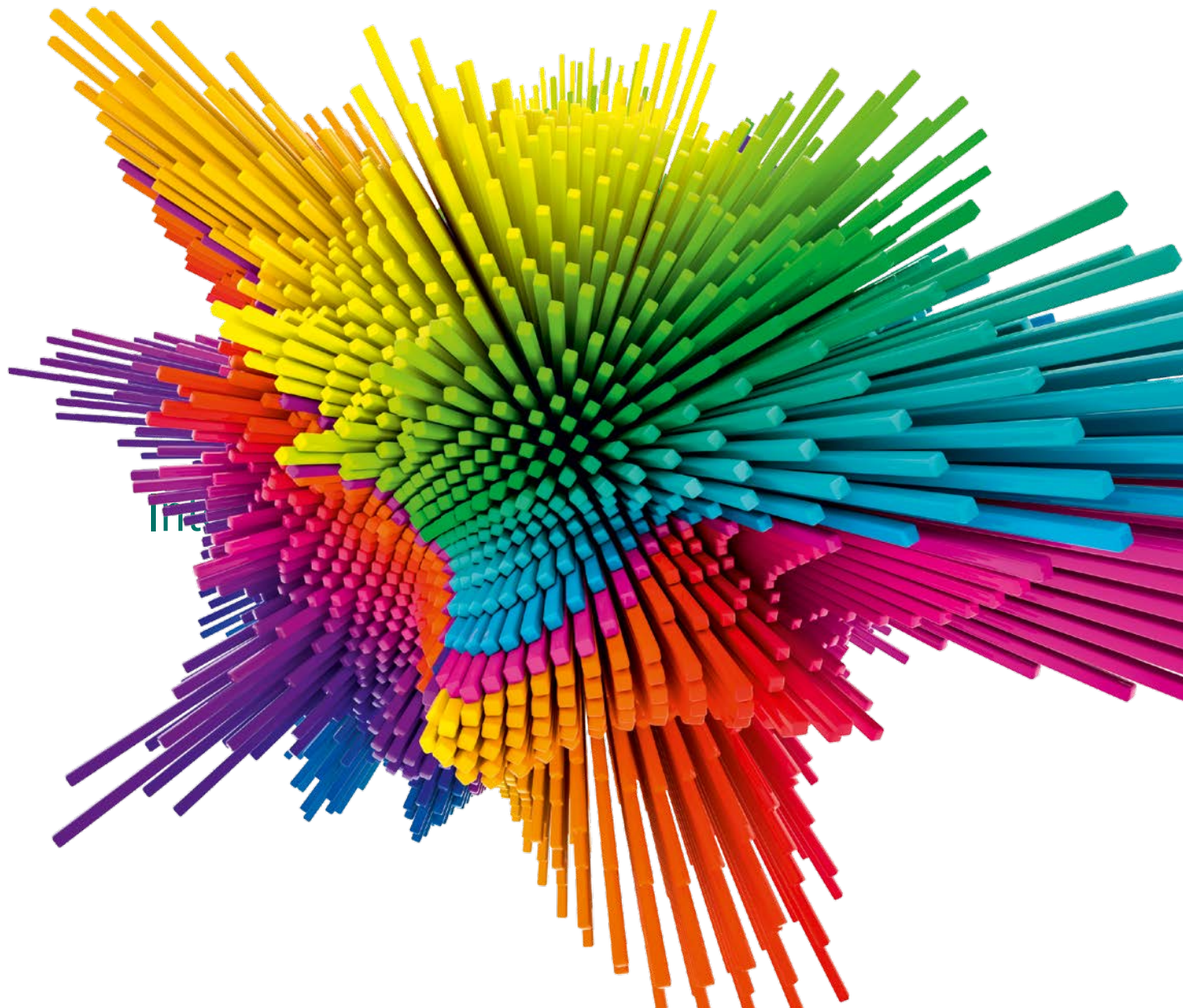


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Capillary Rheology: Interpretation of Data by Application





From Soup to ... Polymers?

Rheology is being studied on almost every material type that you can imagine and plays a key role in formulation, process optimization and ensuring products perform well in their end uses. The ability to create small batches of trial formulations of a product and run simulated processes on them makes rheology an attractive tool, and generates reproducible and quantitative data. Whether we are evaluating the mouthfeel of chocolate, the longevity of a road surface or precision injection molding of polymers, rheology can lend a hand in making sense of the material behavior. This book gives just a brief overview of the technique of capillary rheometry and some of the common examples of applications and how the data may be used. Please also look at our other booklet for more extensive examples – 'Rotational Rheology – Interpretation of Data by Application'.

We hope you find this book helpful and even if your application isn't specifically mentioned, hopefully you'll be inspired as to how a similar test method can be adapted to give an indication of your material's properties in a specific process.

We hope you enjoy reading!

NETZSCH Rheology Specialists

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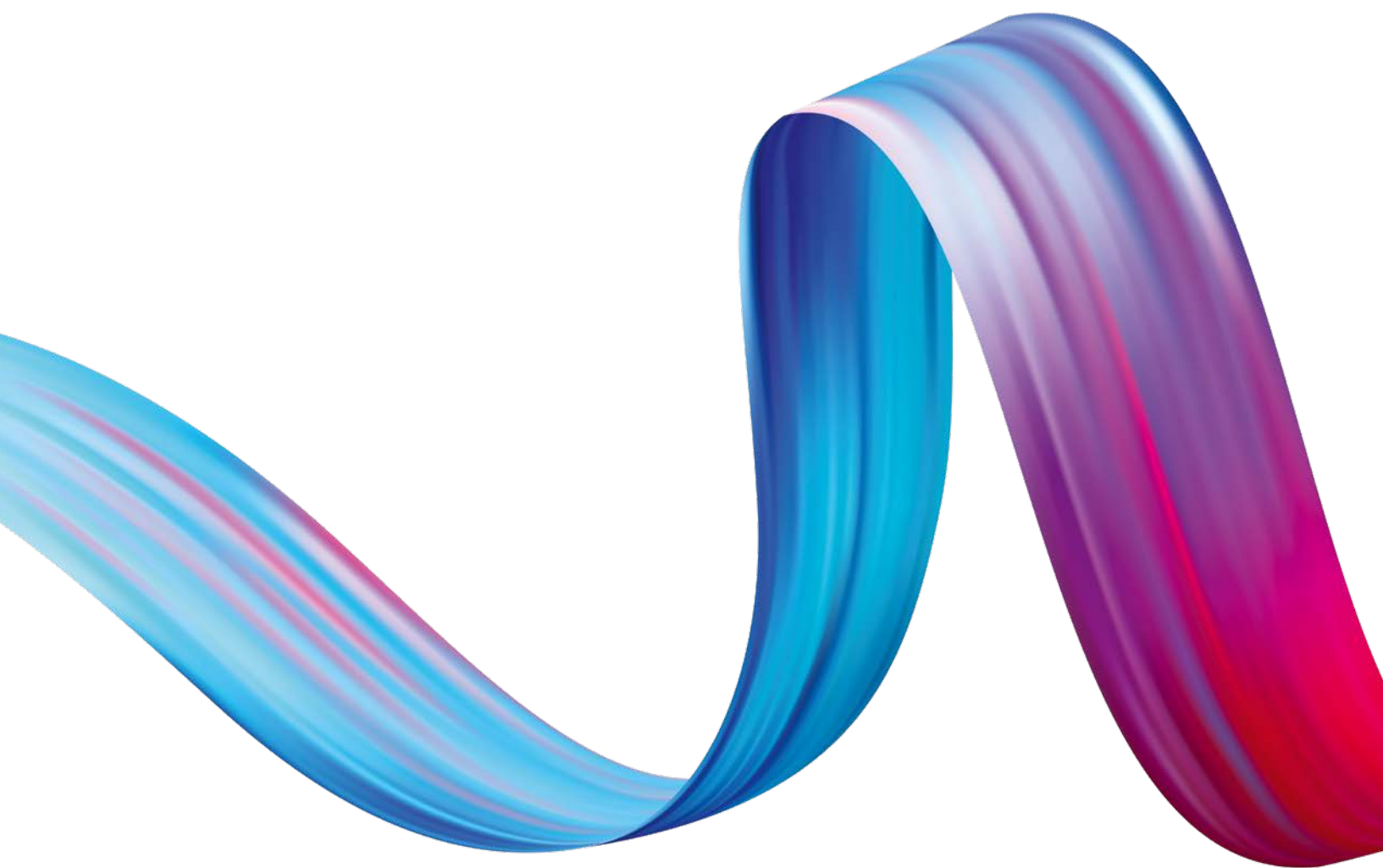
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A Basic Introduction to Capillary Rheology



A Basic Introduction to Capillary Rheology

General

Introduction

Rheometry refers to the experimental technique used to determine the rheological properties of materials; rheology being defined as the study of the flow and deformation of matter which describes the interrelation between force, deformation and time. The term rheology originates from the Greek words 'rheo' translating as 'flow' and 'logia' meaning 'the study of', although as from the definition above, rheology is as much about the deformation of solid-like materials as it is about the flow of liquid-like materials and in particular deals with the behavior of complex viscoelastic materials that show properties of both solids and liquids in response to force, deformation and time.

There are a number of rheometric tests that can be performed on a rheometer to determine flow properties and viscoelastic properties of a material and it is often useful to deal with them separately. In capillary rheometry we predominantly look at viscous flow behavior, however extensional viscosity and also elasticity may be characterized as described in the second part of this introduction.

Viscosity

There are two basic types of flow, these being shear flow and extensional flow. In shear flow fluid components shear past one another while in extensional flow fluid components flow away or towards from one another. The most common flow behavior for pumping, injection molding and extrusion is shear flow and this viscosity introduction will focus on this behavior and how to measure it. Other processes, such as blow molding, fiber spinning and flow through tapered dies is predominantly extensional.

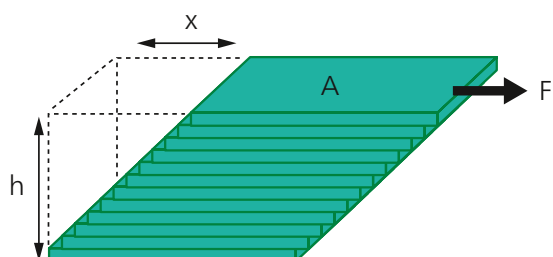


Figure 1. Quantification of shear rate (top) and shear stress (bottom) for layers of fluid sliding over one another

Shear Flow

Shear flow can be depicted as layers of fluid sliding over one another with each layer moving faster than the one beneath it. The uppermost layer has maximum velocity while the bottom layer is stationary. For shear flow to take place, a shear force must act on the fluid. This external force takes the form of a shear stress (σ) which is defined as the force (F) acting over a unit area (A) as shown in Figure 1. In response to this force, the upper layer will move a given distance x , while the bottom layer remains stationary. Hence, we have a displacement gradient across the sample (x/h) termed the shear deformation (γ). For a solid which behaves like a single block of material, the strain will be finite for an applied stress – no flow is possible. However, for a fluid where the constituent components can move relative to one another, the shear strain will continue to increase for the period of applied stress. This creates a velocity gradient termed shear rate or strain rate ($\dot{\gamma}$) which is the rate of change of strain with time ($d\gamma/dt$).

$$\sigma = F/A \quad (\text{Pa}) \quad \text{Eq. (1)}$$

$$\gamma = x/h \quad \text{Eq. (2)}$$

$$\dot{\gamma} = d\gamma/dt \quad (\text{s}^{-1}) \quad \text{Eq. (3)}$$

A derivation of the Hagen-Poiseuille equation gives the shear rate of a Newtonian fluid through a pipe:

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

$$\sigma_a = \frac{R\Delta P}{2L} \quad \text{Eq. (5)}$$

where $\dot{\gamma}_a$ is apparent shear rate, Q is volumetric flow rate, R is tube/capillary radius, σ_a is apparent shear stress, ΔP is the pressure drop over the pipe/capillary, and L the length of the pipe/capillary.

Flow through a tube or capillary die has been well characterized and the Hagen-Poiseuille equation may be used to calculate the shear rate in these situations. When we apply a shear stress to a fluid we are transferring momentum, indeed the shear stress is equivalent to the momentum flux or rate of momentum transfer to the surrounding layers of fluid. That momentum is transferred through the layers of fluid by collisions and interactions with other fluid components giving a reduction in fluid velocity and kinetic energy. The coefficient of proportionality between the shear stress and shear rate is defined as the shear viscosity (η), which is a

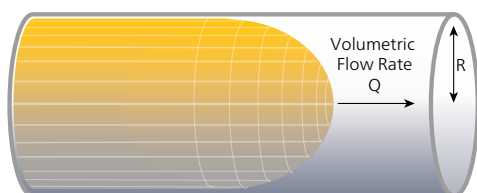


Figure 2. Poiseuille shear flow through a capillary die or tube

quantitative measure of the internal fluid friction and associated with damping or loss of kinetic energy in the system.

$$\eta = \sigma / \dot{\gamma} \text{ (Pa.s)} \quad \text{Eq. (6)}$$

In Newtonian fluids, the viscosity is constant with changing shear rates or shear stresses, such as water, simple hydrocarbons and dilute colloidal dispersions. Non-Newtonian fluids are those where the viscosity varies as a function of the applied shear rate or shear stress. It should be noted that fluid viscosity is both pressure and temperature-dependent, and generally increases with increased pressure and decreasing temperature. Temperature is more critical than pressure in this regard with higher viscosity fluids such as asphalt or bitumen much more temperature dependent than low viscosity fluids such as water.

Generating a Viscosity Flow Curve

The constant shear test is designed to investigate the relationship between shear stress and shear rate for a material, with shear viscosity being the ratio of the two parameters. The test routine involves pre-setting the test temperature, then loading the sample with periodic tamping to ensure a uniform fill to reduce voids and air entrapment. Loading the sample is followed by further pre-test compressions to ensure the sample is de-aerated as much as possible and fully compacted. A series of discrete piston speeds (shear rates) are selected across the shear rate range of interest and the sample is extruded until a pressure equilibrium is detected at each speed. The shear stress is then calculated from the pressure values and the die dimensions based on Eq. (5). To ensure accurate results of the true flow properties of the sample, the user has the option to apply up to three corrections associated with errors of entrance pressure, wall slip, and non-Newtonian flow.

With the Rosand capillary rheometer, a sample is loaded into a cylindrical barrel that is pre-set at the required test temperature. A servo-drive controlled piston is then used to extrude the sample material through a cylindrical or rectangular slot

die in place at the end of the barrel at a very controlled series of speeds. Hence, a well controlled volumetric flow rate (Q) is assured, where Q is determined according to Eq. (7).

$$Q = \pi R_b^2 v \quad \text{Eq. (7)}$$

where v is the piston speed and R_b is the barrel diameter.

The pressure drop across the die is continuously monitored and measured with a pressure transducer placed just above the die. A cut away is shown in Figure 3. The Rosand capillary rheometers (Figure 4) can accommodate a wide range of pressure transducers and dies, making them versatile for measuring a broad spectrum of sample types. Typical sample viscosities can range from inkjet ink to highly-filled, high modulus rubber samples.

Capillary rheometers can be used to determine the viscoelastic properties of materials, e.g., shear viscosity, extensional viscosity and elasticity measurements (the latter from die swell if this is measured). Also, there are modules for thermal degradation tests, flow/no flow testing, pressure volume temperature (PVT) tests, haul-off (fiber spinning), stress relaxation, wall slip analysis and others.

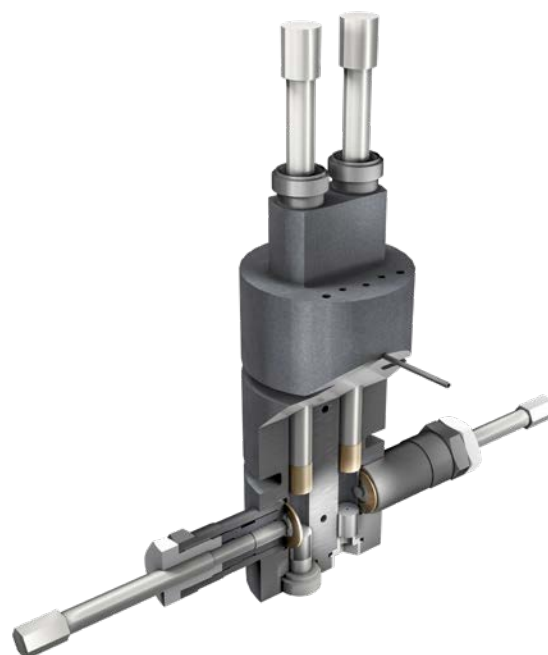


Figure 3. The heart of a Rosand capillary rheometer

A Basic Introduction to Capillary Rheology

A Typical Configuration for the Rosand Capillary Rheometer



Figure 4. The design of the RH7 and RH10 floor-standing capillary rheometer (left) and the RH2000 benchtop capillary rheometer (right)

Shear Thinning

The most common type of non-Newtonian behavior is shear thinning or pseudoplastic flow, in which the fluid viscosity decreases with increasing shear. At low enough shear rates, shear thinning fluids will show a constant viscosity value, η_0 , termed the zero shear viscosity or zero shear viscosity plateau. At a critical shear rate or shear stress, a large drop in viscosity is observed, which signifies the beginning of the shear thinning region. This shear thinning region can be mathematically described by a power law relationship (Eq. 8) which appears as a linear section when viewed on a double logarithmic scale (Figure 5), which is how rheological flow curves are often presented.

$$\sigma = k \dot{\gamma}^n \quad \text{Eq. (8)}$$

At very high shear rates, a second constant viscosity plateau is observed, called the infinite shear viscosity plateau. This is given the symbol η_∞ and may be many orders of magnitude lower than η_0 depending on the degree of shear thinning.

Some highly shear-thinning fluids also appear to have what is termed a yield stress, where below some critical stress the viscosity becomes infinite and hence characteristic of a solid. This type of flow response is known as plastic flow and is characterized by an ever increasing viscosity as the shear rate approaches zero (no visible plateau). Many prefer the description 'apparent yield stress' since some materials which appear to demonstrate yield stress behavior over a limited shear rate range may show a viscosity plateau at very low shear rates.

Why Does Shear Thinning Occur?

Shear thinning is the result of micro-structural rearrangements occurring in the plane of applied shear and is commonly observed for dispersions, including emulsions and suspensions, as well as polymer solutions and melts. An illustration of the types of shear-induced orientation which can occur for various shear thinning materials is shown in Figure 6.

At low shear rates, materials tend to maintain an irregular order with high viscosity due to particle/molecular interactions and the restorative effects of Brownian motion. In the case of yield stress materials, such interactions result in network formation or jamming of dispersed elements which must be broken or unjammed for the material to flow. At shear rates or stresses high enough to overcome these effects, particles can rearrange or reorganize in to string-like layers, polymers can stretch out and align with the flow, aggregated structures can be broken down and droplets deformed from their spherical shape. A consequence of these rearrangements is a decrease in molecular/particle interaction and an increase in free space between dispersed components, which both contribute to the large drop in viscosity. η_{∞} represents the maximum degree of orientation achievable and hence the minimum attainable viscosity which is influenced largely by the solvent viscosity and related hydrodynamic forces.

For non-Newtonian materials, their flow profile through a straight circular pipe is not parabolic as shown in Figure 2, but rather more flow occurs at the walls and less at the center due to the stress distribution across the sample. This results in higher shear rates at the wall and so the data can be further refined with the Rabinowitsch correction to take account of this. This is described in more detail below in the 'Common Corrections Used in the Capillary Rheometry' section.

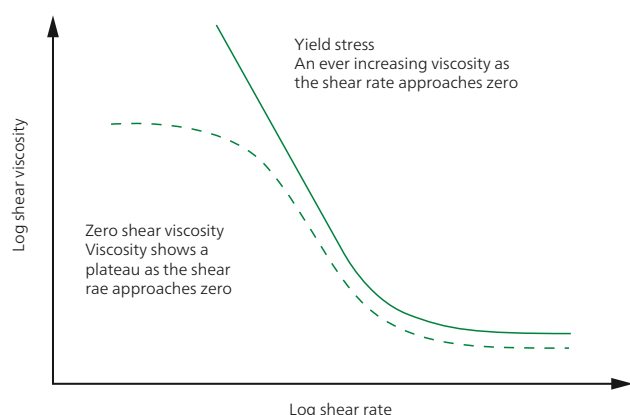


Figure 5. Typical flow curves for shear thinning fluids with and without an apparent yield stress

Shear Thickening

While most suspensions and polymer structured materials are shear thinning, some materials can also show shear thickening behavior where viscosity increases with increasing shear rate or shear stress. This phenomenon is often called dilatancy, and although this refers to a specific mechanism for shear thickening, the terms are often used interchangeably.

In most cases, shear thickening occurs over a decade of shear rates and there can be a region of shear thinning at lower and higher shear rates. Usually dispersions or particulate suspensions with high concentration of solid particles exhibit shear thickening. Materials exhibiting shear thickening are much less common in industrial applications than shear thinning materials. They do have some useful applications such as in shock absorbers and high impact protective equipment but for the most part shear thickening is an unwanted effect which can lead to major processing issues.

For suspensions, shear thickening generally occurs in materials that show shear thinning at lower shear rates and stresses. At a critical shear stress or shear rate the organized flow regime responsible for shear thinning is disrupted and so called 'hydro-cluster' formation or 'jamming' can occur. This gives a transient solid-like response and an increase in the observed viscosity. Shear thickening can also occur in polymers, in particular amphiphilic polymers, which at high shear rates may open-up and stretch, exposing parts of the chain capable of forming transient intermolecular associations.

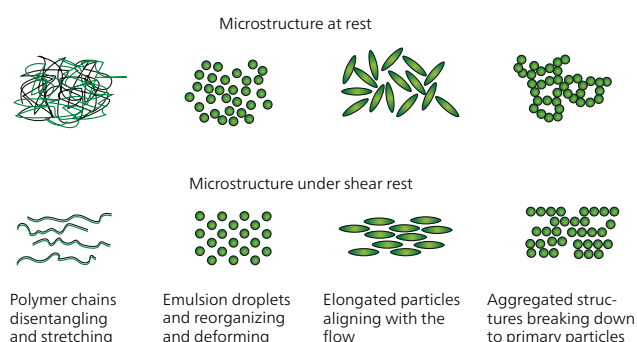


Figure 6. Illustration showing how different micro-structures might respond to the application of shear

A Basic Introduction to Capillary Rheology

Common Corrections Used in Capillary Rheology

The Bagley Correction

Edward B. Bagley derived a correction of the wall shear stress, this accounts for the entrance pressure loss effects of the sample squeezing from the barrel inner diameter to the die's inner diameter. This squeezing process also has both shear and extensional viscosity components, as well some inertia from the sample accelerating. Bagley proposed a few methods for this correction and these are detailed in the section later named 'Three Methods for Correcting for Die Entry Pressure Drop'. Currently, the most commonly applied of these three corrections is the deduction of the pressure of a zero length die from that of a long die. This is known as the Cogswell Orifice Die Method and is described below in the paragraph *Three Methods for Correcting for Die Entry Pressure Drop* later in this book.

The Rabinowitsch Correction

For non-Newtonian materials, their flow profile cross section through a straight circular pipe is not parabolic as shown in Figure 2, but rather more flow occurs at the walls and less at the center due to the stress distribution across the sample. This effect is more and more evident as the material becomes increasingly shear thinning, until ultimately we reach plug flow, where there is a yield stress in the sample that is not exceeded except at the walls of the pipe, see Figure 7.

This results in higher shear rates at the wall and so the data can be further refined by correcting the shear rate with the Rabinowitsch correction to take account of this. Applying the Rabinowitsch correction will increase the shear rates for shear thinning samples.

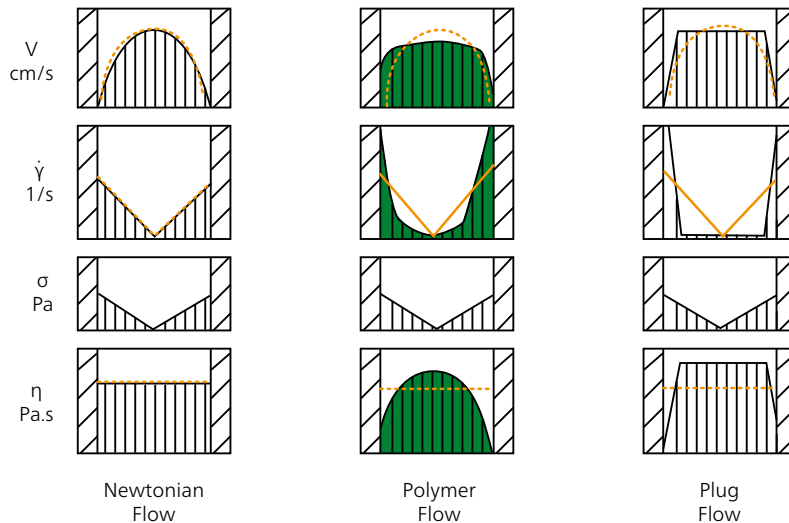


Figure 7. Flow profiles for different sample types

Apparent shear rate
(Newtonian material)

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3}$$

Corrected shear rate
(Rabinowitsch)

$$\dot{\gamma}_c = \frac{4Q}{\pi R^3} \frac{3n+1}{4n}$$

$$n = \frac{d(\log \sigma)}{d(\log \dot{\gamma})}$$

$$\text{If } n = 0.5, \\ \dot{\gamma}_c = 1.25 \cdot \dot{\gamma}_a$$

Eq. (9)

where: $\dot{\gamma}_a$ is apparent shear rate, $\dot{\gamma}_c$ is corrected shear rate, Q is volumetric flow rate, R is tube radius, n is the shear thinning factor.

The Wall-Slip (Mooney) Correction

One of the fundamental assumptions in the correct measurement of the shear viscosity is that the sample is not moving at the wall of die as shown in Figure 7 for Newtonian and Polymer Flow behavior (where the Rabinowitsch correction may be used). However in some situations where the stress on the sample is higher than its adhesion to the walls, the sample starts to slip along the inside wall of the die (see Figure 8). The velocity of wall slip in these cases can be characterized by the Mooney wall slip correction. This correction can be determined using a constant L/D ratio and different die diameters. Later on the apparent shear rate is plotted against $1/R$. The intercept is the apparent shear rate at $R = \infty$ and the slope is 4 times the slip velocity (see Figure 10).

$$\dot{\gamma}_a = \dot{\gamma}_{a\infty} + \frac{4v_s}{R} \quad \text{Eq. (10)}$$

Wall slip is commonly seen in concentrated dispersions and some polymer melts (see Figure 9), such as PVC, HDPE and metallocene catalyzed polymers (above a critical wall stress, typically ~ 0.1 MPa).

- In the case of dispersions, the layer close to the wall are more diluted than the rest and during shear, particle size can take place. This phenomenon is known as concentration depletion and has been described by Barnes.
- In the case of polymer melts: low-molecular weight chains can propagate to the wall leading to slip. Furthermore, flow instabilities (at high stresses) which lead to melt distortions (stick-slip, melt fracture) result in a pressure oscillation and wall-slip may appear as well.

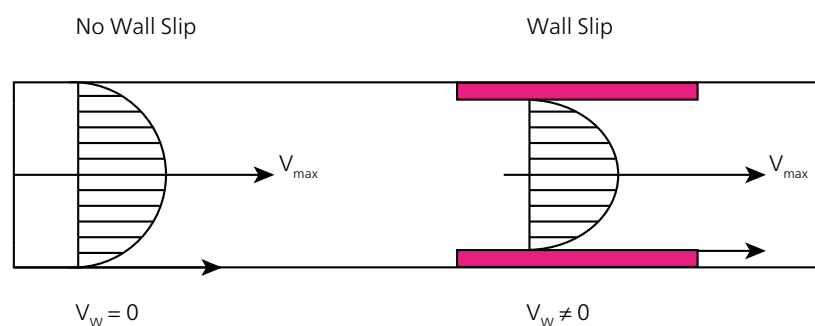


Figure 8. Diagram of the occurrence of wall slip

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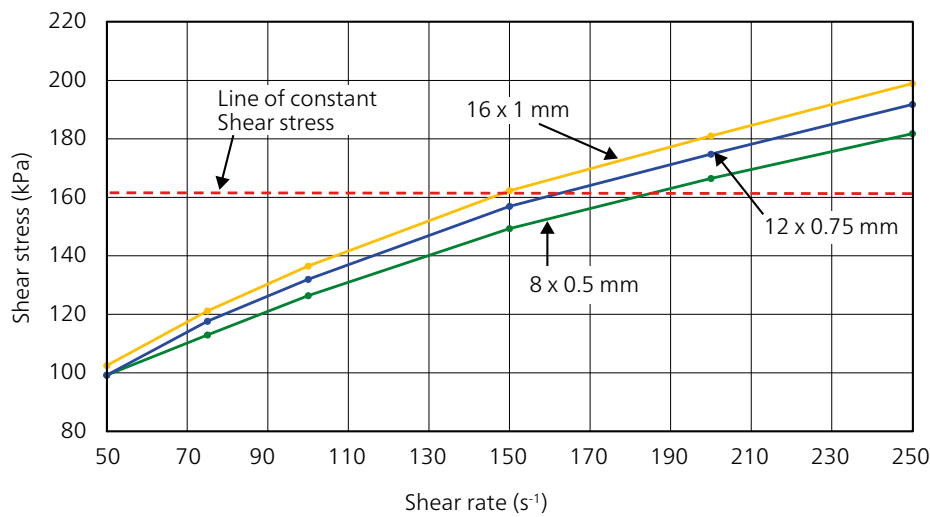


Figure 9. Data from unfilled HDPE at 200°C with three different dies of the same L/D ratio. Theoretically, these shear stress (σ) vs. shear rate ($\dot{\gamma}$) curves should overlay, but due to wall slip, the measured shear stress is lower in smaller dies.

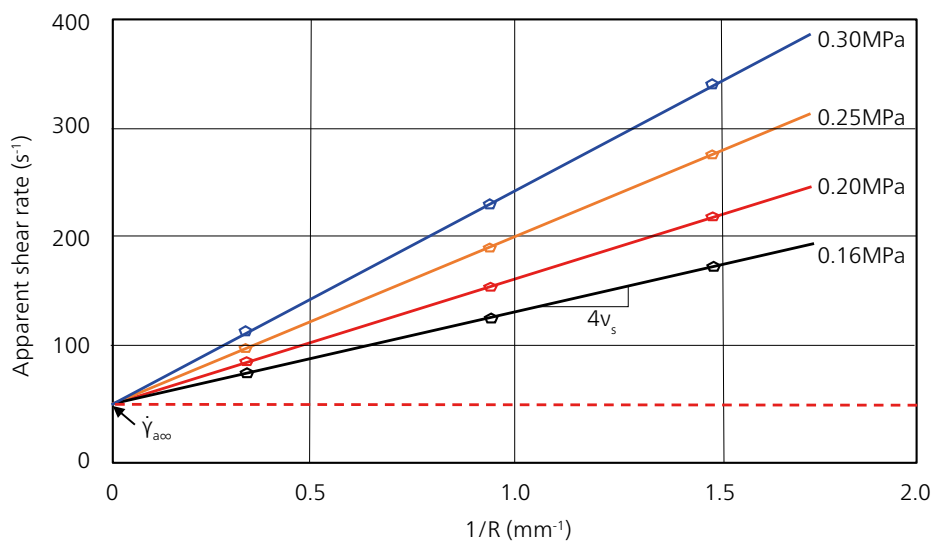


Figure 10. The apparent shear rate results are plotted vs. $1/R$ to determine the wall slip velocity. The intercept value of shear rate shows the apparent shear rate of $R = \infty$ and the slope divided by 4 is the slip velocity. Wall slip does not take place where the line is horizontal (dotted).

Typical slip velocity results:

$$\text{PVC } v_s = 9.5 (\sigma_w/100)^{2.28} \quad \text{Eq. (11)}$$

$$\text{PE } v_s = 1.50 (\sigma_w/100)^{3.20} \quad \sigma_w > 90 \text{ kPa}$$

where units are:

wall slip velocity [v_s] mm/s

wall shear stress [σ_w] kPa

The Hagenbach Correction

When low-viscosity materials are tested with a narrow die, there is a considerable acceleration of the sample from near stationary in the barrel to a high speed through the die length. This acceleration causes an additional pressure drop proportional to the density (ρ) of the sample, change in cross-sectional area from the barrel to the die and also the volumetric flow rate (known as Q). If both the Bagley and Hagenbach corrections are used, the corrected pressure from the Bagley correction would be used in the Hagenbach correction.

$$\eta = \frac{\pi}{8} \frac{\Delta p R^4}{LQ} \quad \text{Eq. (12)} \quad \eta = \frac{\pi R^4 \Delta p}{8LQ} - \frac{\rho Q}{2^{11/3} \pi L} \quad \text{Eq. (13)}$$

Eq. 12. Normal equation for Poiseullian viscosity calculation,

Eq. 13. Hagenbach inertial correction for viscosity

Some finer corrections have also been proposed to Hagenbach's initial inertial correction and these are discussed in the literature cited [6].

Calculation of the Extensional Viscosity

When the shear viscosity of a sample is accurately known (with measurement of a viscosity flow curve, Bagley and Rabinowitsch, Mooney (wall slip) corrections), the extensional viscosity can be calculated from the pressure drop data from the zero length 'orifice' die as proposed by FN Cogswell. In a twin bore Rosand capillary rheometer, these corrections and calculations can all be made automatically if both a long and zero length die are used in parallel in a test method. Cogswell's calculation for the extensional viscosity uses a theoretical flowlines path for a sample flowing in through a flat entry orifice, and are therefore reasonably accurate for a sample that flows to the corners of the barrel and into a flat entry die, although some deviations occur in other situations. A detailed analysis of this was carried out by Kwag and Vlachopoulos.

$$\dot{\epsilon} = \frac{4\eta \dot{\gamma}^2}{3(n+1)\Delta p_e} \quad \text{Eq. (14)} \quad \eta_e = \frac{9(n+1)^2 (\Delta p_e)^2}{32\eta \dot{\gamma}^2} \quad \text{Eq. (15)}$$

Eq. 14. Cogswell's calculation for: a) Extensional rate and,

Eq. 15. Extensional viscosity, where Δp_e is the pressure on the orifice entrance

A Basic Introduction to Capillary Rheology

Typical Setup for a Rosand Twin Bore Capillary Rheometer for Polymer Melt Testing

Instrument Configuration

1. Barrel diameter: 15 mm
2. Dies
 - a) 1.0 mm D x 16 mm L, 180° entrance (long die)
 - b) 1.0 mm D x 0.25 mm L, 180° entrance (orifice)
3. Temperature: RT to 400°C (depending on the polymer type)
4. Pressure transducers: 10 kpsi or 20 kpsi (left) & 1.5 or 5 kpsi (right)
5. Shear rate range: $100 - 10^4 \text{ s}^{-1}$
6. Compression and pre-heat: 10 MPa (left) and 0.5 MPa (right) & 5 minutes and 3 minutes
7. Equilibrium mode: Pressure stability

Typical Equilibrium Conditions Rabinowitsch Correction

Figure 11 shows typical equilibrium and data capture setup within the Rosand Flowmaster software. Raw data arrives and is averaged (3), the equilibrium conditions can then be set with (1) and (2). Maximum samples is when the test will advance irrespective of whether equilibrium has been reached to reduce material being used on speed step.

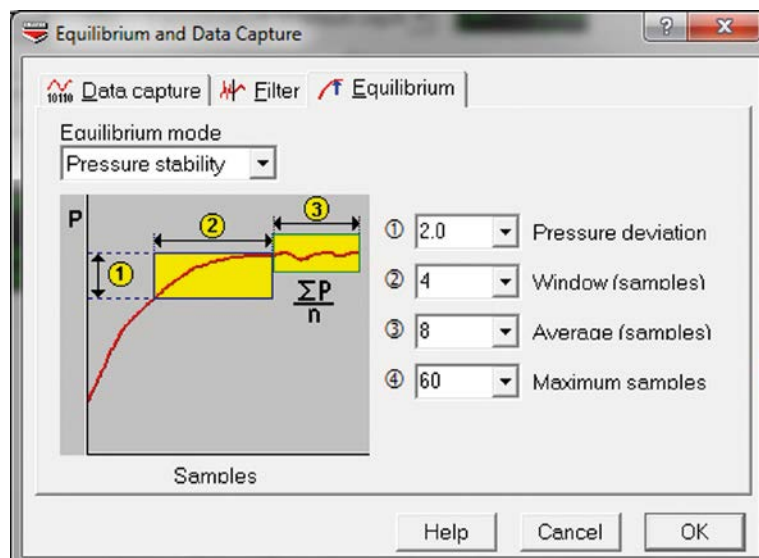


Figure 11. The equilibrium and data capture screen in the Flowmaster software.

Typical Results Obtained With a Capillary Rheometer

Example Results from the Capillary Rheometer

Some example shear viscosity results obtained from the Rosand capillary rheometer can be seen in Figures 12 and 13. Example extensional viscosity results are shown in Figure 14.

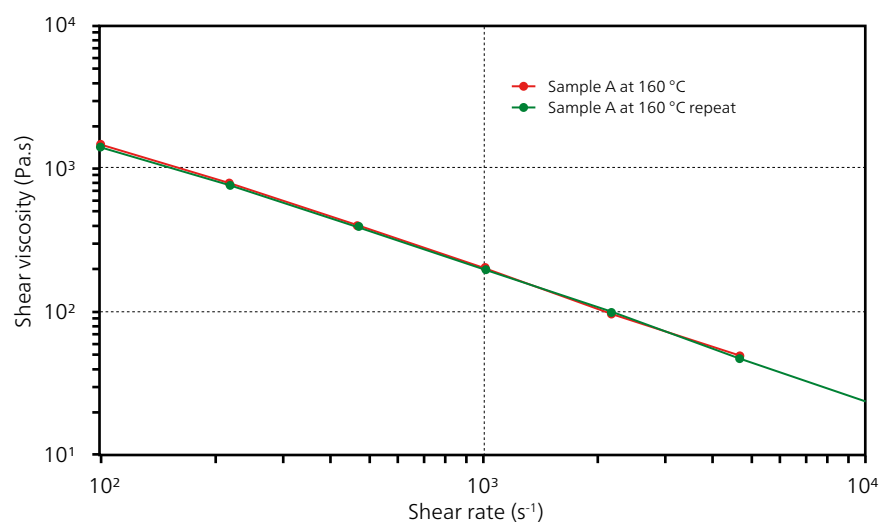


Figure 12. Shear viscosity (η) as a function of shear rate ($\dot{\gamma}$). Two repeat runs are made to check the reproducibility of the method

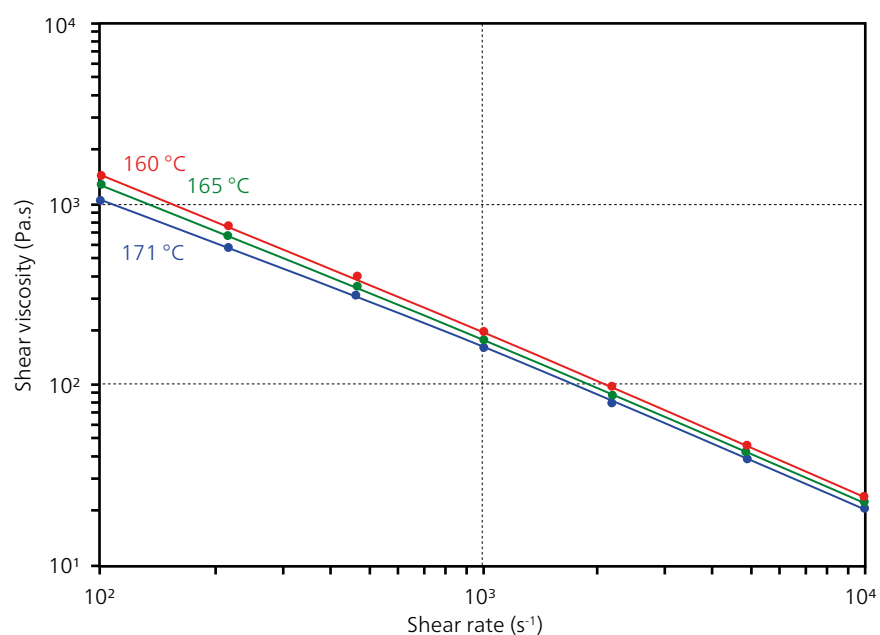


Figure 13. Evaluation of temperature and shear rate ($\dot{\gamma}$) dependence of shear viscosity (η). Flow curves of a sample at 160°C, 165°C and 171°C

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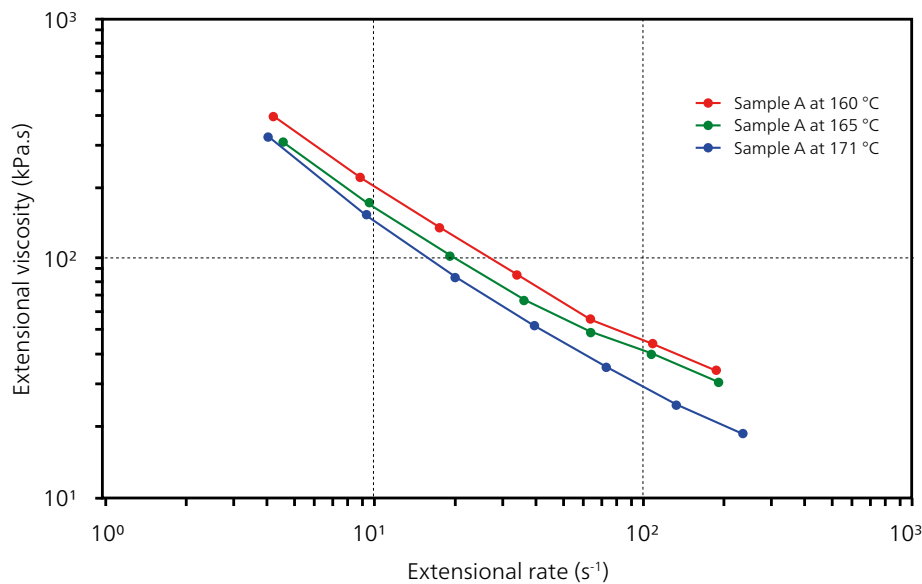


Figure 14. Evaluation of temperature and extensional rate ($\dot{\epsilon}$) dependence of the extensional viscosity (η_e). Flow curves of a sample at 160°C, 165°C and 171°C

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Characterizing Fundamental Material Properties



Characterizing Fundamental Material Properties

Pressure Volume Temperature (PVT) and Injection Molding Tests

PVT Testing

Introduction

When samples are injection molded, it is very important to know the PVT properties of the melt as some melts may be more compressible than others. A compressible melt is likely to require slightly more volume to fill the mold, however, can then bleed from the injection point after molding causing an unsightly sprue or die 'drool'.

Variations in melt compressibility can also cause parts that should have flat surfaces to be made as convex or concave surfaces. This, in turn, can cause problems when the parts are to be fitted together.

The Rosand capillary rheometer is capable of accurately measuring the PVT characteristics of compounds, predicting their suitability and optimizing injection moulder settings. The density of the hot polymer melt can be calculated for any pressure or temperature measured during the test. The rheometer can also measure the high shear rate viscosity characteristics and simulate the injection moulding process.

Interpretation

Figure 15 shows PVT results for two polymer melt samples. The results show that sample A is much less compressible than sample B, needing less volume on injection and is less likely to give drool after molding. The compressibility of a melt is likely to be related to its filler content, the polymer

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: PVT die Transducers: 5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
PVT test detail	Initial descent speed: 30 mm/min Initial volume: 20 mL Compression speed: 2mm/min Record result every: 0.5 min Stop when 10 MPa reached
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

chain structure and the polymer's molecular weight. Sample B is more compressible than sample A, indicating it would need a higher initial injection volume, however with a small withdrawal (slight negative pressure) to reduce the die drool. This reduction of pressure on the die contents whilst the article solidifies for a few seconds may also help to reduce swell (causing convex surfaces).

If the total weight of polymer in the barrel is measured (weight added initially subtracting the weight extruded during pre-compression and initial descent), the density of the melt can also be accurately calculated.

Density of Melt = Wt. of Polymer/Volume (Initially 20 mL)

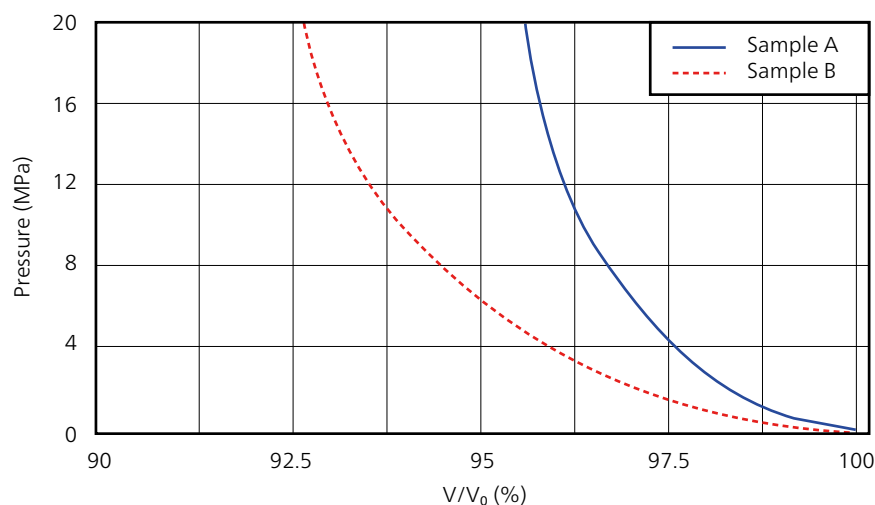


Figure 15. Pressure change versus percentage compression for 2 polymer melt samples. Where V is the sample volume at a given pressure and V_0 is the initial volume before the measurement.

Injection Molding Simulation Tests

Discussion

Figure 16 shows shear viscosity results from the capillary rheometer over a range of shear rates. In this test, the compounds are sheared at similar rates to those in injection molding. As the material is of high viscosity, it is necessary to apply the Bagley and Rabinowitz corrections to give the corrected shear rate. The lower shear rate data indicates how easily the melt fills small mold apertures thus giving better detail definition. The high shear rate data shows how quickly the overall process may be carried out within the limitations of the injection-molder. Sample A, shown above, has a lower viscosity at all measured shear rates indicating easier and quicker filling of the mold details. NB – if the melt viscosity is too low, bleeding between the two touching mold faces may also be a problem.

Conclusion

The Rosand capillary rheometer can be used in conjunction with lab and pilot-scale injection molders to formulate high-quality polymer compounds. PVT testing can show how to optimize the injection molding settings, whilst high shear rheometry can simulate the actual injection process.

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 16 mm x 1 mm x 180°, 0.25 x 1 x 180° Transducers: 10 kpsi 1.5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
IMT test details	Table of shears: 10 - 10,000 s ⁻¹ , 8 steps Temperature: 190°C
Equilibrium	By volume: 60 sample/mL, 0.1 min max interval, no filter, Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, max samples: no limit, trip: 80%

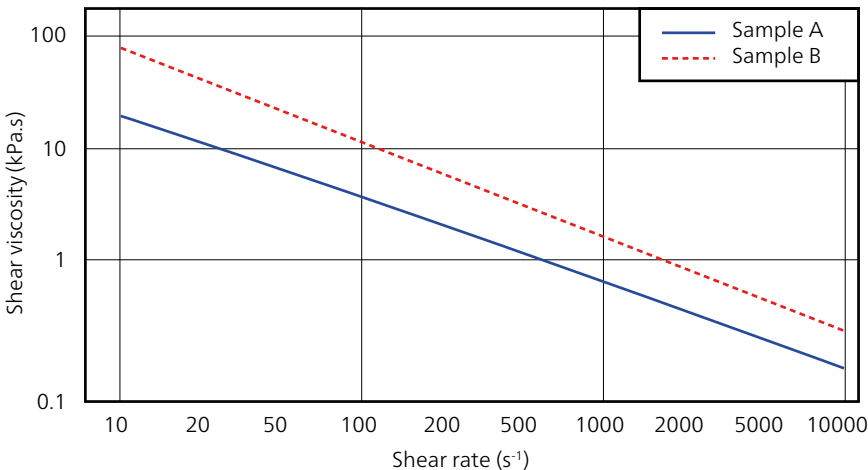


Figure 16. Viscosity (η) during injection molding

Characterizing Fundamental Material Properties

Low-Speed Degradation Testing

Discussion

Figure 17 shows the shear viscosity of a polymer melt over time. During this measurement, the polymer melt is held isothermally at a high temperature and sheared at a low constant shear rate (154 s^{-1} in this example). As the material degrades, the pressure measured at the transducer falls gradually. In this example, it can be seen that sample A has better thermal stability than sample B. Polymers degrade due to several processes occurring, including free radical, monomer reactions and oxidation (when air is present). Oxidation may be largely eliminated by using the nitrogen purge gas option and so this simulates more closely the situation in an extruder or injection-molder.

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 16 x 1 x 180° Transducers: 5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Test details	Low-speed degradation test: 2 mm·min ⁻¹ , samples every 30 s Temperature: 230°C (or appropriate)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Conclusion

The Rosand capillary rheometer can be used to simulate thermal degradation during wait times and the actual injection molding process. The use of small trial polymer lots and the rheometer is ideal to optimize the dosing of anti-oxidants, lubricants and thermal stabilizers.

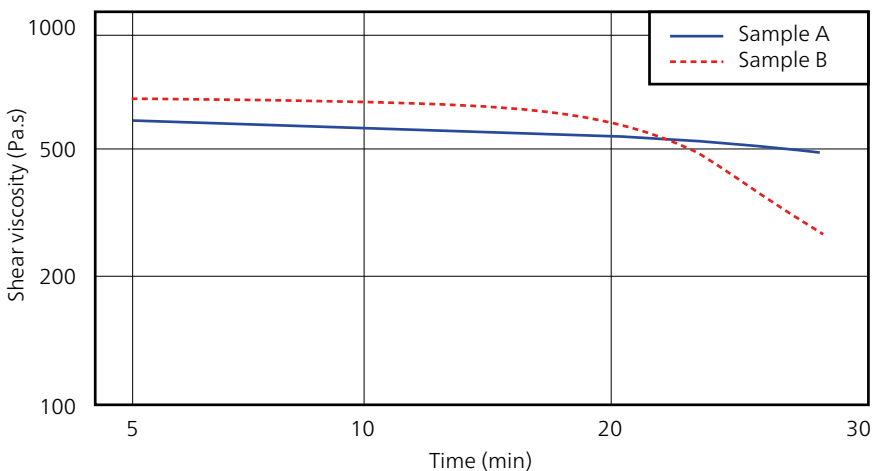


Figure 17. Viscosity (η) as a function of degradation time at 230°C

Flow/No-Flow Test

Introduction

The Flow/No-Flow Test module in the Rosand capillary rheometer is used to investigate the changes in properties of a material with respect to temperature. Of special interest are discontinuities in temperature- pressure graphs that would indicate state changes. A very practical value of the test is that it can be used to determine the approximate no-flow temperature (NFT) of a material. As injection molding simulation programs become more widely used, the influence of the NFT on the main processing parameters is becoming clearer. In the injection molding process, the NFT influences the frozen layer and the filling pressure, and with the effect on the frozen layer, this extends to affecting the estimation of shrinkage and warpage.

The NFT is not well defined, and a standard for measuring polymers does not exist. The Flow/No-Flow test offered on the Rosand capillary rheometers is a simple technique that does not require any components beyond standard rheometer dies and pressure transducers.

Experimental

The test applies a constant shear rate to the material while the barrel cools down naturally; beginning after the sample is loaded and allowed to get to a full melt state. An inflection

Instrument Setup	
Samples	HDPE, LDPE, and polypropylene
Set-up	Dies – 1.0 mm diameter, 16 mm length, 180° entrance angle
Pre-test	Compression/pre-heat -2 stages; compression to 2.0 MPa, then 5 minutes wait, followed by compression to 1.0 MPa then three minutes wait
Test details	15 mm diameter barrel, single-bore mode Piston speed/shear rate – 1.67 mm/min (50 sec-1) Pressure transducer – 10,000 psig (~70 MPa) End pressure – 60 MPa

point with an abrupt change in pressure, close to the melting point, indicates the cessation of flow.

Before performing a flow/no flow test it may be necessary to do some initial investigation. First, determine the softening point of the sample material, and the time it takes the barrel to cool down from the start temperature to this softening temperature. If possible, the relationship between shear rate and resultant pressure at a temperature just above the melting point of the material should also be determined. Selecting an appropriate shear rate avoids a situation where the barrel is prematurely emptied, with the test ending prior to achieving the softening point of the material; starting at the lowest recommended processing temperature for the sample also shortens the time to the softening point.

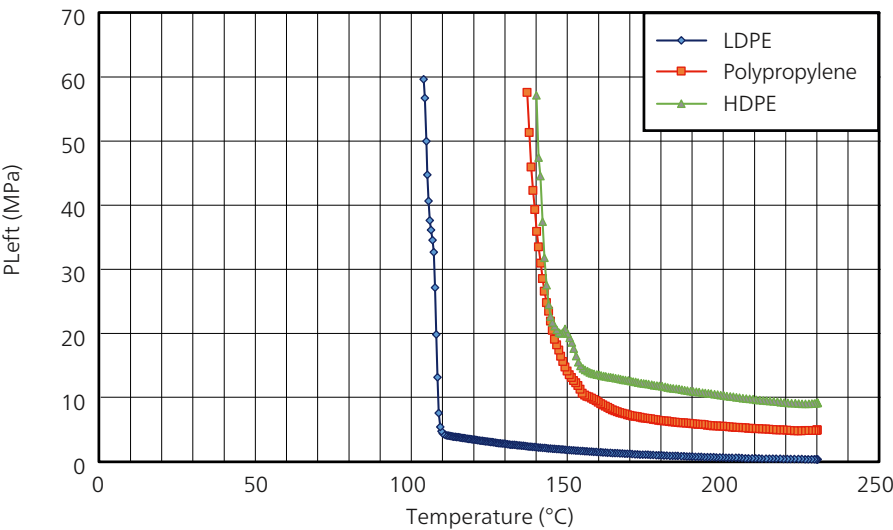


Figure 18. Flow/No-Flow tests on HDPE, LDPE, and Polypropylene showing PLeft (left pressure transducer) pressure with changing temperature.

Results

Figure 18 shows the results from the Flow/No-Flow tests on HDPE, LDPE and polypropylene. The results clearly indicate there is an abrupt increase in pressure of all three samples at their respective no-flow temperature. For LDPE this occurs at 115°C, a significantly lower temperature compared to HDPE (157°C) and Polypropylene (154°C). The results also show the differences in the initial steady state pressure of the three samples at the starting melt temperature of 230°C.



Optimizing the Processability of Materials



Optimizing the Processability of Materials

Characterizing Ceramic Extrusion Properties

Introduction

The rheology of a ceramic body is critical in the ‘plastic making’ of tableware. When the body is extruded, it can cause a large pressure build-up or show signs of cracking on the roller head machine if the solids are too high. If the solids are too low, the body can stick to the roller head or sag after molding. If the ceramic body’s rheology is very poor, (e.g., shear thickening), it can be thrown off the roller head completely.

The Rosand capillary rheometer is capable to simulate the whole range of shear rates seen in extrusion and injection molding (as for kiln furniture, etc.). The rheometer’s rigid design enables high forces to be measured. This enables measurement of the high stresses that occur during extrusion of ceramics.

The experiment discussed is designed to measure the viscosity of the body during the extrusion process. The results can be used to compare with that of ideal body systems, or to optimize the roller head settings. Typical results are shown in Figure 19.

Instrument Setup	
Samples	Fiber-filled ceramic pastes
Set-up	Dies: 16 mm x 2 mm x 90° & 0.25 mm x 2 mm x 90° Transducers: 30 kpsi & 5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 4 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 5 min
Table of shears	Range: 2 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 260°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

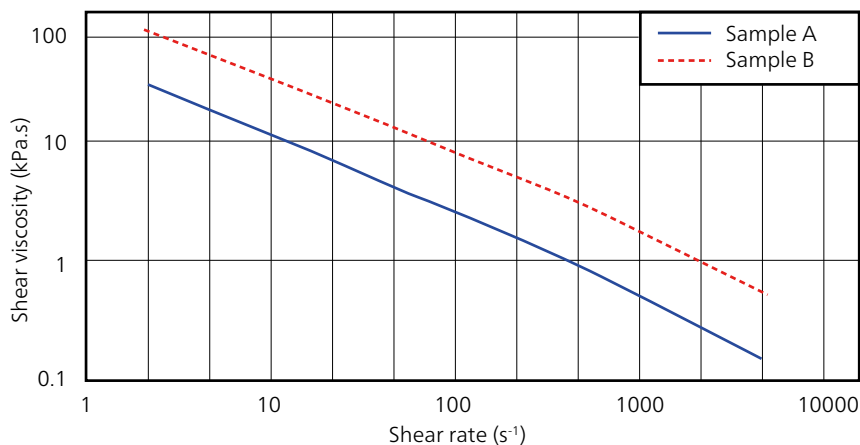


Figure 19. Shear viscosity (η) as a function of shear rate ($\dot{\gamma}$, from Rabinowitsch) for two ceramic extrusion samples

Discussion

The results show that ceramic A has a lower viscosity than B, suggesting easier extrusion and molding with a smoother surface. The shear thinning nature of the body also indicates that it may be suitable for plastic manufacture.

By using a capillary (long) die and an orifice (zero length) die, we can calculate the extensional and shear viscosity properties. The capillary die gives data for the entrance and shear pressure drops, whereas the orifice die only provides entrance pressure information. A Bagley correction may be applied to the results, which subtracts the orifice die pressure from the capillary die pressure, resulting in corrected shear pressure data. The shear viscosity indicates flow properties into molds and in pumping conditions.

The short die gives information about the extensional properties. The P_0 value (pressure at the orifice die) can be plotted to give an indication of the extensional viscosity. A

high extensional viscosity may indicate that the ceramic is likely to give dewatering and processing problems.

If the rheological data of a product can be correlated with its performance in an extruder, any unacceptable formulations can be eliminated without the need for extrusion trials. This dramatically cuts down on wasted time and product.

The Rosand rheometers can also be configured to measure die swell with a laser micrometer system attached to the software. For more information on this please see our section on 'Determining Extrusion and Die Swell Properties of Polymers', page 30.

Conclusion

The Rosand capillary rheometer can be used in conjunction with the lab and pilot scale extruders to formulate high-quality ceramic paste compounds.

Optimizing the Processability of Materials

Characterizing Low-Viscosity Coatings with the Fluids Tip

Introduction

Inkjet inks are often characterized with a rotational rheometer, however because of their very low viscosities, achieving reproducible data at very high shear rates can sometimes be challenging. The samples may be expelled from the measuring gap or transition into vortex flow patterns exhibiting a higher viscosity result than expected.

The Rosand capillary rheometer can be used with a Viton rubber sealed fluids tip (Figure 20) and a small diameter die to generate extremely high shear rate data.

If the ink is not too volatile and has only very small particles ($<1\text{ }\mu\text{m}$), a 0.25 mm die can be used enabling shear rates of up to approximately 10^6 s^{-1} to be reached with a standard 15mm barrel instrument. These very high shear rates will enable the viscosity to be measured at the actual printing shear rate and higher. Using a larger 24 mm barrel, shear rates of up to $2.4 \times 10^6\text{ s}^{-1}$ could theoretically be measured.

Instrument Setup	
Samples	Spray paints
Set-up	Dies: 8 mm x 0.25 mm x 180° & 0.25 mm x 0.25 mm x 180° Transducers: 5 kpsi & 1500 psi
Pre-test	No pre-test compression and wait steps required
Table of shears	Range: 20,000 - 960,000 s^{-1} , 5 steps / up / log Temperature: ambient
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%



Figure 20. Fluids piston tip with a Viton O-ring seal

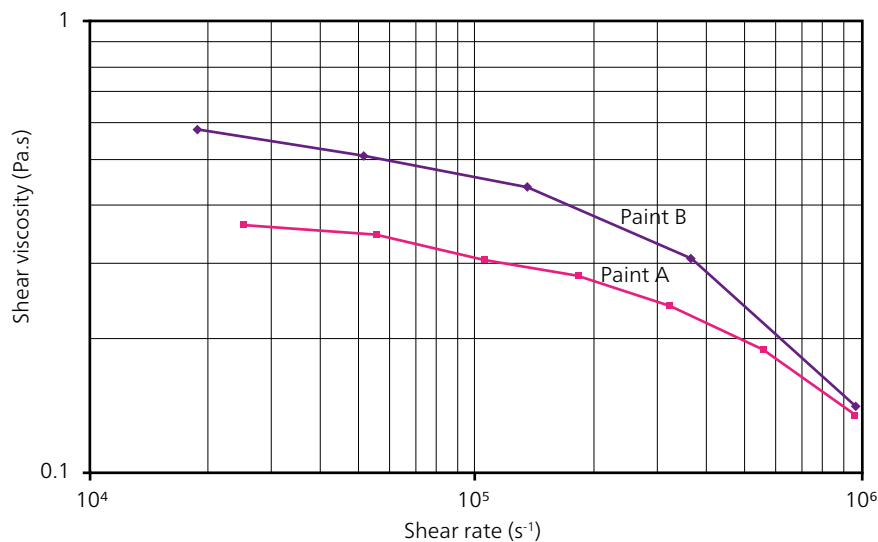


Figure 21. Shear viscosity (η) as a function of shear rate ($\dot{\gamma}$) for 2 coating samples, NB – data taken from a couple of separate runs and combined

Interpretation

The results in Figure 21 show that paint A (pink squares) has a lower viscosity than paint B (purple diamonds) and so will spray more easily but may also run after spraying. Sample B showed a higher viscosity at moderately high shear but low viscosity at very high shear indicating that it may be sprayable, yet not run so easily.

By using a capillary (long) die and an orifice (zero length) die, we can separate the extensional and shear viscosity properties. The capillary die gives data for the combined extensional and shear viscosities, whereas the orifice die only gives extensional viscosity information. A Bagley correction may be applied to the results, which removes the orifice die pressure from the capillary die pressure, resulting in the corrected shear pressure data. To improve the accuracy

further, the Hagenbach and Couette corrections could also be applied. The shear viscosity indicates flow properties through tubes and in pumping conditions.

The short die gives information about the extensional properties. For very low viscosity liquids, the P_0 value (pressure at the orifice die) is usually plotted rather than the Cogswell extensional viscosity, due to limitations of the Cogswell flow model.

Conclusion

Spray paints and other low viscosity coatings can be characterized at extremely high shear rate in the Rosand capillary rheometer to measure the shear and extensional viscosities at printing and spraying shear rates.



Optimizing the Processability of Materials

Determining Extrusion and Die Swell Properties of Polymers

Introduction

Traditional methods of measuring viscosities of polymer melts include melt flow indexing (MFI) and moving die rheometers, however, these units only give low shear rate information. The Rosand capillary rheometer can measure across a broad range of shear rates and is capable to simulate the high shear rates seen during extrusion processes. The polymer's extrusion characteristics can therefore be accurately evaluated, eliminating the need for many injection molding trials.

Common problems experienced during extrusion include melt fracture, shark-skinning, poor finish due to too much work input to the melt and excessive die swell (see Figure 22). All of these problems can be identified with the capillary rheometer and eliminated by good formulation.

In this test, the polymer melt is subjected to a table of shear rates giving equilibrium viscometry data at each step. The lower the shear viscosity, the more easily the polymer will be extruded and if the extrudate is under tension, the section will be thinner.

The die swell properties can be directly measured with a laser die swell unit, giving uni- or bi-axial dimensions of the

Instrument Setup	
Samples	PVC polymers (in this case)
Set-up	Dies: 16 mm x 0.25 mm x 180° & 0.25 mm x 1 mm x 180° Transducers: 5 kpsi & 1.5 psi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 2 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 180°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

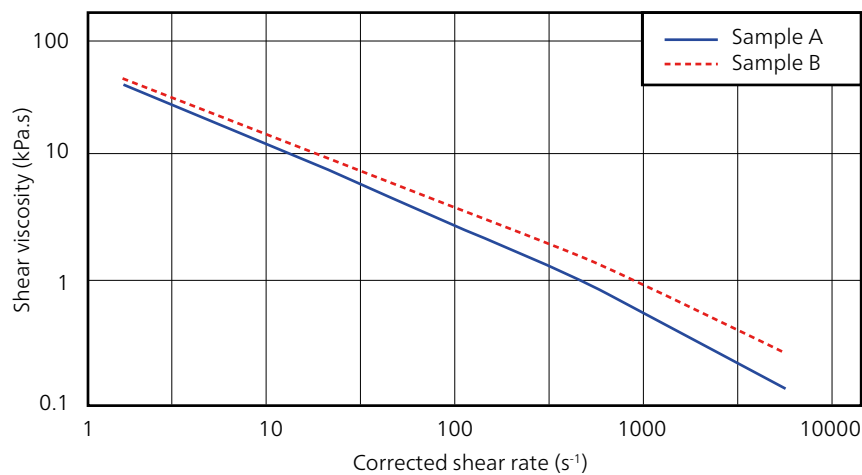


Figure 23. Shear viscosity (η) vs. corrected shear rate ($\dot{\gamma}$) from standard flow curve tests



Figure 22. Die swell during polymer extrusion. At higher shear rates die swell occurs further from the exit of the die as seen in this example. At slower shear rates, die swell may be seen immediately at the die exit.

extrudate at an adjustable height below the die. The die swell measured on the rheometer will therefore be an accurate indicator of the degree of die swell that could be expected during extrusion.

Interpretation

The results in Figure 23 show that sample A has a lower shear viscosity than sample B indicating it may extrude more easily with a smoother surface. The lower viscosity will also allow the material to fill small mold apertures giving a better definition for details.

Discussion

The die swell results in Figure 25 show that sample A gave almost twice the die swell of sample B, and therefore may give an enlarged profile during extrusion. Excessive die swell can cause a large number of part rejections and hence, a considerable waste of polymer compound. Parts such as UPVC double glazing frames, guttering and trunking need to be able to fit together tightly and so accurate dimensions are required. Polymers can vary from batch to batch in their molecular weight and molecular weight distribution, sometimes in such a way that the traditional tests such as Melt flow indexing cannot detect. The Rosand rheometers are capable to simulate actual extrusion shear rates and measure the die swell by means of a laser micrometer. This is

shown in Figure 24 below. The polymer batches can then be blended to give acceptable properties and reduce waste.

Conclusion

The Rosand capillary rheometer can be used in conjunction with the lab and pilot-scale extruders to formulate high-quality polymer compound melts.



Figure 24. Die swell measurements with a laser micrometer

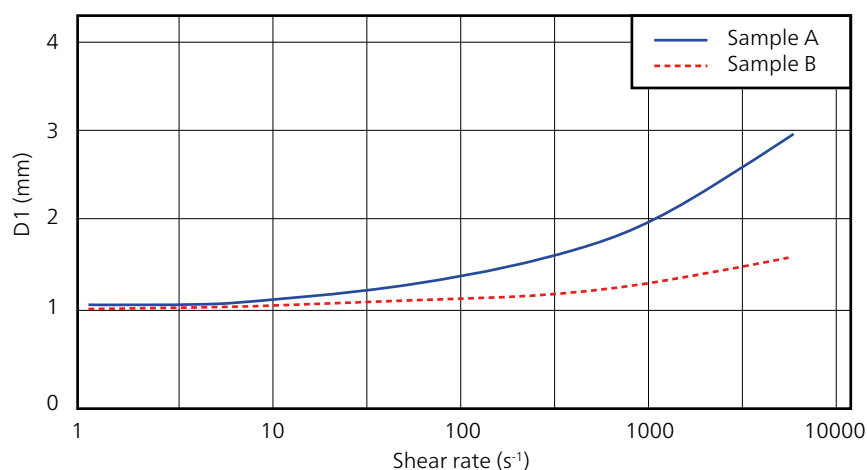


Figure 25. Extrudate diameter vs. shear rate ($\dot{\gamma}$) showing the die swell of the polymers at different shear rates, in addition to the data shown in Figure 23.

Optimizing the Processability of Materials

Determining Extrusion Performance of Rubbers

Introduction

When a rubber is extruded to give a certain section, it can sometimes exhibit die swell or melt fracture resulting in a poorly dimensioned part or an unattractive rough surface. The moving die rheometer and Mooney viscometer provide limited information and only show a low shear rate response (approximately 1 s^{-1}), however, the Rosand capillary rheometer is capable to simulate the whole range of shear rates seen in extrusion. The Rosand capillary rheometer can obtain very high shear rates due to its rigid H-frame design which enables forces of up to 100 kN to be measured. Extrusion shear rates often exceed 10^4 s^{-1} and the low shear viscosity is usually very different than that at high shear.

The lower the shear viscosity of the rubber, the more easily it will be extruded and if under tension, the extrudate section will be thinner.

Interpretation

The results in Figure 26 show that sample A has a lower viscosity than sample B indicating it may extrude more easily with a smoother surface.

By using a capillary (long) die and an orifice (zero length) die, we can separate the extensional and shear viscosity properties. The capillary die gives data for the combined entrance and shear pressures, whereas the orifice die mainly

Instrument Setup	
Samples	EPDM (Ethylene-propylene-diene-monomer copolymer) rubber samples
Set-up	Dies: 8 mm x 1 mm x 180° & 0.25 mm x 1 mm x 180° Transducers: 30 kpsi & 10 psi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 5 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 2 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 180°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

gives extensional pressure information. A Bagley correction may be applied to the results, which removes the orifice die pressure from the capillary die pressure, resulting in the corrected shear pressure data. The shear viscosity indicates flow properties into molds and in pumping conditions.

The short die gives information about the extensional properties as shown in Figure 27. Either the P_0 value (pressure at the orifice die) or the calculated extensional viscosity (by the Cogswell model) may be plotted. A high extensional viscosity may indicate that the rubber is likely to give a different shape section in thermoforming or blow molding, etc.

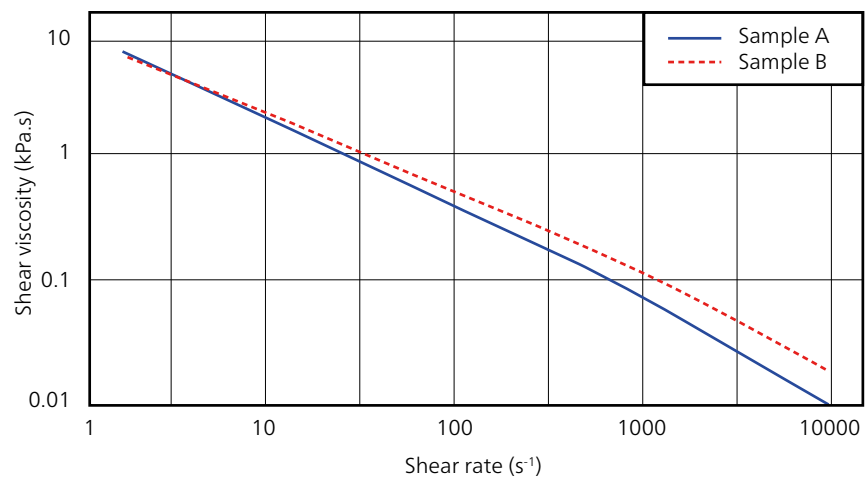


Figure 26. Shear viscosity (η) vs. shear rate ($\dot{\gamma}$) for 2 rubber compounds

If the rheological data of a product can be correlated with its performance in an extruder, any unacceptable formulations can be eliminated without the need for extrusion trials. This dramatically cuts down on wasted time and product.

The effect of screw and barrel temperatures on the viscosity during the extrusion process can be studied by running the shear viscosity test at various temperatures (Figure 28). This allows us to determine the acceptable temperature limits for the process.

Initially on heating, a rubber softens as expected, however, many rubbers become more viscous at higher temperatures due to the acceleration of crosslinking and other reactions. The optimum processing temperature may therefore be

identified by studying the shear and extensional viscosities over a range of temperatures.

The Rosand rheometers can also be configured to measure die swell with a laser micrometer system attached to the software. For more information on this please see our section on 'Determining Extrusion and Die Swell Properties of Polymers', page 30.

Conclusion

The Rosand capillary rheometer can be used in conjunction with the lab and pilot-scale extruders to formulate high quality polymer compound melts.

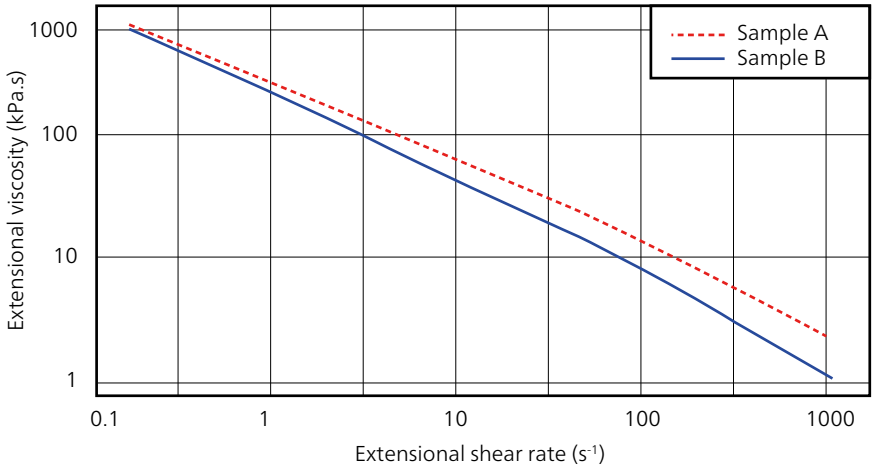


Figure 27. Extensional viscosity (η_e) vs. extension rate ($\dot{\epsilon}$)

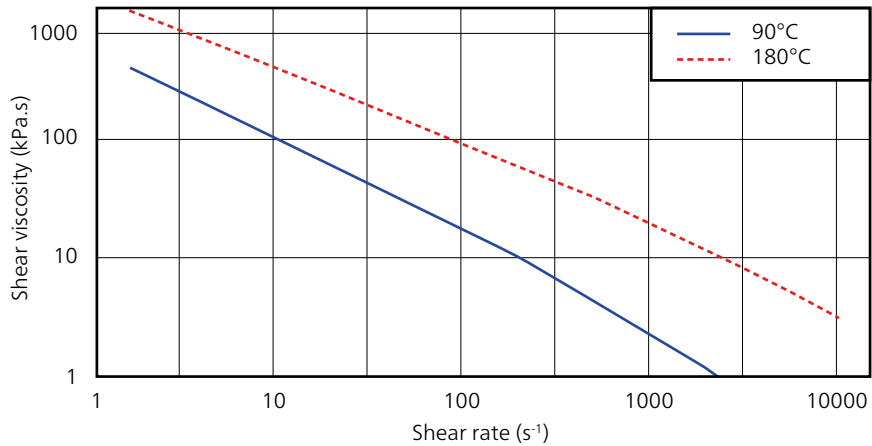


Figure 28. Shear viscosity (η) vs. shear rate ($\dot{\gamma}$) at two different temperatures

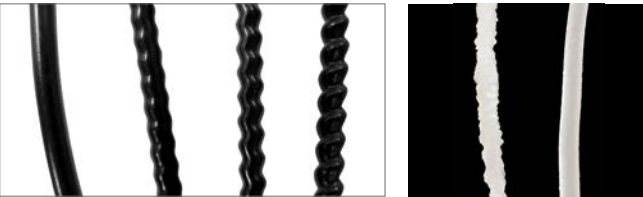


Optimizing the Processability of Materials

Eliminating Melt Fracture and Flow Instabilities

Introduction

A common problem encountered when extruding plastics is they exhibit melt fracture or ‘shark-skinning’. This is seen as a jagged or poor surface finish on the extrudate. Examples of different surface defects caused by melt flow instabilities can be seen below:



The problem is caused by localized slippage inside the die first occurring on one side and then the other. When the shear rate is increased, the flow becomes more plug-like and the surfaces are seen to be smooth again. If the melt fracture can be moved outside of the shear rate region used for extrusion, then it will no longer be a problem. The Rosand capillary rheometer is capable to simulate the whole range of shear rates seen in extrusion and so we can recreate this problem and eliminate it by reformulating the compound.

Initially, a table of shears is carried out to identify the melt fracture region approximately. Figure 29 shows the pressure plot results of sampled data from a table of shear rate measurement.

Instrument Setup	
Samples	Polyethylene (in this case)
Set-up	Dies: 16 mm x 1 mm x 180° Transducers: 20 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 4 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 5 min
Table of shears	Range: 100 - 15,000 s ⁻¹ , 8 steps / up / log Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Interpretation

The results show that melt fracture occurred on the fifth step of the shear rate table indicating that it is in the region of 3000 s⁻¹. Using a shear rate ramp, the exact shear rate range of the melt fracture can now be ascertained.

Discussion

Figure 30 illustrates the set-up of a melt fracture measurement within the Rosand Flowmaster software. Figure 31 displays pressure plotted against shear rate indicating the onset and cessation of melt fracture. The formulation can now be modified so that the fracture area

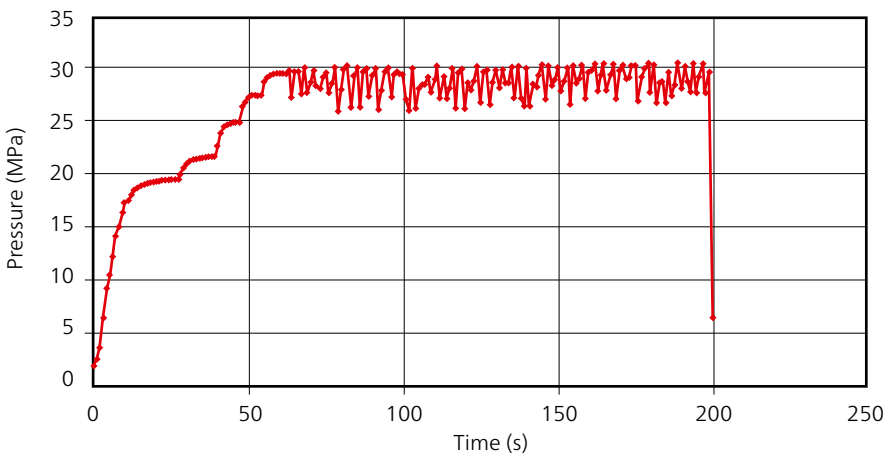


Figure 29. Results of the sampled data

Melt Fracture Shear Ramp Test	
Set-up	Dies: 16 mm x 1 mm x 180° Transducers: 10 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 4 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 5 min
Shear Ramp	Range: 2,000 - 5,000 s ⁻¹ , auto-range ramp rate Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By speed (v6 mode), Variation on standard rate = 1, no filter, Trip: 80%

falls outside extrusion shear rates. Formulations are often modified by addition of different fillers, plasticizers, waxes and other additives.

Conclusion

The Rosand capillary rheometer can be used to help formulate polymer compounds that will not give melt fracture or shark skinning problems during extrusion, thus eliminating many pilot scale trials. The rheometer only requires small sample volumes (approximately 50 mL) making it ideal for research and development testing.

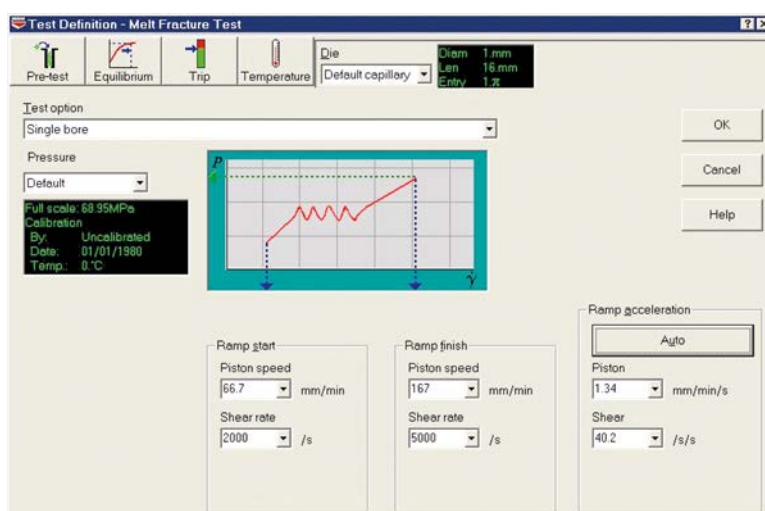


Figure 30. Measurement set-up

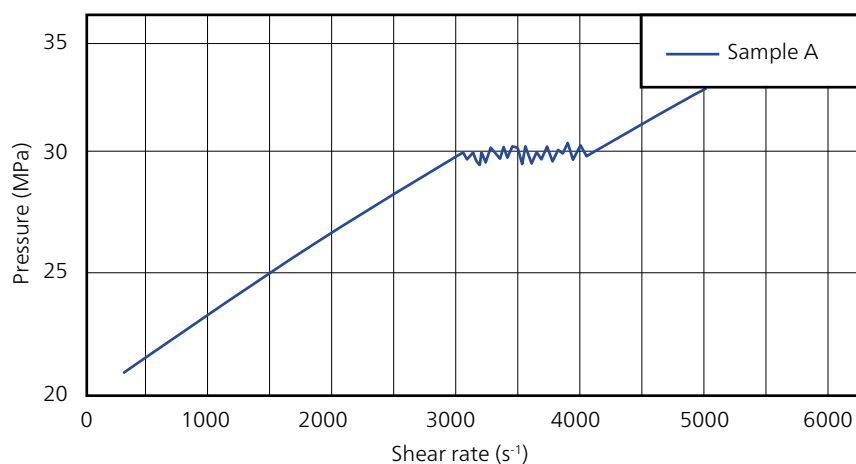


Figure 31. Sampled pressure vs. corrected shear rate ($\dot{\gamma}$) showing the start and end of melt fracture

Optimizing the Processability of Materials

Haul-off, Melt Strength and Fiber Spinning Tests

Introduction

Polymer compounding often suffers problems with the melt breaking therefore requiring repetitive feeding through the pelletizer. Similarly, the fibers can break during fiber spinning, especially when a high draw-down ratio is required. The Rosand capillary rheometers can be used to accurately measure the melt strength of the extrudate, simulate fiber spinning and calculate the maximum draw ratio of a compound or polymer. Testing conditions are highly controlled to give good reproducibility. The rheometer also only requires small amounts of test material and minimal cleaning, making an attractive alternative to pilot-scale extruder equipment.

Two system configurations are available for this work:

- 1) rheometer with a haul-off and balance
- 2) as 1) but also with a laser die swell attached (allowing measurement of extensional viscosity as illustrated in Figure 32)

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 20 mm x 2 mm x 180° Transducers: 10 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Threading	Piston speed: 10 mm·min ⁻¹ Haul-off speed: 5 - 1,000 s ⁻¹ , 7 steps Diameter axis: 1 Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 4 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Interpretation

Figure 33 shows results for a haul-off measurement which determines the melt strength of the polymer. The results show sample A breaking at around 150 m/min whereas sample B was capable to be hauled at over 500 m/min.

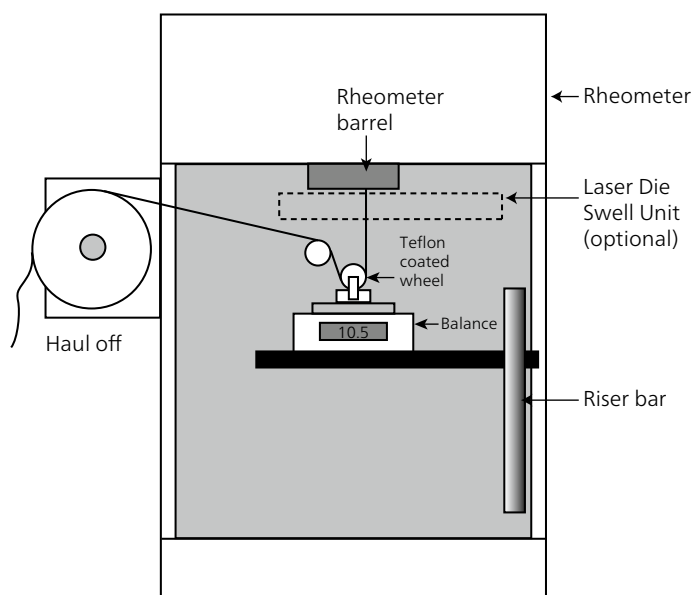


Figure 32. Illustration of the Rosand RH7 or 10 with a haul-off system attached

Where long drops are used for the fiber spinning, the Haul-off force at the break point may be more important to the user than the Haul-off speed.

The maximum 'draw ratio' (hauled length / original extruded length) may be determined when an oven is used to keep the extrudate hot. If an oven is not present, the fiber will cool quickly as it leaves the die, and draw is restricted. In this case, the fiber is likely to break at the die. The use of an oven allows the sample to be freely drawn giving a very narrow diameter extrudate.

The results also show that sample A has a higher Haul-off force than sample B and therefore expected to have a higher extensional viscosity. A comparative value of extensional viscosity can be calculated from the measured stress divided by the extensional rate, the latter being calculated from the change in length over the original length per second.

- Extensional stress, σ_e (Pa) = Haul-off force (N) / extrudate cross-sectional area (m^2)
- Extrudate speed (m/s) = piston speed (m/s) \times (barrel radius/die radius)²
- Extensional rate (s^{-1}) = extensional deformation / time
- Extensional viscosity, η_e (Pa.s) = extensional stress / extensional rate

This could also be correlated with the Cogswell extensional viscosity calculated from the P_0 values with an orifice die in the overlapping rate range. It can be seen from the above formulae that the extrudate diameter needs to be measured with a die swell system to calculate an absolute value of extensional viscosity. Other assumptions, such as the fiber being isothermal, the extrudate stretching at a constant rate throughout its length and no localized necking occurring in the fiber make the method more comparative than absolute, however results are still valid¹.

Conclusion

The Rosand capillary rheometer and Haul-off system is a versatile method of analyzing small batches of polymers and compounds to determine their suitability for fiber spinning or other extensional viscosity dominated processes (thermoforming, blow molding, film blowing, etc). The Rosand software is programmed to automatically control the Haul-off speed as a table of discrete speed or an accelerating ramp and all variables are recorded. Where extra analysis is required, the data may also be exported easily to other spreadsheet applications.

¹ D M Jones et.al, 1987. Rheol Acta 26, 20-30

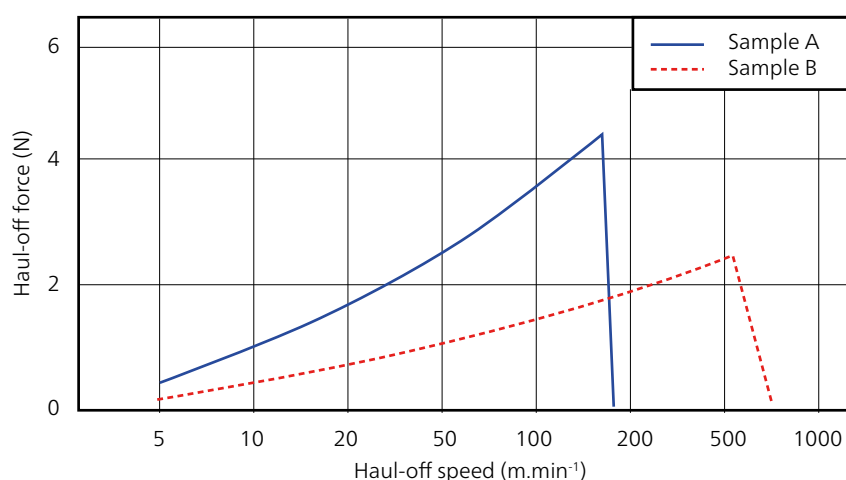


Figure 33. Haul-off force vs. haul-off speed. This is useful to show both the melt strength and maximum attainable haul-off speed

Optimizing the Processability of Materials

Capillary Rheometry in Additive Manufacturing

Introduction

Recently, there has been tremendous growth in additive manufacturing (AM) as a technique for the fabrication of parts directly from digital 3D-printing. This is resulting in the production of high-value, customizable, complex parts in much shorter time compared to the traditional machining methods. Polymeric materials are attractive for use in AM due to their large range of properties and similarities between some AM techniques and commonly used polymer processing methods. However, there remain some challenges such as reducing cost, improving quality and thereby full commercialization. Rheology and the processing aspects of this manufacturing technique are key elements to developing the pathway to better optimization of materials and processes.

Material Extrusion (ME) or Fused Deposition Modeling (FDM) is an additive manufacturing technique that operates very much like a capillary rheometer when the feedstock is a solid or liquid. When a polymer is used in FDM, a filament of the material is fed through a heated barrel where it is melted and exits via a conical nozzle with a small capillary onto a layered moving substrate to build an object.

PLA (polylactic acid) and ABS (acrylonitrile butadiene styrene) are polymers that are widely used in ME because of their favorable flow characteristics; polyethylene (PE) on the other hand is not as its fast crystallizing creates problems with welding onto the substrate. Generally, polymers that abruptly decrease in viscosity after melting are not ideal for ME as they tend to destabilize the deposited material.

A capillary rheometer can be a useful tool in several key areas of the material development and process modeling by optimizing process parameters, material evaluation, and small-scale production of filaments. Viscosity as a function of temperature and shear, extensional flow assessment, die swell, flow instability (melt fracture), and thermal stability, are the key areas where the rheometer is used for the initial screening of different polymer compounds. These topics are covered in other sections of this publication.

The example below (Figure 34) highlights the temperature effect on the viscosity of an ABS compound.

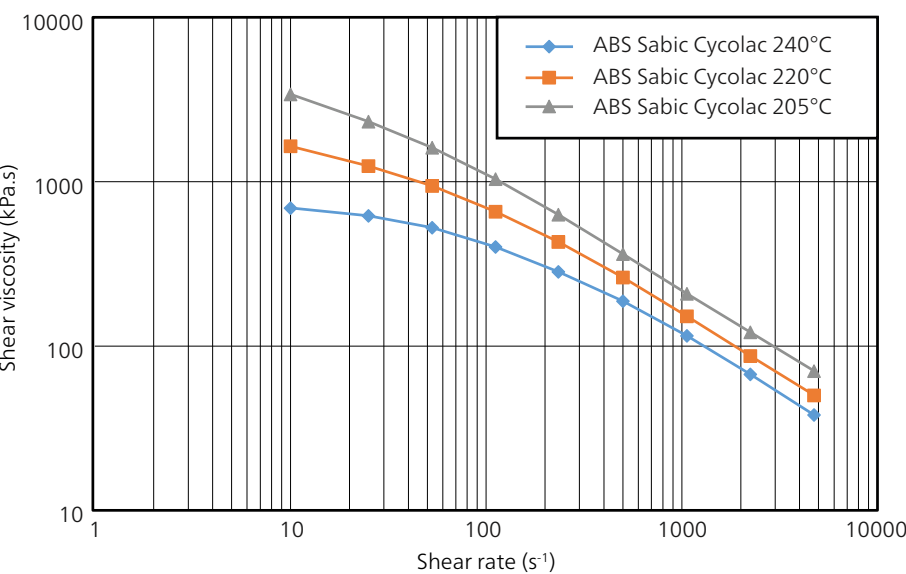


Figure 34. Shear viscosity (η) of ABS at three temperatures, 205°C, 220°C and 240°C

Instrument Setup	
Samples	PLA and ABS polymers
Set-up	Dies – 1.0 mm diameter, 16 mm length, 180° entrance angle & 1.0 mm diameter, 0.25 mm length, 180° entrance angle
Pre-test	compression/pre-heat -2 stages; compression to 2.0 MPa, then 5 minutes wait, followed by compression to 1.0 MPa then three minutes wait
Test details	15 mm diameter barrel, single-bore mode Pressure transducer: 10 kpsi (~70 MPa) & 1.5 kpsi (10.5 MPa)

Conclusion

ABS can be used across a wide range of temperatures; printing filament can be extruded as low as 200°C depending on the grade, melt flow measurements are usually made between 200°C and 220°C. 3D printing can be performed in the range of 230°C – 250°C.





Advanced Capillary Rheology



Advanced Capillary Rheology

Three Methods for Correcting for Die Entry Pressure Drop

Introduction

When a sample is sheared through a capillary die, the dominant factor will be the shear viscosity, however, there will also be some pressure contribution from the extensional viscosity of the sample as well as acceleration and squeezing into the die entrance. The sample undergoes extension as it is introduced into the entrance of the die and contraction when it leaves the exit of the die. To obtain the corrected shear viscosity, a method called the Bagley correction is used. Three methods for carrying out the Bagley correction are described here. The one most applicable will depend on the dies that the user has available.

Method 1: Cogswell Orifice Die Method

This method is the most modern and commonly used method for applying the Bagley correction. The user carries out the viscometry experiment using both a capillary and a 'zero length' die, known as an orifice die (actually 0.25 mm in length). The capillary die will show contributions from both extensional and shear pressures, whereas the orifice die gives mainly the extensional viscosity pressure (shown in Figure 35). The true shear flow pressure can then be calculated by deducting the orifice from the capillary die pressure.

$$P_c = P_L - P_o$$

$$\eta \propto P_c / L_L$$

where

P_c = Corrected shear pressure

η = Shear viscosity

P_o = Orifice die pressure

P_L = Long capillary die pressure

L_L = Long capillary die length

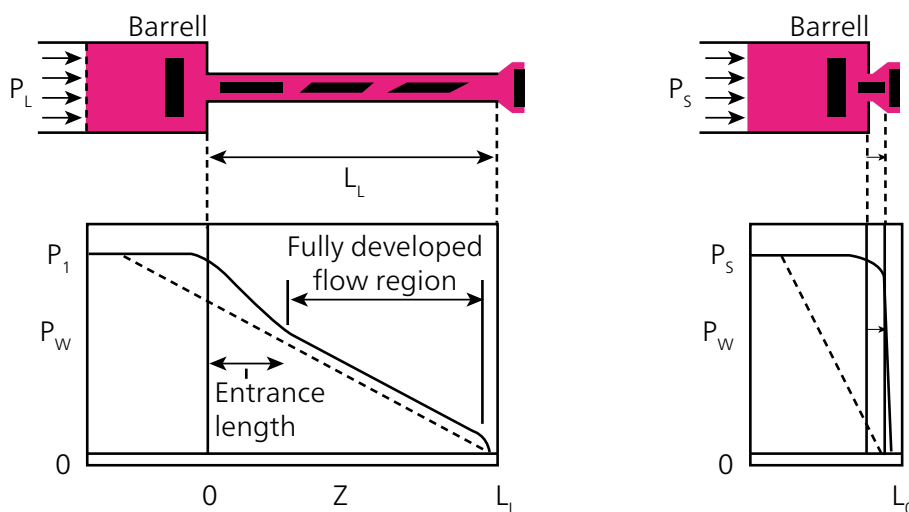


Figure 35. Extensional and shear effects of the capillary and orifice dies

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 20 mm x 1 mm x 180° & 0.25 mm x 1 mm x 180° Transducers: 5 kpsi & 0.5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 20 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Discussion

This method is considered the best method, as the orifice die pressures are generally accepted as being an accurate representation of extensional viscous flow. In addition, it doesn't give any of the non-linear extrapolation errors such as negative values unlike the historical Bagley method. Results are simple to calculate and when a twin bore rheometer is used, both capillary and orifice die pressures may be measured simultaneously. Typical data is shown in Figure 36.

Typical Results

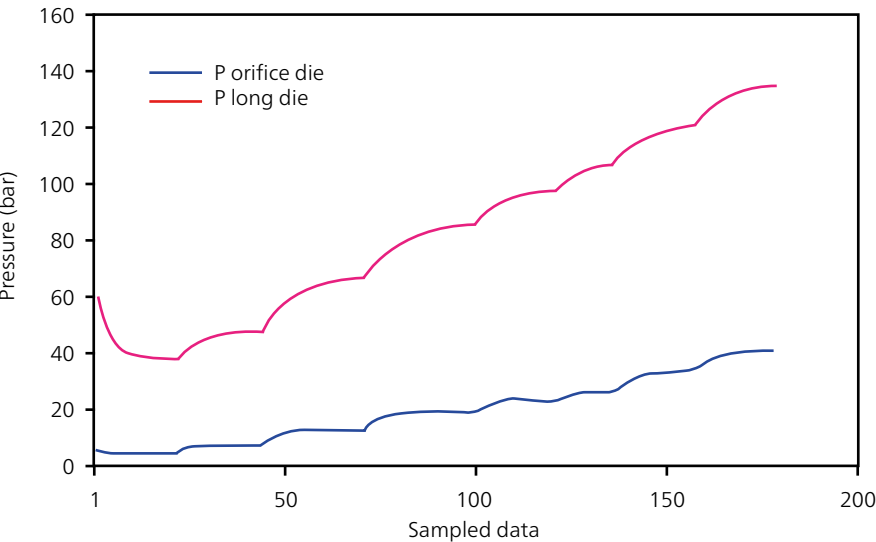


Figure 36. Pressure graphs of the orifice and long dies vs. datapoint

Advanced Capillary Rheology

Method 2: Two Different Length Dies of the Same Diameter

In this method, long and short (but not zero length) capillary dies of the same diameter are used. It can be seen (Figure 37) that the samples in both the long and short dies undergo extension and shear flow. However, the sample in the longer die undergoes only extra shear flow and no extra extensional flow. Therefore, the difference in pressure measured must be due to the shear viscosity of the material in the extra length of barrel. The method assumes that the material has zero slip and is incompressible.

In this classical Bagley method, the correct shear pressure is taken as the long die stress less the short die pressure and the die length taken as the difference in length between the two dies. The true shear viscosity is therefore calculated from the difference between the two dies. To obtain accurate results, the long die should be much longer than the short die.

$$P_c = P_L - P_s$$

$$L_c = L_L - L_s$$

$$\eta \propto P_c / L_c$$

where

P_c = Corrected shear pressure

L_c = Corrected die length

η = Shear viscosity

P_L = Long capillary die pressure

L_L = Long capillary die length

L_s = Short capillary die length

P_s = Short capillary die pressure

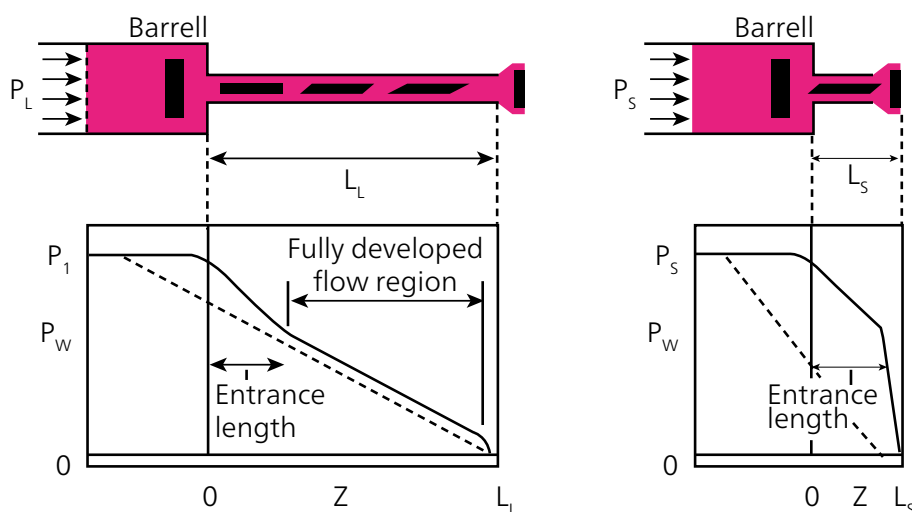


Figure 37. Shear and extensional flow effects of long and short dies

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 20 mm x 1 mm x 180° & 10 mm x 1 mm x 180° Transducers: 10 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 20 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Discussion

This method is a satisfactory substitute for method 1 if the user does not have an orifice die of the same diameter as the capillary die. It does not give any of the non-linear extrapolation errors such as negative values unlike the historical Bagley method. However, both dies should be long enough to allow the material to establish fully developed laminar flow. When a twin bore rheometer is used, both long and short die pressures can be measured simultaneously. Typical data is shown in Figure 38.

Typical Results

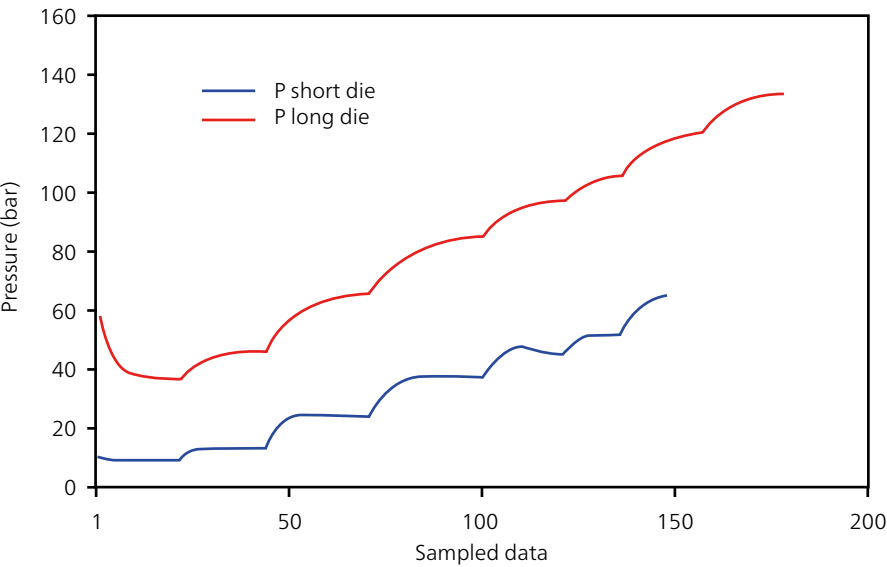


Figure 38. Pressures of the 20 mm and 10 mm dies in red and blue, respectively

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Method 3: Historical Method – Two or Three Dies of Different Length

In this method, two or three different diameter capillary dies with very different lengths are used. The flow curve is analyzed with all three dies. For each shear rate, a graph is plotted of pressure against length/radius (L/R) ratio (for the three dies used) and extrapolated back to zero pressure (see Figure 39). If the material only underwent shear flow, the graph would have an intercept at the origin, however, as there is a degree of extensional flow, the intercept at ΔP equals zero is at a negative L/R value (known as 'e'). This 'e' value can then be used to calculate the true shear stress at the wall by the formula shown.

The true shear viscosity is therefore calculated from the calculated wall stress

$$\eta \propto \sigma_w / L$$

where

η = Shear viscosity

σ_w = Corrected stress

L = Length of capillary die

$$\sigma_w = \frac{R \Delta P}{2(L + eR)} = \frac{\Delta P}{2(L/R + e)} = \frac{R(\Delta P - P_{end})}{2L}$$

where

σ_w = Shear stress at the wall

R = Radius

ΔP = Pressure drop

L = Length

e = L/R correction

P_{end} = Sum of entrance and exit pressure

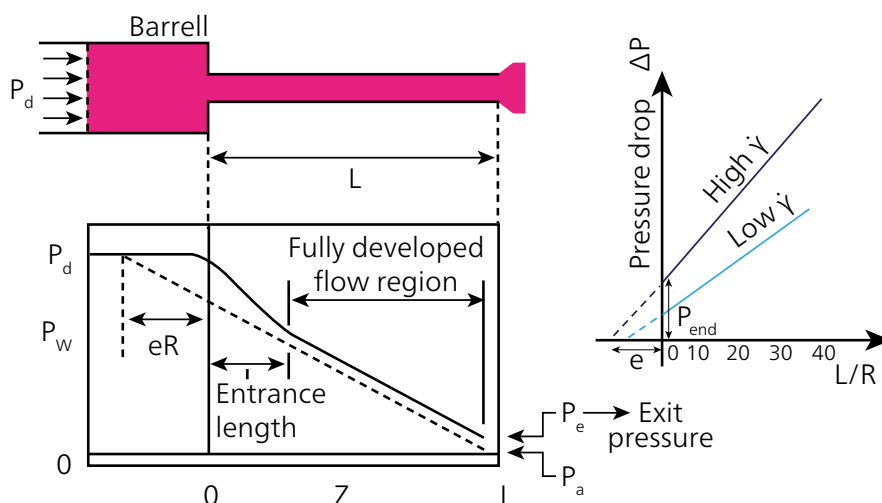


Figure 39. The pressure drop across a die is proportional to the L/R ratio plus an extensional component at any one shear rate; therefore, the pure shear entrance pressure can be calculated from the gradient of the graph and the calculated 'e' value from the above equation.

Instrument Setup	
Samples	PP polymer (in this case)
Set-up	Dies: 4 mm x 1 mm x 180° 16 mm x 1 mm x 180° 24 mm x 1 mm x 180° Transducers: 5 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 20 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 190°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%

Discussion

Typical pressure plots of three different die lengths can be seen in Figure 40. This method is the most laborious and slightly less accurate but can be useful when the dies necessary for method 1 are not available or when the user does not have a variety of die lengths. For reliable results, dies spanning a large L/R ratio range should be used. If the data is non-linear, this may be attributed to melt compressibility or some wall slip occurring. It is not advisable to fit a quadratic model to extrapolate, as the curve only has three points and errors will be created.

Conclusion

The Bagley correction is a versatile method of calculating pure shear flow data when using a capillary rheometer. The Rosand capillary rheometers can automatically carry out the orifice die (method 1) Bagley correction without the need for a complex set up, giving immediate true shear viscosity results. This method is also the only method that can generate extensional properties in the processing shear rate range (i.e., above 50 s⁻¹). Where extra analysis is required, the data may simply be exported to other spreadsheet applications.

Typical Results

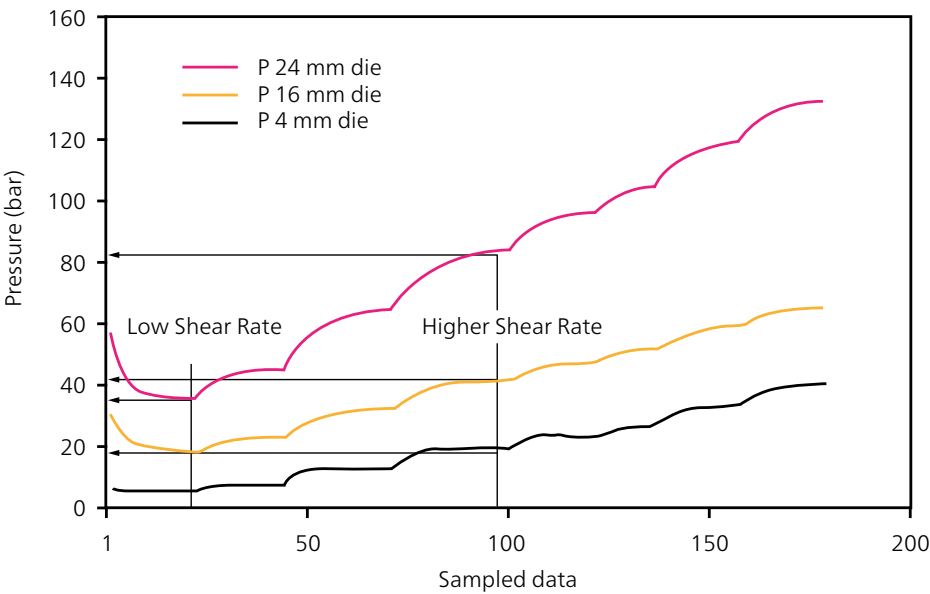


Figure 40. Pressures of the 24 mm, 16 mm and 4 mm dies against sampled data

Advanced Capillary Rheology

The Zero Length Die and Extensional Viscosity Measurement

Introduction

The Rosand capillary rheometer can measure across a broad range of shear rates and is capable to simulate the high shear rates seen during extrusion processes. The Rosand rheometer can also measure the extensional viscosity properties directly indicating how the polymer may behave during blow molding or fiber spinning.

In this test, the polymer melt is subjected to a table of shear rates obtaining equilibrium viscometry data at each step. The lower the extensional viscosity, the more easily the fiber will break during fiber spinning, or the larger the profile a bag may be during blow molding.

The extensional stress can be measured simply by using the pressure value from the orifice die (P_o), or calculated from the Cogswell model (this requires both capillary and orifice dies).

$$\dot{\epsilon} = \frac{4\eta\dot{\gamma}^2}{3(n+1)\Delta p_e} \qquad \eta_e = \frac{9(n+1)^2(\Delta p_e)^2}{32\eta\dot{\gamma}^2}$$

where:

- η_e = Extensional viscosity (Pa.s),
- n = Shear thinning index,
- ΔP_o = Extensional entrance pressure (Pa),
- $\dot{\gamma}$ = Shear rate (s^{-1}),
- $\dot{\epsilon}$ = Extensional shear rate (s^{-1})

Instrument Setup	
Samples	PVC polymers (in this case)
Set-up	Dies: 16 mm x 1 mm x 180° & 0.25 mm x 1 mm x 180° Transducers: 10 kpsi
Pre-test	Stage 1: 2 MPa/50 mm·min ⁻¹ hold for 3 min Stage 2: 2 MPa/50 mm·min ⁻¹ hold for 6 min
Table of shears	Range: 2 - 5,000 s ⁻¹ , 8 steps / up / log Temperature: 180°C (or normal extrusion temperature)
Equilibrium	By volume: 60 samples/mL, 0.1 min max. interval, no filter Pressure deviation: 0.5%, Window: 6 samples, Average: 4 samples, Max samples: no limit, Trip: 80%



Interpretation

The calculated extensional viscosity curves (by the Cogswell model) are shown for two polymers². A high extensional viscosity, as shown for sample B, indicates that the polymer is less likely to break during fiber spinning and would give a smaller blow molding diameter with standard conditions than sample A. It is possible that sample B could exhibit greater die swell than sample A (Figure 41), causing extruded profiles to be larger than expected. This can equally result in a waste of the polymer compound.

If a long capillary die and a 'zero' length are both used for the test, the Bagley correction may be applied to the results, which removes the orifice die pressure from the capillary die pressure, resulting in the corrected shear pressure data.

Conclusion

The Rosand capillary rheometer can be used in conjunction with lab and pilot-scale extruders to formulate high-quality polymer compound melts.

² NB. results are illustrative only

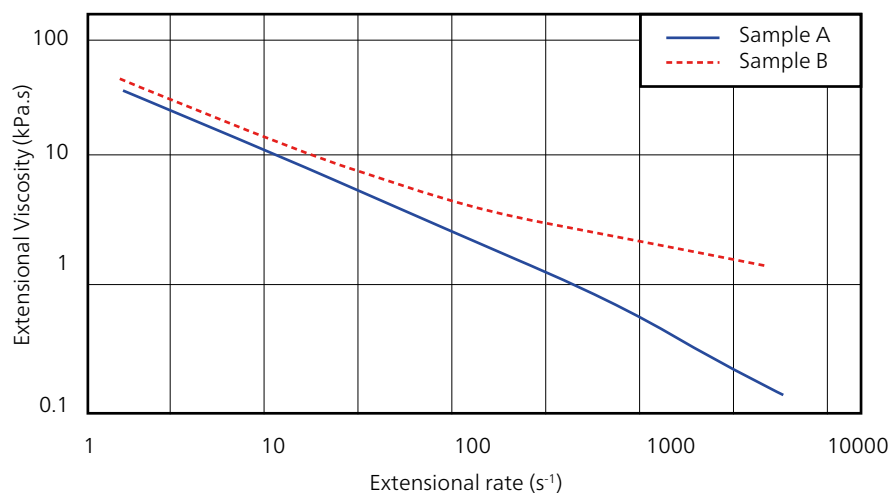


Figure 41. Extensional viscosity (η_e) vs. extensional rate ($\dot{\epsilon}$)

Advanced Capillary Rheology

Low Level Tests

There are several standard tests in capillary rheometry that are designed to investigate different properties of materials. These include but are not limited to: Constant Shear Rate, Material Degradation, Melt Fracture and Stress Relaxation, all based on routines that are directed by ASTM and ISO standards and universally accepted.

For users who may want to perform experiments that are non-standard, the low-level test sequence is a means for defining 'custom' tests, via a scripting language (see Figure 43). This allows a user to venture outside the confines of the standard tests, enhance the functionality of the software and take full advantage of the versatility of the rheometer. A user can define their own test types, with the test definition that consists of a script, constructed from low level statements that provide control over the machine and data logging.

Low-level tests can be as simple as incorporating a prompt for user intervention into a standard test, as shown in Figure 42, or involve operations that are more complex. The low-level test definition/test sequence shown below is from a pVT test that includes multiple test temperatures in sequence whilst controlling pressure levels and piston position.

Perhaps the best way to get started with low-level sequencing is to choose the standard test that is closest to your requirements, and convert it to a low-level sequence. That sequence can then be modified to match your requirements. The graph in Figure 44 shows the results of a standard low speed degradation test that was converted to low-level sequence and modified to include a temperature 'ramp'.



Figure 42. Cleaning prompt pop-up window

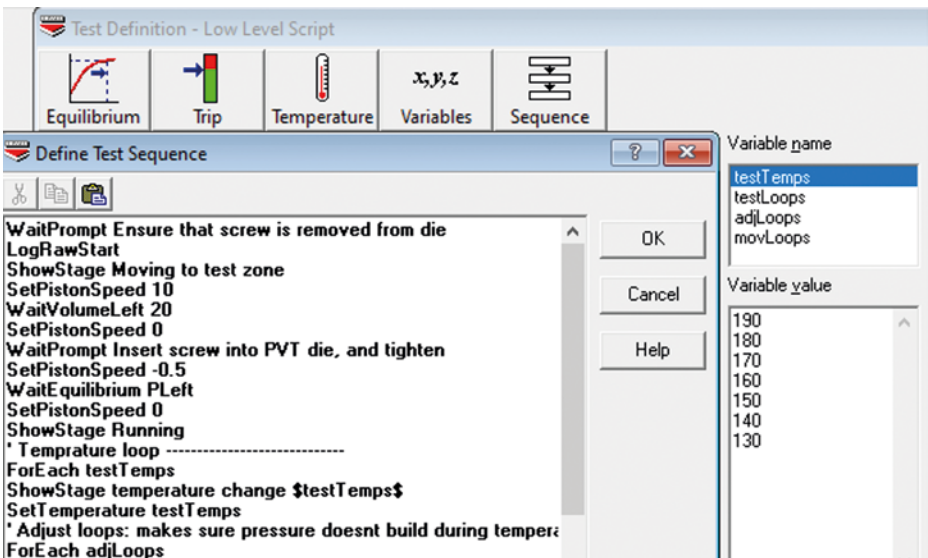


Figure 43. Low level script custom measurement set-up

Low-level test statements fall into four categories:

1. Machine control statements. These directly control the machine, allowing the sequence to do such things as set a piston speed, set a haul-off ramp or set temperatures.
2. Wait statements. These hold the progress of the test until a certain condition is met. Conditions include the detection of equilibrium, waiting for time to elapse, waiting for a user response to a prompt.
3. Data logging statements. These control the recording of sampled data and result data.
4. Sequence control statements. This category is concerned with control of the sequence itself, rather than any external effects. It includes statements to implement loops (in conjunction with multiple-valued variables), the display of the manual control panel, and the display of information on the test panel on the main screen.

To allow the creation of 'generic' low-level sequences, which may be easily modified to produce a range of individual tests, low-level sequences incorporate the concept of test variables. Any number of variables that are used within the test definition can be defined. The concept of using variables is taken further instead of a single value, variables can be assigned a list of values. Statements within the test sequence allow you to execute a series of statements once for each value that is contained within the list. This allows you to define a test sequence that operates in the same way, for example, as the standard constant shear rate test. The sequence itself does not have to include details of either the shear rates that you want to test, or the number of test stages that you want to perform. Both of these are controlled by the definition of the appropriate test variable.

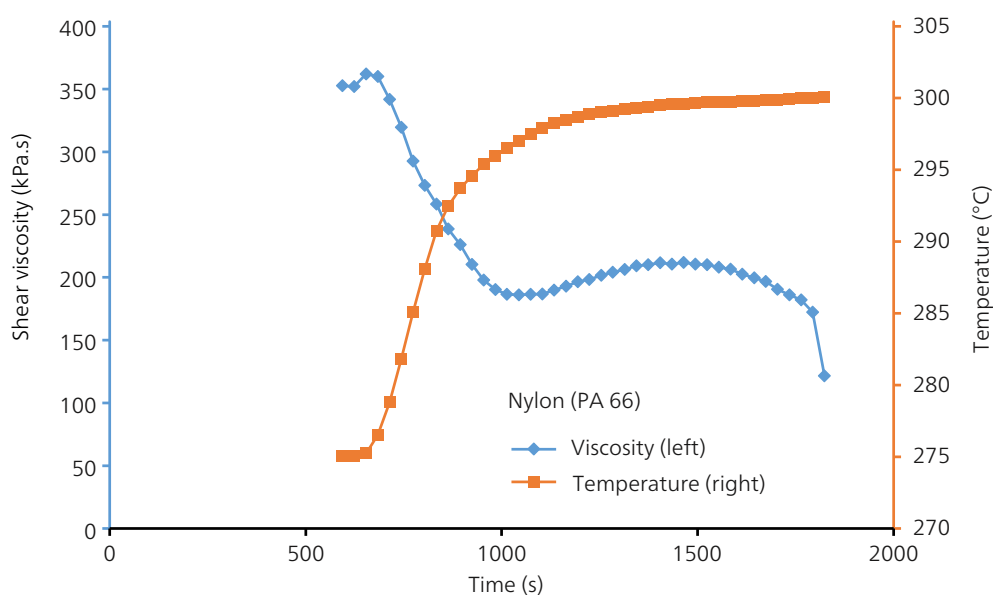


Figure 44. Shear viscosity (η) as a function of time and temperature

Nomenclature

γ	Shear deformation
$\dot{\gamma}$	Shear rate
$\dot{\gamma}_a$	Apparent shear rate
$\dot{\gamma}_{a\infty}$	Slip corrected apparent shear rate
$\dot{\gamma}_c$	Corrected shear rate
$\dot{\epsilon}$	Extensional rate (elongation rate)
η	Shear viscosity
η_0	Zero shear viscosity
η_∞	Infinite shear viscosity plateau
η_e	Extensional viscosity
ρ	Density
σ	Shear stress
σ_a	Apparent shear stress
σ_c	Corrected shear stress
σ_e	Extensional stress
σ_w	Wall shear stress
e	L/R correction
Δp_e	Pressure on the orifice entrance
p_{en}	Pressure drop in the capillary due to converging flow from reservoir to capillary
p_{ex}	Non-zero pressure at the capillary die exit due to fluid elasticity
p_c	Corrected shear pressure
n	Shear thinning index (power law index)
Q	Volumetric flow rate
v_s	Wall slip velocity
P_o	Orifice die pressure
P_L	Long capillary die pressure
P_s	Short capillary die pressure
P_C	Corrected pressure
P_{end}	Pressure used for end correction during Bagley correction
L_L	Long capillary die length
L_s	Short capillary die length
L_c	Corrected die length
L	Length
R	Radius
R_b	Barrel diameter
ΔP	Pressure drop
ABS	Acrylonitrile butadiene styrene
EPDM	Ethylene propylene diene monomer copolymer (a type of rubber)
HDPE	High-density polyethylene
LDPE	Low-density polyethylene
PE	Polyethylene
PLA	Polylactic acid
PP	Polypropylene
PVC	Polyvinyl chloride
UPVC	UV resistant polyvinyl chloride (a polymer often used for window frames and guttering)
A	Surface
ASTM	American Society for Testing and Materials
ISO	International Organization for Standardization
F	Force
MFI	Melt flow index
MW	Weight average molecular weight
MWD	Molecular weight distribution
PLeft	Pressure in the left bore
PVT	Pressure-volume-temperature test (compressibility)

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