

Guide to the measurement of the flow properties of polymeric materials

In processing plastics the material is melted, transferred and then solidified. The transfer or flow process is critical to processing and the properties of the final product. An understanding of the flow properties of the material is therefore crucial to the manufacture of products.

The flow properties of materials can be measured using a wide range of techniques. However, each technique has its limitations and advantages, and selection of the appropriate method to be used is dependant on many factors, not least the intended application of the data obtained, for example for quality control, materials development or process design through computer simulation. This guide provides information to assist in the identification and selection of the appropriate measurement methods. For a more extensive version see NPL Measurement Note MATC(MN)42 Guide to the measurement of the flow properties of polymeric materials.

Introduction to rheometry

The complete rheological¹ response of a polymer melt is comprised of both its viscous and elastic components. In addition, flows can be shearing, for example as in flow through a cylindrical tube, or extensional (stretching), for example as occurs in blow moulding². To describe the rheological behaviour in these different flow fields requires several largely independent components. These flows may also be steady or transient; an example of the latter being stress relaxation. Properties are typically shear rate, temperature and pressure dependent. Changes in material properties may also result from moisture uptake or loss, and degradation or cross-linking. Furthermore, materials may also exhibit changes in properties due to changes in their structure during flow, particularly for heavily filled materials. Thus the rheological behaviour of a material can be very complex. Consequently its characterisation can vary from the basic to the very complex. The level of complexity required is dependant on the application for which the data is being sought. Quality control applications, for example, do not require the same accuracy and amount of quantitative data as is required for flow simulation.

In selecting the appropriate rheological technique it is important to consider various issues, in particular; the intended use of the data, the deformation modes in the processing of the material, and any additional complicating factors. These issues are summarised in Table 1.

Processes that involve considerable extensional flow deformations (stretching flows) are, for example, blow moulding, fibre spinning, film extrusion and blowing, thermoforming and wire coating. The extensional flow behaviour of polymers will therefore have a significant affect on their processability. However, the more established rheological techniques predominantly characterise the behaviour of polymers in shear and it can prove difficult to relate the behaviour measured in shear with that observed in processing. Thus characterisation using extensional flow methods will be more appropriate. For processes that are dominated by shear flow, for example injection moulding and to a lesser degree extrusion moulding, the

¹ Rheology is defined as the study of the flow and deformation of materials.

² It is noted that there are three basic types of extensional deformation: uniaxial, biaxial, and planar. In a production process the actual deformation is likely to be a complex combination of them [1,2].

emphasis should be more on shear flow characterisation. As a general rule, it is recommended to select a technique that mimics the process for which the data are being sought.

Shear and strain rates vary in processing significantly making it difficult to be specific about their magnitudes. However, in selecting an appropriate technique it is important to consider the shear rates or strain rates that occur during processing. For example, in injection moulding shear rates can be very high, whereas in the extrusion of thick-walled pipe they tend to be significantly lower. Similarly, extensional strain rates can be very high in wire coating, but very low in the extrusion of thick-walled pipe. It is desirable to match the rates of the characterisation technique with those occurring in processing.

Definitions and units

In accordance with the Nomenclature Committee of the Society of Rheology, rheological terminology and notation is presented by Dealy [3]. Furthermore, additional terms are defined in the relevant international Standards.

Shear viscosity is given by the shear stress divided by the shear rate in steady shear flow. To differentiate it from kinematic viscosity it is also referred to as dynamic viscosity.

Shear (or dynamic) viscosity is normally given the units of Ns/m^2 or $\text{Pa}\cdot\text{s}$ (these units are equivalent as $1 \text{ N/m}^2 = 1 \text{ Pa}$). Alternative units used for viscosity are poise where:

$$10 \text{ poise (g/cm s)} = 1 \text{ kg/m s} = 1 \text{ Ns/m}^2 = 1 \text{ Pa}\cdot\text{s}$$

The kinematic viscosity, not normally used for plastics melts, is given by:

$$\text{kinematic viscosity} = \text{dynamic viscosity} / \text{density}$$

It has units of m^2/s , although Stokes are often quoted where:

$$1 \text{ Stoke} = 1 \times 10^{-4} \text{ m}^2\text{s}^{-1}.$$

Table 1: Issues that need to be considered when selecting appropriate test techniques.

Issue	Options
Requirement for data	<ul style="list-style-type: none"> • materials development • materials selection • quality control / troubleshooting • tool design • process design • process optimisation
Deformation mode	<ul style="list-style-type: none"> • shear • extensional: e.g. uniaxial, biaxial, planar or complex extensional flow • complex: combinations of shear and extension
Material response	<ul style="list-style-type: none"> • viscous • viscoelastic
Complicating factors	<ul style="list-style-type: none"> • shear rate dependence • temperature dependence • time dependence of properties: e.g. degradation, cross-linking, thixotropy • pressure dependence • slip flow

Selection of rheological techniques

There is a wide range of rheological techniques available and each one has its advantages and disadvantages. To maximise the value of the data generated it is obviously important to ensure that the most appropriate technique is used for the application. A simple rule of thumb is to employ a technique that mimics the process for which the data is required. For example, for extrusion then an extrusion based characterisation technique is appropriate, and for film blowing, in which the melt is deformed in a predominantly extensional fashion, an extensional technique is appropriate. Table 2 summarises details of the more commonly used rheological techniques.

Table 2: Summary of rheological techniques

Technique:	Dominant deformation mode	Relevant Standards	Properties normally measurable	Additional comments
Melt mass or melt volume flow rate (MFR/MVR)	Shear flow dominated extrusion technique. Viscous response	ISO 1133 ASTM D1238	Melt mass flow rate* Melt volume flow rate*	Shear viscosity and entrance pressure drop can be determined, albeit using an additional die.
Capillary die / slit die extrusion rheometry	Shear flow dominated extrusion technique. Viscous response	ISO 11443	Shear viscosity Entrance pressure drop	Shear viscosity and entrance pressure drop data can be combined and interpreted as approximate extensional viscosity data: see 'Entrance flow measurement' category below. Technique can be used, with modification, for measuring pressure dependence of viscosity.
Oscillatory rheometry	Shear flow oscillatory rotation technique. Viscoelastic response	ISO 6721-10	Viscoelastic behaviour: storage modulus and loss modulus	Normally parallel plate geometry. Often same instrument as used for steady shear rotational measurements
Rotational rheometry	Shear flow rotational technique. Viscous and viscoelastic responses	ISO 3219	Steady shear viscosity. First & second normal stress differences. Stress relaxation & creep	Normally cone and plate geometry. First and second normal stress differences and stress relaxation and creep are measures of the viscoelasticity of the melt. Often same instrument as used for oscillatory measurements.
Extensional rheometry – Filament stretching	Extensional flow technique. Viscoelastic response.	ISO 20965 [§]	Transient extensional stress growth data (i.e. transient extensional viscosity)	Isothermal measurement of transient extensional properties under controlled conditions of constant strain rate or constant stress.
Extensional rheometry - Fibre-spinning	Extensional flow technique. Viscoelastic response	ISO 16790 [§]	Melt strength*	Tensile strength of a melt strand usually under non-isothermal, non-constant strain rate and stress conditions.

Technique:	Dominant deformation mode	Relevant Standards	Properties normally measurable	Additional comments
Extensional rheometry - Entrance flow measurements	Extensional flow dominated technique. Viscous response.	ISO 11443	Approximate extensional viscosity values ⁺	Approximate extensional viscosity derived from entrance pressure drop and shear viscosity data (from capillary extrusion rheometry) using one of variety of models.
Extrudate swell measurements	Complex/extensional flow technique. Viscoelastic response.	ISO 11443	Extrudate swell values*.	Measure of viscoelastic response of polymer melt. Approximate extensional viscosity ⁺ from draw-down of extrudate.
On-line rheometry	Shear flow dominated extrusion technique. Viscous response	-	Approximate melt flow rate parameters* Shear viscosity Entrance pressure drop*	Melt flow rate geometry and test conditions not reproduced in instruments therefore only approximate melt flow parameters deduced.

* Not fundamental rheological properties.

+ Approximate values are derived as the methods do not operate under conditions of constant strain rate or constant stress.

\$ Standard under development.

Melt flow rate (MFR/MVR)

The melt flow rate method is a measure of the ease of flow of a material. The principle is to determine how much material is extruded through a die in a given time when a load is applied to the molten sample in a barrel [4]. Testing is carried out under tightly specified conditions of temperature, load and test geometry thereby maximising the comparability of results obtained.

The melt flow rate technique is appropriate for quality control purposes and provides a simple, qualitative measure of the processability of the material. The results obtained are not fundamental rheological properties, and tend to be obtained at relatively low shear rates. However, recent work at the NPL has demonstrated that the melt flow rate instrument, with minor modifications, can be used to determine quantitatively accurate shear viscosity and entrance pressure drop data [5].

NPL Facility: Instrumented melt flow rate instrument for testing wide range of thermoplastics materials.

Capillary and slit die extrusion rheometry

Capillary and slit die extrusion rheometers [6] are used predominantly to determine the shear viscosity of molten materials. The principle is to measure the pressure drops across one or more dies for various volume flow rates, from which shear viscosity is calculated. Corrections can be applied to the data to take into account errors in the measurement procedure and for that reason various “shear viscosities” - end-corrected and Rabinowitsch

corrected - exist. Results of an international intercomparison and an analysis of measurement uncertainties are reported by Rides [7].

The method can also be used to determine entrance pressure drop values as a function of flow rate. These values can be related to the extensional viscosity of the material [8, 9]. Such values, particularly when comparing similar types of material, are considered to be qualitatively valuable, for example in ranking materials. Through modification the method can also be used to determine the pressure dependence of viscosity.

The method is suitable for generating quantitatively accurate data for modelling as well as for quality control.

NPL Facility: Two capillary extrusion rheometers, suited for molten polymers, covering a wide range of temperatures and shear rates using dies from 0.5 mm to 2 mm in diameter. Capability to measure pressure dependence of materials.

Oscillatory rheometry

The viscoelastic properties of polymer melts can be measured using oscillatory rheometry [10]. The principle of the technique is to subject a specimen, held between two plates, to a sinusoidal torque or displacement. The response of the sample to that input is measured. Typically, shear storage G' and shear loss G'' moduli are determined.

The results of an international intercomparison on the method and the determination of the uncertainties of the measurement of the dynamic properties are presented by Rides [11].

The method is suitable for generating quantitatively accurate data for modelling as well as for quality control.

NPL Facility: Controlled stress oscillatory rheometer covering a wide range of temperatures and frequencies, suited for measurement of stable and curing/degrading materials having viscosities in the range from approximately 1 mPa.s to 10,000 Pa.s.

Rotational rheometry

Rotational rheometers can be used to determine transient and steady shear flow properties of materials; typically shear viscosity, creep or stress relaxation. Furthermore, the first and second normal stress differences, indicative of the elasticity of the material, can also be measured. The principle, and often the instrument, is the same as for the oscillatory rheometer except that the deformation of the sample is obtained by rotating rather than oscillating one plate relative to the other.

The standard, ISO 3219, describes the measurement of shear viscosity [12]. Such measurements tend to be limited to an upper shear rate of approximately 10 s^{-1} as at higher rates some of the sample can be ejected out from between the plates thereby critically changing the sample geometry.

NPL Facility: Controlled stress oscillatory rheometer covering a wide range of temperatures and shear rates, suited for measurement of stable and curing/degrading materials having viscosities in the range from approximately 1 mPa.s upwards.

Extensional rheometry

Extensional rheometry can be divided into two basic categories: ones in which quantitatively accurate transient extensional viscosity data are determined, and the other in which qualitative data are determined. Stretching rheometers of the sort defined by ISO/DIS 20965 [13, 14] fit into the first category. Fibre spinning [15] and entrance flow measurements [8] typically fit into the second category.

In the first category the measurements are more complex but are generally easier to interpret. They are suitable for generating transient extensional viscosity data for modelling or for more involved materials characterisation. In comparison, fibre-spinning and entrance flow measurements are more appropriate for quality control type functions. Both of these qualitative techniques can be carried out using an extrusion device, e.g. an extrusion rheometer. For the fibre spinning method a haul-off device is required. The test is normally carried out under non-isothermal conditions. For entrance flow measurements approximate extensional viscosities are derived using analytical models, for example the Cogswell model [9].

NPL Facility: Measurement of extensional viscosity using (a) Cogswell method with capillary extrusion rheometry entrance pressure drop measurement, (b) by a fibre drawing method.

Extrudate swell and draw down

The measurement of extrudate swell is best as a qualitative measure of flow behaviour, although attempts to correlate it with fundamental rheological properties have been attempted. The measurement of extrudate swell of polymer melts using capillary extrusion rheometers is specified by the standard ISO 11443 [6]. An intercomparison of extrudate swell measurements using a high density polyethylene [16] indicated that the reproducibility of results was poor. This was not entirely unexpected due to the differences in the procedures used by the laboratories, but is an indication of the difficulty of such measurements.

NPL Facility: Measurement of extrudate swell and draw down using either a capillary extrusion rheometer or a melt flow rate instrument.

On-line rheometry

On-line measurement of the rheological properties of polymers is less well established than laboratory based measurements. Instruments tend to operate on the use of capillary or slit dies, with pressure drop measurement along the length of the die. The approach is suitable for near real-time monitoring of production processes that are typically extrusion based. Approximate melt flow rate or shear viscosity values may be obtained, depending on the geometry used. The technique is most suited to quality control applications.

References

1. Mackosko, C.W., Rheology – Principles, Measurements and Applications, VCH Publishers Inc., 1994.
2. Whorlow, R.W., Rheological Techniques, Ellis Horwood Ltd, 1992.
3. Dealy, J.M., J. Rheology 39(1) Jan/Feb 1995, pp.253-265.
4. ISO1133: Plastics - Determination of the melt flow rate and melt volume flow rate of thermoplastics.
5. Measurement Good Practice Guide No. 61. Improved testing using the melt flow rate instruments – multi-rate and extensional flow measurements, M. Rides C.R.G. Allen and A. Dawson, National Physical Laboratory.
6. ISO 11443: Plastics - Determination of the fluidity of plastics using capillary and slit die rheometers.
7. M. Rides and C.R.G. Allen, Capillary extrusion rheometry intercomparison using polyethylene and glass-fibre filled polypropylene melts: measurement of shear viscosity and entrance pressure drop, NPL Report CMMT(A)25, May 1996.
8. Measurement Good Practice Guide No. 16. Extensional flow properties of polymer melts using converging flow methods, March 1999, M Rides and C Allen, National Physical Laboratory.
9. Cogswell, F.N., Polym. Eng. Sci., 12 No.1 (1972) pp.64-73.
10. ISO 6721-10: Plastics - Determination of dynamic mechanical properties, Part 10: Complex shear viscosity using a parallel plate oscillatory rheometer.
11. M. Rides and C.R.G. Allen, Round robin for parallel plate oscillatory rheometry using polyethylene and polypropylene melts, NPL Report CMMT(A)11, January 1996.
12. ISO 3219: Plastics - Determination of viscosity using a rotational viscometer with defined shear rate.
13. ISO/DIS 20965 Plastics – Determination of the transient extensional viscosity of polymers melts.
14. Measurement Good Practice Guide No. 18. Extensional flow properties of polymer melts using stretching flow methods, May 1999, M Rides and C Allen, National Physical Laboratory.
15. ISO/DIS 16790: Plastics - Determination of drawing characteristics of thermoplastics in the molten state (under development).
16. M. Rides and C.R.G. Allen, Intercomparison of extrudate swell measurements using capillary extrusion rheometers for a polyethylene melt, NPL Report CMMT(A)9, January 1996.