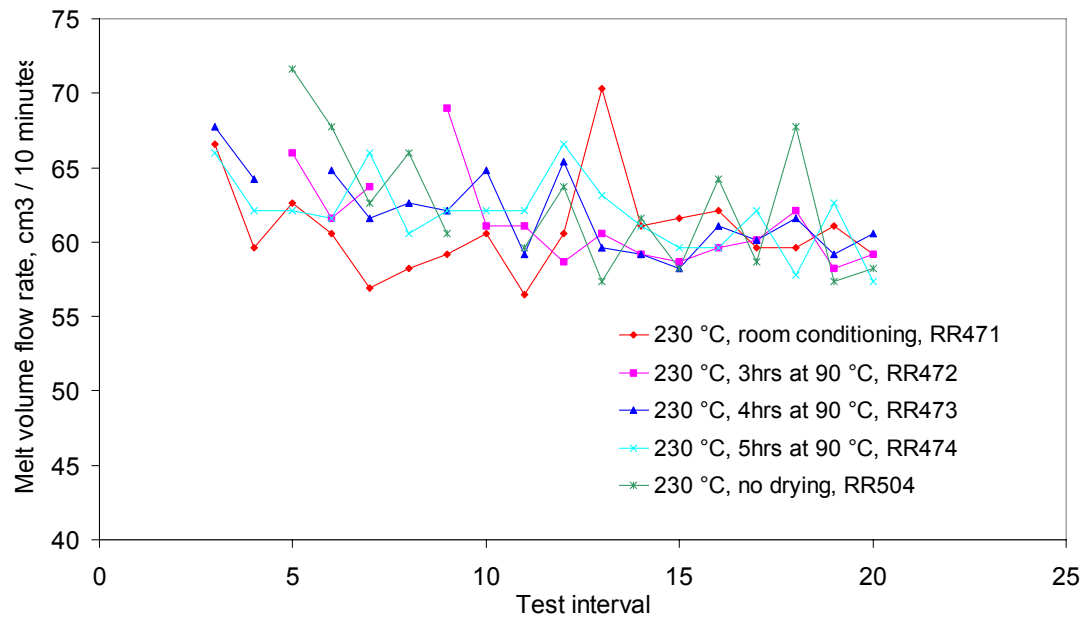


Figure 9: Effect of drying conditions on melt volume flow rate values for PP. 2.16 kg load.

Test temperature, drying conditions, test reference	MVR, cm ³ /10 minutes	% of average*
230 °C, room conditioning 24hrs, RR471	60.89	98.5
230 °C, no drying, RR504	63.07	102.0
230 °C, 3hrs at 90 °C, RR472	61.25	99.1
230 °C, 4hrs at 90 °C, RR473	61.89	100.1
230 °C, 5hrs at 90 °C, RR474	61.92	100.2
Average MVR	61.80	100.0*
Repeatability, 1 standard deviation	0.83	1.3%

Table 2: Effect of drying conditions on melt volume flow rate values for PP. 2.16 kg load.

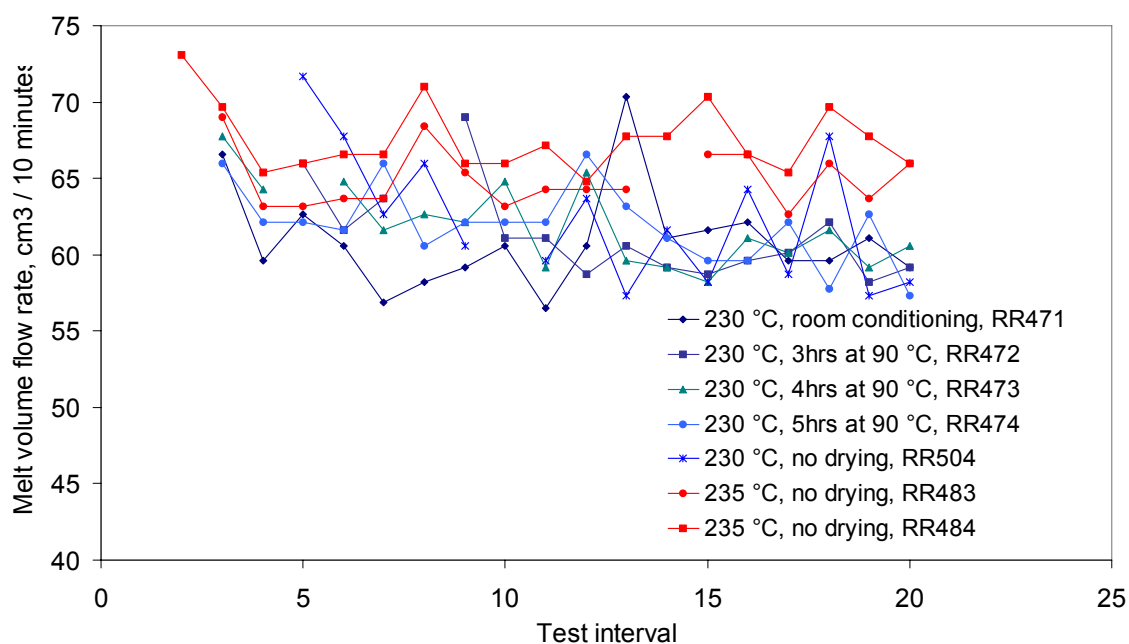


Figure 10: Effect of temperature on melt volume flow rate of PP. 2.16 kg load.

Test temperature, drying conditions, test reference	MVR, cm ³ /10 minutes	% of average*
230 °C, room conditioning 24hrs, RR471	60.89	98.5
230 °C, no drying, RR504	63.07	102.0
230 °C, 3hrs at 90 °C, RR472	61.25	99.1
230 °C, 4hrs at 90 °C, RR473	61.89	100.1
230 °C, 5hrs at 90 °C, RR474	61.92	100.2
Average MVR	61.80	100.0*
Repeatability, 1 standard deviation	0.83	1.3%
235 °C, no drying, RR483	64.93	105.1
235 °C, no drying, RR484	67.53	109.3

Table 3: Effect of temperature on melt volume flow rate of PP. 2.16 kg load.

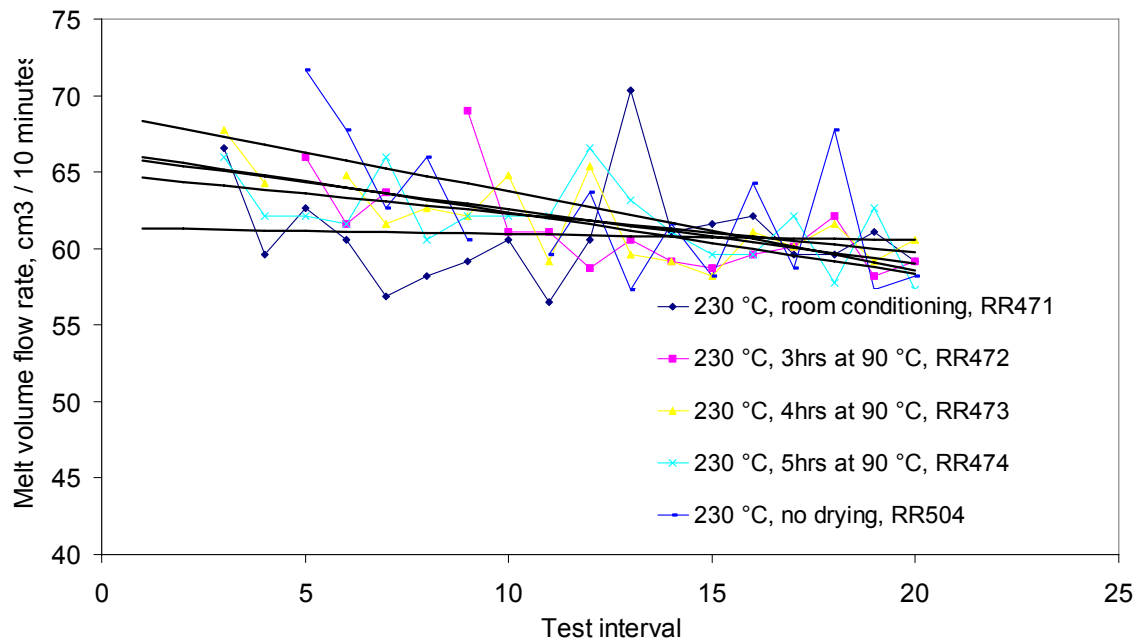


Fig 11: Effect of duration of test on PP at 230 °C with a 2.16 kg load.

Test No.	RR471	RR472	RR473	RR474	RR504	Average
Average MVR, cm ³ /10 minutes	60.9	61.3	61.9	61.9	63.1	61.6
Standard deviation, cm ³ /10 minutes	3.3	3.0	2.7	2.5	3.5	3.2
Standard deviation, %	5.3	4.9	4.4	4.1	5.6	5.1

Table 4: Repeatability of MVR measurements of PP at 230 °C with a 2.16 kg load.

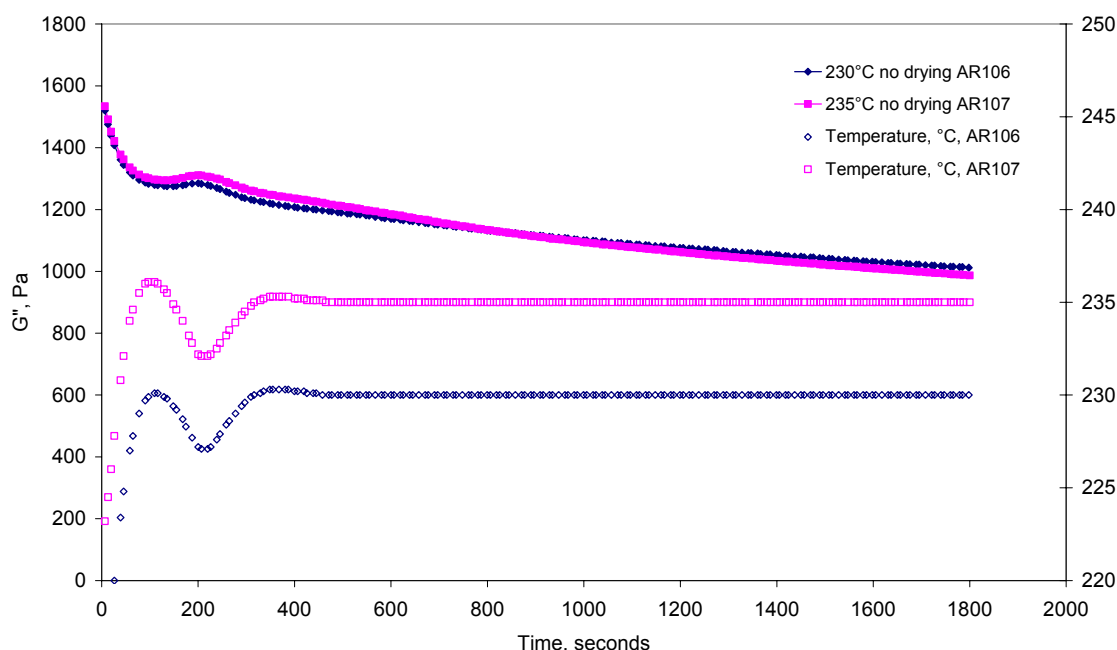


Figure 12: Effect of test time on measurement of shear loss modulus G'' of PP.

6.2.2 Poly(butylene terephthalate)

The results for PBT are presented in Figures 13 to 17 and Tables 5 to 7. Very large transients were observed with in one case a transient lasting for a significant proportion of the test duration, Figure 13. With that exception the transients were restricted to the start of the test.

The effect of drying of the PBT was negligible, Figure 15, the scatter in results being comparable to that obtained for samples of the same drying conditions, Figure 16. Drying the sample for 20 hours at 90 °C in a vacuum oven resulted in a 0.043% weight loss, presumably due to moisture loss, suggesting a moisture content in excess of 430 ppm in the as-received sample. Drying for 4 days in a vacuum oven at 80 °C resulted in the same weight loss suggesting that the drying procedure of 20 hours at 90 °C was sufficient. This was considered to be due to the fact that the material had been packaged in a dry state in moisture proof bags. This was confirmed by exposure of a sample to the laboratory atmosphere for 24 hours prior to testing, resulting in an increase in melt flow rate by approximately 15% compared with the as-received sample, Figure 14 and Table 5. This illustrates that precautions need to be taken to prevent water absorption by the polymer.

The effect of temperature on melt flow rate results in presented in Figure 15. For the PBT the temperature dependence of MVR was approximately 3 %/°C, and the repeatability of measurements was of the order of 3% (1 standard deviation), Table 6. This will include a contribution due to variations in the moisture content of the polymer and factors that may affect it.

There was no significant variation in melt flow rate of PBT with test duration, Figure 16. For this material with a MVR of 20 cm³/10 minutes the extrusion period was of the order of 75 seconds (300 s to 375 s), with a total test duration including charging the

barrel of ≈ 435 seconds. The oscillatory rheometry tests indicate that there is little variation in the shear loss modulus G'' in this time interval, Figure 18. Again a greater change in G'' occurs at the higher temperature of 255 °C compared with 250 °C.

The repeatability of melt flow rate testing of the PBT was estimated to be of the order of 6% (1 standard deviation).

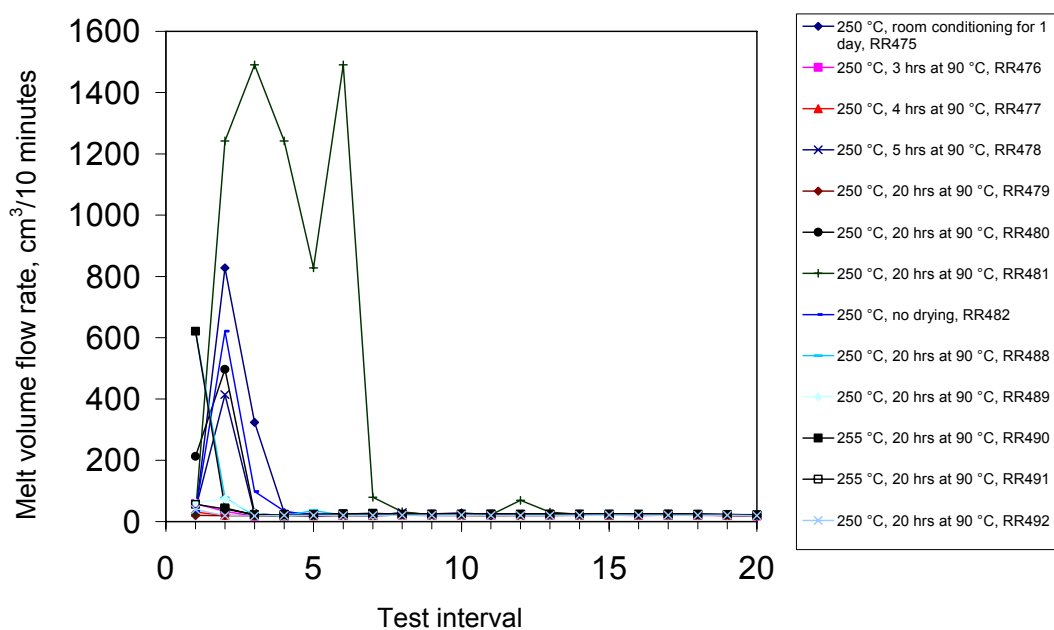


Figure 13: Initial transient results observed in melt volume flow rate testing of PBT. 2.16 kg load.

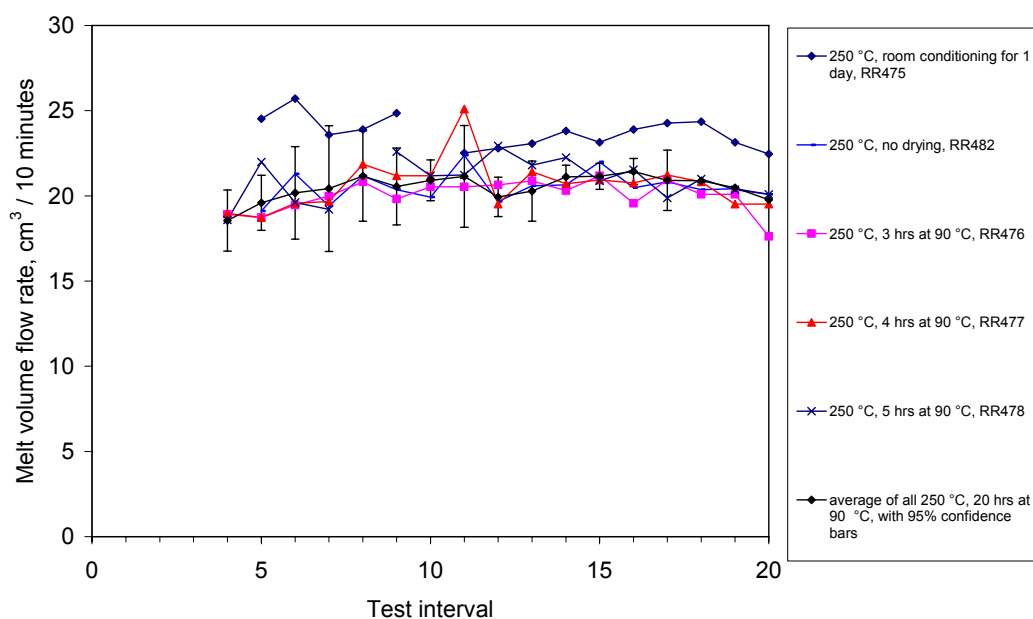


Figure 14: Effect of drying conditions on melt volume flow rate values for PBT (averaged values with 95% confidence bars for 20 hours drying condition). 250 °C and 2.16 kg load.

Test temperature, drying conditions, test reference	MVR, cm ³ /10 minutes	% of average*
250 °C, 20 hrs at 90 °C, RR479	19.96	96.7
250 °C, 20 hrs at 90 °C, RR480	21.25	103.0
250 °C, 20 hrs at 90 °C, RR481	21.42	103.8
250 °C, 20 hrs at 90 °C, RR488	20.76	100.7
250 °C, 20 hrs at 90 °C, RR489	19.95	96.7
250 °C, 20 hrs at 90 °C, RR492	20.43	99.0
Average MVR	20.63	100.0*
250 °C, room conditioning 24hrs, RR475	23.73	115.1
250 °C, no drying, RR482	20.55	99.6
250 °C, 3 hrs at 90 °C, RR476	20.01	97.0
250 °C, 4 hrs at 90 °C, RR477	20.63	100.0
250 °C, 5 hrs at 90 °C, RR478	20.94	101.5

Table 5: Effect of drying conditions on melt volume flow rate values for PBT (averaged values with 95% confidence bars for 20 hours drying condition). 250 °C and 2.16 kg load.

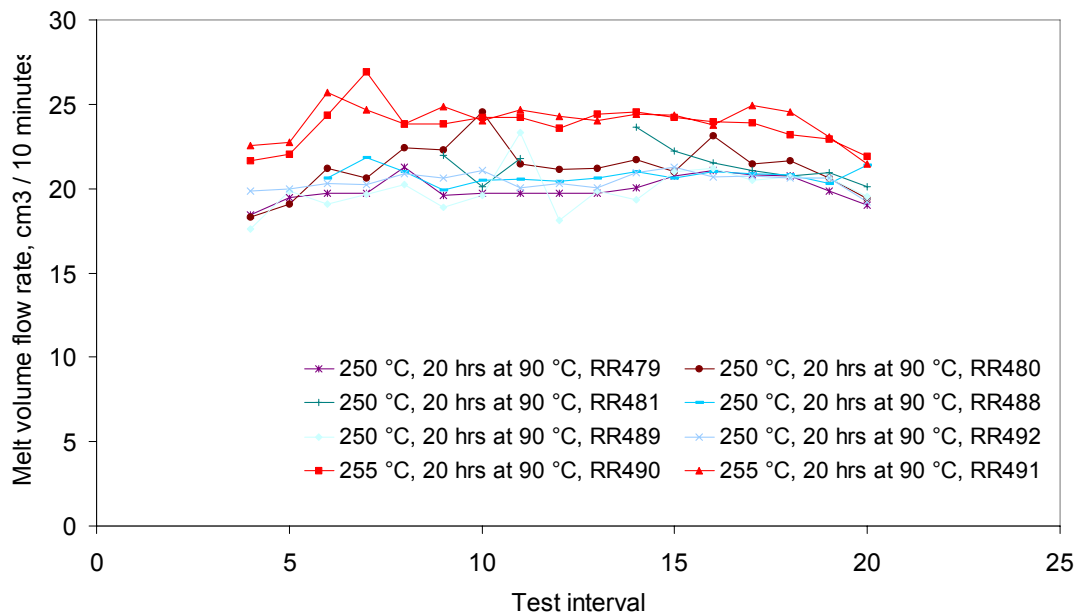


Figure 15: Effect of temperature on melt volume flow rate values for PBT with 2.16 kg load.

Effect of temperature on PBT	MVR, cm ³ /10 minutes	% of average*
250 °C, 20 hrs at 90 °C, RR479	19.96	96.7
250 °C, 20 hrs at 90 °C, RR480	21.25	103.0
250 °C, 20 hrs at 90 °C, RR481	21.42	103.8
250 °C, 20 hrs at 90 °C, RR488	20.76	100.7
250 °C, 20 hrs at 90 °C, RR489	19.95	96.7
250 °C, 20 hrs at 90 °C, RR492	20.43	99.0
Average MVR	20.63	100.0*
Repeatability, 1 standard deviation	0.63	3.0
255 °C, 20 hrs at 90 °C, RR490	23.75	115.1
255 °C, 20 hrs at 90 °C, RR491	23.99	116.3

Table 6: Effect of temperature on melt volume flow rate values for PBT with 2.16 kg load.

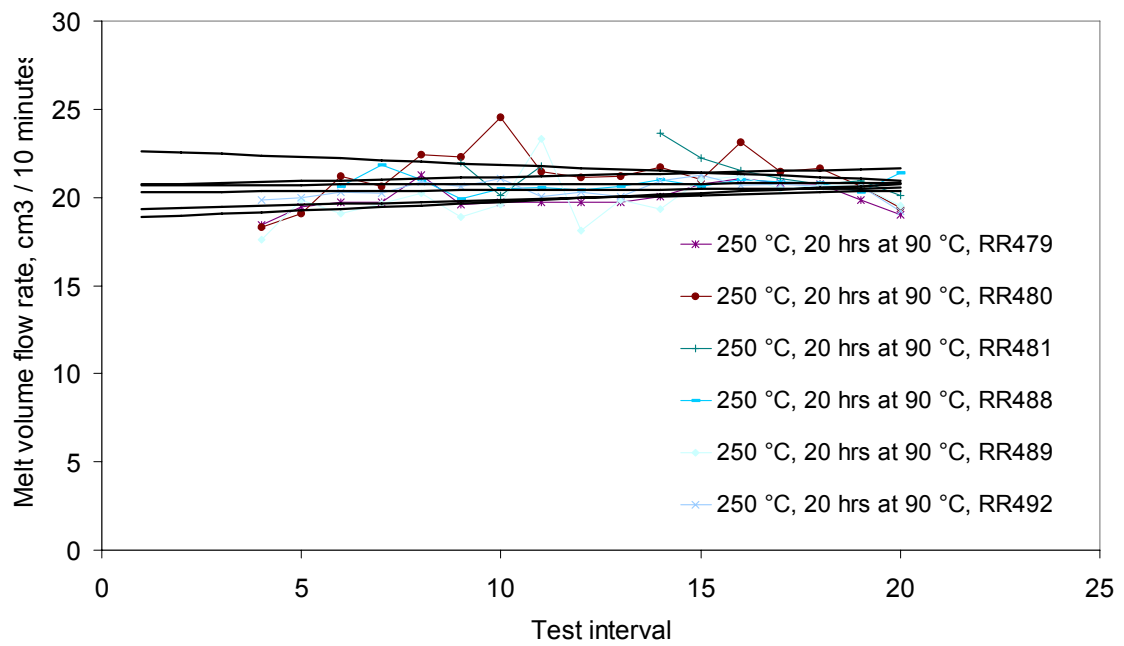


Figure 16: Effect of test duration on MVR of PBT at 250 °C with 2.16 kg load. Drying conditions: 90 °C for 20 hours.

Test No.	RR479	RR480	RR481	RR488	RR489	RR492	Average
Average MVR, cm ³ /10 minutes	20.0	21.3	21.4	20.8	20.0	20.4	20.6
Standard deviation, cm ³ /10 minutes	0.7	1.5	1.1	0.5	1.3	0.5	1.1
Standard deviation, %	3.7	7.0	5.0	2.2	6.5	2.5	5.5

Table 7: Repeatability of MVR measurements of PBT at 250 °C with 2.16 kg load. Drying conditions: 90 °C for 20 hours.

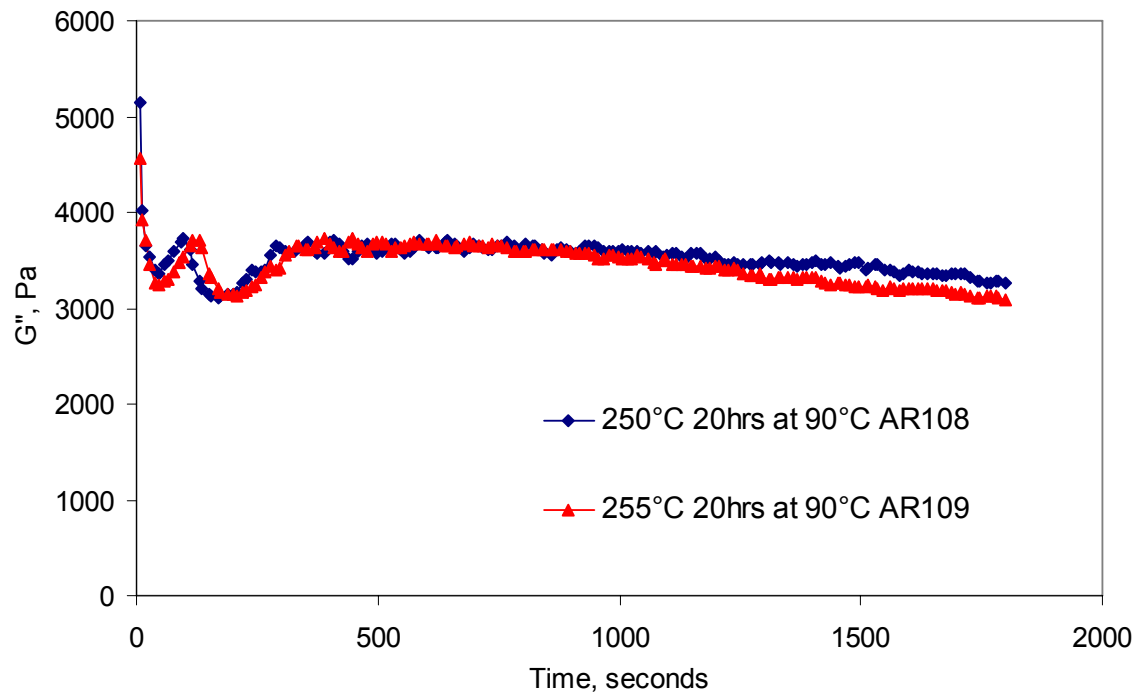


Figure 17: Effect of test temperature and time on measurement of shear loss modulus G'' of PBT.

6.2.3 Poly(ethylene terephthalate)

The PET material exhibited a very significant effect of moisture on MVR values. For a sample conditioned in the laboratory atmosphere for 24 hours prior to tests melt flow rate values of the order of $1000 \text{ cm}^3/10 \text{ minutes}$ were obtained, Figure 18. The effect of drying on the behaviour of the PET was quite marked, Figure 19, with MVR values decreasing with longer drying periods.

A 3 hour drying period resulted in MVR values approximately 45% higher than obtained for a 5 hour drying period. A 4 hour drying period resulted in MVR values that were approximately 20% higher than for the 5 hour drying period. Drying the PET for 3 hours at 130°C resulted in a 0.235% weight loss, and for 5 hours at 130°C a 0.247% weight loss occurred. The latter value was the same as when drying for 22 hours at 130°C and also 4 days at 80°C . These drying measurements suggest that 5 hours was sufficient to dry the material, and that the as-received material had a moisture content in excess of 0.247% (2470 ppm).

It was observed that even short exposures of the material to the atmosphere caused significant variations in MVR value: tests RR505, RR506 and RR507 were carried out sequentially on samples of the same batch of dried PET, where the samples were taken consecutively from the same jar that was kept sealed during test. The results show a progressive increase in the MVR values from $10.12 \text{ cm}^3/10 \text{ minutes}$ to $11.91 \text{ cm}^3/10 \text{ minutes}$ (an 18% increase). This increase is considered to have been due to moisture uptake by the material between tests. The repeatability of these nominally identical measurements was of the order of 10% (1 standard deviation), Table 8.

The effect of temperature on MVR was estimated to be of the order of $5 \text{ }^\circ\text{C}^{-1}$, Figure 20 and Table 9, a value considerably greater than the $\approx 1 \text{ }^\circ\text{C}^{-1}$ to $2 \text{ }^\circ\text{C}^{-1}$ that was observed for the relatively stable PP. Again there was little indication of a variation in measured MVR with test duration, Figure 21. The repeatability of measurements was of the order of 10% (1 standard deviation) although the repeatability within a single measurement was significantly better and averaged 3%. For this material (MVR $\approx 11 \text{ cm}^3/10 \text{ minutes}$) the total test duration was of the order of 440 seconds with an extrusion period of 90 s ($\approx 350 \text{ s}$ to 440 s). In oscillatory testing, Figure 22, there was a $\approx 1.5\%$ reduction in G'' over this extrusion period. The shear loss modulus G'' plot shows that the rate of degradation was higher at a test temperature of 285°C compared with 280°C .

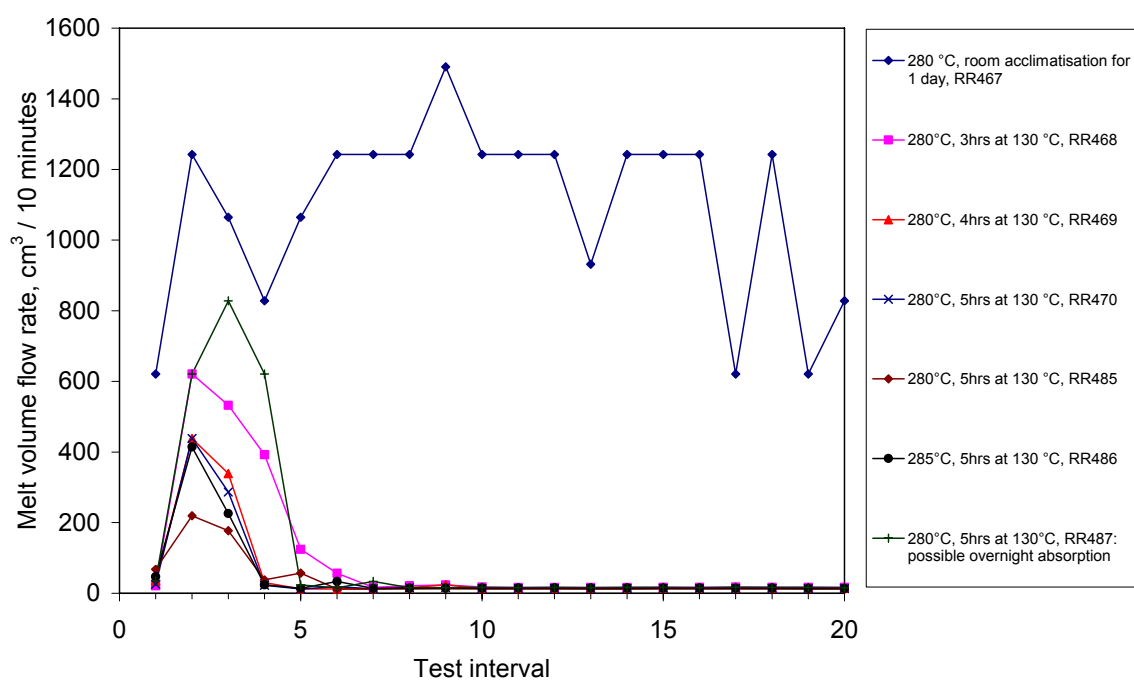


Figure 18: Initial transient results observed in melt volume flow rate testing of PET at 280 °C with a 5 kg load.

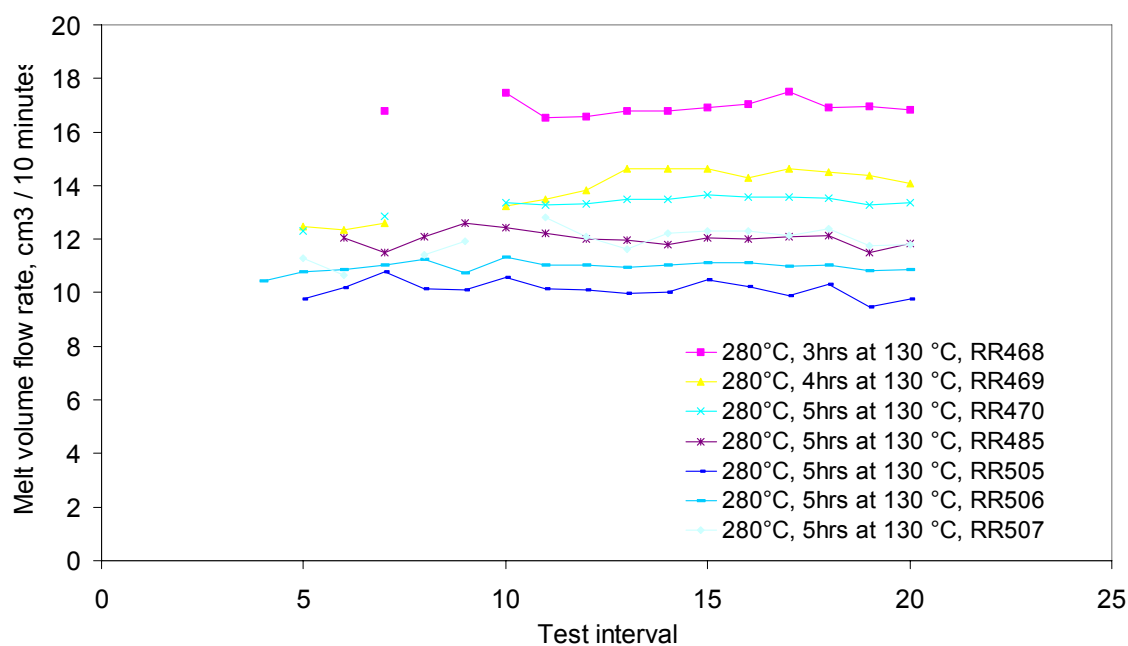


Figure 19: Effect of drying conditions on melt volume flow rate values for PET at 280 °C with a 5 kg load.

Test temperature, drying conditions, test reference	MVR, cm ³ /10 minutes	% of average*
280°C, 5hrs at 130 °C, RR470	13.32	114.1
280°C, 5hrs at 130 °C, RR485	12.02	103.0
280°C, 5hrs at 130 °C, RR505	10.12	86.8
280°C, 5hrs at 130 °C, RR506	10.97	94.0
280°C, 5hrs at 130 °C, RR507	11.91	102.1
Average MVR	11.67	100.0*
Repeatability, 1 standard deviation	1.20	10.3%
280°C, 3hrs at 130 °C, RR468	16.92	145.0
280°C, 4hrs at 130 °C, RR469	13.84	118.6

Table 8: Effect of drying conditions on melt volume flow rate values for PET at 280 °C with a 5 kg load.

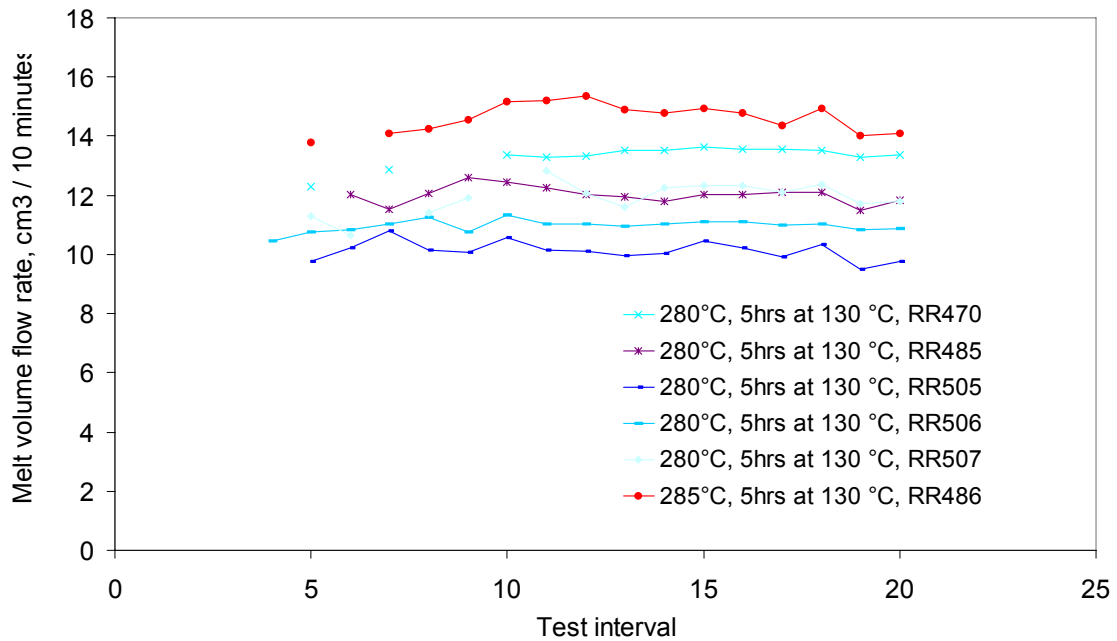


Figure 20: Effect of temperature on melt volume flow rate values for PET with a 5 kg load.

Test temperature, drying conditions, test reference	MVR, cm ³ /10 minutes	% of average*
280°C, 5hrs at 130 °C, RR470	13.32	114.1
280°C, 5hrs at 130 °C, RR485	12.02	103.0
280°C, 5hrs at 130 °C, RR505	10.12	86.8
280°C, 5hrs at 130 °C, RR506	10.97	94.0
280°C, 5hrs at 130 °C, RR507	11.91	102.1
Average MVR	11.67	100.0*
285°C, 5hrs at 130 °C, RR486	14.62	125.3

Table 9: Effect of temperature on melt volume flow rate values for PET with a 5 kg load.

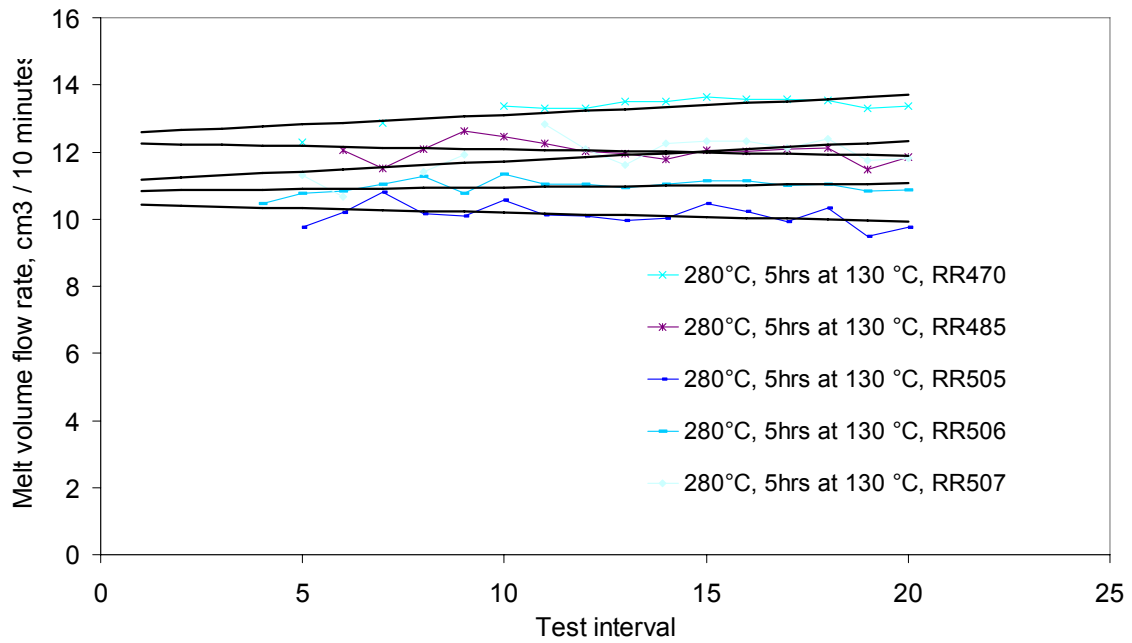


Figure 21: Effect of test duration on MVR of PET at 280 °C with a 5 kg load.
Drying conditions: 130°C for 5 hours.

Test No.	RR470	RR485	RR505	RR506	RR507	Average
Average MVR, cm ³ /10 minutes	13.3	12.0	10.1	11.0	11.9	11.6
Standard deviation, cm ³ /10 minutes	0.4	0.3	0.3	0.2	0.5	1.1
Standard deviation, %	2.7	2.5	3.2	1.9	4.6	9.7

Table 10: Repeatability of MVR measurements of PET at 280 °C and 5 kg load.
Drying conditions: 130°C for 5 hours.

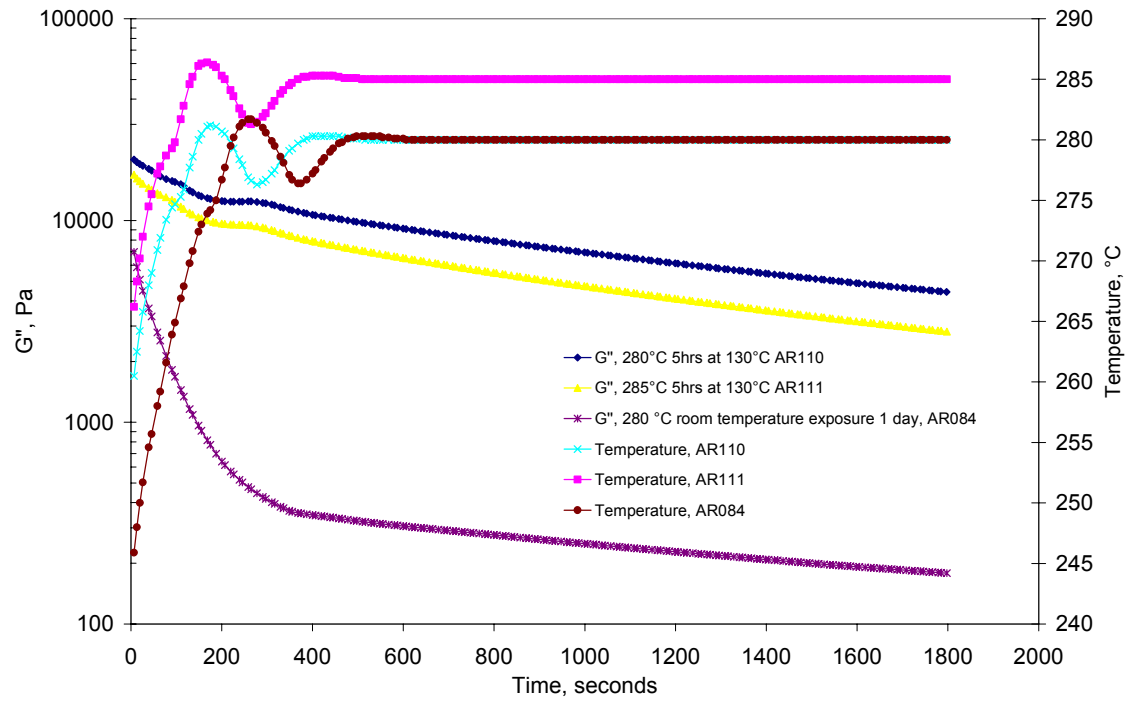


Figure 22: Effect of test temperature and time on measurement of shear loss modulus G'' of PET.

6.2.4 Polyamides

Results for the three polyamides are presented in Figures 23-25 and Tables 11-13. The results for the polyamide 66 indicate a possible reduction in melt flow rate as the test progressed, Figure 23. The MVR for the PA66 was approximately $56 \text{ cm}^3/10 \text{ minutes}$ with a standard deviation values of $\approx 5\%$. The two polyamide 6 materials had similar MVR values, averaging $26 \text{ cm}^3/10 \text{ minutes}$, with the PA6(2) having a slightly higher standard deviation of 6% compared with 5% for PA6(1). Noticeably and reassuringly, there was no significant difference in the standard deviation values despite the difference in test loads between the two materials.

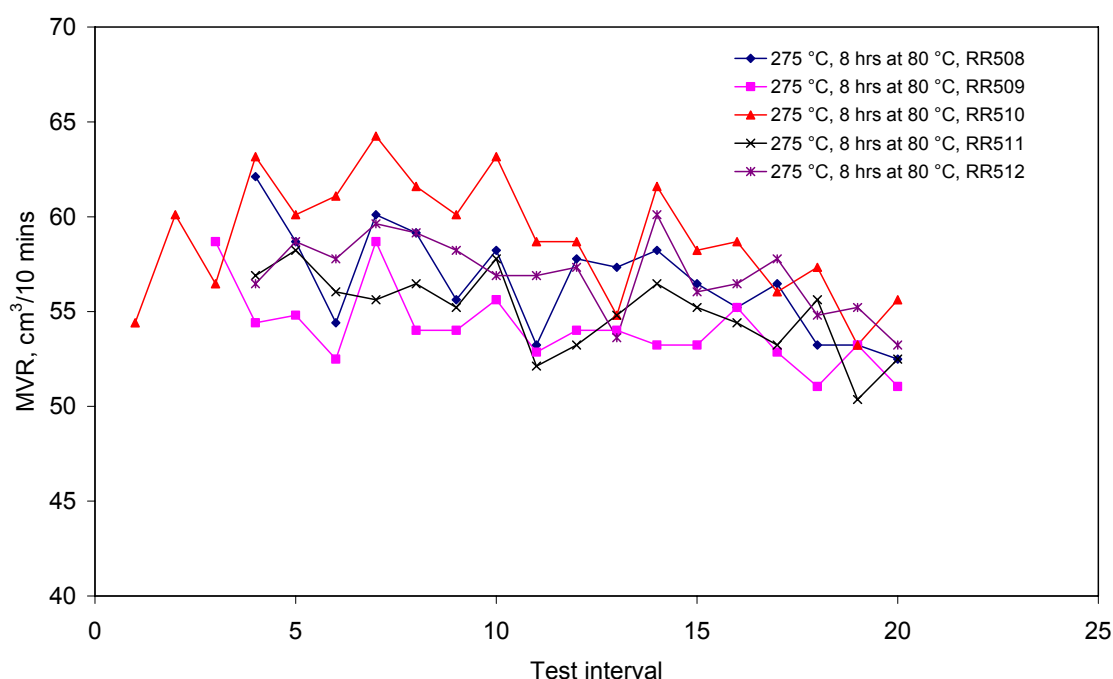


Figure 23: Repeatability of MVR measurements of PA66 at 275 °C with a 2.16 kg load. Drying conditions: 80°C for 8 hours.

Test No.	RR508	RR509	RR510	RR511	RR512	Average
Average MVR, $\text{cm}^3/10 \text{ minutes}$	56.6	54.1	58.9	55.0	57.0	56.4
Standard deviation, $\text{cm}^3/10 \text{ minutes}$	2.7	2.1	3.1	2.1	2.0	3.0
Standard deviation, %	5	4	5	4	3	5

Table 11: Repeatability of MVR measurements of PA66 at 275 °C with a 2.16 kg load. Drying conditions: 80°C for 8 hours.

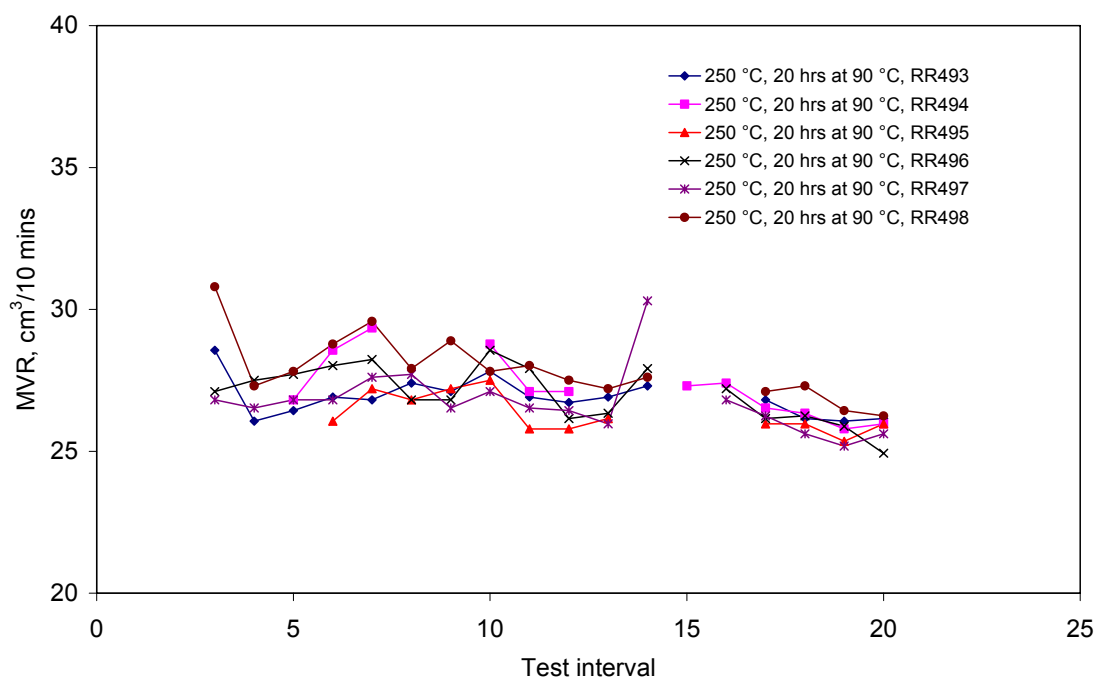


Figure 24: Repeatability of MVR measurement of PA6(1) at 250 °C with a 1.2 kg load. Drying conditions: 90°C for 20 hours.

Test	RR493	RR494	RR495	RR496	RR497	RR498	Average
Average MVR, cm ³ /10 minutes	26.9	27.3	26.3	27.0	26.7	27.9	27.0
Standard deviation, cm ³ /10 minutes	0.7	1.1	0.7	1.0	1.1	1.2	1.1
Standard deviation, %	3	4	3	4	4	4	4

Table 12: Repeatability of MVR measurements of PA6(1) at 250 °C with a 1.2 kg load. Drying conditions: 90°C for 20 hours.

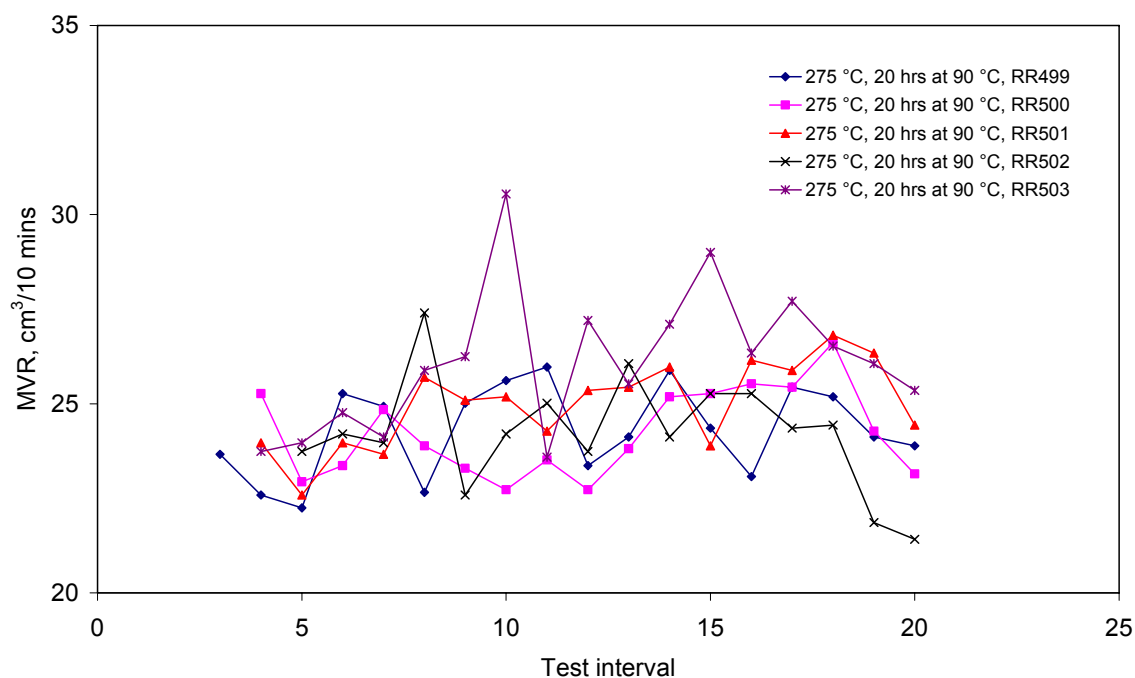


Figure 25: Repeatability of MVR measurement of PA6(2) at 275 °C with a 5 kg load. Drying conditions: 90°C for 20 hours.

Test No.	RR499	RR500	RR501	RR502	RR503	Average
Average MVR, cm ³ /10 minutes	24.3	24.2	25.0	24.2	26.1	24.8
Standard deviation, cm ³ /10 minutes	1.2	1.2	1.1	1.5	1.9	1.5
Standard deviation, %	5	5	5	6	7	6

Table 13: Repeatability of MVR measurements of PA6(2) at 275 °C with a 5 kg load. Drying conditions: 90°C for 20 hours.

7. Discussion and conclusions

The visual representation of MVR and MFR test envelopes clearly shows that the specifications for MVR and MFR testing are inconsistently presented in the standard. When combined with figures presenting uncertainties in MVR and MFR the figures clearly illustrate that the current specifications for MVR and MFR testing [1] are not optimised to minimise uncertainties. In particular, the recommendation for an extrudate cut-off length of between 10 mm and 20 mm results in high uncertainties in MFR values. It is recommended that such figures are used to assess the optimal testing conditions for measurement of MVR and MFR values. The data presented illustrate that relative uncertainties of up to approximately 20% (1 standard deviation) can be achieved if non-ideal test conditions are used.

The initial transients observed for these high melt flow rate materials could potentially introduce significant lack of repeatability into the method. As these transients can be identified using the instrument used herein, they can be discarded in determining the “average” value for melt flow rate. However, where test instruments do not have this facility then allowance for initial transients cannot easily be made and thus a significant contribution to scatter in results may occur. The cause of these transients is thought to be associated with trapped air and/or poor packing of the material in the barrel. This is in part due to its tendency to leak through the die thus preventing significant pressure being applied to the material in the barrel to obtain adequate compaction of the material.

The melt flow rate measurements on the PP, PBT and PET materials identify several issues that need to be addressed in developing the melt flow rate standard for materials that are sensitive to their time-temperature history, in particular those materials that are sensitive to absorbed moisture. For the PET material in particular MVR values were found to increase with subsequent tests possibly due to moisture absorption in handling the sample from one test to the next, even though the “dried” material was kept in a sealed container.

The MVR temperature sensitivities of the PBT (3 %/°C) and PET (5 %/°C) were higher than that of the PP (1 %/°C to 2 %/°C). Thus to achieve similar uncertainties in MVR of these moisture sensitive materials as is achieved for the stable material, the tolerances on temperature would need to be reduced by a factor of approximately x3, i.e. a range in tolerances of ± 0.66 °C and ± 1 °C, depending on the temperature range. However this does not take into account the effect that an error in the absolute temperature has on the degradation rate and thus amount of degradation present in the material during the test. This would further increase the error in MVR, although oscillatory rheometry testing would indicate that for a 1 °C discrepancy the effect would be relatively small over the duration of the MVR test.

The repeatability of measurements (1 standard deviation) was observed to be up to approximately 10% for the PET. The high value for repeatability was considered to be due to the suspected tendency for this material to rapidly absorb moisture thus resulting in a high sensitivity of the measured values to the handling of the samples prior to testing and during charging of the barrel. This compared with a value of 2% for the relatively stable PP and from 4% to 6% for all the other moisture sensitive materials.

The duration of the extrusion part of the melt flow rate test is relatively short, being of the order of between 30 seconds and 130 seconds for MVR values of 40 cm³/10 minutes and 10 cm³/10 minutes respectively. In most cases there was little evidence of a consistent trend for increasing (or decreasing) melt flow rate suggesting that the test duration was sufficiently short to avoid the materials changing behaviour over the course of the tests. For PA66 material there was possibly a slight decrease in MVR values as the test proceeded, i.e. higher viscosity values. This could be due further polymerisation occurring at the test temperature due to over-drying of the material prior to testing. However, there was also a possible reduction in MVR for the PP. In both case the duration of the extrusion was estimated to be of the order of 20 seconds to 25 seconds. It is suggested that this could be due to temperature gradients in the barrel of the instrument. The temperature at the top of the barrel was lower than in the die region and thus material passing from the top through the die at the end of the test would be cooler resulting in lower measured melt flow rate values. For lower melt flow rate materials this effect may not be observable as such materials might have sufficient time to heat up to the test temperature as it passes slowly along the length of the barrel toward the die, thus reducing the effect of any temperature gradients.

On the basis of this work it has been shown that for certain materials the most important parameter to control is the moisture content of the material. It is recommended that the high sensitivity to moisture content should be addressed through the specification of appropriate procedures for the preparation and handling of samples, and that procedures should be specified for carrying out to establish the sensitivity of measured values to drying procedures (or moisture content) and test temperature. Criteria should be established such that if the measured melt flow rate varies by more than $\pm 10\%$, for example, on doubling the drying time or on changing the temperature by 2 °C then the method is not suitable for that material and should not be used. Furthermore, it is recommended that uncertainty statements, based in part on such sensitivity studies, are prepared and reported when quoting results.

An international intercomparison on these materials has been carried out, the findings of which will be reported in a subsequent publication. It is anticipated that the intercomparison will provide additional evidence to enable appropriate setting of tolerances, particularly of permitted temperature variations within the barrel.

The findings of this work are being fed into the development of the standard ISO 1133 on melt flow rate testing to improve the current standard and also to develop a Part 2 for testing materials that are sensitive to their time-temperature history.

8. Acknowledgements

This work was carried out as part of a programme of underpinning research sponsored by the National Measurement System Directorate of the Department of Trade and Industry, UK. The advice, guidance and contributions from members of the Polymeric Materials Industrial Advisory Group are also gratefully acknowledged.

The authors would also like to thank the members of the ISO Melt Rheology Working Group (TC61/SC5/WG 9) of the Plastics Technical Committee.

9. References

1. ISO 1133: 2005 Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics.
2. CAMPUS plastics database: www.CAMPUSplastics.com
3. Rides, M., Review of melt mass flow rate and melt volume flow rate measurement for polymer melts, NPL Report CMMT(A)231, October 1999.
4. Shenoy, A.V. and Saini, D.R., Advances in Polymer technology, 6 No.1 pp.1-58 (1986).
5. Rangaprasad, R., Melt flow index test – a critical review, Popular Plastics and Packaging, 39 Part 11, Nov 1994, pp.55-57.
6. Wakefield, N., MFI – the pitfalls, Plastics and Rubber News, May 1985, pp.26-27.
7. ASTM D1238 Standard test method for flow rates of thermoplastics by extrusion plastometer
8. Kandil, F.A., Manual of codes of practice for the determination of uncertainties in mechanical tests on metallic materials, Code of practice No. 2: The determination of uncertainties in low cycle fatigue testing, National Physical Laboratory, September 2000.
9. Fahrenholz, H., private communication
10. ISO 6721-10: 1999 Plastics - Determination of dynamic mechanical properties – Part 10: Complex shear viscosity using a parallel plate oscillatory rheometer
11. ISO 11443: 2005 Plastics - Determination of the fluidity of plastics using capillary and slit-die rheometers

APPENDICES

Appendix 1: Nomenclature

For the purpose of this document the following terminology is used:

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 cm^3 although it is expressed as $\text{cm}^3/10$ minutes indicating it is the volume extruded in cm^3 in 10 minutes

m is the mass extruded in time t , grams

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

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

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

t time, s

Q volume flow rate, m^3/s

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

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

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

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

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

P pressure drop, Pa

P_e entrance pressure drop, Pa

P_s shear flow pressure drop along the capillary die, Pa

D barrel diameter, m

R die radius, m

L die length, m

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

Appendix 2: Analysis of melt flow rate testing

General

The melt mass flow rate (MFR) is given, according to ISO 1133 [1], by the expression

$$MFR = \frac{m t_{ref}}{t} \quad (A2.1)$$

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

$$MVR = \frac{MFR}{\rho} \quad (A2.2)$$

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

Thus the melt volume flow rate is given by the expression

$$MVR = \left[\frac{m t_{ref}}{t} \right] \times \frac{1}{\rho} \quad (A2.3)$$

Alternatively, as the quotient of the mass extruded to its density is equivalent to the volume extruded then this may be re-written as

$$MVR = \left[\frac{t_{ref}}{t} \right] \ell \frac{\pi D^2}{4} \times 10^6 \quad (A2.4)$$

where ℓ is the distance moved by the piston in time t and D is the diameter of the barrel. The factor of 10^6 is introduced here and elsewhere below to account for the differences in units used for the various parameters (for units see Nomenclature Appendix 1). MVR is determined experimentally by measuring the time taken for the piston to move a given distance or vice-versa.

Apparent shear rate

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

$$Q = \frac{MVR \times 10^{-6}}{600} \quad (A2.5)$$

or, substituting for MVR using equation A2.4, by

$$Q = \frac{\ell \pi D^2}{4t} \quad (\text{A2.6})$$

The apparent shear rate $\dot{\gamma}_a$ in the melt at the wall of the die is given [11] by

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (\text{A2.7})$$

and thus in the melt flow rate die, substituting for Q using equation A2.6, by

$$\dot{\gamma}_a = \frac{\ell D^2}{R^3 t} \quad (\text{A2.8})$$

Alternatively, the apparent shear rate is given, using equations A2.5 and A2.7, by

$$\dot{\gamma}_a = \frac{4(MVR / 600) \times 10^{-6}}{\pi R^3} \quad (\text{A2.9})$$

or in terms of MFR by

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

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, polymer melts 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

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \dot{\gamma}_a \quad (\text{A2.11})$$

or

$$\dot{\gamma} = \left(\frac{3n+1}{4n} \right) \frac{4Q}{\pi R^3} \quad (\text{A2.12})$$

where n is a power law index. The value of n-1 is equivalent to the gradient of the plot of log(apparent shear viscosity) versus log(apparent shear rate).

Apparent shear stress and apparent shear viscosity

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

$$Wg = \frac{P\pi D^2}{4} \quad (\text{A2.13})$$

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

$$P = \frac{4Wg}{\pi D^2} \quad (\text{A2.14})$$

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

$$P\pi R^2 = 2\pi RL\tau_a \quad (\text{A2.15})$$

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

Thus

$$\tau_a = \frac{PR}{2L} \quad (\text{A2.16})$$

or, substituting for P using equation A2.14, by

$$\tau_a = \frac{4Wg}{\pi D^2} \frac{R}{2L} \quad (\text{A2.17})$$

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

$$\underline{\eta}_a = \frac{\tau_a}{\dot{\gamma}_a} \quad (\text{A2.18})$$

Thus the apparent shear viscosity is given, using equations A2.10 and A2.17, by

$$\underline{\eta}_a = \frac{300Wg\rho R^4}{D^2 L \times MFR \times 10^{-6}} \quad (\text{A2.19})$$

or in terms of MVR by

$$\eta_a = \frac{300WgR^4}{D^2 L \times MVR \times 10^{-6}} \quad (\text{A2.20})$$

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

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

$$P_s = P - P_e \quad (\text{A2.21})$$

Thus replacing P_s for P in equation A2.14 yields the true shear stress τ in the die at the wall

$$\tau = \frac{P_s R}{2L} \quad (\text{A2.22})$$

Thus shear viscosities, corrected for entrance effects, could be determined given entrance pressure drop data.

An analysis of the effect of viscous heating in the melt flow rate test is presented in Appendix 4.

Appendix 3: Summary of constraints on melt flow rate testing for ISO 1133

The following presents a summary of the specifications for melt flow rate testing in accordance with ISO 1133 that are used to prepare Figures 2 and 3 showing the region of permissible operation of the instrument in melt flow rate testing. It is emphasised that the Standard presents further specifications and recommendations not presented here that are essential for carrying out melt flow rate testing.

Parameter	Units	Nominal	Tolerance
Barrel diameter	mm	9.550	± 0.025
Barrel length	mm	115 to 180	not reported
Die length	mm	8.000	0.025
Die diameter	mm	2.095 mm	± 0.005 mm
Piston head length	mm	6.35 mm	± 0.10 mm
Piston head diameter	The diameter of the piston head shall be less than the internal diameter of the barrel by $0.075 \text{ mm} \pm 0.010 \text{ mm}$		
Piston rod markings	Two marks 30 mm apart, upper one when piston 20 mm above die entry plane. Measurements shall be made within this 30 mm travel only.		
Load	kg	various	$\pm 0.5\%$
Timer	$\pm 0.1 \text{ s}$ for melt mass-flow rates $< 100 \text{ g}/10 \text{ minutes}$ $\pm 0.01 \text{ s}$ for melt mass-flow rates $> 100 \text{ g}/10 \text{ minutes}$ Also compare with a calibrated timing device over a period of 15 minutes to 20 minutes and ensure that the tolerance is within $\pm 0.07 \%$ of the total time measured.		
Displacement	$\pm 0.02 \text{ mm}$ for melt flow rates $< 1 \text{ cm}^3/10 \text{ minutes}$ or $1 \text{ g}/10 \text{ minutes}$ $\pm 0.1 \text{ mm}$ for melt mass-flow rates $> 1 \text{ cm}^3/10 \text{ minutes}$ or $1 \text{ g}/10 \text{ minutes}$		
Temperatures	Tolerances are dependent on absolute temperature and are specified with respect to position with the barrel and with time - see Table 1 of ISO 1133. Tolerances range from $\leq \pm 2 \text{ }^\circ\text{C}$ to $\leq \pm 3 \text{ }^\circ\text{C}$. The temperature-calibration device has a resolution of $\leq 0.1 \text{ }^\circ\text{C}$.		
MFR measurement – Method A	Extrudate cut off time intervals are specified and are dependant on the absolute MFR value. Cut-off intervals range from 240 s for MVR (or MFR) less than $0.5 \text{ cm}^3/10 \text{ minutes}$ ($0.5 \text{ g}/10 \text{ minutes}$) to less than 15 seconds for MVR (or MFR) greater than $10 \text{ cm}^3/10 \text{ minutes}$ ($10 \text{ g}/10 \text{ minutes}$)- see Table 2 of ISO 1133. Extrudate cut-off length at least 10 mm and preferably not more than 20 mm. Mass of cut-off at least 0.04 g. Weighing to the nearest 1 mg (balance accurate to $\pm 0.5 \text{ mg}$) Not recommended for MFR $> 100 \text{ g}/10 \text{ minutes}$		

MVR measurement – Method B	Minimum piston displacements recommended ranging from 3 mm to 20 mm (see clause 9.2 of ISO 1133).
Charging barrel	Complete charging the barrel in less than 1 minute.
Total test time	The time between the end of charging the barrel and the last measurement shall not exceed 25 minutes.
Single measurement duration	No single measurement shall take more than 240 s
Half die:	For use for MFR > 75 g/10 min or MVR > 75 cm³/10 min: • 4.000 mm ± 0.025 mm in length • bore of nominal diameter 1.050 mm ± 0.005 mm • no spacer shall be used with this die to increase the apparent length to 8.000 mm (i.e die entry 4 mm lower compared with standard die)

Appendix 4. Analysis of viscous heating in the flow

This analysis based on an energy balance and assumes that all the work done by the piston is converted to heat in the sample. Thus it is assumed that no heat energy is lost to the surroundings. This will result in the estimated viscous heating to be an overestimate of the actual amount. The work done by the piston per unit time w_F is given by

$$w_F = \frac{Wg\ell}{t} \quad (\text{A4.1})$$

The energy in heating the flowing material per unit time is given by

$$w_\theta = \rho C_p \Delta\theta \frac{\ell}{t} \frac{\pi D^2}{4} \quad (\text{A4.2})$$

where ρ is the melt density, C_p is the specific heat capacity and $\Delta\theta$ is the temperature rise in the sample. Thus from the energy balance

$$w_F = w_\theta \quad (\text{A4.3})$$

then

$$\rho C_p \Delta\theta \frac{\ell}{t} \frac{\pi D^2}{4} = \frac{Wgl}{t} \quad (\text{A4.4})$$

or, using equation A2.14

$$\Delta\theta = \frac{Wg}{\rho C_p \left(\frac{\pi D^2}{4} \right)} = \frac{P}{\rho C_p} \quad (\text{A4.5})$$

Thus using typical values for a polymer:

$$W = 2.16 \text{ kg}$$

$$g = 9.81 \text{ m.s}^{-2}$$

$$D = 9.55 \times 10^{-3} \text{ m}$$

$$\rho = 1000 \text{ kg/m}^3$$

$$C_p = 2000 \text{ J/(kg.K)}$$

the maximum average temperature rise $\Delta\theta$ is estimated to be $\approx 0.15^\circ\text{C}$ for a 2.16 kg load test. For a 21.6 kg load test the effect is estimated to be $\approx 1.5^\circ\text{C}$ and for a 50 kg load it is $\approx 3.4^\circ\text{C}$.

These estimates assume that all the energy was dissipated as heat evenly through the specimen and that no heat was dissipated from the melt to the surrounding environment. These factors would result in a reduction of the temperature increase. For a HDPE (HGH000) the shear flow temperature dependence was estimated to be less than 1 %/°C. The effect on the flow behaviour can thus be estimated. Uncertainty analysis has shown that a 1.5 °C error in set temperature would result in a 3% - 4% error in MVR for such a material. The effect on MFR and MVR testing would be expected to be less as these temperatures would be the maximum reached, i.e. that at the exit of the die: the average temperature of the material in the die would be less. The effect of the lower load of 2.16 kg is therefore considered negligible, but at higher loads the effect becomes potentially significant. Although the effect is perhaps not relevant when using the MFR test for comparative purpose it may be significant when using the data to extrapolate to higher shear rates.

Appendix 5: Comments on melt flow rate testing

The melt flow rate method is widely used in quality control within the polymer industry and is likely to remain as a dominant tool for quality control and assurance. It is the most widely used method for characterising the rheological or flow properties of polymer melts.

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

The particular strengths of the melt flow rate method, identified through consultation with industry, can be summarised as:

- Tests can generate useful data that are easily understood.
- Yields a single value that characterises the resistance to flow of the material: ideal for quality control applications and ease of understanding.
- Tests are relatively simple to perform.
- The tests occur typically at low shear rate. This results in a greater ability to resolve differences between the flow behaviour of similar materials than if measurements were carried out at high rates.
- Relatively cheap rheological method, both in terms of the cost of the equipment and its operation.
- Relatively short test time. The results are rapidly available.

The particular disadvantages of the melt flow rate method, identified through consultation with industry, can be summarised as:

- Repeatability and reproducibility can be poor. Variations are often obtained between different operators. This results in lack of confidence in the method and an uncertainty as to whether a measured variation is real or due to the method.
- Errors can become significant for very low viscosity and very high viscosity materials, particularly when using the melt mass flow rate method. In these cases either very little material is extruded or the material extrudes very rapidly resulting in a test of very short duration. Trends in injection moulding indicate that higher melt flow rate materials will be more commonly used thus increasing the need for an accurate, high melt flow rate measurement capability. High melt flow rate problems are also encountered with additives, e.g. lubricants and masterbatches.

- Yields only a single value that characterises the resistance to flow of the material. The flow of polymer melts is complex and cannot be described adequately by a single value.
- The test normally occurs at a low shear rate. In comparison, processing is normally carried out at high shear rates and thus extrapolation of melt flow rate data to processing conditions is not recommended. To illustrate this point, the ranking of the ease of flow of several materials at a low shear rate may not be the same as that at a higher shear rate.
- The method is predominantly a shear flow method whilst processing, with the exception of injection moulding, tends to be dominated by extensional flows. In the melt flow rate method the entrance pressure drop in the entry region to the die has been estimated to comprise approximately 20% of the total pressure drop in the instrument for an unfilled thermoplastic. The measurements are therefore dominated by the shear flow behaviour which tends to be less sensitive to variations in materials, and is less relevant to the majority of processing methods.
- Lack of suitable and traceable reference materials for checking measurements.
- In using the MFR method, cutting the extrudate is a potential source of error and can be problematic.
- The test duration can be long and degradation may occur and affect results. Conversely melt flow rate may also be used to monitor degradation. Of relevance particularly to polymer producers and compounders is that a longer test time equates to, potentially, a greater quantity of scrap being produced if the material is found to be out of specification.
- The sample size is too small and is not necessarily representative of the batch from which it is taken.
- Loading procedures are not always consistent between operators or laboratories, and cleaning procedures for melt flow rate equipment are not always adequate. Inappropriate loading procedures can result in air entrapment in the extrudate which then falsifies the measured values if it not noticed and the results discarded. The polymer form, e.g. pellets or flakes can have an effect on the measurements through their effect on loading efficiency.
- Fillers can cause problems with blockage of the die, resulting in erroneous readings.
- There is difficulty in comparing data obtained under different test conditions, for example the use of various loads for polyethylenes, or between different material types in which case both the temperature and load may differ.
- Lack of convenience and safety concerns when using higher load values.

- Uncertainty in the value to use for density to calculate MFR from MVR or vice versa. It can be calculated by measuring both the MFR and MVR but that defeats, in part, the objective of measuring only one value and then calculating the other.

The melt mass flow rate (MFR) value appears to be the more commonly used criteria within industry for specification of the behaviour of polymer melts. The reason for this is likely to be historical as the MVR method is a more recent development of the melt flow rate test. However, and for example, within the CAMPUS plastics properties database [2] MVR rather than MFR is quoted. MVR is more appropriate to polymer processing as such processes are volume rather than mass controlled: the mould cavity has a defined volume and thus a specific volume of material is required to fill it. The weights of a filled and an unfilled material that are required to fill the cavity will differ due to the difference in their densities. Thus it is more important to control the volume of material rather than the weight of material. Comparing the flow properties of materials should therefore be on a melt volume flow rate (MVR) basis.

A further advantage of the MVR over the MFR approach is that it is more amenable to automation and hence a reduction in labour costs as cutting and weighing of extrudate samples is not necessary.

An important consideration is the need to keep the cost of testing down, although the view was also expressed that additional costs are acceptable provided that there is confidence in the data obtained and that the information provided is relevant.

Finally, a potential future trend for materials producers and compounders is for on-line process monitoring rather than off-line melt flow rate testing to reduce costs and delay times and to tackle materials that are difficult to measure using off-line testing. However, current on-line methods that can be used to determine melt flow rate are not compliant with melt flow rate standard, although corrections to account for differences can be applied. Standardisation of on-line methods for determining MFR or MVR is desirable if on-line measurements are to be carried out in place of off-line melt flow rate measurements for quality control.

File reference: MVR development report H4_D2 v#22.doc, 05/10/2007 10:36