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Review of melt mass flow rate and melt volume flow rate measurements for polymer melts

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ABSTRACT

The melt flow rate method is widely used in quality control within the polymer industry and is likely to remain as a dominant tool for quality control and assurance. However, it is general accepted within the industry that the melt flow rate method has limitations. The advantages and disadvantages, as perceived by industry, of the current melt flow rate method have been presented. To address these limitations various developments to the melt flow rate method have been proposed. These developments address:

- the measurement of melt flow rate at higher shear rates thus making the method more reliable in predicting the performance of materials in processing,
- the characterisation of the extensional flow behaviour of polymer melts: a property that is important in both processing and quality control yet is normally overlooked by traditional characterisation methods, and also
- improvements to the current melt flow rate method and procedure to improve confidence in its use.

It is noted that these developments are not intended to replace the melt flow rate method but to supplement it to enhance the capability and value of the method by providing additional, appropriate information on the flow behaviour of polymer melts.

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1. INTRODUCTION

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

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

All test conditions are tightly specified by the ISO standard on melt flow index [1]. The only parameters that are allowed to vary are the test 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. 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].

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.

The purpose of this review, carried out principally through a number of meetings and discussions with materials suppliers, instrument manufacturers and converters, was to identify those weaknesses and to present potential solutions in the form of improvements to the current method and development of new methods that are suited principally for the purposes of materials selection and quality control.

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

2. CURRENT STATUS OF RHEOLOGICAL METHODS FOR QUALITY CONTROL

The melt flow rate method is the most widely used method for characterising the rheological or flow properties of polymer melts. The data obtained using the melt flow rate method is used for two basic purposes, either to check on the quality of the material, or to give some indication as to how the material will behave during processing, whether that processing is by, for example, injection moulding, extrusion, blow moulding, thermoforming or compounding.

Methods such as capillary extrusion rheometry, oscillatory and rotational rheometry and tensile extensional rheometry [2, 3] can also be used to provide such information, albeit at greater cost. However, these methods are suited more to advanced applications where detailed, quantitative information on the rheological behaviour are required, for example for flow simulation. In comparison with melt flow rate testing, measurements using these equipment are generally more involved and require a higher skill level to carry out and, in particular, to interpret the multi-point data generated. Furthermore, testing can take significantly longer and the equipment is considerably more expensive. This is not to say that these methods do not have a role to play in quality control - these method can be used to obtain better information than that obtained from a melt flow rate test - but these factors do limit their suitability for such a purpose.

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

- Tests can generate useful data that is 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 a 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 hazardous. 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 a suitable and traceable reference material 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 [4] 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. The feasibility of such standardisation will be considered during the work on development on the off-line melt flow rate method.

3. PROPOSED DEVELOPMENTS BASED ON THE MELT FLOW INDEX METHODS

3.1 GENERAL

An essential requirement for developments based on the melt flow rate method is that the current method should neither be replaced by an alternative method, nor changed to the extent that current instruments would no longer comply with the standard. The melt flow rate technique is too ingrained in the global polymer industry for the successful introduction of a replacement or substantially modified method. The proposed developments have also been restricted, at this stage, to those that utilise the basic melt flow rate instrument, rather than requiring the purchase of significant additional test equipment. This approach is likely to maximise the uptake by industry of such measurement technology. The approach adopted has therefore been to consider improvements in the current method and the associated ISO standard, and to develop methods that can be carried out utilising the basic melt flow rate instrument.

The proposed developments consider a three-pronged approach and address the needs for:

- improvements to the existing method to improve its precision, i.e. the repeatability and reproducibility, and thus confidence in the data generated,
- testing at higher flow rates to provide data to improve the prediction of the behaviour of materials in processing, and
- measurements of the extensional flow behaviour to improve both the quality control of materials and the prediction of their processing behaviour.

A general comment made on the requirements for such testing is that the information obtained must be simple to understand and easy to relate to the processability of the materials.

3.2 IMPROVEMENTS TO THE EXISTING METHOD

The improvements to the melt flow rate method will be addressing that specified by ISO 1133: Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics.

Various improvements to this standard have been and will be proposed to the ISO committee TC61/SC5/WG9 on rheological properties of polymer melts. Such improvements have been identified through discussion with instrument manufacturers, materials suppliers and users. This standard is currently under revision and further comments on its development can be addressed either to the author or through the BSI, addressed to Mr E Levio, Secretary, PRM/21.

3.3 HIGHER FLOW RATE TESTING

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

At the same time as carrying out these developments, efforts will be made to tighten the specification on the capillary extrusion rheometry standard ISO 11443 [5] which currently permits a large degree of flexibility in terms of testing a material. This will be achieved through, for example, specification of the diameter and lengths of the dies, the test temperature and the apparent shear rates to be used for a given material class, e.g. polypropylene.

3.4 EXTENSIONAL FLOW TESTING

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

The methods to be developed are:

- the use of a zero length or short die,
- measurement of extrudate draw-down under load (similar to parison sag), and
- the measurement of extrudate swell.

The principle behind the use of a zero or short length die is to obtain a measure of the resistance to flow in a converging region which can then be correlated with the extensional flow behaviour of the material [6, 7, 8]. The measurement of the die swell and that of the extrudate draw down will correlate directly with the behaviour of melts in extrusion and blow moulding (parison sag). Whereas parison sag is predominantly governed by the extensional flow behaviour of the material, extrudate swell is a complex phenomena that is governed more by the full rheological behaviour of the material. Nevertheless for polymer melts the extensional flow behaviour can have a significant affect on the extrudate swell behaviour and more importantly extrudate swell is a measure that is of direct relevance to converters. It is thus considered a very valid approach to pursue as a quality control measure. The principle difficulties perceived with these methods will be in developing the necessary procedures to cover the range of behaviours and to obtain repeatable and reproducible results [9] thus giving the user confidence in the data generated.

4. CONCLUSIONS

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 for some time. However, it is general accepted within the industry that the melt flow rate method has limitations as a quality control tool. The advantages and disadvantages, as perceived by industry, of the current melt flow rate method have been presented. To address these limitations various developments have been proposed. These developments address:

- the measurement of melt flow rate at higher shear rates thus make the method more appropriate for predicting the performance of materials in processing,

- the characterisation of the extensional flow behaviour of polymer melts - a property that is important in processing yet is normally overlooked by traditional characterisation methods, and also
- improvements to the current melt flow rate standard ISO 1133.

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

Comment on this report will be welcomed by the author.

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6. REFERENCES

1. ISO 1133: Plastics - Determination of the melt mass flow rate (MFR) and melt volume flow rate (MVR) of thermoplastics.

2. Rheology: Principles, Measurements, and Applications, C.W. Macosko, 1994, VCH Publishers (UK) Ltd, Cambridge, England.

3. Melt rheology and its role in plastics processing: theory and applications, J.M. Dealy and K.F. Wissburn, 1995, Chapman and Hall, England.

4. CAMPUS plastics database: www.CAMPUSplastics.com

5. ISO 11443: Plastics - Determination of the fluidity of plastics using capillary and slit-die

rheometers

6. Rides M. and Allen C.R.G., Measurement Good Practice Guide No. 16. Extensional flow properties of polymer melts using converging flow methods, March 1999, National Physical Laboratory.

7. Rides, M., and Allen, C.R.G., Entrance pressure drop measurements by capillary extrusion rheometry: a measure of the extensional flow behaviour of polymers, Polymer Rheology '99 Conference: Polymer Rheology - A practical approach to quality control for the Plastics and Rubber Industries, Paper 13, Pages 1-4, RAPRA Technology Ltd, Shawbury, UK, 13-14 October 1999.

8. Rides, M., Allen, C.R.G. and Chakravorty, S., Intercomparison of extensional flow characterisation techniques for polymer melts: tensile stretching and converging flow methods, NPL Report CMMT(A)171, April 1999.

9. Allen, C.R.G. and Rides, M., Intercomparison of extrudate swell measurements using capillary extrusion rheometers for a polyethylene melt, NPL Report CMMT(A)9, January 1996.

Ref: cmmt(A)231 review MFI report format 25Oct99#8.doc

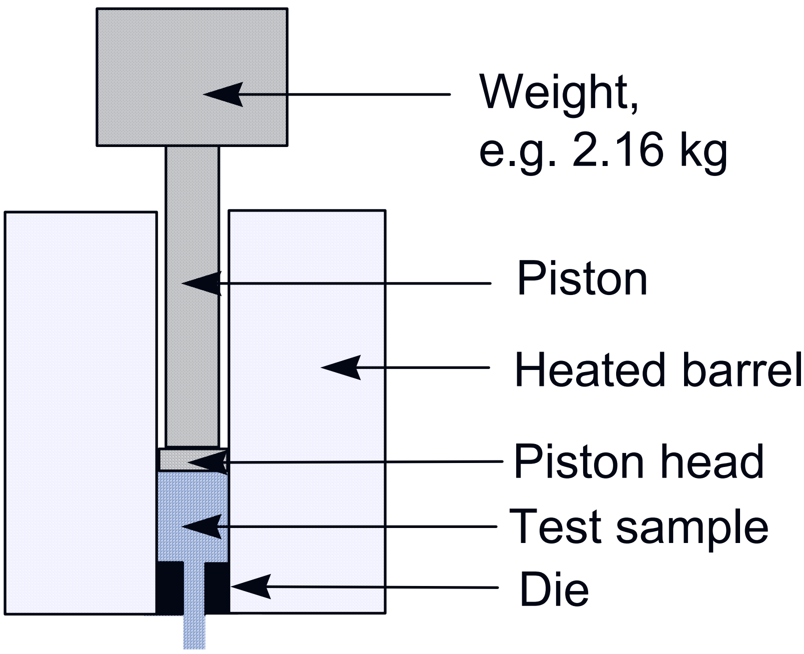

Figure 1: Schematic of a melt flow rate instrument