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## Capillary Rheometry

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### INTRODUCTION

Rheology is the study of the deformation of materials. This includes the elastic deformation of solids such as metals as well as the viscous behavior of fluids such as water or oil. There is a wide range of materials that exhibit both a viscous and an elastic response to an applied force, and polymers fall into this group. One of the best ways to determine the viscous nature of these materials is with a capillary rheometer.

A capillary rheometer operates by measuring the force required to extrude a material through a small channel at a known flow rate. High temperatures and forces are required to work with polymers; capillary rheometers are robust instruments that are capable of reaching the temperatures and shear rates typical of a wide range of processing equipment, from compression molders to extruders to injection molders. This makes them the instrument of choice for evaluating the suitability of a new polymer for a specific process. Other types of rheometers, such as cone-and-plate-type rotational rheometers, are designed to study materials at very low deformation rates and cannot reach the shear rates necessary to directly evaluate the processability of polymers. Capillary rheometers are also very useful in quality control applications, for process troubleshooting, and process flow modeling.

The basic output of a capillary rheometer is the viscosity curve (or flow curve), the viscosity of a test sample expressed as a function of shear rate at a single test temperature. Many things influence the shape of the viscosity curve. Viscosity data can be used to study the effects of temperature, additives, and/or fillers on material processability, and to determine optimum process conditions. Viscosity may also be correlated with other, more difficult to measure properties such as molecular-weight distribution.

This chapter starts with a presentation of the basic equations used to calculate viscosity, the limitations of their assumptions, and the procedures used to correct for these problems. A basic capillary rheometer is described, and then a detailed description of the steps used to set up and run an experiment is presented. Methods of interpreting the data and some procedures to gather data other than viscosity curves are also discussed.

## THEORY

Rheology studies the relationship between force and deformation in a material. To investigate this phenomenon we must be able to measure both force and deformation quantitatively. Steady simple shear is the simplest mode of deforming a fluid. It allows simple definitions of stress, strain, and strain rate, and a simple measurement of viscosity. With this as a basis, we will then examine the pressure flow used in capillary rheometers.

Before starting, the following Greek symbols are used in the field of rheology and throughout this chapter:

- $\gamma$  (gamma): shear strain
- $\dot{\gamma}$  (gamma dot): shear rate
- $\sigma$  (sigma): shear stress
- $\eta$  (eta): viscosity

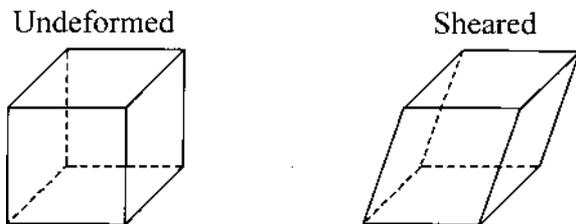
### Steady Shear Viscosity

The most important mode of deformation during flow is shear. Shearing deformation results when the material is moved in a direction parallel to the surface as shown in [Fig. 1](#). This can be visualized as layers of material sliding across one another, similar to shearing a deck of cards.

The amount of deformation is measured by the shear strain as defined below:

$$\gamma = \frac{x}{h} = \frac{X}{H} \quad (1)$$

The shear strain is normalized by the height of the sample and is zero when the sample is undeformed. Each element in the sample sees the same amount



**Figure 1** Shear strain of a cube.

of strain regardless of the size of the element (see Fig. 2). Strain is dimensionless and is often reported as a percentage.

Fluids flowing in a capillary rheometer see a shearing mode of deformation. Since fluids are always in motion and cannot hold a shape, a static measure of the strain is not useful; a continuous deformation rate must be determined. Differentiating the shear strain with respect to time gives the shear strain rate or “shear rate”:

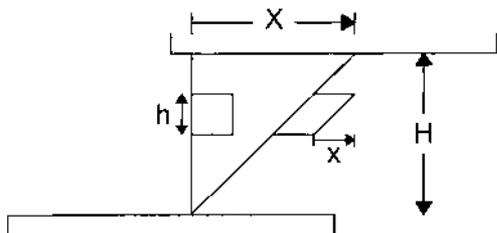
$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{1}{H} \frac{dX}{dt} = \frac{V}{H} \quad (2)$$

which is a measure of how fast the shearing process is occurring. The units of shear rate are reciprocal seconds ( $s^{-1}$ ), with parameters  $V$  and  $H$  as defined in Fig. 3.

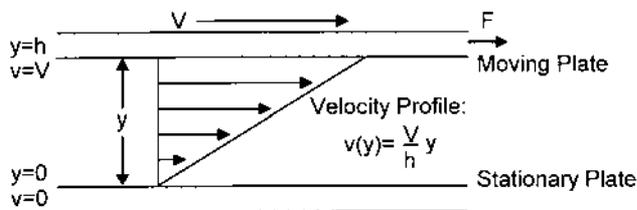
Once the deformation is determined, the force causing the deformation must be measured. A stress,  $\sigma$ , is defined as a force  $F$  applied to an area  $A$ :

$$\sigma = \frac{F}{A} \quad (3)$$

$A$  is the area of the sample over which the force is applied; in Fig. 1 it corresponds to the area of the top of the cube and in Fig. 3 it corresponds



**Figure 2** Shear strain—the top plate is moved to the right by distance  $X$ .



**Figure 3** Simple steady shear of a fluid between two infinite plates. The fluid is stationary at the fixed plate and moves at velocity  $V$  at the moving plate.

to the area of the sample that wets the plates. A shear stress acts parallel to the surface to which it is applied, and the units of stress are force per unit area, or Pa ( $\text{N/m}^2$ ) in the SI system.

Figure 3 illustrates a steady simple shear flow between infinitely large plates (hence no edge effects, leakage, etc., which would be experienced in a real-world experiment). The top plate moves with a constant velocity  $V$  and shears a fluid sample of height  $H$ . The shear rate is constant across the gap so that all material sees the same deformation. The force  $F$  is that which is required to keep the plate moving at constant speed  $V$ . The stress and shear rate are determined from the force and the plate speed and geometry using Eqs. (2) and (3). The viscosity, defined as the fluid's resistance to flow, is determined from the ratio of the force and the deformation rate:

$$\eta = \frac{\sigma}{\dot{\gamma}} \quad (4)$$

The units for viscosity are Pa-s. A Newtonian fluid is a fluid that follows Newton's law of viscosity, which states that the viscosity is independent of shear rate. This implies a linear relation between force and plate speed; doubling the force on the plate will double its velocity.

### Newtonian Equations for Round-Hole Capillary Flow

The flow in Fig. 3 is called a *drag flow*; the top plate is dragging the material across the stationary plate to create the velocity profile that is shearing the fluid. In contrast, flow in a capillary rheometer is *pressure-driven flow*. All of the wall area inside the capillary is stationary so that the material has zero velocity at the walls and a maximum velocity along the centerline. Calculating the shear rate in a capillary is not as straightforward as with steady simple shear. Each fluid element still sees steady simple shear, but the shear rate is no longer constant; it varies across the radius of the die. It runs

from zero at the centerline to a maximum at the wall. Since the shear rate is not constant, a point must be chosen where the shear rate and stress can both be determined. The forces that generate stress interact with the material at the wall, and at this point the shear rate is a maximum. Thus this is where the viscosity is calculated.

Assuming Newtonian fluid behavior (constant viscosity), the no-slip assumption ( $v = 0$  at the die wall), and fully developed flow, a parabolic velocity distribution can be derived for the material flowing down the capillary:

$$v(r) = 2v^* \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \quad (5)$$

where  $v^*$  is the average velocity of the fluid and  $R$  is the radius of the capillary. This average velocity can be defined in terms of the cross section of the die and the volumetric flow rate of the fluid,  $Q$ , as follows:

$$v^* = \frac{Q}{\pi R^2} \quad (6)$$

The shear rate profile can now be calculated by differentiating the velocity profile. The shear rate at the wall ( $r = R$ ) is determined and expressed as a function of the volumetric flow rate:

$$\dot{\gamma}_{\text{ap}} = \left. \frac{dv}{dr} \right|_{r=R} = \frac{4Q}{\pi R^3} \quad (7)$$

The meaning of the subscript “ap” is discussed in the section on the Rabinowitch correction.

Once the shear rate is established, the stress required to drive the flow must be determined. A force balance between the driving pressure across the cross section of the capillary and the shear stress experienced along the wetted surface inside the capillary links the measured pressure drop across the die ( $\Delta P$ ) to the stress at the wall ( $\sigma_W$ ):

$$\Delta P \cdot \pi R^2 = \sigma_W \cdot 2\pi RL \quad (8)$$

where  $L$  is the length of the die. This can be rearranged to give

$$\sigma_W = \frac{\Delta P \cdot R}{2L} \quad (9)$$

Pressure is measured in units of pascals (Pa, the same unit as stress); other common usages are MPa ( $10^6$  Pa) and bar ( $10^5$  Pa). Using eqs. (7) and (9), the Newtonian viscosity can then be determined from the flow rate and the pressure drop:

$$\eta_{\text{ap}} = \frac{\sigma_W}{\dot{\gamma}_{\text{ap}}} = \frac{\pi \cdot \Delta P \cdot R^4}{8 \cdot Q \cdot L} \quad (10)$$

Again, the units for viscosity are Pa-s (Pascal-seconds).

### Slit Die Capillaries

In addition in round-hole capillaries, it is possible to use a slit die to perform viscosity measurements. Theoretically such a die would have no side walls (be infinitely wide), but in practice it has been found that wall effects are negligible if the slit die is at least 10 times wider than it is high. The equations for slit flow are similar to those for round-hole capillaries:

$$\dot{\gamma}_{\text{ap}} = \frac{6Q}{H^2 W} \quad (11)$$

$$\sigma_W = \frac{\Delta P \cdot H}{L} \quad (12)$$

$$\eta_{\text{ap}} = \frac{\sigma_W}{\dot{\gamma}_{\text{ap}}} = \frac{\Delta P \cdot H^3 \cdot W}{12 \cdot Q \cdot L} \quad (13)$$

where  $H$  is the height and  $W$  is the width of the slit.

The main advantage of a slit die is that, since it has flat walls, the pressure transducers can be mounted directly in the die. This eliminates the entry and exit effects discussed in the section on the Bagley correction below. A slit die's disadvantages tend to be of a practical nature. While slit dies can usually be made wide enough to avoid edge effects, they are much more difficult to flush clean with a new sample, especially near the edges. They are usually multipiece dies that require much more effort to disassemble and clean. Round-hole dies are more convenient and are the die of choice unless a special test procedure specifically requires a slit die. (This might happen if a tapelike extrudate is desired for further testing, or if three or more pressure transducers are to be mounted along the die to study the pressure profile along the die.)

### Rabinowitch Correction

The steady simple shear flow in [Fig. 3](#) is fully controllable, because the velocity profile of the flow depends only on the geometry and motion of the plates, regardless of the rheological properties of the fluid. Fully developed flow in a capillary tube is only partially controllable. The material properties can affect the velocity profile, which must be known in order to calculate the shear rate that the sample is experiencing. If a Newtonian fluid

(constant viscosity at all shear rates) is assumed, then a parabolic flow profile can be calculated as in Fig. 4 with  $n = 1$ . Shear rates and viscosities calculated using this assumption are termed “apparent” values, with the subscript “ap.” Apparent values are correct for Newtonian fluids. Most materials, including most polymers and polymer solutions, are not Newtonian fluids because their viscosity is not constant with changing shear rate.

Figure 5 shows some of the basic curve shapes and names for materials whose viscosity varies with shear rate. Most polymers are pseudo-plastic, or shear thinning; as the shear rate increases, their viscosity decreases. Figure 6 shows a typical flow curve for a molten polymer. It can be divided into three regions: the Newtonian plateau at low shear, the power law region at high shear, and the transition zone in between. At very low shear rates (often  $\ll 0.01 \text{ s}^{-1}$  for polymer melts),  $\eta$  is independent of  $\dot{\gamma}$ ; this constant value is called the zero-shear viscosity ( $\eta_0$ ). As the shear rate is raised, the structure of the molecular chains begins to break down and the viscosity is reduced. At higher shear rates, this can be modeled with the power law model,

$$\tau = k\dot{\gamma}^n \quad (14)$$

which has parameters  $n$  and  $k$ . When combined with Eq. (4), this gives

$$\eta = k\dot{\gamma}^{n-1} \quad (15)$$

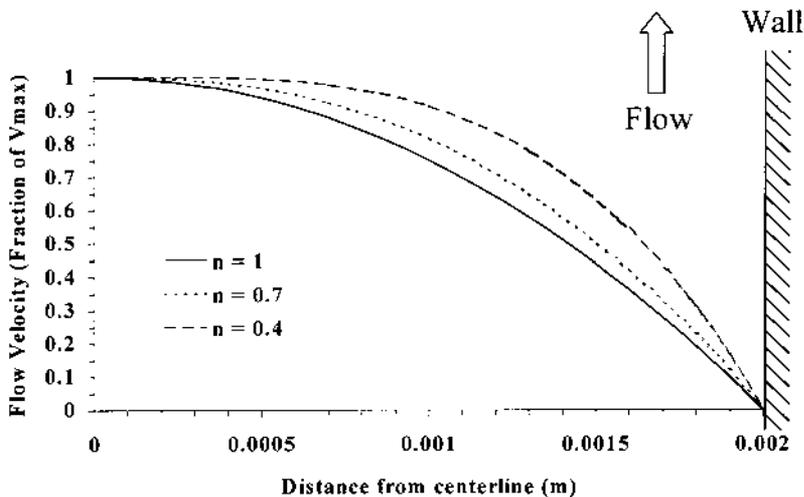
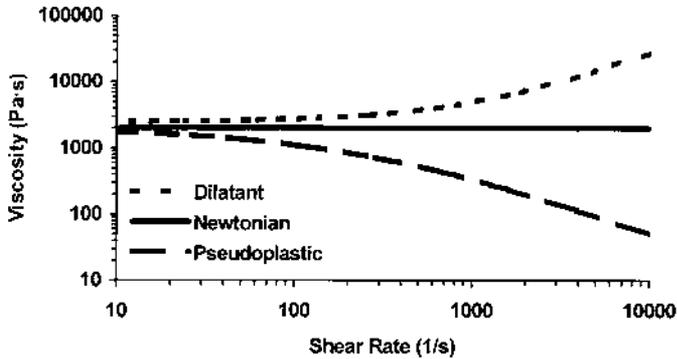


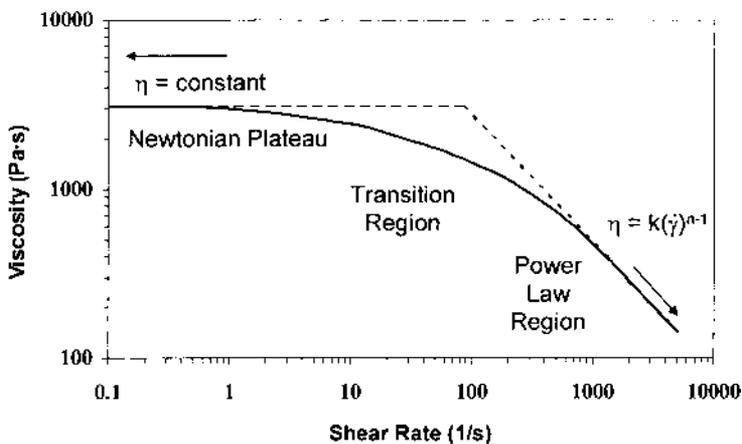
Figure 4 Velocity profiles as a function of the power law exponent.



**Figure 5** Viscosity curves varying with shear rate.

Because viscosity is nonconstant, it must be measured across a range of shear rates to fully characterize a material. The equations used to calculate the apparent viscosity are not exactly correct due to the shear-thinning phenomenon. A correction has been developed (by Rabinowitch [1]) that uses the slope of the  $\sigma_{ap}(\dot{\gamma}_{ap})$  curve,

$$n = \frac{d \log(\sigma_{ap})}{d \log(\dot{\gamma}_{ap})} \quad (16)$$



**Figure 6** Regions of a typical flow curve for a shear-thinning polymer.

to correct for the non-constant viscosity. For a Newtonian fluid,  $n = 1$ . The smaller the value of  $n$ , the more shear thinning is occurring and the larger the correction that is required. The true wall shear rate is calculated using

$$\dot{\gamma}_w = \dot{\gamma}_{ap} \left( \frac{3n + 1}{4n} \right) \quad (17)$$

with  $n$  calculated at the point of the measurement to be corrected. Note that multiple measurements must be available so that the calculation of a slope is possible; it is not possible to correct a single point measurement. Most modern capillary rheometers perform this correction automatically in their software, and then use the true shear rate values in eq. 4 to calculate the true viscosity.

Another approach that is available involves calculating the viscosity at a point different from the wall. The Schümmer correction [2] involves determining where the actual velocity profile intersects with the Newtonian profile; at this point,

$$\eta(\dot{\gamma}^*) = \eta_{ap}(\dot{\gamma}_{ap}) \quad (18)$$

i.e., the apparent viscosity equals the true viscosity at the Schümmer-corrected shear rate. If the Schümmer shear rate is

$$\dot{\gamma}^* = x\dot{\gamma}_{ap} \quad (19)$$

then for a power law fluid,

$$x = \left( \frac{3n + 1}{4n} \right)^{n/n-1} \quad (20)$$

The value of  $x$  varies by only a small amount over a wide range of values of  $n$ , so that a representative value of  $x^*$  may be chosen for a material with very little loss in accuracy. This method can therefore be used to correct the shear rate of single point measurements if an approximate value of  $n$  is known for the tested material. Schümmer suggests that if a constant value of  $x = 0.83$  is used for all materials, the error in the viscosity will be 3% or less.

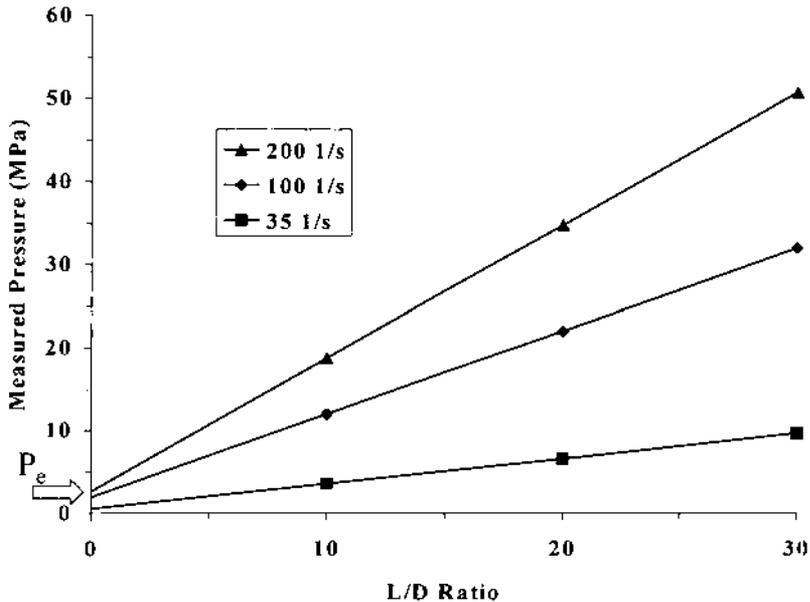
### Bagley Correction

Most capillary rheometers use round-hole dies with the pressure (or force) measured above the die in the barrel. The melt flow undergoes a large contraction as it moves from the barrel into the die and an expansion as it leaves the die to the atmosphere. These entrance and exit effects add an extra pressure drop ( $P_e$ ) to the measured pressure ( $P_m$ ) in addition to the pressure drop due to flow through the die ( $\Delta P$ ). This will result in a viscosity measurement that is erroneously high due to the  $P_e$  component.

Bagley [3] developed a method to determine  $P_e$  so that capillary data could be corrected. The method requires multiple measurements using dies of the same diameter and varying lengths. By keeping the diameter the same, the entrance and exit effects will be the same for each die; the total measured pressure  $P_m$  can be determined as a function of die length for each shear rate. Extrapolating the pressure back to a die with zero length allows the determination of  $P_e$ . In other words, whatever pressure still remains after  $\Delta P$  is removed is the pressure due to entrance and exit effects.

The following steps are taken for a Bagley correction.

1. Determine the apparent flow curve for the sample using at least two different die lengths (three or more improves accuracy). The same apparent shear rate points must be used for all tests.
2. Construct a Bagley plot from this data (see Fig. 7). The measured pressures are plotted against the  $L/D$  of the die for each apparent shear rate. (*Note:* By convention, the Bagley plot



**Figure 7** Bagley correction performed for a three-point curve run three times with 30/1-, 20/1-, and 10/1-mm dies. For each shear rate,  $P_e$  is determined by extrapolating back to  $L/D = 0$ .

uses the  $L/D$  ratio instead of just the die length, but since  $D$  is held constant the results are the same using  $L$  or  $L/D$ ).

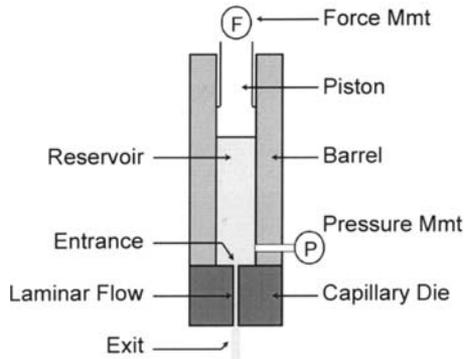
3. For each shear rate, perform a linear extrapolation back to zero. The value of pressure at  $L/D = 0$  is  $P_e$ , the extra pressure due to entrance and exit effects.
4. To apply the correction, subtract  $P_e$  from the measured pressure  $P_m$  to get the correct pressure for each data point. Use the corrected pressure to calculate the stress and viscosity for that point. Once each curve (from the different dies) has been corrected, the curves can be averaged and Rabinowitch corrected to get a final true viscosity curve.

The entrance and exit effects are often quite small relative to the measured pressure, especially if longer dies are used that increase the magnitude of  $\Delta P$  compared to  $P_e$ . A study of the effect of both the Bagley and Rabinowitch corrections [4] demonstrated that the corrections become more substantial with shorter dies and higher shear rates. As a rule of thumb, dies with an  $L/D$  ratio of 20 or greater often have  $P_e$  values that are 5% or less of  $P_m$ , in which case the effort of performing the Bagley correction is probably not necessary. However, there are many materials (especially with strong elastic components) that have appreciable  $P_e$  values even with long dies, so it is wise to check an unknown material at least once to determine the magnitude of the Bagley correction before deciding if it is necessary.

## CAPILLARY RHEOMETERS

A capillary rheometer measures the viscous properties of a fluid by determining the pressure required to cause it to flow through a small cylindrical tube or rectangular slit (the capillary) at a set flow rate. Many rheometers control the flow rate (by setting the piston speed) and measure the pressure drop across the capillary; some gas- or weight-driven models fix the pressure and measure the flow. The American Society for Testing and Materials has issued a standard entitled “Standard Test Method for Determination of Polymeric Materials by Means of a Capillary Rheometer,” designated D3835–96 [5]. This method covers the measurement of the viscosity of materials at temperatures and shear rates found in common plastics processes. Issues such as temperature control and calibration, rheometer and die specifications, common temperature ranges, procedures, data analysis, and reproducibility are addressed.

Figure 8 shows a schematic of a typical capillary rheometer. The molten polymer is held in a cylindrical reservoir and heated to the desired temperature. A motor-driven piston is used to force the material down the barrel

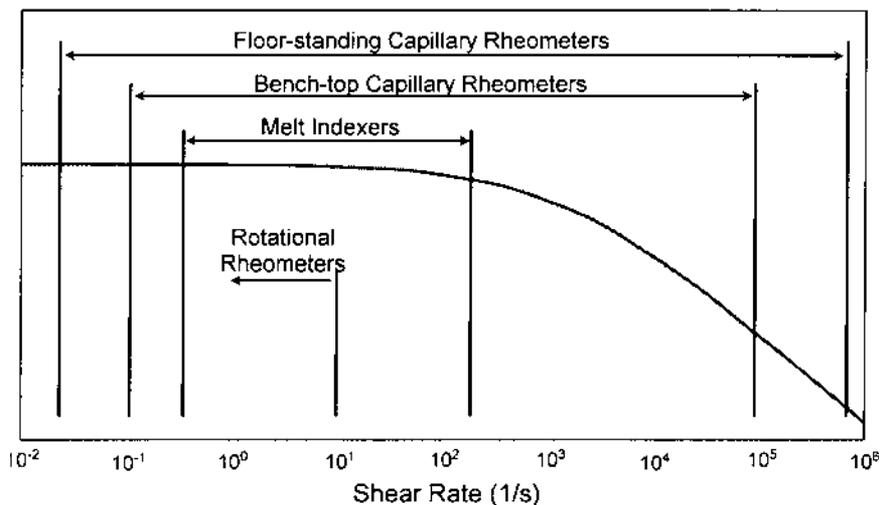


**Figure 8** Schematic of a capillary rheometer.

and through the die, with the flow rate determined by the speed of the piston. Once the pressure has reached equilibrium it is noted, and the piston speed may be changed to measure the material at a different rate. The important parameters in this measurement to be controlled and/or measured are the temperature, pressure (or force on the piston), the material flow rate (calculated from the piston speed and the barrel cross section), and the die geometry.

The geometry of the capillary rheometer, both the barrel and the die, must be known exactly. Typical barrels range in size from 9 to 15 mm in diameter. Larger barrels hold more material and achieve higher flow rates for the same piston speed but require longer holding times for the samples to reach temperature equilibrium before a test can begin. Barrel, piston, and die are made of very hard metals to resist wear over time, but tolerances must be checked for wear on a regular basis. The piston must seal well with the barrel to prevent backflow of the material. Often a double-land or O-ring design is used.

The capillary dies must be very smooth, accurately machined, and hard. They are often made of tungsten carbide. Accuracy is especially critical. In a round-hole capillary, for example, the shear rate is a function of the radius cubed [see Eq. (7)]. A 1% error in the radius will result in a 3% error in the shear rate determination. Some dies have entry angles machined into their entrance to ease the abruptness of the transition from barrel to die and reduce the entrance pressure losses (see Bagley correction). Typical dies have diameters in the range of 0.5 to 2 mm, but specialty dies are available in almost any practical dimension. Depending on the piston speed and die selection, a wide range of shear rates can be achieved on capillary rheometers (see Fig. 9).



**Figure 9** Shear rate ranges of common rheometers.

Once the flow rate (and thus the shear rate) is determined from the piston speed and the geometry, the pressure drop across the die must be determined. This is measured with a pressure transducer in the barrel near the die or a force transducer situated on top of the piston. Each method has pros and cons, so choosing the best method depends on a particular situation (Table 1).

Pressure transducers are often preferred when high-accuracy measurements on a broad range of materials are required. Force transducers see use in quality control labs, where ease of operation and cleaning are important, or when maximum corrosion resistance is desired. Further discussions will assume that a pressure measurement system rather than a force transducer is used. (To calculate stress, the force measurement is converted into a barrel pressure by dividing by the cross-sectional area of the barrel, so no generality is lost.)

Often the pressure measurement is the limiting factor determining the maximum shear rate range of a single experiment. Pressure and force transducers typically have 0.5% of full scale total accuracy (linearity, repeatability, and hysteresis). This means that a measurement registering 1% of full scale has a relative accuracy of  $\pm 50\%$ ! Manufacturers often recommend measuring pressures between 10% and 100% of full scale for this reason. This is a range of only a single decade, while most rheometers can accurately control piston speeds over a range of four decades or more. New transducers

**Table 1** Pros and Cons of Measurement with Pressure and Force Transducers

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Pressure measurements	Pressure is measured right at the die entrance Transducers are less expensive and easier to change, allowing a better match range to material viscosity But a pressure hole error is generated (usually negligible since material flows slowly in the barrel)
Force measurements	Easier to clean (no pressure tap to collect material) Transducer will not come in contact with corrosive or very-high-temperature samples But piston friction can be significant and material flow along barrel as well as through die is measure; the measurement is dependent on the amount of material in the barrel

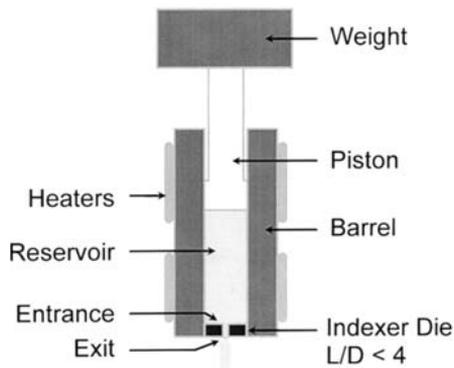
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are being released with better accuracy as high as  $\pm 0.1\%$ , a significant improvement but not enough to remove the restriction completely.

One of the most important criteria for any instrument is repeatability, not only with the same instrument running the same sample, but between different machines with different manufacturers in different laboratories. As well as machine design and setup, repeatability depends on the actual test procedure used and the consistency of sample conditioning. ASTM D3835 includes the results of a round-robin test in which a number of different labs measured flow curves on a number of materials. It was found that, within a single lab, the standard deviation in the viscosity results was typically less than 2%. Between the labs, considerably higher variability was seen; most measurements had between 3% and 8% standard deviation. An important observation is that the standard deviations tended to be much higher for the lower shear rate points. This is because stress measurements taken at the low end of the pressure/force transducer ranges, as mentioned above, have much higher relative errors.

## MELT INDEXERS

The melt index is an industry standard test used to assess the processability of a polymer melt. A schematic of a melt indexer is shown in Fig. 10. It is essentially a stress-controlled capillary rheometer using a weight-driven piston to force material through a round-hole capillary die. A melt index is obtained by measuring the amount of time required for a specific volume of material to be extruded from the die, with the results presented in units of g/10 min.



**Figure 10** Schematic of a melt indexer.

ASTM Method 1238, “Standard Test Method for Flow Rates of Thermoplastics by Extrusion Plastometer” [6], completely defines the melt index, both the instrument and the experimental procedure. Temperatures and instrument configurations for common materials are given along with recommended calibration procedures and round-robin results. This method must be strictly followed if consistent melt index results are to be obtained. A melt index measurement is performed at low stress levels compared to capillary rheometers measurements (typical weights are in the range of 1.2–21.6 kg) and is sensitive to variations in operating procedure, instrument cleanliness (between tests), and operator bias (items such as packing and sample preparation).

The melt index itself is not a material property like temperature or viscosity, but a machine dependent index. This is because the die is short relative to its length (8 mm long and 2.1 mm in diameter), with an  $L/D < 4$ . Typical  $L/D$  values for capillary rheometers are greater than 15. As a result, the melt index results are heavily influenced by entrance and exit effects at the die (see the section on the Bagley correction) that cannot be exactly duplicated on anything other than another melt indexer. While it is possible to calculate a viscosity from the flow data generated by the melt indexer, the entrance and exit effects also negatively influence its accuracy.

## TECHNIQUES

### Setup Parameters

Before running tests on a polymer sample, a number of parameters must be chosen for the instrument. These include the test temperature, shear rate

ranges, and the die and pressure transducer selections. This section discusses these considerations.

## Temperature

Temperature is one of the most important parameters to be specified, as viscosity is a strong function of temperature. The temperature must be high enough to melt the sample completely and low enough that the sample will not degrade during the test. Once a temperature is chosen, a thermal degradation study should be performed to determine the maximum residence time of the material in the rheometer.

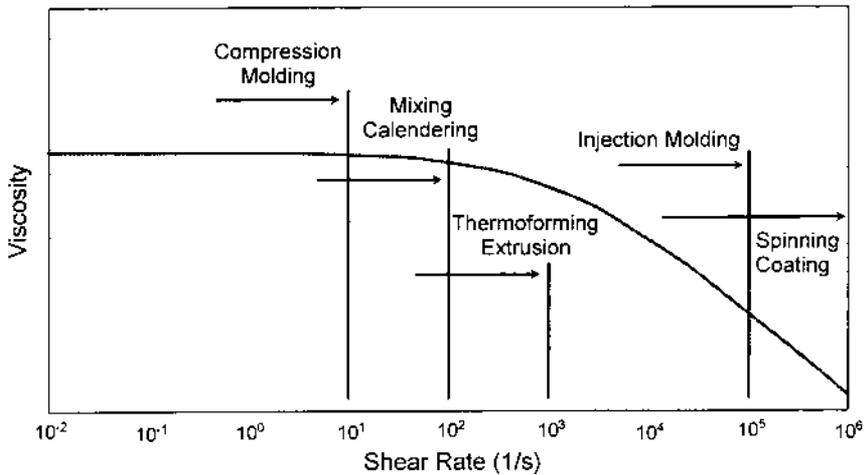
Meaningful test temperatures can often be found in two places: an ASTM specification or a processing temperature. A standard testing temperature suggested by ASTM (either in D3835 or in the melt index specification, D1238) is often used if available, because it has been chosen by experts to provide a good molten sample with a reasonable dwell time in the rheometer. Also, it will likely be chosen by other people, allowing comparison of results with other laboratories and literature sources. The ASTM temperature is often not, however, the temperature at which the material is processed. Using the process temperature will give the most relevant results when the test is performed as part of a troubleshooting effort or to screen candidate samples for a process.

A pretest heating period must be specified to allow a material to melt and come to temperature before a test is begun. Polymers are notoriously poor conductors of heat and require time for the material in the center of the barrel to come to temperature. The amount of time required depends on the temperature and the barrel size: higher temperatures and larger barrel sizes require longer times for temperature stabilization. If too long a period is specified, the duration of the test may be extended to the point that polymer degradation occurs. Typical times for barrels from 9.5 to 12 mm in diameter in the 150–300°C range are 4–7 min.

## Shear Range and Die Diameter Selection

Before selecting a die or transducer, the desired shear rate range for the flow curve must be determined. The process for which the material is intended usually determines this. Some typical ranges are listed in [Fig. 11](#).

A typical test range for an average extrusion process might be from 20 to 2000  $\text{s}^{-1}$ , whereas testing for an injection molding process might be more relevant across a range of 200–20,000  $\text{s}^{-1}$ . Keeping in mind that pressure and force transducers have a maximum usable range of two decades, it is usually a good idea to also limit the shear rate range to two decades in a single test, even if the rheometer is capable of more. Once you are familiar



**Figure 11** Shear rate ranges for common polymer processes. Compare these ranges with the rheometer capabilities in Fig. 9 to see why capillary rheometers are more suited to test polymer processability.

with a material, you may find that you can add extra points at either the high or low end of the range.

Once the shear rate range is determined, the appropriate die can be selected. The radius of the die,  $R$ , is selected first; it should be such that the piston speeds required to generate the selected shear range fall into the mid-range (if possible) of the piston speed range of the instrument. Using Eq. (7) to relate shear rate and volumetric flow rate, and the cross-sectional area of the barrel piston ( $\pi R_B^2$ , where  $R_B$  is the rheometer barrel radius), the piston speed is calculated as

$$v = \frac{\dot{\gamma} R^3}{4R_B^2} \quad (21)$$

The piston speed is a linear function of the shear rate that is strongly affected by the geometry of both the barrel and die. Usually the barrel geometry is fixed and the die geometry is variable; reducing the radius of the die by one-half will increase the shear rate through the die by eight times for the same piston speed. For an instrument with  $R_B = 6\text{mm}$  and  $R = 0.5\text{mm}$  (1-mm diameter), the 20–2,000  $\text{s}^{-1}$  range mentioned above would correspond to piston speeds of 0.0174–1.74 mm/s, easily achievable by most rheometers. On the same instrument, a die with  $R = 0.25\text{mm}$  would be more suitable for testing an injection molding-grade material.

## Die Length and Pressure Transducer Selection

The length of the die controls the magnitude of the pressure drop the sample will generate and determines the range of the pressure transducer that will be required. In many cases, a rheometer has only a single transducer available and so the die length must be properly selected to assure test results in a range suitable for the transducer. The pressure drop is linear with the die length; doubling the length doubles the pressure drop at the same flow rate.

In considering die length, a second criterion is the  $L/D$  (length/diameter) ratio of the die. In order to assure fully developed flow, an  $L/D > 15$  is recommended, with values in the range of 20–30 being common. If a die is too short, then entrance and end effects will form a large percentage of the pressure drop and the viscosity measurement will be incorrect (see the Bagley correction). If a die is too long, the pressure drop may be too great for the rheometer to handle, or pressure/density effects may begin to become significant in the viscosity measurement.

With a material that is completely unfamiliar, one or two trial tests may be required before the best transducer selection can be determined. Usually the rheometer is equipped with a transducer that covers the high end of its capabilities. (Most capillary rheometers can generate pressures up to 1000 bar; most floor-standing units can achieve close to 2000 bar.) Obviously, the first test should use a high-range transducer to avoid possibly overpressuring a more sensitive transducer. Most transducers will take 25–50% overload before damage occurs—check the unit's specifications. If more sensitive transducers are available for your unit, the maximum pressure generated in your first experiment will tell you which transducer to choose for subsequent tests. Note that pressures below 1 bar are extremely difficult to measure even with sensitive transducers.

## Determining the Number of Shear Rate Points per Curve

The number of points that can be achieved in a single test is highly dependent on the piston speed required to generate the desired shear rates. The higher the piston speed, the more material is extruded for the given point. Generally, only a few high-speed points (where the test piston is traveling more than  $\sim 1$  mm/s) can be obtained with a single sample. Rheometers with longer barrels will hold more melt and are able to generate more points. Some experimentation is usually necessary to before a final shear rate configuration can be achieved.

The speed with which a point can be taken depends on how fast the pressure stabilizes after the piston reaches the correct speed. The transient nature of the pressure response in a capillary rheometer has been discussed and modeled by Dealy and Hatzikiriakos [7]. The pressure will stabilize

quickly at high extrusion rates but can take 4–5 min at low rates. This affects both the overall length of the test and the amount of material expended for a given point.

Various algorithms exist to determine automatically when the pressure is stable. One procedure is outlined in an appendix to ASTM D3835. Usually, the operator sets a tolerance (a percentage change in the pressure) over a specified period of time. When the pressure changes less than the tolerance over the comparison interval, then the pressure is considered steady and the viscosity point is taken. If the pressure is still changing, the routine waits for another comparison interval to pass and then checks again.

If the tolerance is made small and the comparison interval long, the pressure will have to be very level before it is considered stable. If the tolerance is relaxed or the comparison interval shortened, then the viscosity point will be taken quickly, while the pressure is still slowly changing. There is a trade-off between speed and accuracy: viscosity points taken more quickly may not be as accurate. Generally, one chooses a reasonable pressure tolerance and a long comparison interval to start (for many materials, a 1% tolerance over a 10–20-s interval is a good starting point). Gradually reducing the length of the interval until the viscosity measurement starts to change allows the determination of the optimum parameters, which in turn determines the number of points that can be obtained in a single test (7–10 points is reasonable in most cases).

### Shear Rate Order

The order in which the shear rate points are run during a test influences the dynamics of the experiment. Running in decreasing order (from high to low rates) as opposed to increasing order will affect the speed of the measurement. When low shear measurements are performed at the end of an experiment rather than the beginning, there is much less material in the rheometer barrel. Therefore there will be less material that must equilibrate before a stable pressure reading is generated; faster stabilization means that the viscosity points can be taken faster.

Unfortunately, the amount of sample saved by taking points faster at low shear rates is offset by extra sample required by the first points at high shear rates, so in most cases the number of viscosity points obtainable with a single barrel of material is about the same. However, running decreasing shear rates can reduce the overall length of an experiment by 30–50% compared to increasing shear rates and in most cases is the preferred mode of operation. One must be careful, however, with unknown materials: starting at a high piston speed can damage an undersized pressure or force transducer.

Sometimes the shear rate order is randomized to ensure that the viscosity measurement is independent of the order in which the points are taken. This causes no problems but, with the piston speed and the pressure swinging up and down, more time will be needed for stabilization. It may not be possible to get as many points as when the shear rates are ordered.

## **Running a Test**

Running a test involves three steps: preparing the sample, preparing and loading the rheometer, and running the test.

### Sample Preparation

Preparation of the sample may involve drying the sample; moisture absorbed from the air can cause some polymers (e.g., polyesters and polycarbonates) to degrade chemically when melted. These samples must be dried in a heated convection oven or vacuum oven to drive off moisture before testing. Since the presence of moisture dramatically affects the rheological properties of the material, it is very important that the drying protocol be followed consistently to ensure repeatable test results.

To develop a drying protocol, test materials that have been in the oven for varying lengths of time. The shortest length of time that gives consistent results should be considered the drying time. In general, higher temperatures (especially over 100°C, if the material does not begin to melt or degrade) and the application of a vacuum will reduce the amount of drying time required. Typical times range from 2 to 6 h.

When loading moisture-sensitive materials into the rheometer, speed is usually the best defense against the material picking up any moisture. Ensure that the drying oven is close to the rheometer and that any sample removed from the oven is immediately loaded or discarded. Some rheometers have a nitrogen system available that blows dry nitrogen into the barrel to keep a blanket over the sample as it is loaded.

### Preparing the Rheometer

Preparing the rheometer involves bringing it to the correct temperature, installing the selected die and pressure transducers, and ensuring that it is clean. When installing cold transducers or dies into a hot instrument, the items should be inserted and tightened only loosely until they have had a chance to reach the rheometer temperature. Final tightening should be performed with items at the test temperature.

One of the most common causes of sample variation is an improperly cleaned rheometer. Making sure the barrel walls and piston are clean will free up piston travel and ensure that degraded material will not contaminate

new material as it flows through the die. Swabbing the barrel with cotton patches and using a rotating brass brush are typical methods of cleaning out the barrel. The barrel wall is often not very dirty, since the close tolerance between the piston and barrel keeps it scraped clean. However, piston travel usually ends a predetermined distance from the die, leaving a disk of material on the top of the die that needs to be removed. Often the cotton patches are sufficient to remove this material. If in doubt, remove the die after cleaning the barrel to see how much material is left behind.

If a pressure tap is present, it must be cleaned at least on a daily basis. Often the material trapped inside the tap degrades very slowly, since it is not exposed to oxygen, and the material does not leave the tap to contaminate the new sample. As long as the material does not carbonize and block the opening into the barrel, it often does not need to be cleaned after each experiment. (Be careful when operating with materials at high temperatures, 300°C or above: the high heat is more likely to carbonize the sample. It is usually better to clean the tap more often in this case.)

The die itself must be purged of the old material before a new test can begin. Often when loading and prepressuring the sample a small amount will be purged through the die; this will suffice to clean the die if the tested materials are similar or if the new material is more viscous than the old. To further aid purging, a high to low shear rate profile causes a large amount of material to flow through the die at the start of the test. By the time the pressure has leveled out for the first point, the die is well purged.

When a lower-viscosity material is used for purging, a half or full barrel of material might be required to remove the old sample before the new sample can be tested. (*Note:* If the sample being tested is very different in viscosity from the previous sample, then a “blank” test should be run, in which the die is purged with an entire barrel of new material to ensure that the previous sample is completely removed.)

If a muffle furnace or sand bath is available, the old sample can be burned out of the die (usually at  $\sim 500\text{--}550^\circ\text{C}$ ) to assure that only the new sample will be present during the test. This is time consuming, however, so often it is done only at the end of the day to prevent buildup from occurring in the die. Not all materials can be successfully burned out of a die; materials that carbonize (such as rubbers and some high-temperature engineering plastics) can permanently plug a die if burning is used to try to remove them. They should be purged with another material (such as a polyolefin) before cleaning.

### Loading the Rheometer

Samples for testing come in many forms, including pellets, powder, cut strips, pourable liquids, or molded slugs. The material is loaded into the

barrel with the aid of a tamping rod. After pouring in a small amount of material, use the tamping rod to press it to the bottom and compact it to remove as much air as possible. Repeat this step roughly 6–10 times, until the barrel is full. Liquids may be poured slowly down one wall of the barrel to avoid air pockets. Semiliquid pastes may have to be loaded with a syringe having a tube attached that is long enough to reach the bottom of the barrel (considerable effort may be involved to get the material to flow down the tube). Every effort must be taken to avoid the introduction of air bubbles, as they will interfere with the measurement.

Once the sample is in place, the piston should be inserted and slowly driven down on top of the sample until a small flow is extruded from the die. This will compress the sample and drive out air bubbles. Usually, by the time the piston is inserted into the barrel the material at the bottom is melted enough to flow, though care should be taken not to overpressure the system. Pushing a small amount of material through the die will help to purge any old material left from previous testing. A pressure spike indicates that the material has filled the pressure tap and no blockage is present.

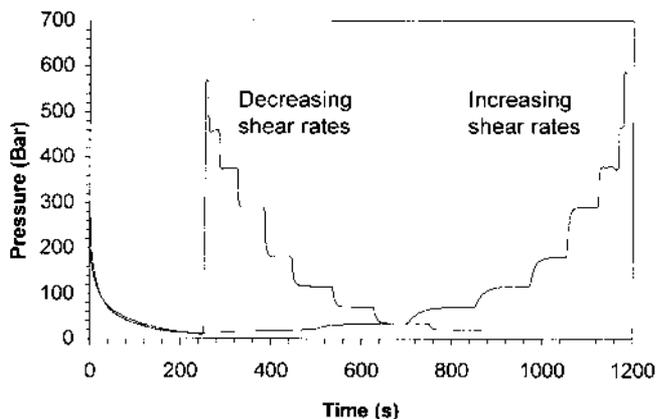
At this point, the melt timer is started and the instrument holds the sample to allow it to come to temperature. Once the allotted time is over, the piston begins to move and the first data point is begun. [Figure 12](#) shows a typical pressure trace from a nine-point viscosity curve for polyethylene.

### Possible Problems

Once operators gain some experience, they will find a large number of indicators telling them if there is something wrong with their experiment. The first check is to compare your data with previous runs on similar samples to make sure it is reasonable. The viscosity–shear rate function should be a smooth curve similar to the typical curve shown in [Fig. 6](#). If the points are very noisy, check to make sure that the pressure readings are at or above 10% of the full scale of the pressure transducer. Often the low-shear-rate points are not, but some noise in the low-pressure measurements might have to be accepted to get a pressure transducer large enough to measure the high-rate points.

If the data are different than expected, check to make sure the pressure/force transducer that was used was calibrated properly, that the correct die was inserted in the rheometer, and that the instrument's temperature controllers accurately reflect the temperature in the rheometer barrel. Most laboratories keep a well-characterized “lab standard” material available that can be run on an instrument to make sure it is giving the correct results.

When working with an unknown material, double check your results by running the sample at least twice to ensure that your results are repeatable. Exactly what else might occur depends heavily on the material being tested,



**Figure 12** Two typical pressure traces from a polyethylene flow curve at 190°C, one with an increasing shear rate profile and one with decreasing rates. Each time the pressure levels off, the instrument saves the point and changes the piston speed to move to the next shear rate. The resulting flow curve is similar to [Fig. 14](#).

but the following list gives some situations that might require special handling.

1. *No pressure reading.* If no pressure is indicated across the range of shear rates for the experiment, check for a blocked pressure tap. Other possible causes are a faulty transducer or a transducer that is not sensitive enough to register the pressures that are generated.

2. *Viscosity curve is shifted.* There are a number of items that can cause the viscosity curve to shift up or down. Check to see that the proper calibration values have been entered for the pressure/force transducer. Check the die to ensure that it is not partially blocked, causing greater than normal pressure drops. Lastly, check for a shift in either the barrel or die temperature. Burned-out heater bands or maladjusted temperature controllers will cause large shifts in experimental results.

3. *Thermal degradation.* Examine the polymer extrudate for discoloration or other signs of degradation. The residence time of the material in the rheometer may need to be shortened if significant degradation occurs. A thermal degradation test, described later in this chapter, can be performed to determine the maximum residence time in the rheometer.

4. *Chemical degradation.* Look for the formation of bubbles, as this often exhibits itself as off-gassing; listen for hissing and popping as the sample is extruded. The bubbles are often evident in the extruded strand.

Reducing the residence time and/or lowering the test temperature can help with this problem. Improper drying of the material can also cause this problem.

5. *Melt fracture and distortion.* The phenomena occur in materials at higher stresses and can be an indication of slip/stick in the die. The extrudate can display a wide variety of distortions from simple sharkskin (a very rough surface on the strand) to twists and kinks in the strand (gross melt distortion). These distortions usually occur at the exit of the die and do not affect the viscosity curve as long as the material does not slip.

6. *Slip/Slip-stick.* Slip occurs when the material “slips” through the die. The start of melt slip usually manifests as an abrupt change in slope in the stress-versus-shear rate curve; the curve suddenly levels off and there is little or no increase in stress as the shear rate increases. The stress on the material has become high enough that it slips along the wall (the mechanism of this failure to adhere to the wall is still being debated). Once the material begins to slip, the equations used to calculate shear rate become invalid: the no-slip wall boundary condition (material velocity is zero at the wall) is no longer true. Viscosity measurements are not possible without using a multi-experiment procedure [8] to determine the wall speed of the material. Since slip occurs once the material reaches a critical stress ( $\sigma_c$ ), increasing the test temperature (and thus reducing the melt viscosity) will allow testing at higher flow rates until the  $\sigma_c$  is reached again.  $\sigma_c$  is a strong function of the type of wall material

Slip-stick occurs when the material is on the verge of slipping. This manifests as a sawtooth-shaped oscillation in the pressure signal. The pressure builds to the point that the material slips. As it slips, the pressure in the barrel is relieved until the material begins to stick and the pressure builds again [9].

7. *Shear heating.* Shear heating occurs at high shear rates due to viscous dissipation in the material. Some of the flow energy is converted into thermal energy. It is difficult to detect and monitor shear heating because it is extremely difficult to get an accurate measurement of the temperature of the melt strand exiting the die. The thermal generation term varies according to

$$E_{\text{Thermal}} \sim \eta \dot{\gamma}^2 \quad (22)$$

and can raise the temperature significantly (i.e., 10–20°C or more) when testing high viscosity materials at high rates. Since viscosity is a strong function of temperature, erroneously low viscosity measurements will occur.

8. *Compressibility/density effects.* Compressibility and density effects will not affect most materials at typical testing pressures (less than 100 MPa). Polymeric materials are considered incompressible at normal pressures and temperatures, and the equations used to calculate shear rates and

viscosity assume this. It is also assumed that viscosity is not a function of the material density. Capillary rheometers, however, can generate such high pressures (when testing very tough materials or if a die with a very large  $L/D$  ratio is used) that the density of a material can change appreciably as it flows through a die. The material sees the barrel pressure as it enters the die and atmospheric pressure when it exits, a pressure drop that can reach up to 2000 times on a powerful rheometer! The material will swell as the pressure decreases along the die, increasing the shear rate. Also, viscosity is actually a weak function of density; this can become significant for some materials when large density changes occur. One way to check for compressibility effects is to perform a Bagley correction as discussed earlier in the chapter. Curved lines on a Bagley plot rather than straight lines can indicate the possibility of pressure effects in the viscosity. Note that when performing high-pressure, high-rate measurements, shear heating and pressure effects can both occur, complicating data interpretation.

## DATA INTERPRETATION

The main uses for capillary rheometers fall into two broad categories, quality control functions and material characterization for research, design, or trouble shooting applications. The use of models for data presentation and interpretation is also discussed.

### Material Characterization

The main purpose of a capillary rheometer is to generate a viscosity–shear rate curve over as wide a range of shear rates as possible. The effect of temperature on the viscosity can also be determined by running curves across a range of temperatures. The selection of specific dies and pressure transducers tailor the shear rate range to match a desired process window. This information can be used in many ways.

1. *Material selection.* Flow curves can be used to screen new materials for a process by ensuring that their viscosity is suitable at process shear rates.
2. *Polymer development.* The effect of additives, recipe changes, or adding or changing fillers in a material can be determined to see if the material is still in (or has now achieved) a desired process window.
3. *Effect of processing.* Virgin material is tested and compared with material that has been run through a process. Differences in the viscosity curves can indicate if any significant property degradation has occurred.

4. *Process troubleshooting.* The viscosity curve of a troublesome material can be run and compared against previous materials that have performed well. If the viscosity is the problem, determining the viscosity–temperature relation for the material by running curves at several temperatures will determine if a simple temperature adjustment to the process will bring the viscosity back to an appropriate value. A thermal stability test can be used to determine the maximum residence time of a material in a process before its properties begin to degrade.
5. *Process modeling/equipment design.* A viscosity function is necessary for computer simulations of polymer flow through extrusion dies, injection molds, or almost any type of equipment.
6. The viscosity function can be correlated with other, more difficult to measure material properties such as the molecular-weight distribution [10–12].

The last item above deserves to be expanded upon, since one of the most common questions asked is “What does this viscosity curve say about the molecular-weight distribution of this material?” The answer is “quite a bit,” but much of the information is qualitative in nature rather than quantitative. It is often used to compare and/or rank samples rather than generate absolute numbers defining the distribution.

As shown in Fig. 6, the viscosity at low shear rate approaches a constant value called the zero-shear value ( $\eta_0$ ). In almost all cases  $\eta_0$  is independent of the shape of the molecular-weight distribution and depends on the weight-average molecular weight ( $M_w$ ) only. Above a critical value of  $M_w$  ( $M_c$ ), there is a very strong correlation between  $\eta_0$  and  $M_w$ .

$$\eta_0 \sim M_w^{3.4} \quad (23)$$

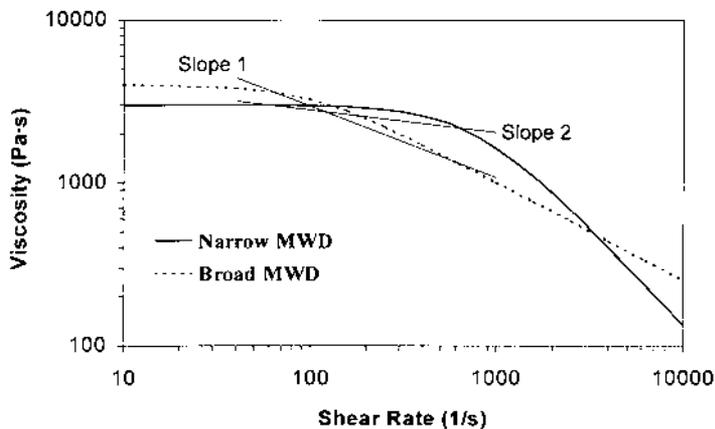
$M_c$  varies by material, but almost all commercial polymers have  $M_w > M_c$ .

Capillary rheometers cannot measure accurately at shear rates low enough to determine  $\eta_0$  directly. For many polymers, this determination would require measurements in the 0.01–0.001 s<sup>-1</sup> range. Correlations are sometimes made using the lowest reproducible shear rate possible instead of  $\eta_0$ , or models (such as the Carreau or Yasuda model) are used to extrapolate back to  $\eta_0$ . When comparing viscosity curves that extend to sufficiently low shear rates (where the curve begins to flatten out), it is possible to make the statement that material A has a higher  $M_w$  than material B because its low-shear viscosity is higher.

The second item of information that can be gleaned from the flow curve has to do with the breadth of the molecular-weight distribution. Broader distributions tend to have an earlier onset of shear thinning and a more gradual transition into the power law region. Narrow distributions have a relatively sharp transition and achieve a steeper slope in the power law region. This relation is illustrated graphically in Fig. 13. It is much more difficult to get quantitative correlations for this kind of information. Attempts made to correlate viscosity curve slopes or “shape factors” from the transition region with parameters such as polydispersity, a measure of the breadth of a log-normal molecular-weight distribution, have met with limited success for specific materials [13].

### Data Presentation

The viscosity curve generated by a capillary rheometer is a series of viscosity–shear rate points. Depending on how the data are to be used, it is often convenient to fit a model to the data. This reduces the amount of data to the parameters of the chosen model and allows easy interpolation of viscosity values between the measured points. It is also the preferred form for use in computer modeling of process flows. Usually a viscosity curve for this purpose is fitted to a model so that the computer program can deal with an equation rather than a series of data points. This way the form of the



**Figure 13** The shape dependence of flow curves on the molecular-weight distribution. Viscosity curve tangents taken from the transition region can quantify the shape of the curve.

equation can be programmed ahead of time and the actual viscosity data are entered as the parameters for the model.

There are a number of models in common use, a few of which will be listed here. The most common two-parameter model is the power law model (parameters  $n$  and  $k$ ), whose form is given in Eq. (15). This model corresponds to a straight line on a log-log plot, and fits viscosity data well at high shear rates. It is the simplest model to account for shear thinning. In logarithmic form, the equation for the model becomes

$$\log \eta = \log k + (n - 1) \log \dot{\gamma} \quad (24)$$

If  $\log(\eta)$  is plotted against  $\log(\dot{\gamma})$  on linear axes, then the slope of the curve is  $n - 1$  and the intercept is  $\log k$ .

Two more complicated models are the three-parameter Carreau model [14],

$$\eta = \eta_0 (1 + (\lambda \dot{\gamma})^2)^{-p} \quad (25)$$

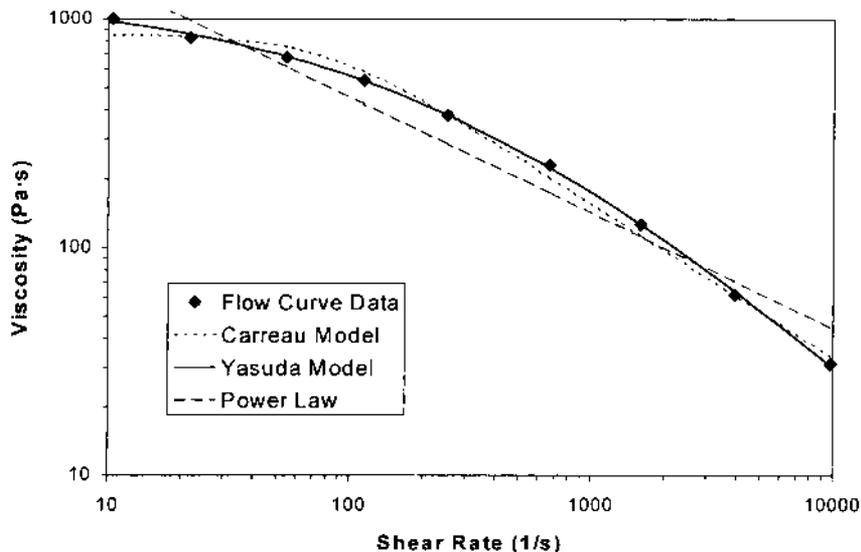
and the four-parameter Yasuda model [15],

$$\eta = \eta_0 [1 + (\lambda \dot{\gamma})^a]^{n-1/a} \quad (26)$$

These models are useful because their mathematical structure mimics the shear-thinning curve expected for a viscosity function. This gives more reliable extrapolation beyond the data used to determine the model parameters. A four-parameter polynomial, for example, does not have a predefined shape; it may fit the data well but gives unpredictable extrapolation results. Also, the parameters in these equations have physical significance, which aids in data interpretation. The  $\eta_0$  parameter contains the model's estimate of the zero-shear viscosity, while the  $n$  and  $p$  parameters correspond to the power law behavior seen at high shear rates. Also, the transition region of the viscosity curve occurs in the shear rate range around  $\dot{\gamma} = 1/\lambda$ . The Yasuda equation contains an extra shape factor,  $a$ , which allows it to better fit the transition region. [Figure 14](#) compares the fit of these models with the viscosity data from a nylon sample. The disadvantage of these models is that the parameters are more difficult to determine: non-linear optimization routines must be used. Fortunately, most modern instruments have software with curve-fitting capabilities already included.

## Quality Control

Quality control laboratories use the capillary rheometer to monitor incoming and outgoing material. In general, the emphasis is to search for any differences between the tested material and previously established standards and norms. The test procedures are repetitive and the general nature of the



**Figure 14** A comparison of three common viscosity models. Increasing the number of parameters improves the fit of the model to the data.

results is known beforehand. Often only a single, process-relevant shear rate is selected for monitoring. The sample passes the test if the measured viscosity falls within a specified range of the target viscosity. Multipoint measurements, whether a two-point, high-/low-shear rate test, or an entire 3- to 10-point curve, provide a more thorough evaluation of a polymer. In this case, each point must fall within specifications for a material to pass.

When performing quality control measurements a major goal is to optimize the sensitivity and repeatability of the results for a specific test [16]. Especially for a single point measurement, the pressure or force transducer can be selected so that the measurement falls at the upper end of the transducer's range to ensure the best accuracy. The die can be selected so that the desired shear rate is generated at a reasonable piston speed. This ensures that the test finishes in a reasonable amount of time, and that it will not run out of material before finishing. Often Bagley and Rabinowitch corrections are not made for these tests, as it is consistency (and convenience) rather than absolute accuracy that is desired. This introduces a small instrument dependency to the results, but this is usually neglected since many company labs are standardized on a single brand of rheometer, and the data are not for outside consumption.

Many laboratories use a melt indexer to generate a single-point property measurement for quality control. A capillary rheometer offers a number of advantages over a melt indexer. First, the capillary rheometer measures the viscosity rather than a machine-dependent index. Viscosity results can be compared to tests from other types of rheometers, including on-line process rheometers that measure directly from the process. Reproducibility tends to be better as well: operating at higher pressures and flow rates often makes the measurement less sensitive to operator bias in the sample preparation and loading procedures.

The most important advantage that the rheometer holds over the indexer, however, is the shear rate at which the test occurs. The melt index measurement occurs at shear rates that fall into the lower ranges of a capillary rheometer's capabilities (see Fig. 9). In most cases, these shear rates are also considerably below the shear rate range of the process for which the polymer is intended (see Fig. 11). Two materials with differently shaped viscosity curves could easily have the same viscosity at low shear rates and different viscosities at high rates. They would have the same melt index, pass QC inspection, and behave completely differently on the production floor. The ability of the rheometer to test at shear rates pertinent to the process allows the development of more relevant quality control test procedures.

## OTHER MEASUREMENTS

While the basic function of the capillary rheometer is to produce viscosity–shear rate curves, there are a number of procedures that can be performed which extend the range of the viscosity curve. There are also tests that measure completely different material properties.

### Time–Temperature Superposition

The viscosity of polymeric materials is a very strong function of temperature. A temperature difference of 10°C can make a 30–50% difference in the viscosity of many polyolefins, and as much as 200% for some engineering polymers such as polyvinyl chloride (PVC). Time–temperature superposition determines the effect of temperature by shifting viscosity curves measured at different temperatures onto a single, temperature-independent master curve. The shift factor is

$$a_T = \frac{\eta_0(T)}{\eta_0(T_0)} \quad (27)$$

where  $T$  is the actual temperature of the viscosity test and  $T_0$  is the reference temperature of the master curve. Once the shift factor is determined for each

curve, plotting  $\eta(\gamma)/a_T$  versus  $a_T\gamma$  produces the master curve. The master curve will cover a larger shear rate range than the individual curves because the curves are shifted along the shear-rate axis.

Once the shift factor has been determined for a large enough number of curves, the shift factors themselves may be fitted to a model. This allows the determination of shift factors and master curves at arbitrary temperatures. For viscosity curves taken within 100°C of a material's glass transition temperature ( $T_g$ ), the WLF (Williams-Landel-Ferry) equation [17] is used:

$$\log a_T = \frac{A(T - T_0)}{B + (T - T_0)} \quad (28)$$

The parameters  $A$  and  $B$  are the model parameters used to fit the shift data. When the temperatures are more than 100C above  $T_g$ , an Arrhenius equation,

$$a_T = \exp\left[\frac{E_A}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (29)$$

is useful, where  $R$  is the universal gas constant and  $E_A$ , an activation energy, is the parameter adjusted to fit the data.

## Thermal Stability

One important item of information that can be determined with a capillary rheometer is the thermal stability of a material, or how long it can be maintained at a specific temperature before it begins to degrade. This information is critical for process designers and can be used to test the performance of stabilization-additive packages. This simple test involves loading the rheometer barrel with a sample and running intermittent viscosity tests over a period of time, each test requiring only a small portion of the material in the barrel.

The rheometer is set up at the desired temperature and a single (or usually not more than two) shear rate at which to perform the test is chosen. Usually a low shear rate is chosen for two reasons: low shear viscosity is more sensitive to the effects of degradation (the main effect is usually a reduction in the average molecular weight) and the piston speed should be low enough to allow for many tests on the same barrel of material. Make sure a proper pressure transducer is selected, one that is sensitive enough to track the low-shear measurements accurately. Perform the viscosity measurement at specified intervals until the barrel is empty or a sufficient time period is covered.

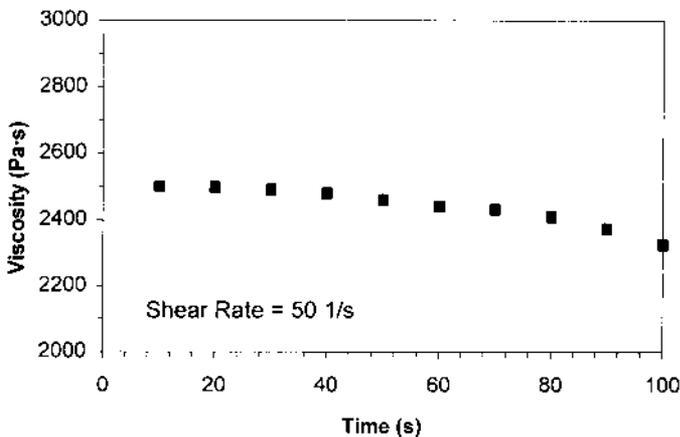
A constant viscosity measurement implies that there is no significant degradation of the material. If the viscosity drops off over time, degradation

is occurring and a maximum recommended residence time recommendation can be made based on when the viscosity reduction becomes significant. A sample test result is shown in Fig. 15.

### Melt Density

Determining the melt density of a material with a capillary rheometer is simple. It involves only extruding and weighing a known volume of sample. Most rheometers show piston displacement values, but even with instruments that do not it is possible to measure piston travel with a ruler. Perform the measurement as follows:

1. Load a sample into the rheometer carefully, to avoid air bubbles, and allow it to come to temperature.
2. Purge some material through the die to ensure that no air is in the system.
3. Note the initial position of the piston and use a brass scraper or similar tool to remove any drool from the die.
4. Extrude and collect a sample of the material. When the piston stops, wait until the barrel pressure drops before using the scraper to ensure that all extruded sample is collected.
5. Note the final position of the piston and determine how far it traveled. Multiply the distance traveled by the cross-sectional area of the piston ( $\pi R^2$ ) to get the volume of the material extruded.



**Figure 15** Sample stability test performed on polyethylene at 190°C.

6. Weigh the extruded sample.
7. Divide the weight by the volume to get the density.

Typical values fall between 0.7 and 1.2 g/cm<sup>3</sup>.

### Common Accessories

A number of common accessories are available to further enhance the capabilities of a capillary rheometer. The rheometer is designed to determine viscous data and minimize the effects of other properties. These other instruments work in conjunction with the rheometer to produce other types of measurements.

### Die Swell Measurement

A die swell measurement of a strand extruded from a capillary die is used to measure the elastic properties of a material. As a polymer flows down a capillary tube, its molecules become stretched out and aligned in the direction of the flow. Once the material leaves the confines of the die, the molecules recoil and draw back up to themselves, causing the extrudate to swell beyond the size of the opening in the die. The amount of swell displayed by a polymer is a characteristic of its elastic nature.

Die swell is measured by determining the diameter of the extruded strand after it has exited the capillary die. Usually a noncontact laser measuring system is used to get accurate strand diameter measurements. Die swell is a strong function of shear rate, so most systems are configured to get a die swell measurement each time a viscosity point is taken by the rheometer. Die swell data are usually presented as a ratio of the cross-sectional area of the die to the cross-sectional area of the strand:

$$\text{Die swell} = \frac{A_{\text{Strand}}}{A_{\text{Die}}} = \left( \frac{D_{\text{Strand}}}{D_{\text{Die}}} \right)^2 \quad (30)$$

### Melt Tensile Tests

In polymer processes such as film blowing, fiber spinning, and blow molding, the extensional properties and melt strength of a material are crucial pieces of information. Melt tensile testers are devices which pull on a melt strand as it is extruded from the capillary die and measure the force necessary to generate a desired draw ratio or melt extension. These instruments are capable of measuring very small forces and can generate the extensional strain rates found in many processes.

The melt strand is exposed to the atmosphere and is not at a constant temperature, complicating efforts to determine extensional viscosity directly. However, the data from these tests are very useful for qualitative testing of materials to rank their suitability for a process, troubleshoot, or perform quality control. Much work has been done recently to expand the usefulness of this measurement, including techniques that can generate temperature- and process-independent master curves [18].

## CONCLUSION

The capillary rheometer is a versatile and robust instrument. Easily interchangeable transducers and dies give the instrument the flexibility to study a wide range of materials over a wide range of shear rates, especially in the high-shear-rate ranges. It can handle tough materials at the temperatures, pressures, and flow rates typically found in high-performance plastics processes. The viscosity curve that the instrument produces finds many practical applications in quality control, process design, and troubleshooting, as well as in the study of the material properties themselves.

Aside from viscosity curves, the capillary rheometer can be used to determine other material properties. The effects of time and temperature on processability and chemical stability can be studied, and other properties such as the melt density can be measured. Elastic data can be collected with accessories such as a die swell measurement system, and extensibility measurements can be performed with a melt tensile tester. The capillary rheometer is the instrument of choice for any practically oriented polymer laboratory.

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