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

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

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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 handing 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.

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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 material[1]. MFR is expressed in g/10 minutes and MVR in cm^3/10 minutes. The MFR and MVR are thus measures of the ease of flow: the higher the 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 = density × 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].

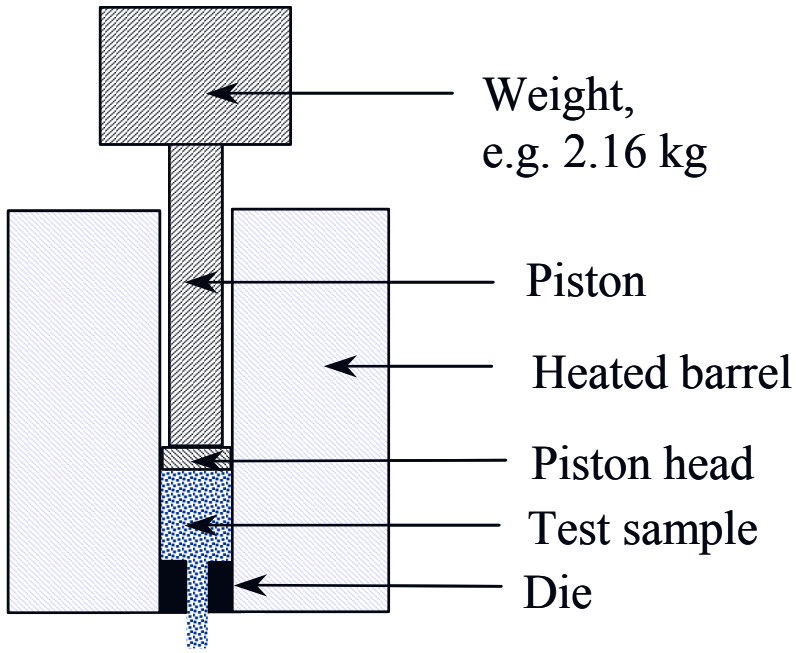

Figure 1: Schematic of a melt flow rate instrument.

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 cm^3/10 minutes (or MFR > 10 g/10 minutes) and preferably less than 40 cm^3/10 minutes (or MFR < 40 g/10 minutes). The lower constraint (10 cm^3/10 minutes) results in an extrusion time of not more than ≈ 130 seconds and the upper constraint (40 cm^3/10 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 cm^3/10 minutes (or MFR < 10 g/10 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:

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

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.

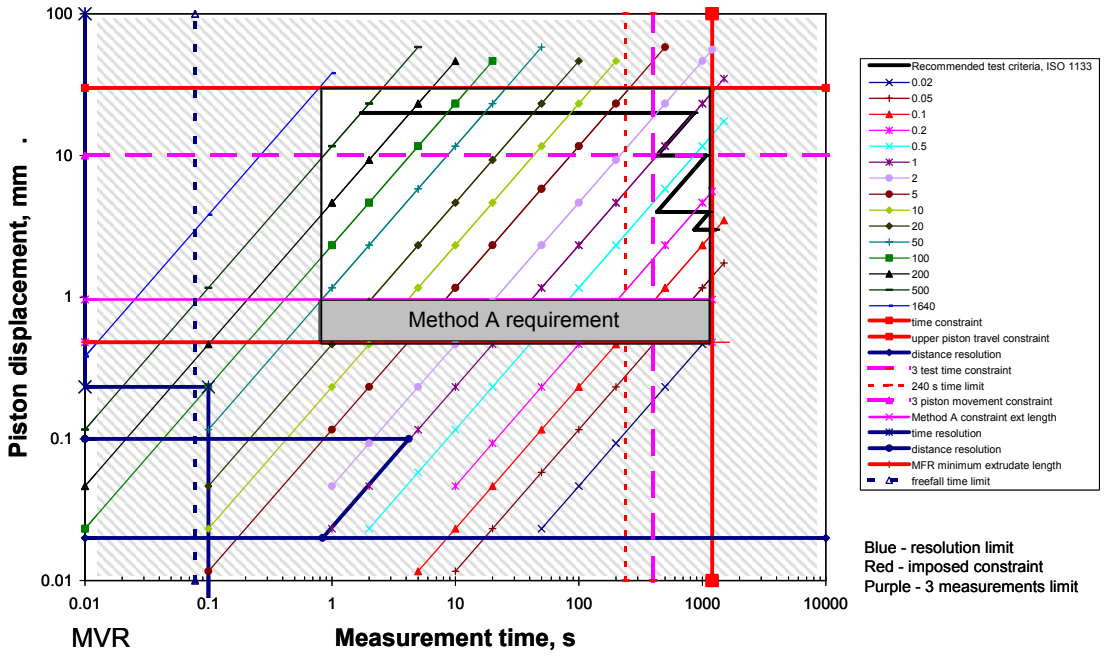

Figure 2: MVR constraints diagram (light-grey outer shaded area indicates region outside measurement range).

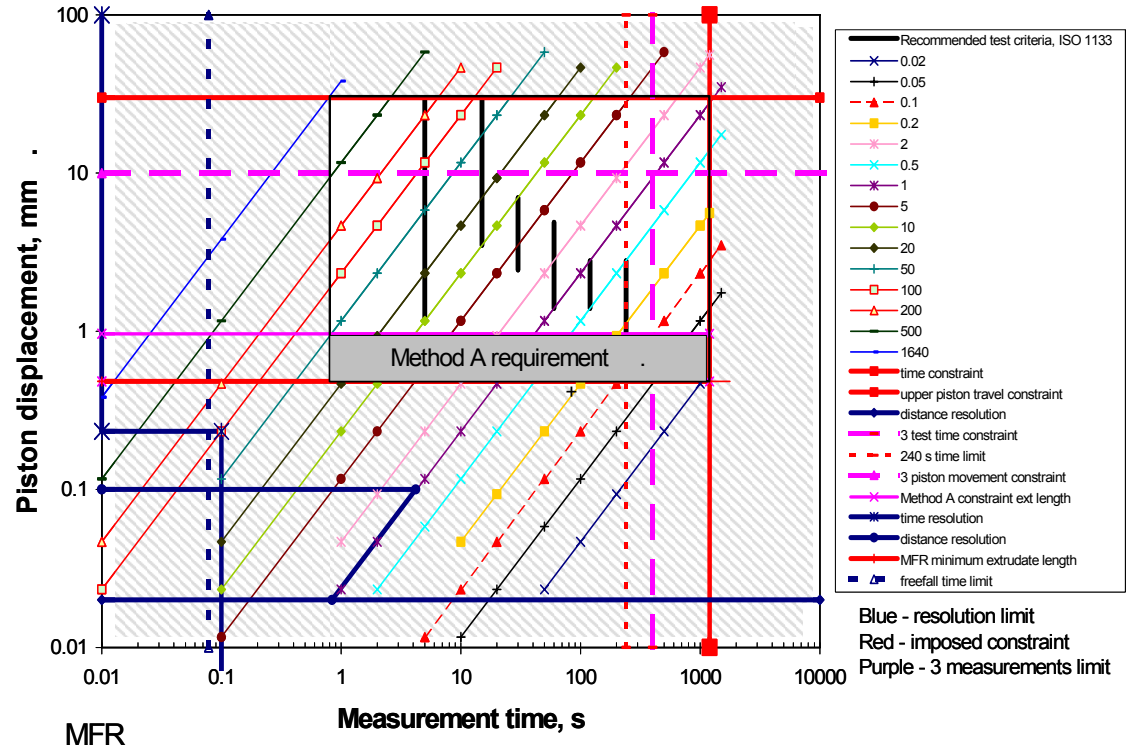

Figure 3: MFR constraints diagram (light-grey outer shaded area indicates region outside measurement range).

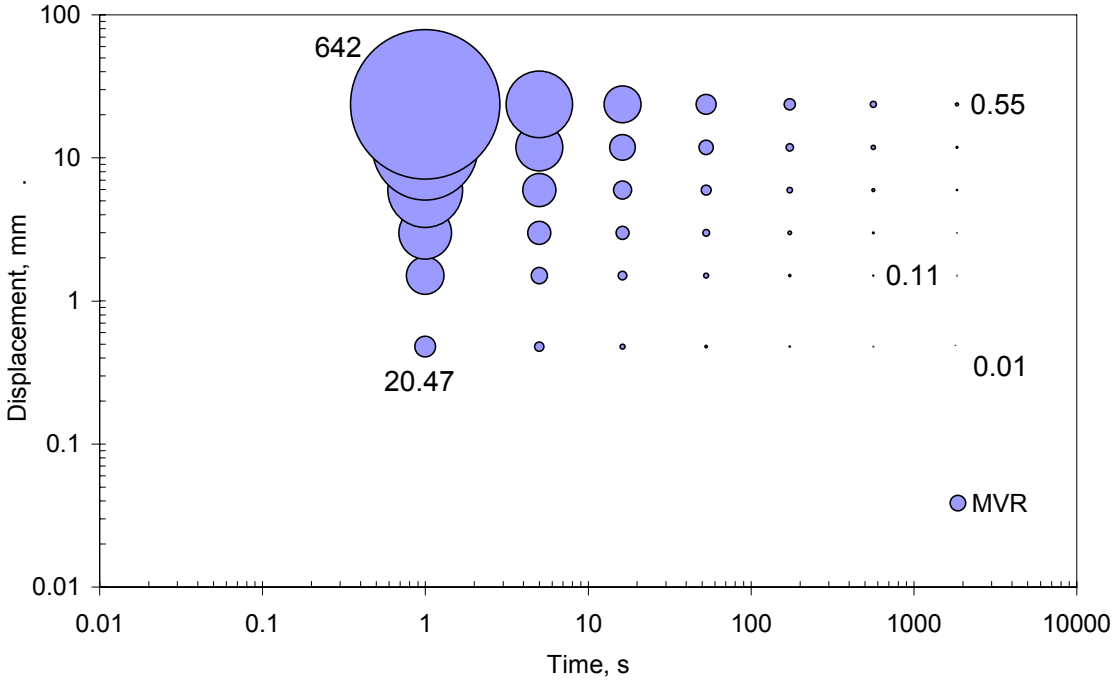

Figure 4: MVR values as a function of piston displacement and time.

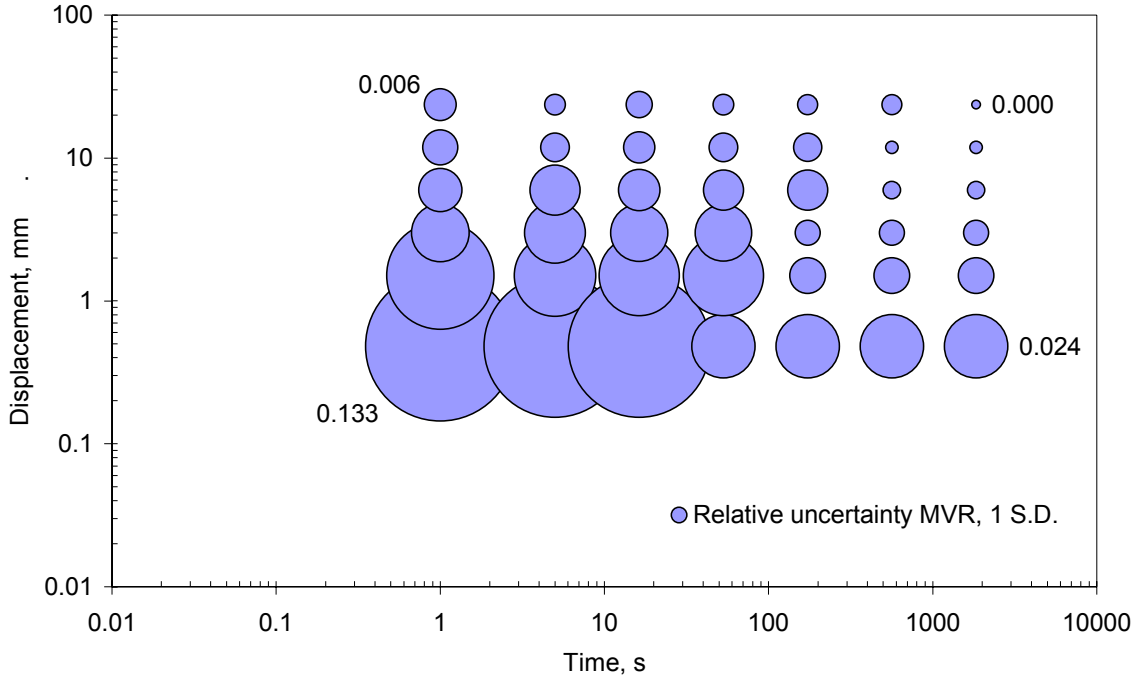

Figure 5: MVR relative uncertainties as a function of piston displacement and time (1 standard deviation values presented).

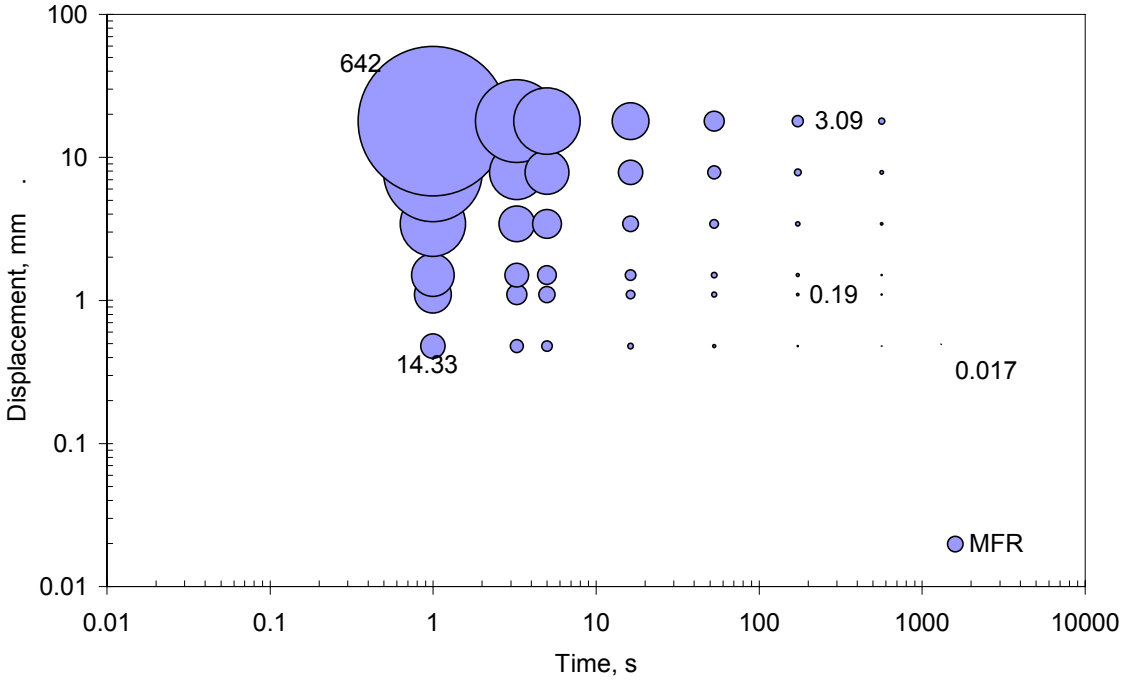

Figure 6: MFR values as a function of piston displacement and time.

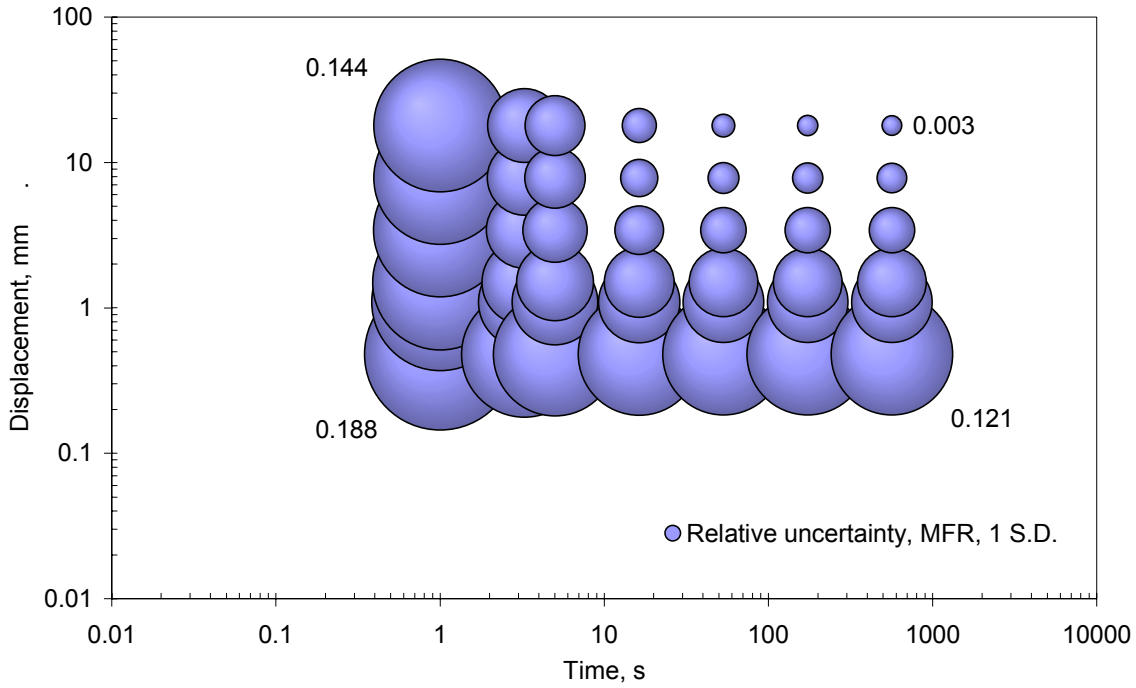

Figure 7: MFR relative uncertainties as a function of piston displacement and time (1 standard deviation values presented).

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 ± 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 cm^3/10 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.

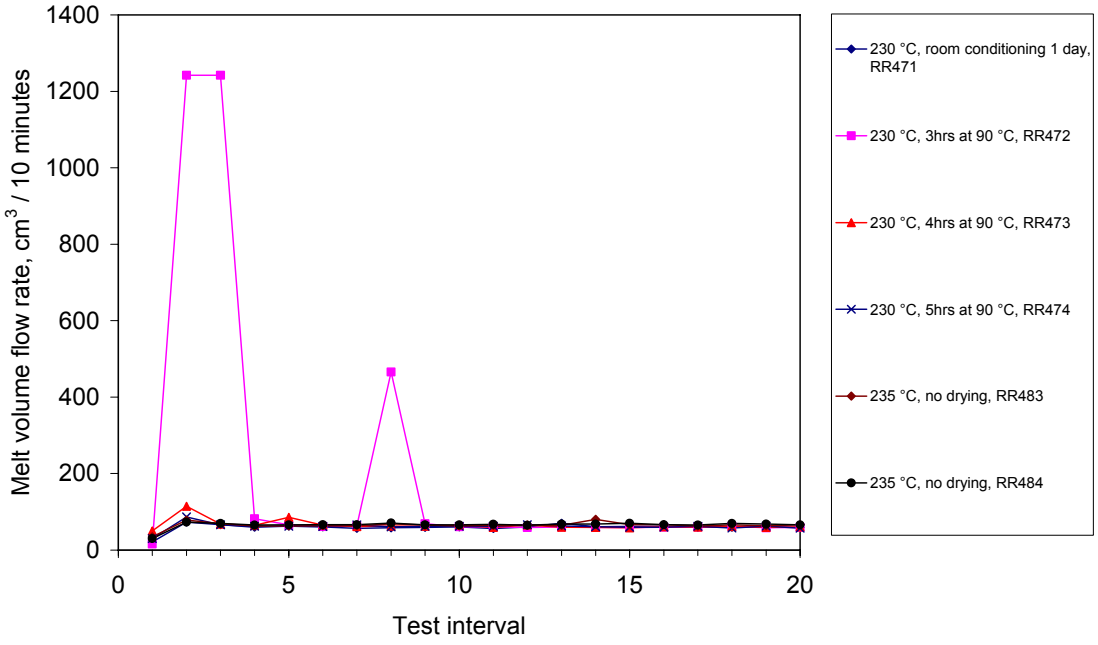

Figure 8: Initial transient results observed in melt volume flow rate testing of PP. 2.16 kg load.

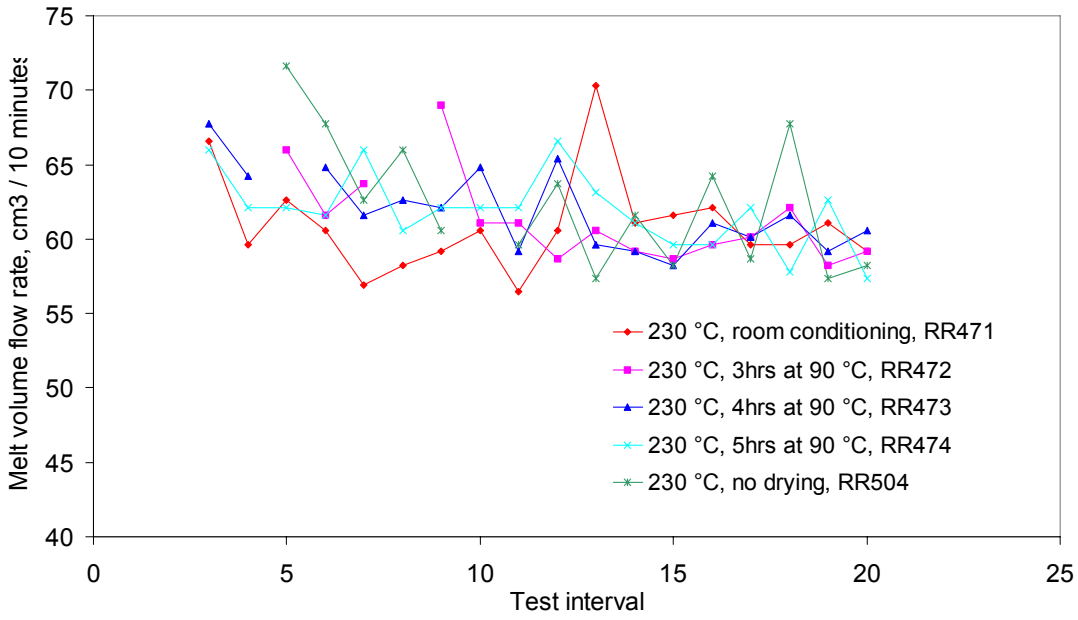

Figure 9: Effect of drying conditions on melt volume flow rate values for PP. 2.16 kg load.

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.

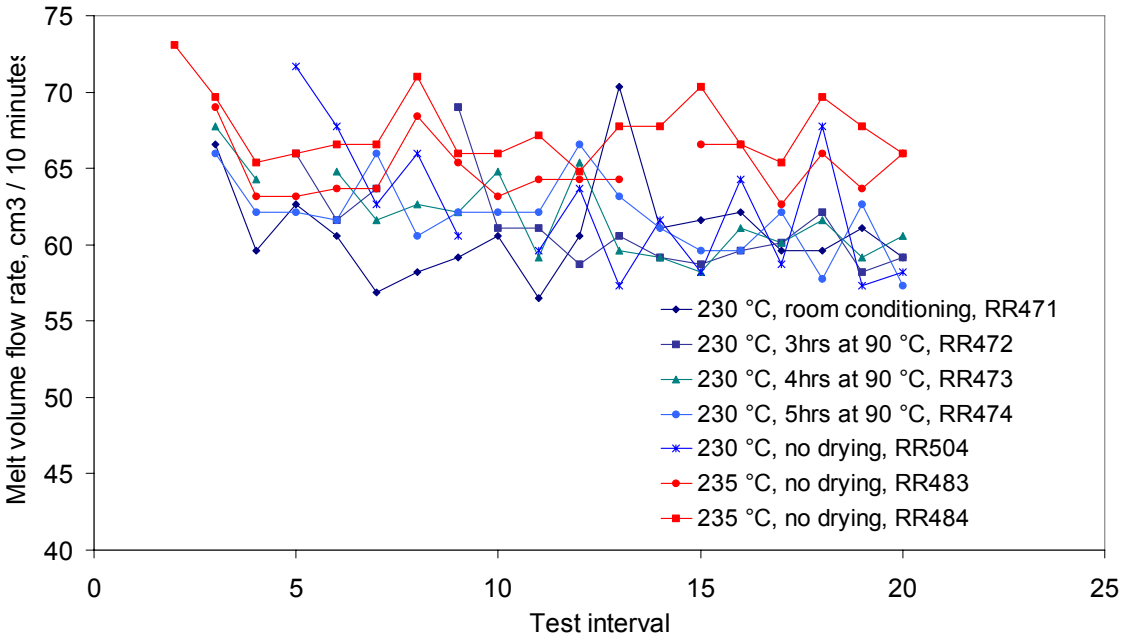

Figure 10: Effect of temperature on melt volume flow rate of PP. 2.16 kg load.

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.

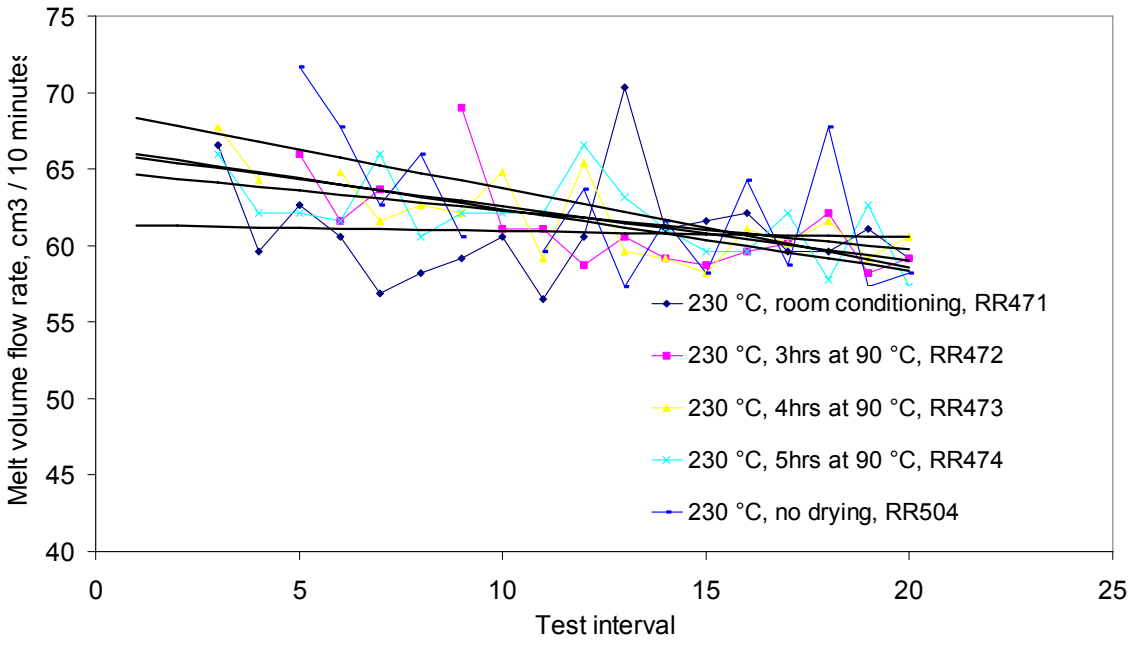

Fig 11: Effect of duration of test on PP at 230 °C with a 2.16 kg load.

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.

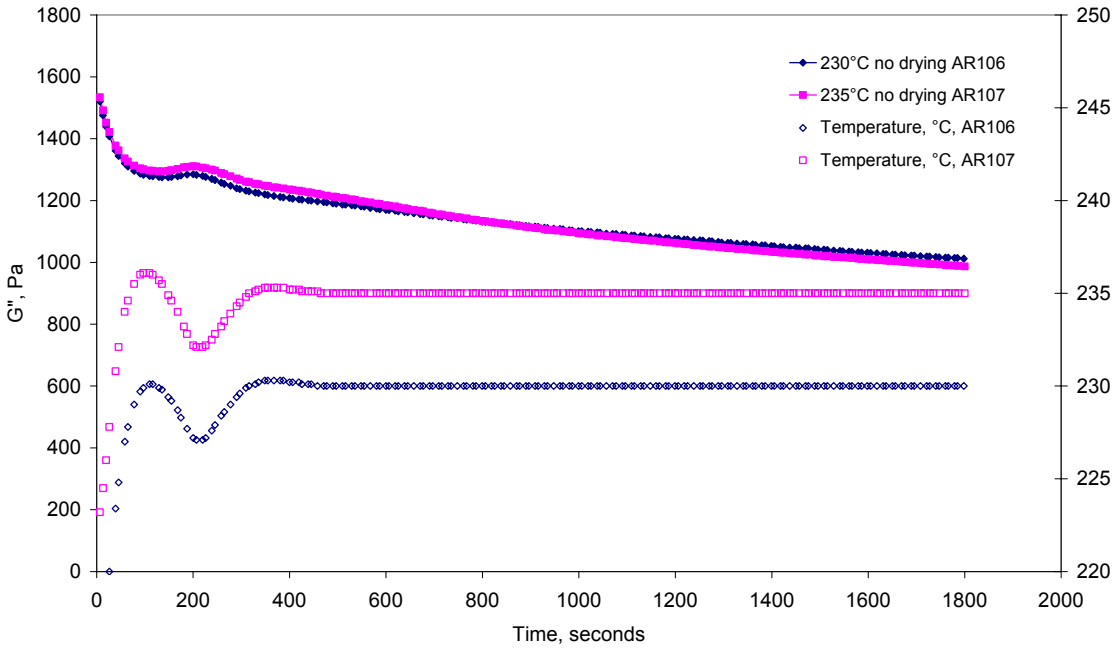

Figure 12: Effect of test time on measurement of shear loss modulus G'' of PP.

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 cm^3/10 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).

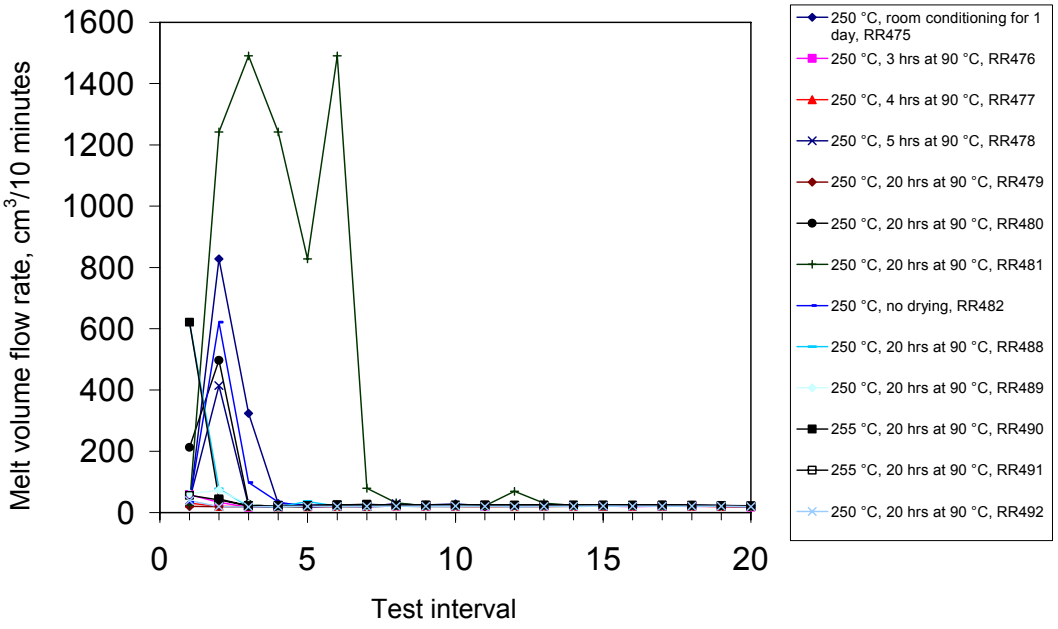

Figure 13: Initial transient results observed in melt volume flow rate testing of PBT. 2.16 kg load.

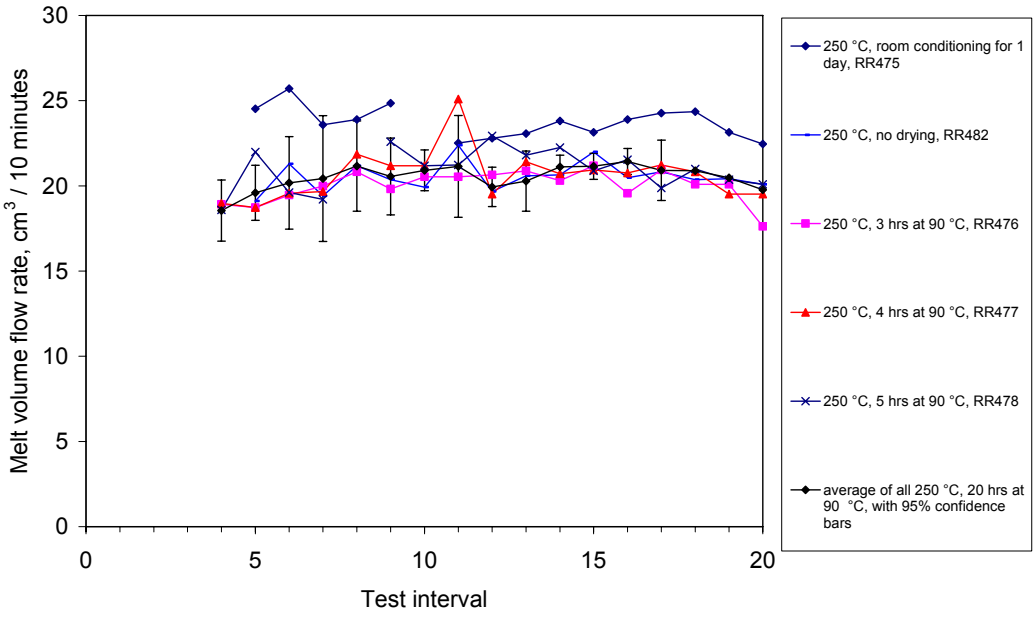

Figure 14: Effect of drying conditions on melt volume flow rate values for PBT (averaged values with 95% confidence bars for 20 hours drying condition). 250 °C and 2.16 kg load.

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.

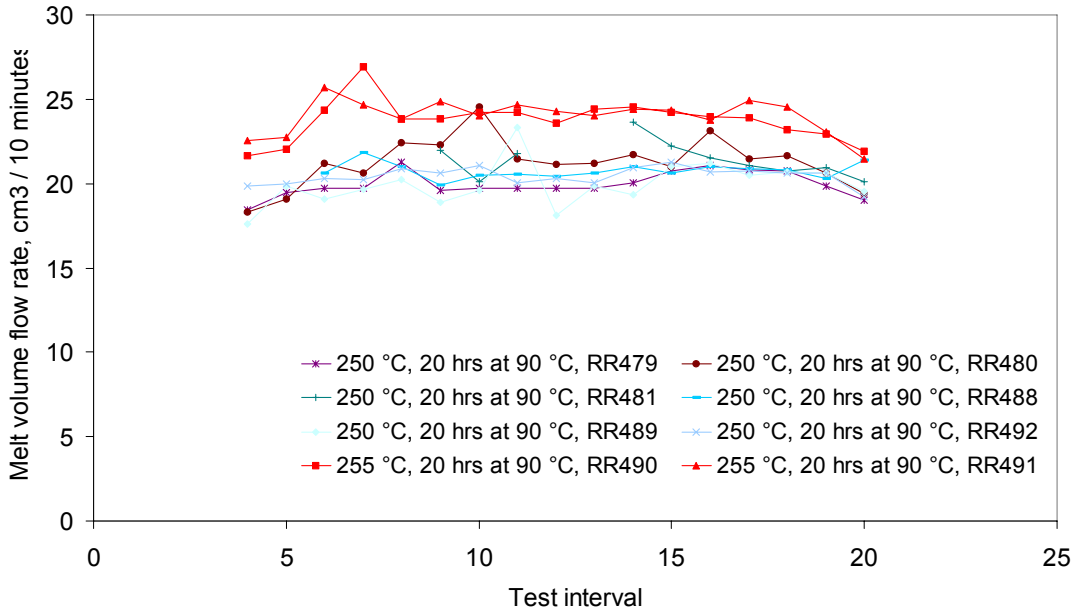

Figure 15: Effect of temperature on melt volume flow rate values for PBT with 2.16 kg load.

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.

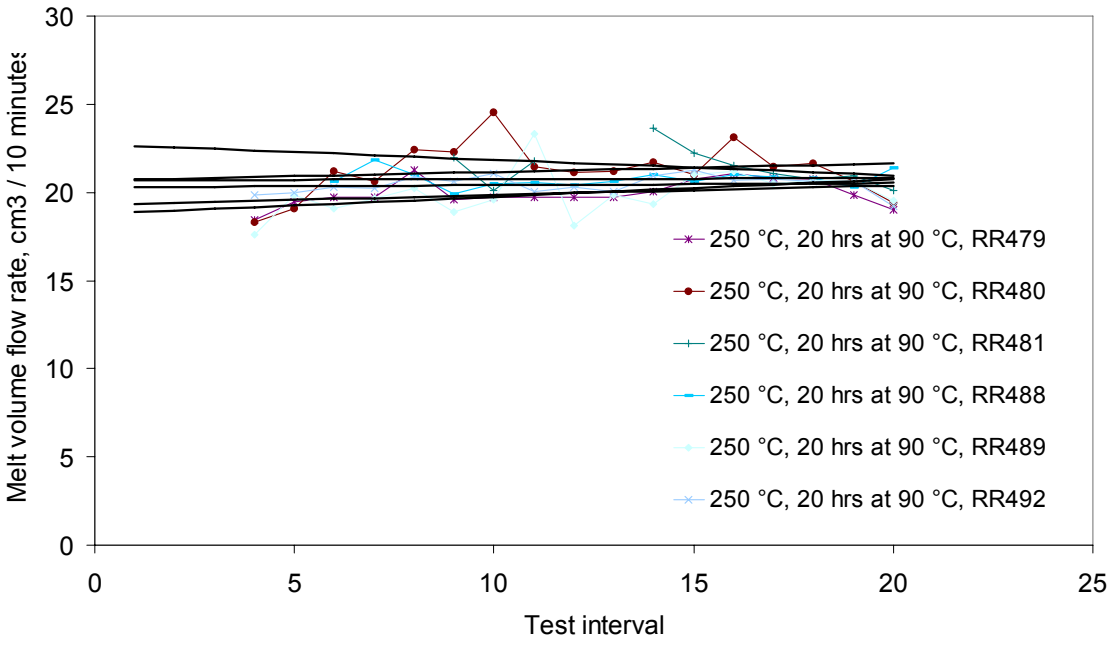

Figure 16: Effect of test duration on MVR of PBT at 250 °C with 2.16 kg load. Drying conditions: 90 °C for 20 hours.

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.

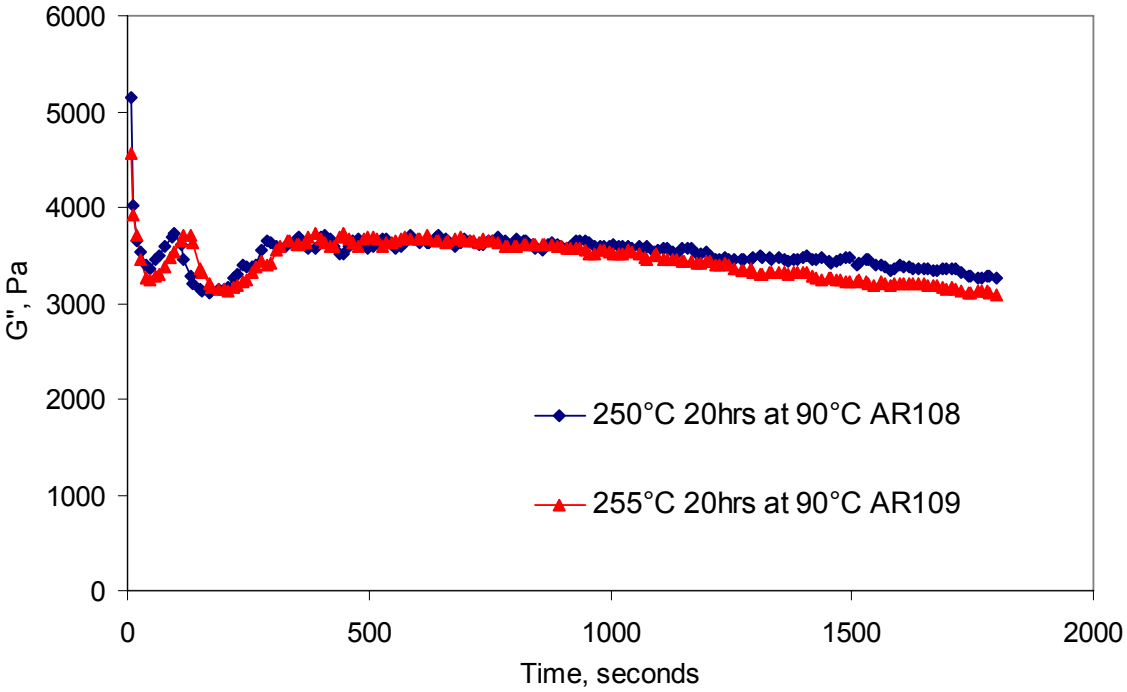

Figure 17: Effect of test temperature and time on measurement of shear loss modulus G'' of PBT.

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 cm^3/10 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 cm^3/10 minutes to 11.91 cm^3/10 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 %/°C, Figure 20 and Table 9, a value considerably greater than the ≈ 1 %/°C to 2 %/°C 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 ≈ 11 cm^3/10 minutes) the total test duration was of the order of 440 seconds with an extrusion period of 90 s (≈ 350 s to 440 s). In oscillatory testing, Figure 22, there was a ≈ 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.

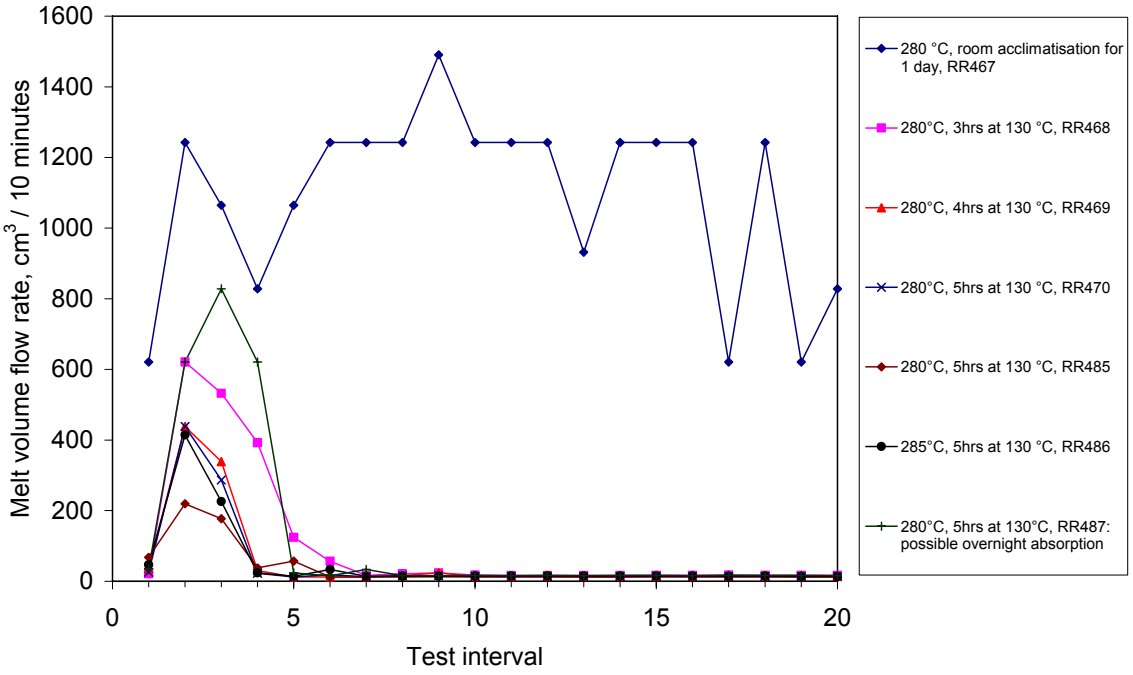

Figure 18: Initial transient results observed in melt volume flow rate testing of PET at 280 °C with a 5 kg load.

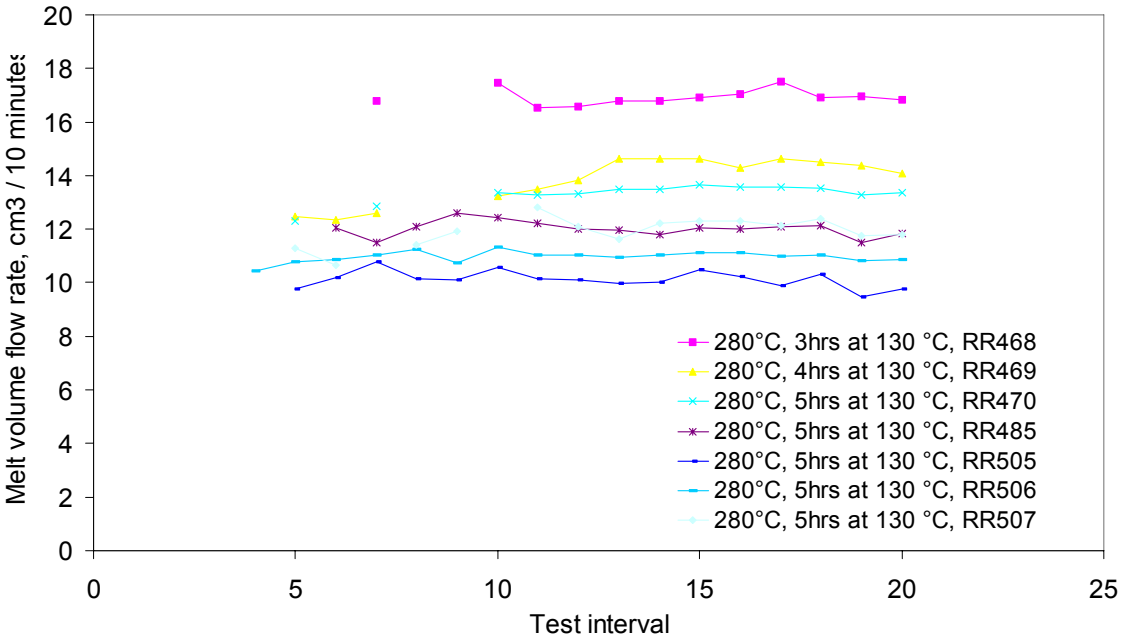

Figure 19: Effect of drying conditions on melt volume flow rate values for PET at 280 °C with a 5 kg load.

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.

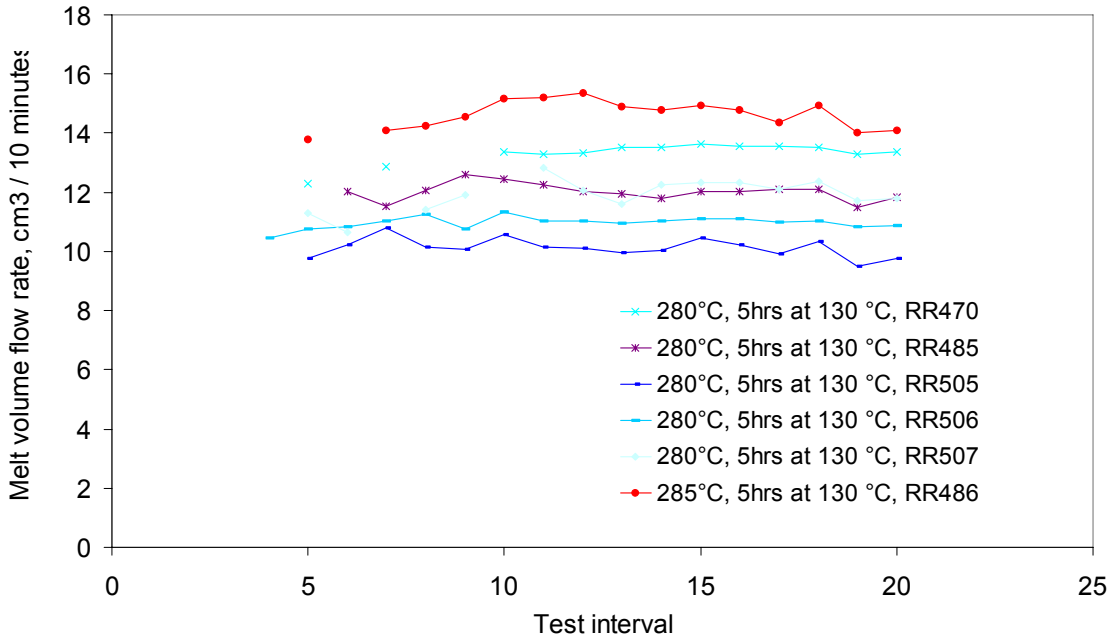

Figure 20: Effect of temperature on melt volume flow rate values for PET with a 5 kg load.

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.

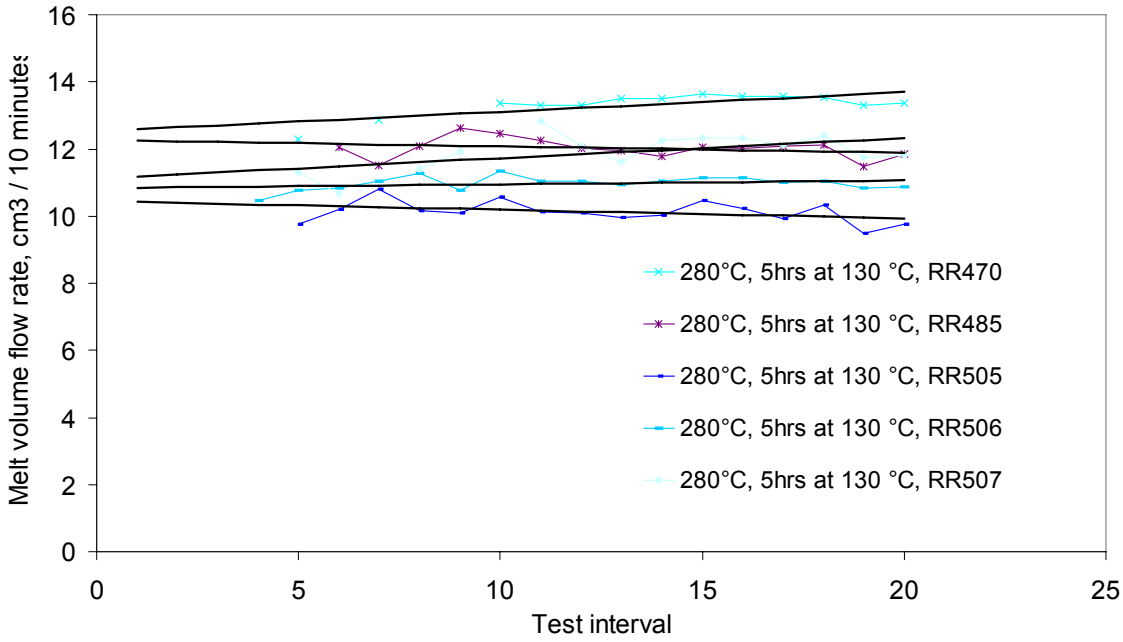

Figure 21: Effect of test duration on MVR of PET at 280 °C with a 5 kg load. Drying conditions: 130°C for 5 hours.

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.

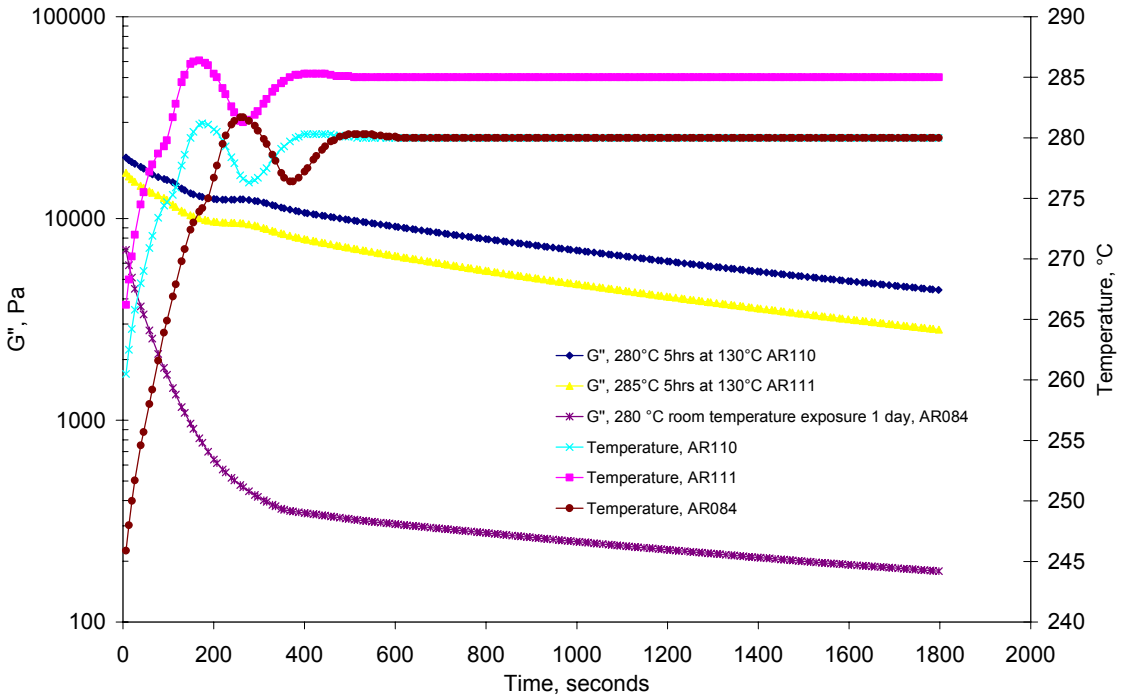

Figure 22: Effect of test temperature and time on measurement of shear loss modulus G'' of PET.