Capillary Rheology Training Course

Introduction to capillary rheometer theory & technology
Application introduction and discussion

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Overview

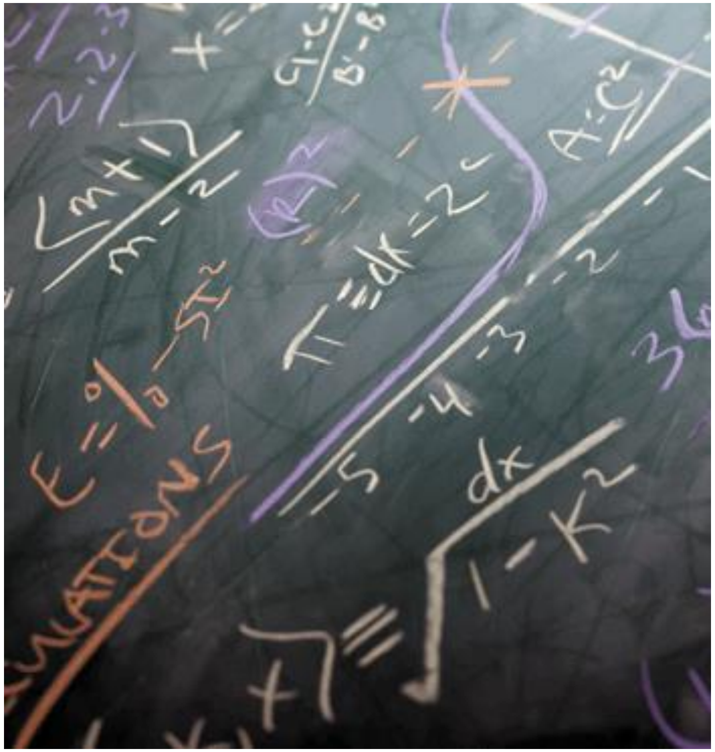
- Will give you a general understanding of what is **"rheology"**
- Details some of terms and definitions for **shear viscosity**

What is rheology…?

- The technical definition is:

“The science of deformation and flow”

- **But**, what does this **really** mean?



Why Measure Rheology?

- **Polymers** - we need to understand how the melt flows and to design moulds
- **Foods** - to give the correct appearance, texture and processing characteristics

- **Paints** - to give shelf life and correct surface finish
- **Inks** - to give print clarity and good metering

- **Pharmaceuticals** - for accurate dosing, sedimentation characteristics and effectiveness to the patient
- also important in: mud slurries, drilling fluids, bitumens, rubbers, etc...

Examples of Polymer Processing

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Rosand Product Range

- The **capillary** instruments

- From the entry level bench top instrument to the research level floor standing instrument

Rosand RH2000

Rosand RH7 / 10

Studying Flow

- With a capillary rheometer we are mostly focusing on how a material flows under different conditions

- Simply put:
  - Viscosity - the resistance to flow at different…
  - Shear Rates - the conditions

- Viscosity is a function of shear rate – different viscosities under different conditions

What is Shear Rate?

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- Really just a deformation rate. How much work are we putting into the sample?

Process	Typical shear rate range (s^{-1})		
Reverse gravure	100,000	-	1,000,000
Roller coating	10,000	-	1,000,000
Spraying	10,000	-	100,000
Blade coating	1,000	-	100,000
Mixing/stirring	10	-	1,000
Brushing	10	-	1,000
Pumping	1	-	1,000
Extrusion	1	-	100
Curtain coating	1	-	100
Levelling	0.01	-	0.1
Sagging	0.001	-	0.1
Sedimentation	0.000001	-	0.0001

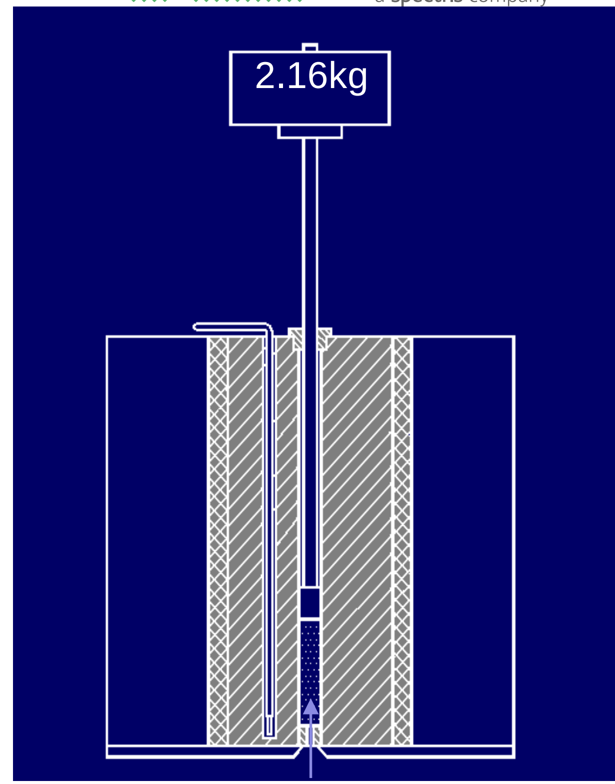
Faster processes, squeezing materials through smaller gaps

Measurable on a **Rosand** capillary rheometer

Measurable on a **Kinexus** rotational rheometer

MFI – Melt Flow Indexers

- Capillary rheometers are, in very simple terms, advanced MFI's
- A rheometer allows a far greater understanding of the materials' property



MFI die (2.095mm diameter)

MFI Shortcomings

- Uses a **weight** (pressure) to extrude the material
  - Industrial processes work in a rate (rather than stress) mode
  - The shear rate depends on the material properties, and is typically very low (lower than typical industrial processes)
  - Only a single stress used
- Results in arbitrary units of grams per 10 min
  - Not engineering units!
- Only able to get an indication of flow at a particular temperature
- A capillary rheometer has far greater sensitivity, control and test procedures

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1 Piston

Drives the sample through the barrel at a defined flow rate using high precision piston tips in order to give the desired shear rate. Wide dynamic speed range up to 1200 mm/min (error <0.1%) and up to 100 kN in force allowing high viscosity and high shear rate measurements.

2 Barrel

Temperature controlled sample reservoir available in a choice of sizes and materials depending on sample properties and application.

3 Electrical heaters

Barrel temperature is maintained using electrical heaters that are optimally positioned to give a uniform and stable temperature along the barrel. Temperature range is 5 - 500°C depending on instrument variant.

4 Temperature control

Temperature is monitored using multiple Platinum Resistance Thermometers (PRTs) which feed into a multi-zone PID algorithm for rapid and accurate temperature control. Set-up also allows automatic temperature calibration.

5 Pressure transducers

Measures the fluid pressure at the die entrance allowing the pressure drop along the die to be determined and the shear stress calculated (following correction for entrance effects). Available pressure transducers cover the range 500 – 30000 psi (error < 0.5%) facilitating accurate viscosity measurements for a variety of materials over a wide range of shear rates.

6 Dies

Flow inside the die can be considered equivalent to pipe flow (Poiseuille flow) where the shear stress is related to the pressure drop, die length and die diameter; the shear rate is related to volumetric flow rate and die diameter. Dies are made of Tungsten Carbide and are available in diameters ranging from 0.5 – 3 mm and with various lengths and entrance angles.

7 Dual bore barrel

Second barrel/die allows entrance pressure to be measured directly and simultaneously using a zero length die. This can be used to correct for entrance effects in the first barrel/die which uses a die of finite length. The entrance pressure can be used to estimate the extensional viscosity.

8 Die holder

Holds die securely within the barrel. Designed to withstand extreme loads and for easy interchange of dies.

9 Transducer mount

Allows accurate positioning of the transducer within the barrel facilitating accurate pressure measurements and easy removal for cleaning.

10 Piston tips

Interchangeable piston tips of different design and material are available depending on the application. These ensure an accurate seal to prevent back pressure leakage and optimize sample flow rate measurements, thus increasing measurement accuracy.

11 Rigid 'H' frame design

The 'H' frame design provides a vertical stiffness well in excess of that achievable with cantilever or 'C' frame designs. The frame is effectively rigid at loads at loads up to 250kN. The floor standing system also provides ample working space below the die assembly and room for optional accessories.

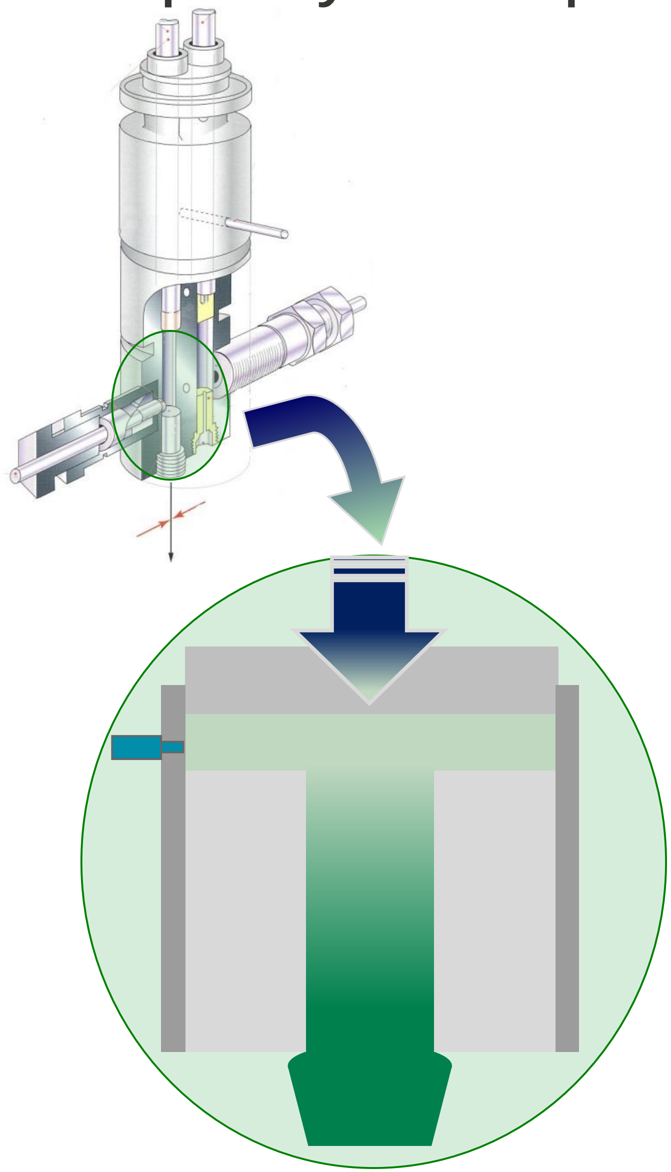
12 Optional accessories

Several accessories are available for particular applications or to enhance the testing capability of the base units.

These include

- Melt tension and melt strength apparatus
- Laser die swell measurement
- Slot die assembly
- PVT test option
- Die and melt cutters

Capillary Principles

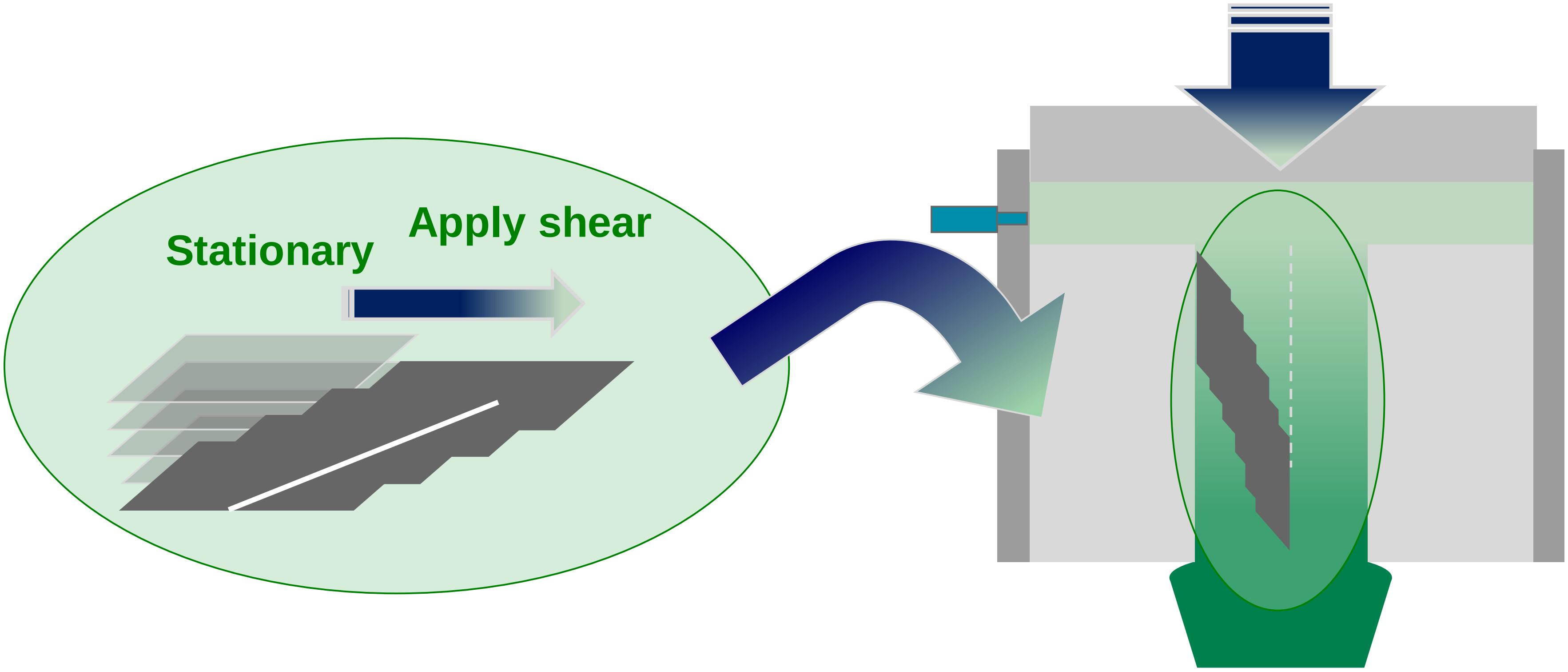


- For a given piston speed (= constant shear rate)
- The **higher the viscosity** the higher it's resistance to flow out of the barrel
- Therefore, a **higher pressure is recorded**
- Pressure is related to shear stress

$$Viscosity = \frac{\textit{Shear Stress}}{\textit{Shear Rate}}$$

Shears the sample through the die

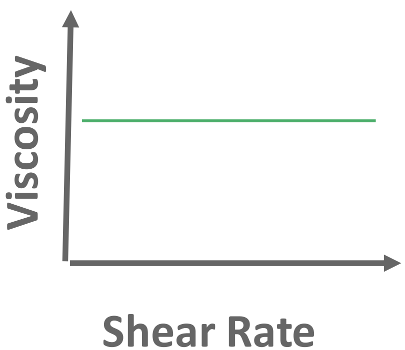
- A shear flow is typically presented as a sliding deck of cards
- This is, in simple terms, what occurs inside the die of a capillary rheometer



Flow Curves

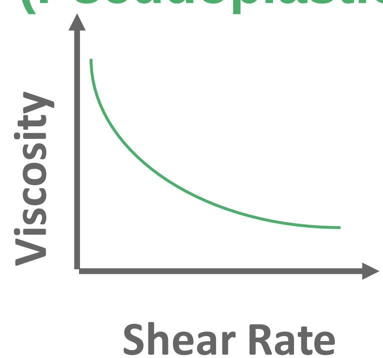
- Three general flow behaviours
  - Viscosity is a function of shear rate

Newtonian



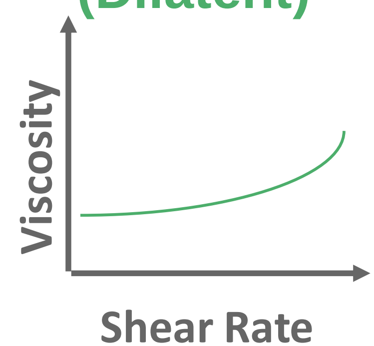
e.g. silicone oil, low concentration dispersions

Shear-Thinning (Pseudoplastic)



e.g. polymers, dispersions

Shear-Thickening (Dilatent)

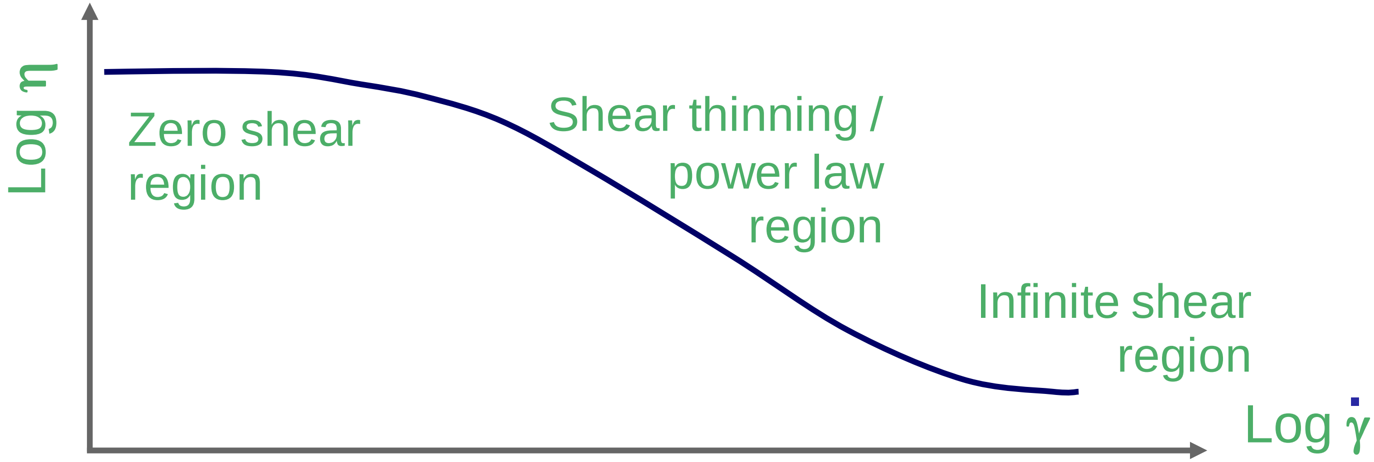


e.g. cornflour, high solid content TiO_2

› Most, real, samples are shear thinning with Newtonian regions

Viscosity Flow Curves

- By changing the **piston speed** we apply **different shear rates** to the sample, and plot the viscosity at each different shear rate

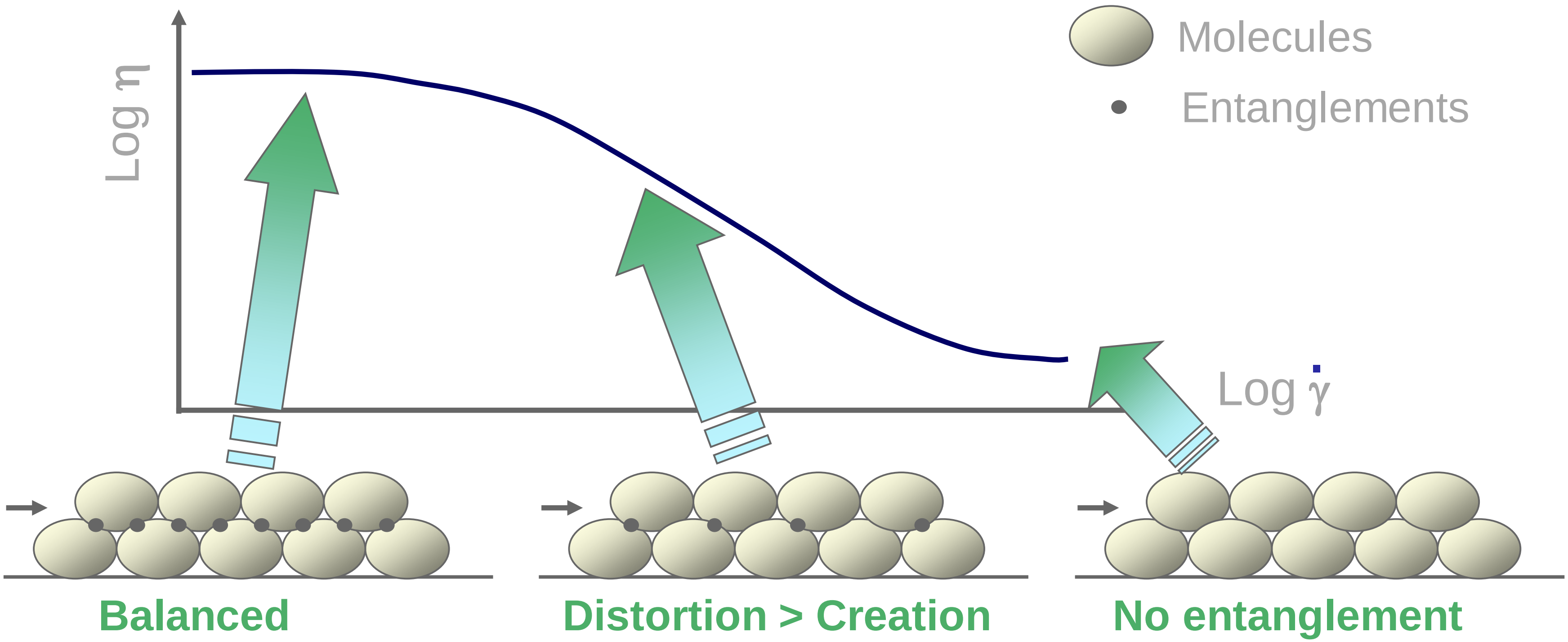


› Most samples, especially polymers will have the above profile

› In practice for polymers only the power law region is usually recorded

Shear Thinning

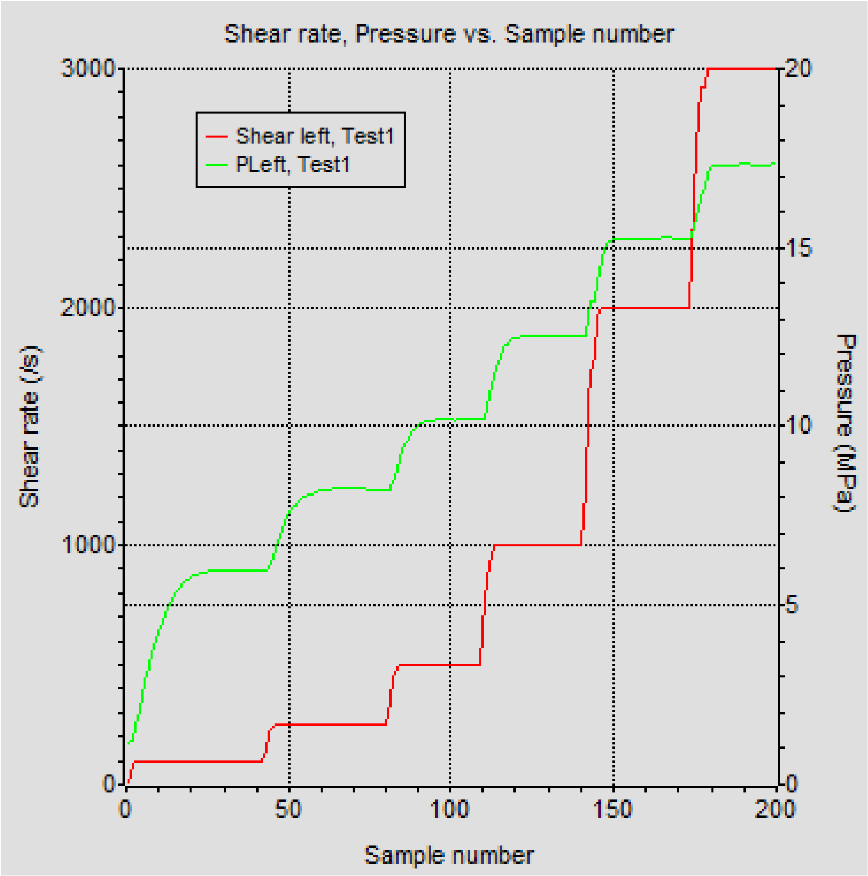
- Why the different regions?



› Entanglement resists flow. Viscosity is resistance to flow, therefore, more greater entanglement, higher viscosity.

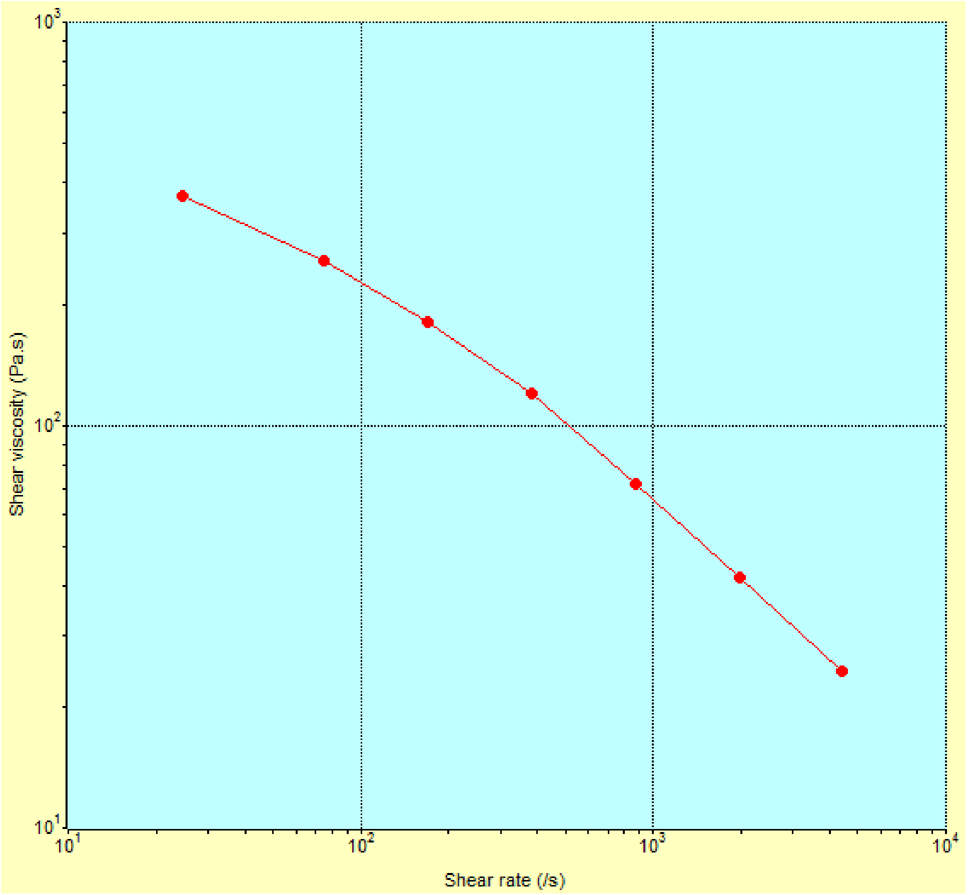
Typical Results 1

- To record a viscosity against shear rate curve we increase the shear rate in a **step** wise fashion
- The shear rate is held constant to record a **stable value** of pressure
- As the shear rate is increased, the **pressure increases**



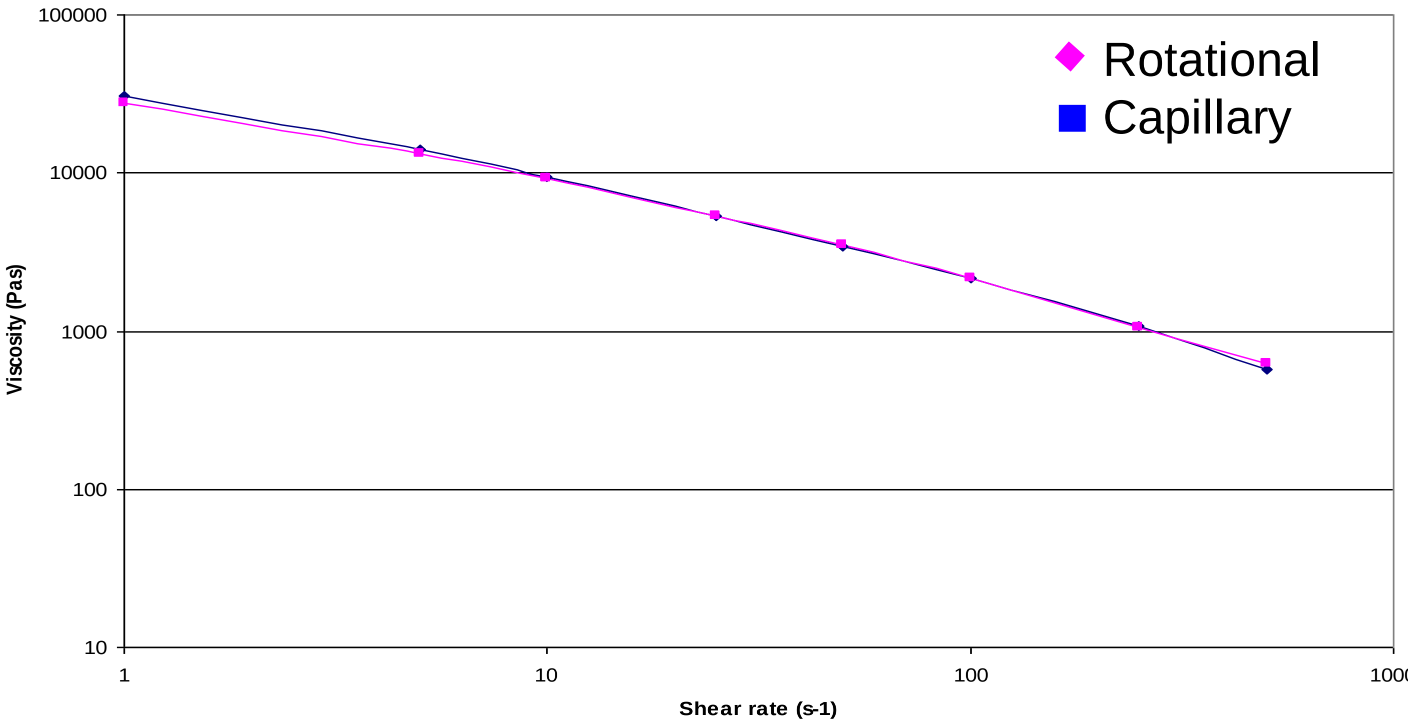
Typical Results 2

- Piston speed is converted to **shear rate**
- Pressure is used to calculate **stress**
- Typically interested in shear viscosity versus shear rate
- Plot both on a logarithmic scale
- However, shear viscosity is only one part of the rheology



Capillary vs. Rotational

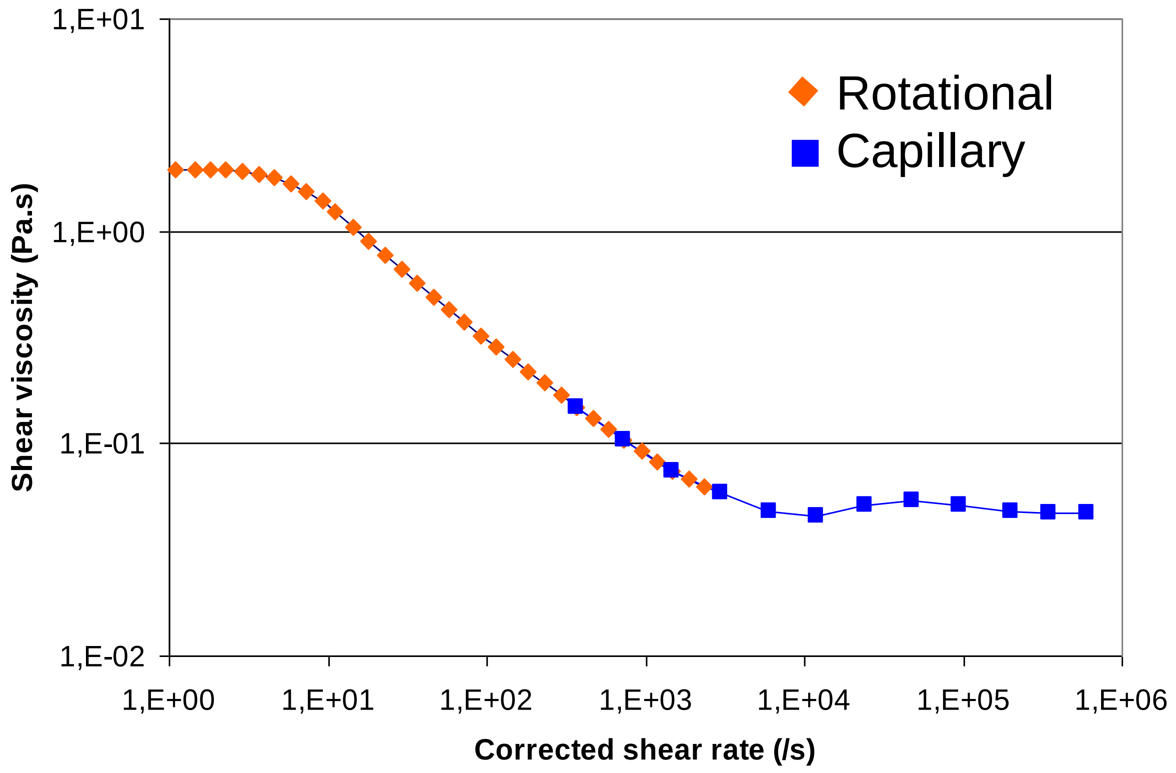
Polypropylene Viscosity



- Polypropylene measured at 190 ºC
- Same results on a capillary and rotational

Capillary vs. Rotational

Covers a wide range of shear rates



- The higher shear rate range of the Rosand rheometers can compliment the range of the Kinexus rotational rheometers

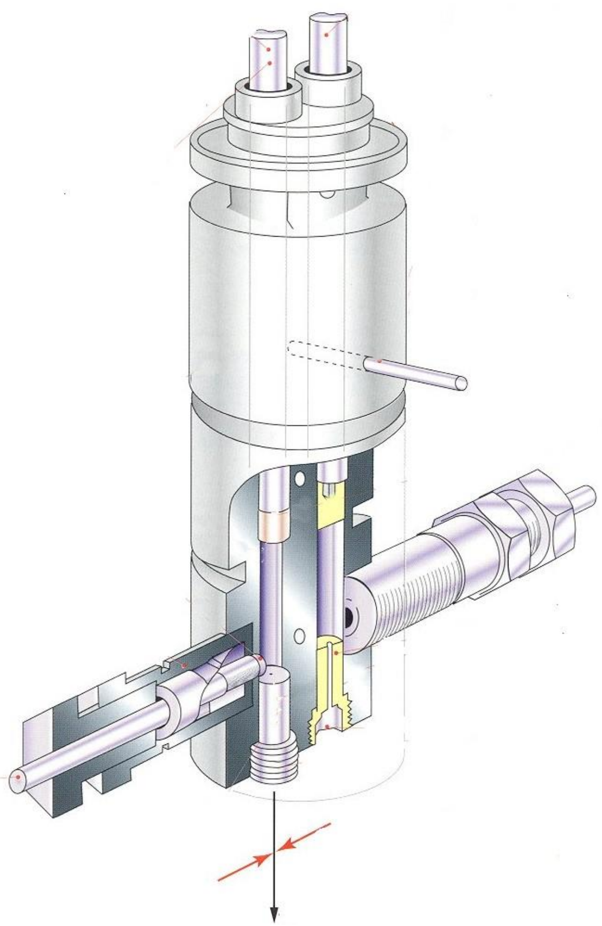
Summary

- Overview of how a **capillary rheometer** works
- Introduced the concept of **viscosity** as resistance to flow

Overview

- Introduces the **Bagley correction**
- Corrects capillary die data for **entrance effects**
- Needed to get **absolute viscosity** results

Twin Bore Design

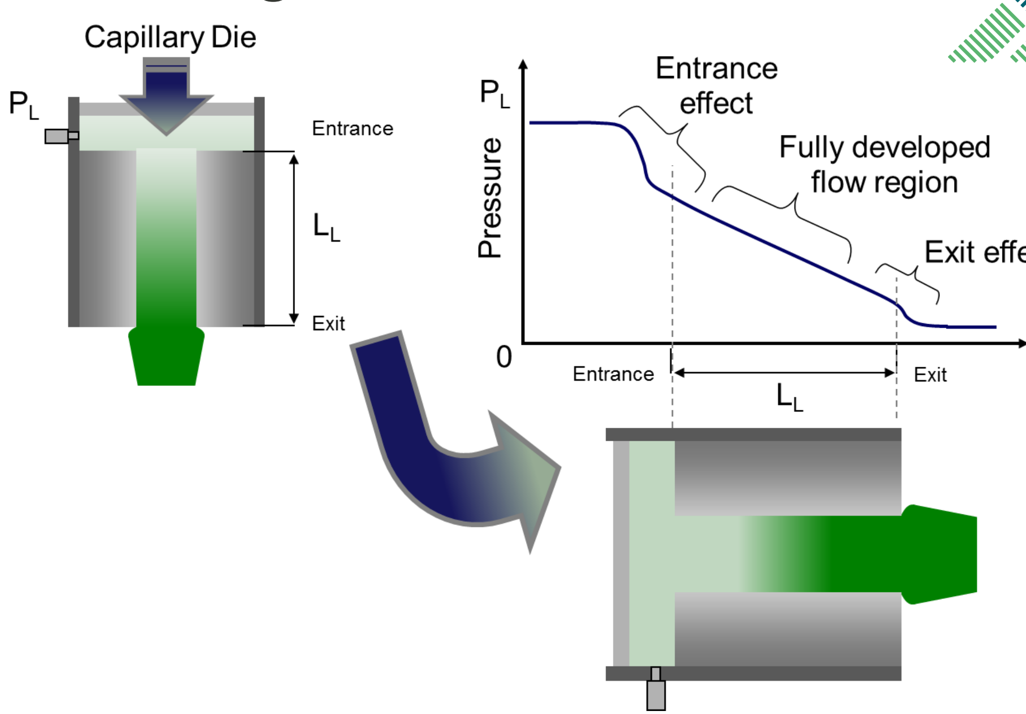


The left bore is used first, typically with the long, capillary die. The orifice die is always on the right for Bagley corrected experiments.

- The twin bore design allows flexible use of the rheometer:

1. **Single bore, uncorrected**
   - Simple shear viscosity measurements, uncorrected for entrance pressure
2. **Twin bore, Bagley corrected**
   - Most common test. Simultaneously uses a shear die and orifice die to measure shear (corrected for entrance pressure) and extensional viscosity
3. **Two materials, uncorrected**
   - Run two samples at the same time
4. **Extended shear rate, uncorrected**
   - Use two different dimension dies for a greater shear rate range

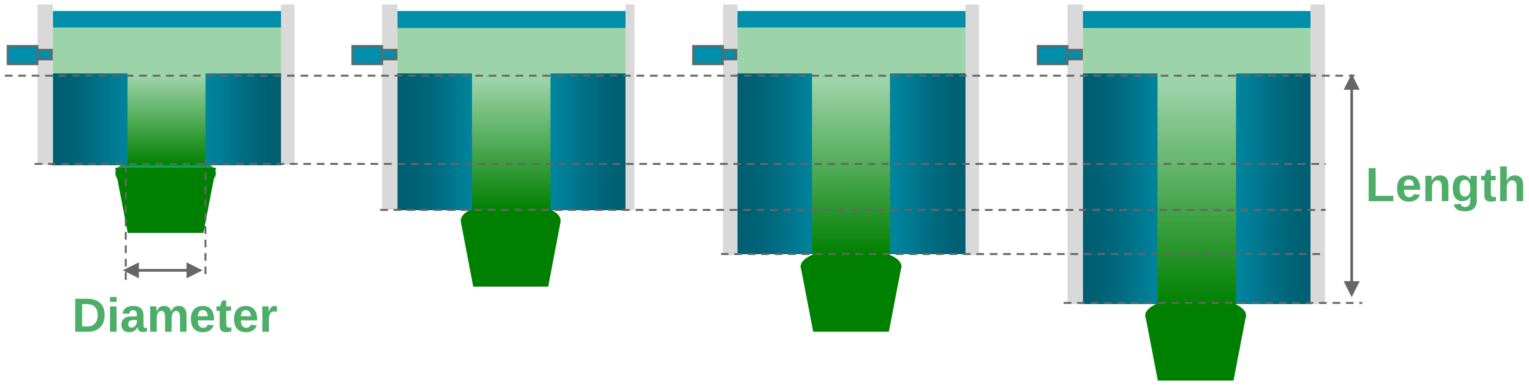
Pressure Changes in a Die



- The pressure in the long die is a resultant of the **entrance effect**, the **shear flow** and the **exit effect**
  - The material through the 1 mm diameter die needs to speed up to maintain the same flow rate as was in the 15 mm diameter barrel
  - This acceleration should be accounted for to obtain "true viscosity"

Historical Bagley (DIN 11443)

- Extrapolating the pressure back to a zero length die should give a zero pressure drop



› However, there is an **entrance pressure effect**

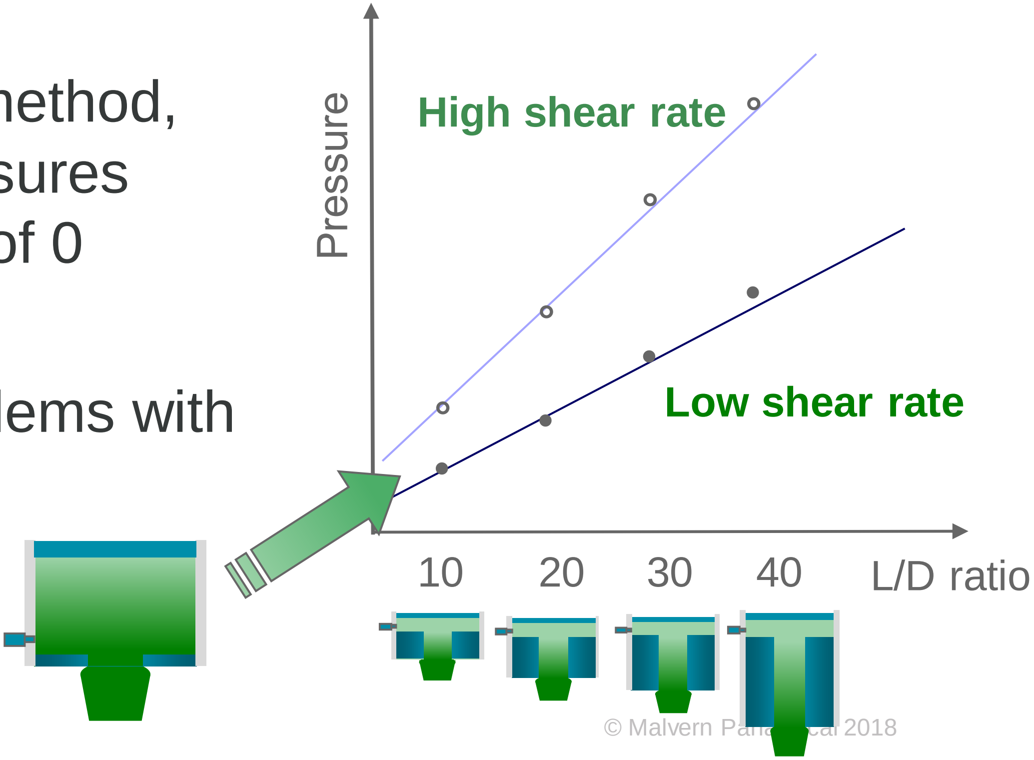
Historical Bagley Extrapolation

- Measure the pressure drop on a series of dies of decreasing length

- Linear extrapolation to a Length : Die (L/D) ratio of 0

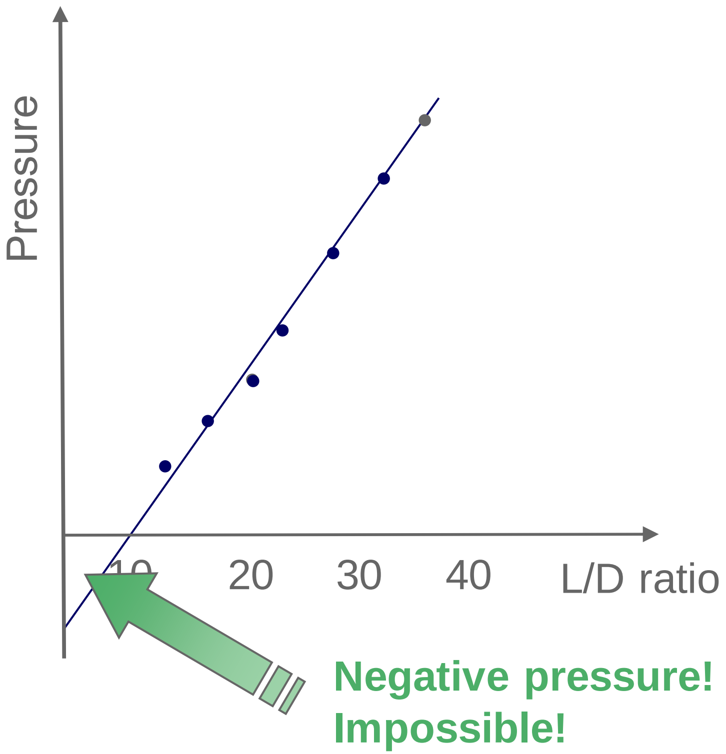
› The alternative method, **orifice die**, measures directly at a L/D of 0

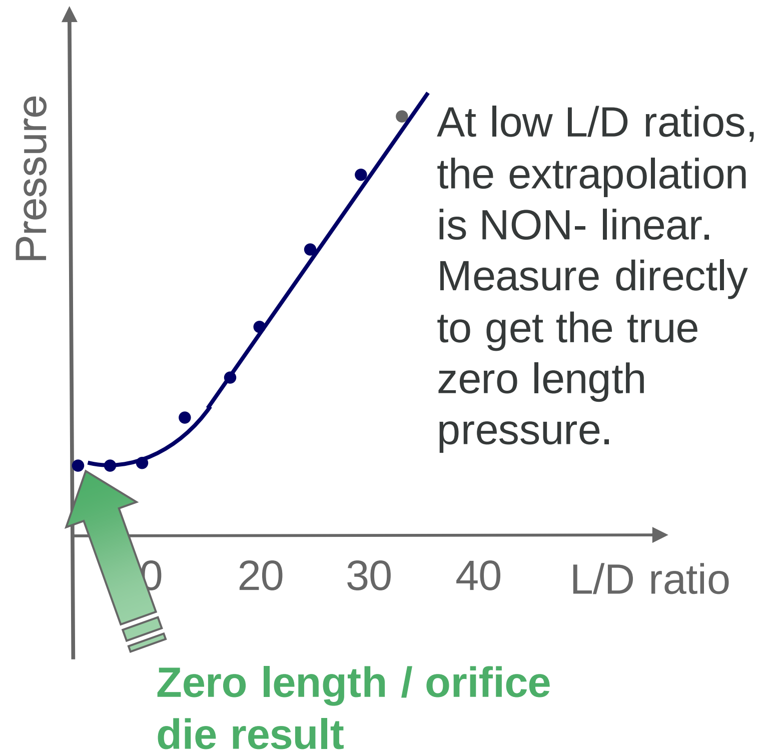
› This avoids problems with extrapolation



Extrapolation Problems & Alternative Methods

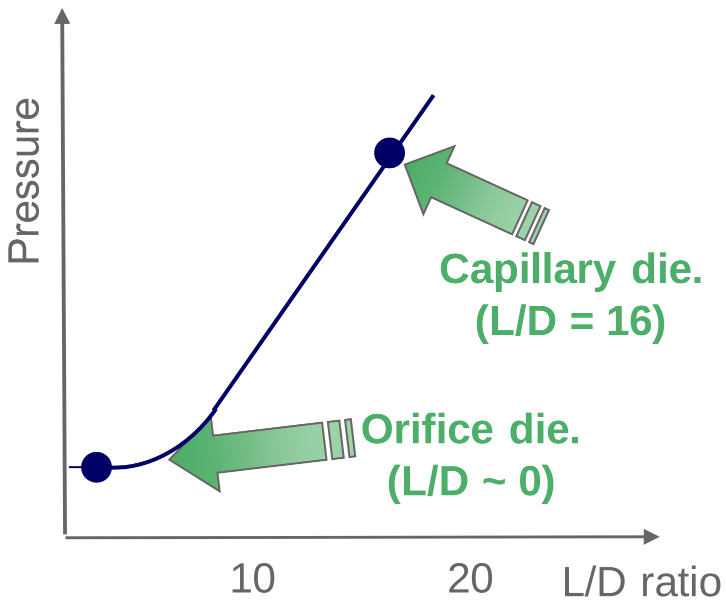
- Measure the pressure drop on a series of dies of decreasing length





Cogswell Orifice Die Method

- With an long capillary and orifice die on a twin bore instrument it is possible to get **direct measure of entrance pressure drop**



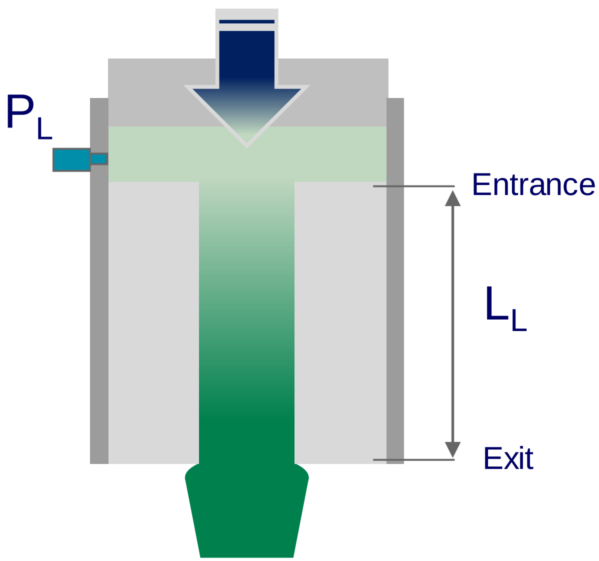
› No extrapolation needed

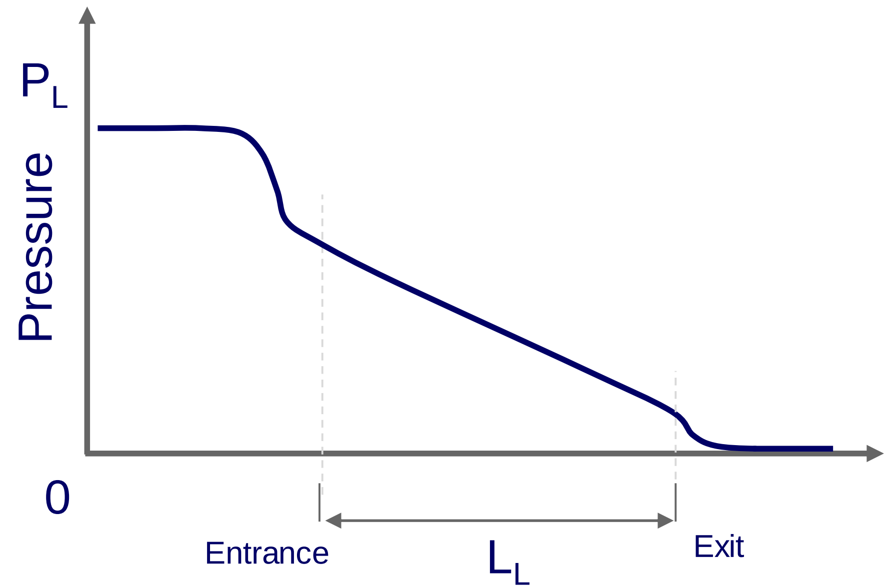
› This allows **Bagley correction** to get **true shear viscosity**

Pressure Effects

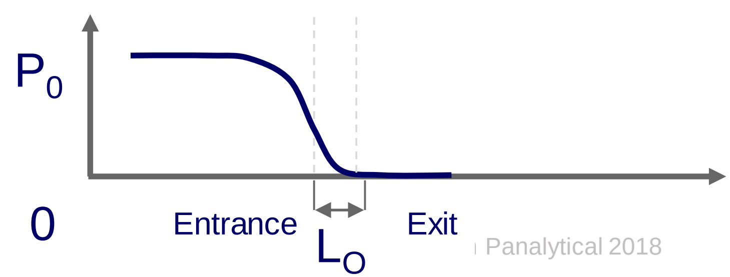
- The capillary die has a shear pressure drop (L_L) that the orifice dies does not

Capillary Die



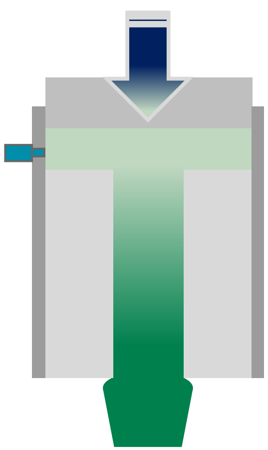


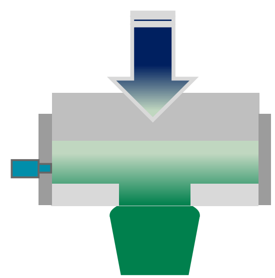
Orifice Die

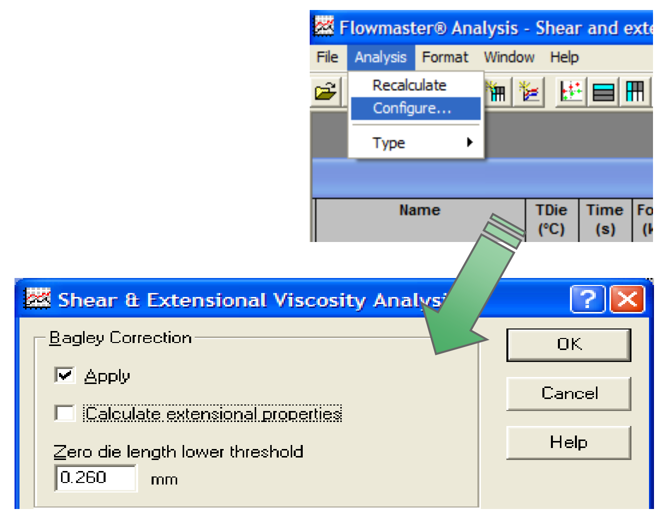


The Bagley Correction

- To account for the pressure drops, a long capillary die accompanied with a short orifice die is used
- An orifice die has a matching die diameter to the capillary die but possesses approximately zero length and will therefore only have entrance and exit effects
- This can be used to remove the entrance and exit effects to leave true shear viscosity
- Apply Bagley Correction and the Flowmaster software automatically subtracts this pressure variation to give you the true viscosity value







Shear & Extensional - **Entrance & Exit effects** = **TRUE Shear Viscosity**

Summary

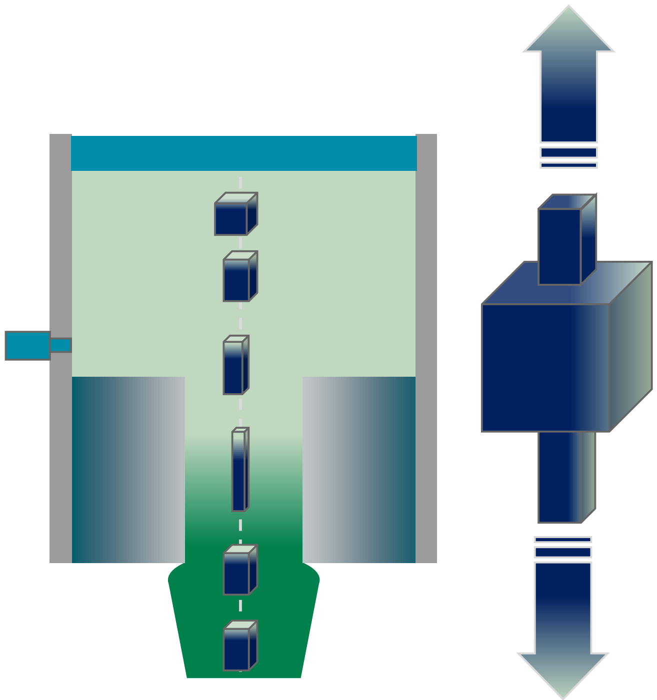
- To get true shear viscosity, the **entrance & exit effects** need to be corrected

- This can be calculated through the **Bagley correction**

Overview

- There is more to viscosity than just shear viscosity; there is also **extensional viscosity**
- This section introduces and defines extensional viscosity

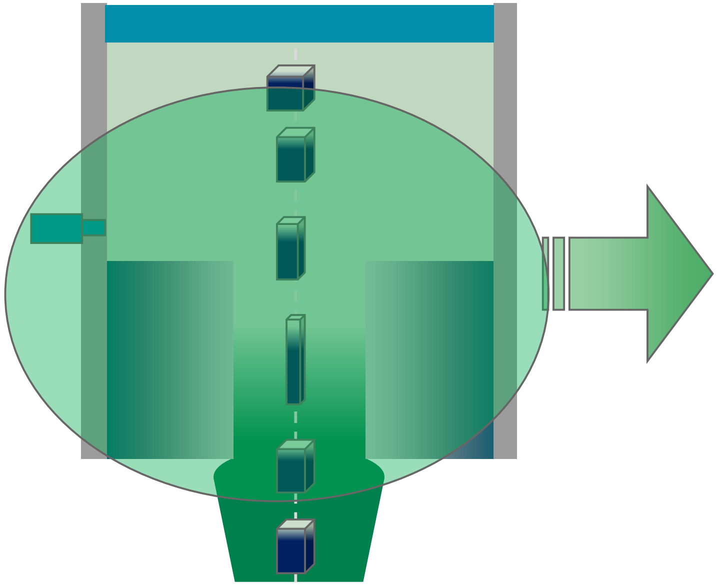
More Than Just Shear Viscosity



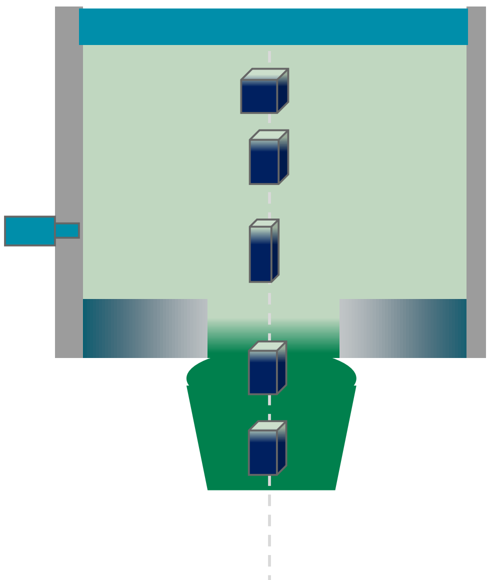
- The orifice die can provide more than just true viscosity values
- To conserve volumetric flow rate through the die (i.e. the same amount of material enters and exits the die), **the material must accelerate from the barrel through the die**
- On accelerating the material stretches – it becomes elongated, or **extends**
- This **resistance to stretch** is called **extensional viscosity**
- The orifice die can be used to calculate this extensional viscosity

Extensional in Action

- Possible to see the coloured polymer:
  1. Accelerate as it is approaching the die
  2. Stretch going into the die



Orifice (Zero Length) Die

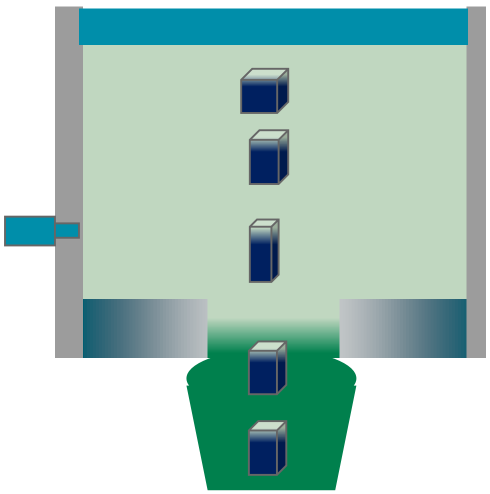


Rosand zero lengths dies have an effective length of 0, but an actual length of 0.25mm.

- A die with an effective zero length will therefore **only have entrance and exit effects**
- This means minimal shearing of the sample
- Therefore the zero length die can be used to:

1. Correct the long die to remove entrance effect to leave **true shear viscosity**
2. Calculate **extensional** (or elongational) viscosity

Cogswell Method



- Effectively, the **only resistance** to flow through a die with an effective zero length (orifice) will be **extensional**
- There is **minimal shearing** of the sample
- The **pressures from the die** with the **piston speed** can be used to calculate **extensional viscosity**

› With the Rosand twin bore design, the long die and orifice die can to run simultaneously to calculate **shear & extensional viscosity**

Viscosity Definition

Extensional Viscosity is resistance to stretch

$$\text{Extensional Viscosity}(\eta_E) = \frac{\text{Extensional Stress}}{\text{Extensional Rate}} = \frac{\tau_e}{\dot{\varepsilon}}$$

- The term **Tensile** or **Elongational** Viscosity is also used, along with **σ for stress**, and **$\dot{\gamma}$ for shear rate**
- It is the dominant effect for fibre spinning, film blowing, blow moulding
- Also affects: flow through dies, gates, runners, mixing elements, etc.

Trouton Ratio

- **Extensional viscosity** tends to be **greater** than the shear viscosity

- For **Newtonian** materials, there is a constant **ratio** between the shear and extensional viscosity:

$$\eta_E = 3\ \eta_s$$

- For polymer melts, this ratio is a lot higher. It can be 1,000 times as high

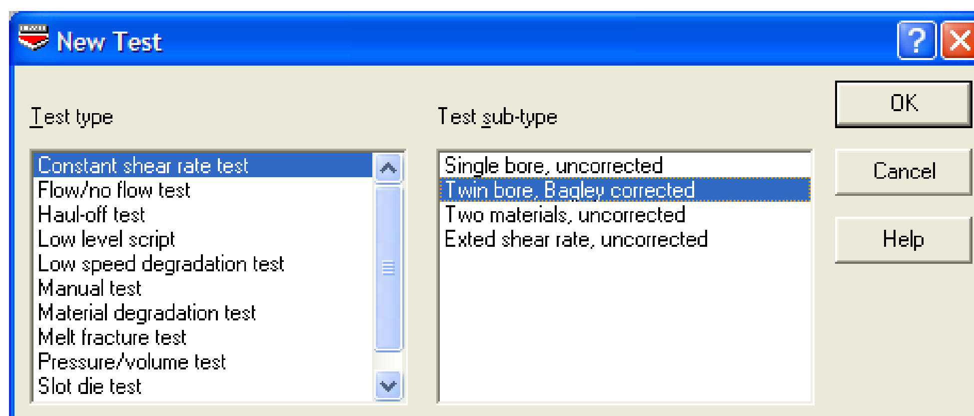
$$\eta_E > 3\ \eta_s$$

Calculating Shear & Extensional Viscosity

- There are a number of ways of calculating extensional viscosity. This training will concentrate on two:

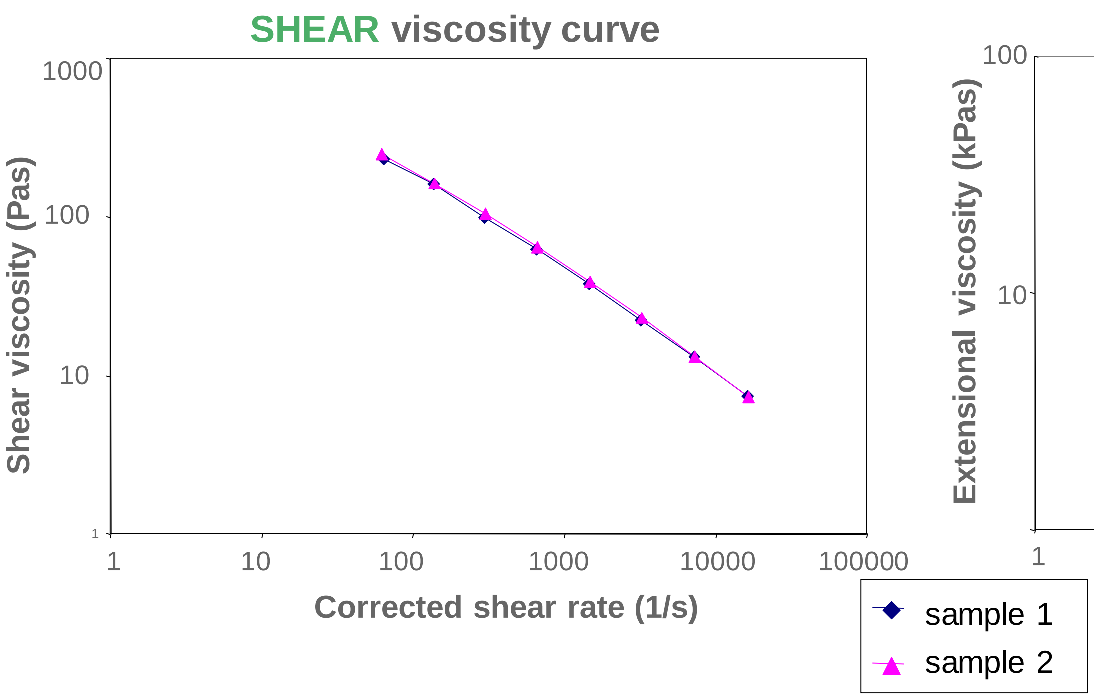
1. Historical Bagley correction
   - Use “Constant shear rate test / Two materials, uncorrected” test

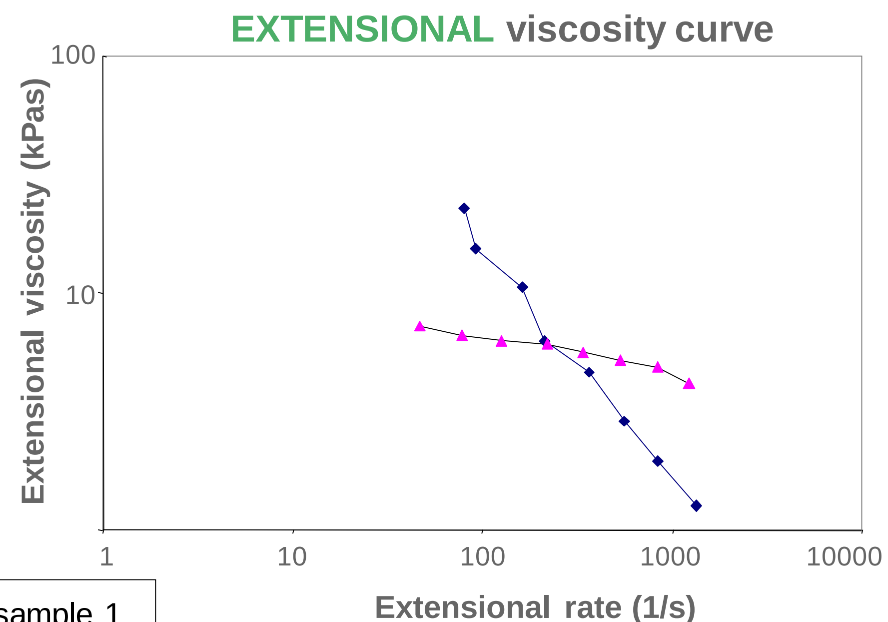
2. Cogswell method using an orifice die
   - Use “Constant shear rate test / Twin bore, Bagley corrected” test



Typical Results

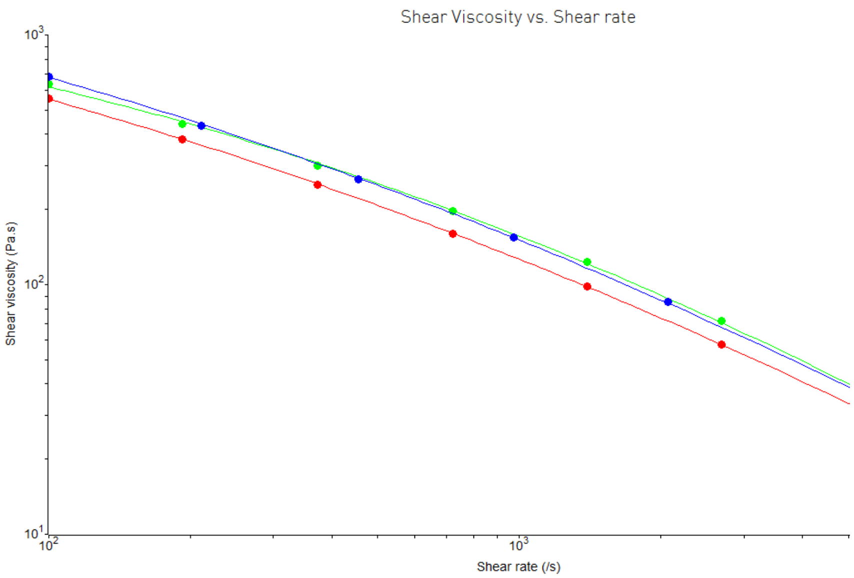
- Extensional viscosity introduces another material property
- Shear viscosity can be the same when comparing two different samples, however, **extensional viscosity can be different.** (Note: **kilo**Pa.s)

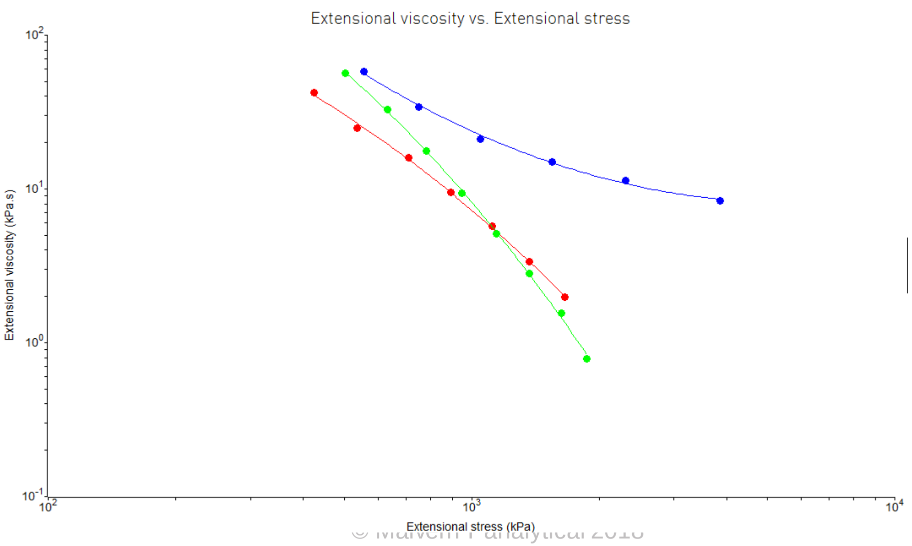




PVC testing – Shear vs. extensional

- Although the three different samples exhibit **similarities** between the **shear viscosities**, the **extensional** properties show significant **differences**





Summary

- Viscosity is more than just **shear viscosity**
- Introduced the term **extensional viscosity**
- Simply put, the **resistance to stretching**