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From lab to production,
providing a window into the process

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Webinar II: Applications for Capillary Rheometers

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Instruments Discussed in This Webinar

- LMI5000 Series
  - Controlled Stress Capillary Rheometer
- LCR7000 Series
  - Controlled Strain Capillary Rheometer

LMI5000 Series Melt Flow Rate Test

- ASTM D1238

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LCR7000 Series Controlled Rate Capillary Rheometer

- ASTM D3835

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Controlled Stress versus Controlled Rate Capillaries

Item	LMI (Stress)	LCR (Rate)
Barrel Dia.	9.55 mm	9.55 mm
Orifice Dia.	2.095 mm	0.5 to 3 mm
Orifice L/D	3.82	0 to ~60
Weights	0.1 to 20 kg	N/A
Rate	N/A	0.03 to 650 mm/min
Shear Rate Range	1 to 500 sec^{-1}	1 to 30,000 sec^{-1}
Main Data	Grams/10 minutes	Apparent Viscosity vs. Shear Rate
Other Data	Cm^3 /10 min	True Viscosity Die Swell Extensional Viscosity
Other Tests	Ratio Test (2 wts.)	Stability Test

Q. What is a capillary rheometer to a customer?

Instrumentation that measures the rheological or flow properties of polymers.

Reasons to Test Rheology of Polymers

- Polymers are complex
- Polymer properties vary significantly and there is a need to control their structure and / or properties
- Rheology measurements are a quick and inexpensive method to control processes

Customers for Polymer Testing with Capillary Rheometers

- Polymer Producers
- Formulators
- Re-Cyclers
- Manufacturers

Expectations of Customers that Produce Polymers

- A specific grade of polymers will have a consistent viscosity
- Polymers products will be produced as quickly as possible

Expectations of Customers that Process Polymers

- Products will be made with a good finish
  - No Degradation
  - No porosity
  - No rough finish
- Processing will occur at the fastest speed possible without producing scrap

Reasons to Test Thermoplastic Polymers in the Melt Phase

- Polymers often processed in melt phase
- Determine rheological behavior of materials under processing conditions.
- Melt conditions allow the characterization of good and bad materials.

Ideal Requirements for Testing Rheological Properties of Polymer Melts

- Measure flow properties of polymers at process temperatures
- Determine the effect of flow speed on the polymer flow properties
- If possible, measure flow properties at the same speed as the process

Reasons that a Capillary Rheometer is a Good Tool for Polymers

- Holds temperature within required range
- Measures change in properties with change in flow speed
- Can cover flow speeds used in polymer processing

Common Thermoplastics in Use Today

- Commodity thermoplastics
  1. Polyethylene (PE, LDPE, LLDPE, HDPE)
  2. Polypropylene (PP)
  3. Polyvinylchloride (PVC)
  4. Polystyrene (PS, TPS, IPS, HIPS)
- Engineering thermoplastics
  1. Nylons or polyamides
  2. Acetals
  3. Polycarbonate (PC)
  4. Polyesters (PET)
- Thermoplastic elastomers or rubbers
  1. TPEs
  2. TPRs
- Blends or alloys

Plastics are Formulated with Additives

- Lubricants
- Antistatic additives
- Nucleating agents
- Pigments
- Fillers (Cost?)
- Reinforcement (Strength?)
- Impact Resistance (Rubber?)
- Anti-oxidants / Anti-UV
- Reclaim
- Degradant

These materials can affect flow properties.

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Applications for the LMI5000 Series

Range of Samples

- Pellets
- Powders

Material must be melted in order to be tested on any capillary rheometer.

Melt Flow Rate Test

- Grams/10 minutes is a relative measure of viscosity
  - Higher value indicates lower viscosity
- Inexpensive method to measure viscosity
- Rapid test
- Well established in industry
- Typically produces a single value at one set of conditions

MFR Sensitive to:

- Viscosity of polymer melt
- Process aids & Lubricants
- Molecular weight
- Molecular weight distribution
- Degradation
- Moisture in material
- Crosslinking agents

Frequency of MFI Test

- 3 Tests per:
  - Tanker
  - Pallet
  - Bag

Characterize Polymers

- High Viscosity Polymers (low MFR) – Products usually have superior impact resistance
- Low Viscosity Polymers (high MFR) – Easier processing especially when thin areas are in the product

Common Use for MFR

- Mold does not fill or part is not well formed
  - Increase MFR with additives
  - Find material with greater MFR
  - Increase temperature

When MFR Test Fails to Detect Problems

- Identical Test Results on Two Batches but different Performance in Manufacturing
  - Run Ratio Test (two different weights / stresses)
  - Use a controlled rate Capillary Rheometer (LCR Series)

Applications for the LCR7000 Series

LCR Measures Flow Properties

- Apparent or True Viscosity
- Dispersion of Additives
    - Check Repeatability of Viscosity
- Die Swell
- Melt Fracture at Critical Shear Rate
- Extensional Viscosity

Range of Samples

- Pellets
- Powders
- Elastomers cut into thin slices

Material must be melted in order to be tested on a capillary rheometer.

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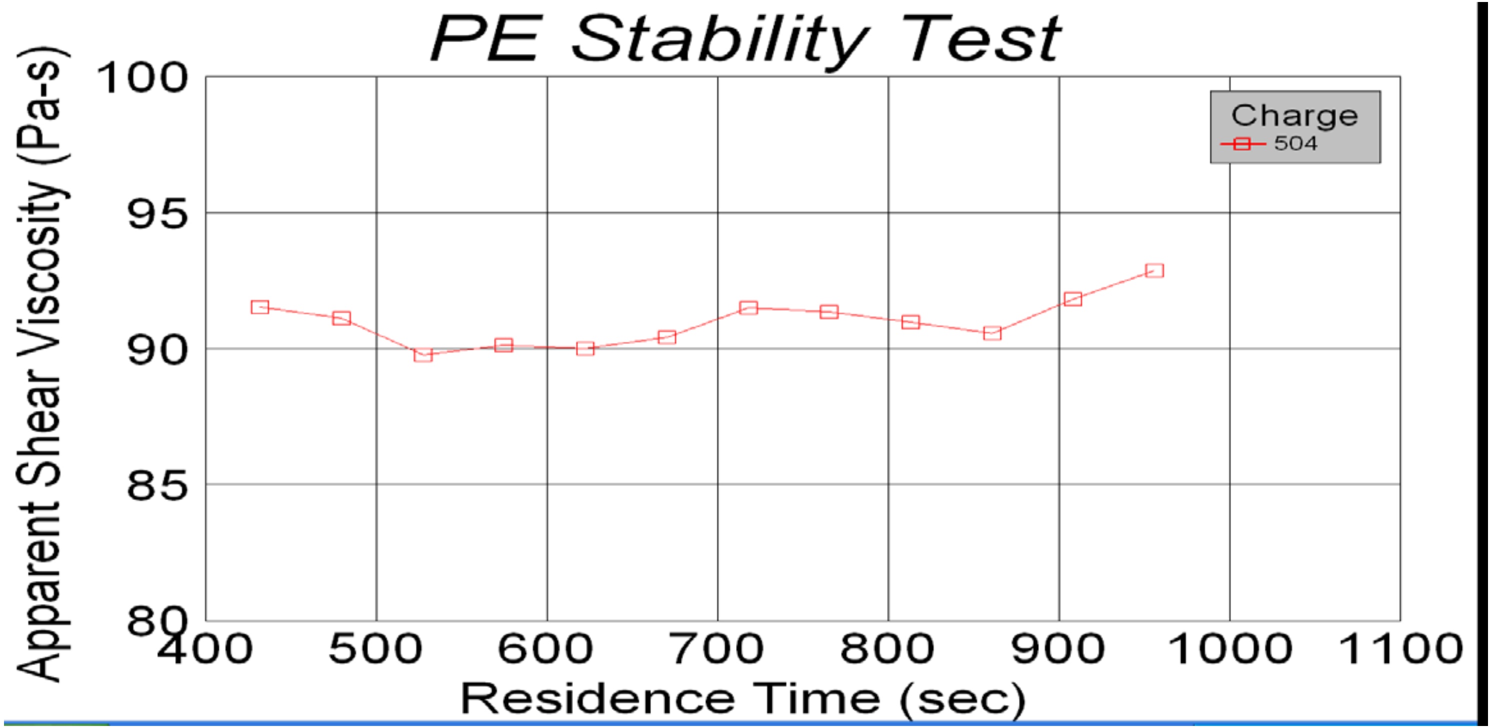
Viscosity Tests

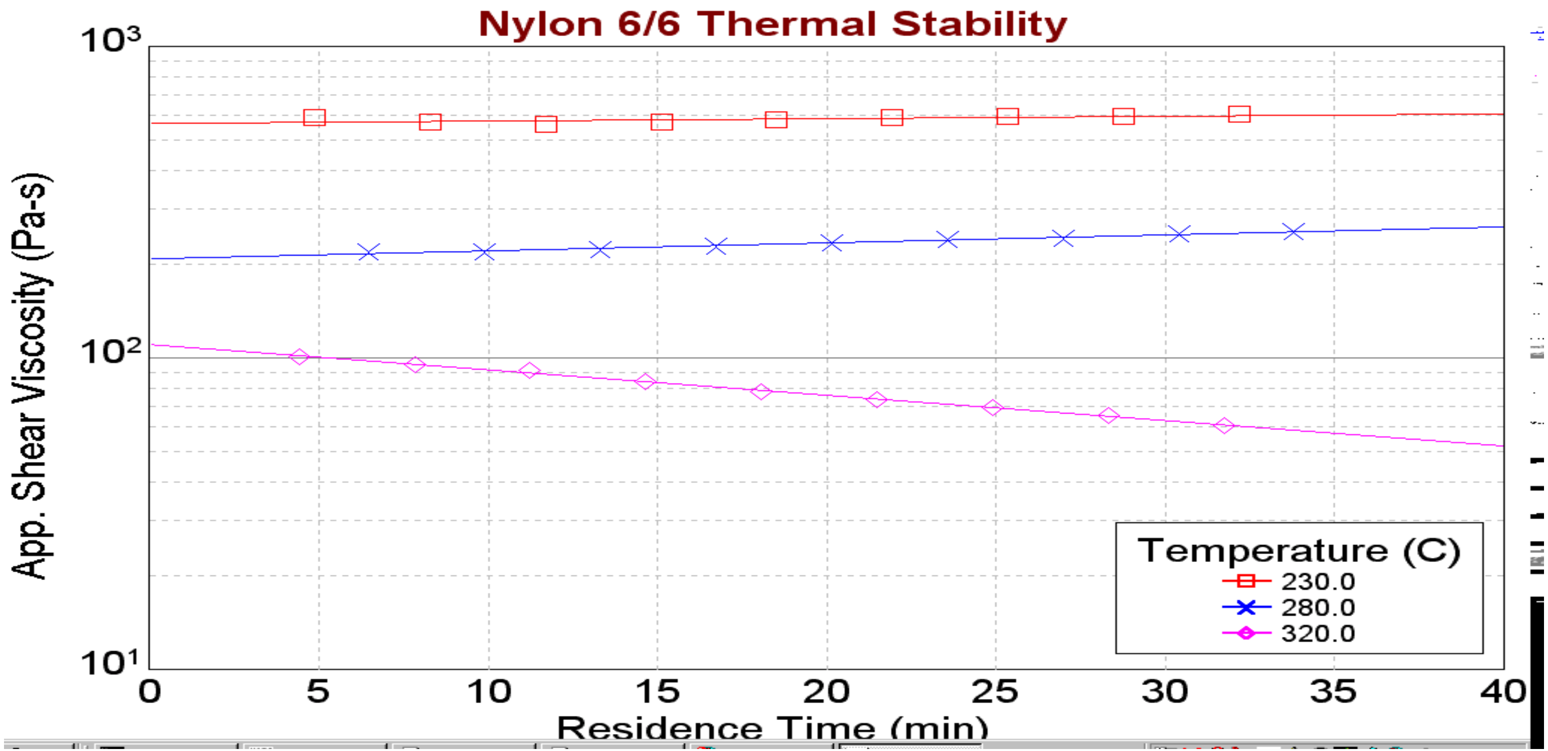
- Stability Test
  - Stability of polymer at processing temperature
- Shear Rate Sweep
  - Behavior of polymers at different shear rates or processing speeds

LCR7000 Series Stability Tests

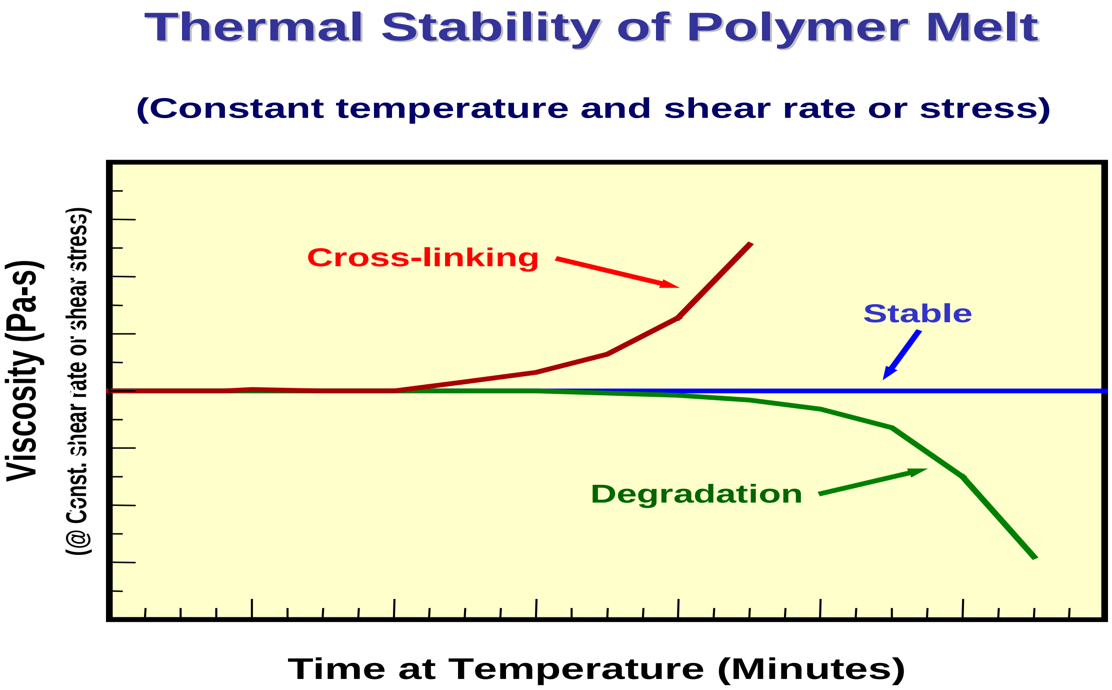
Stable Material on the LCR7000 Series



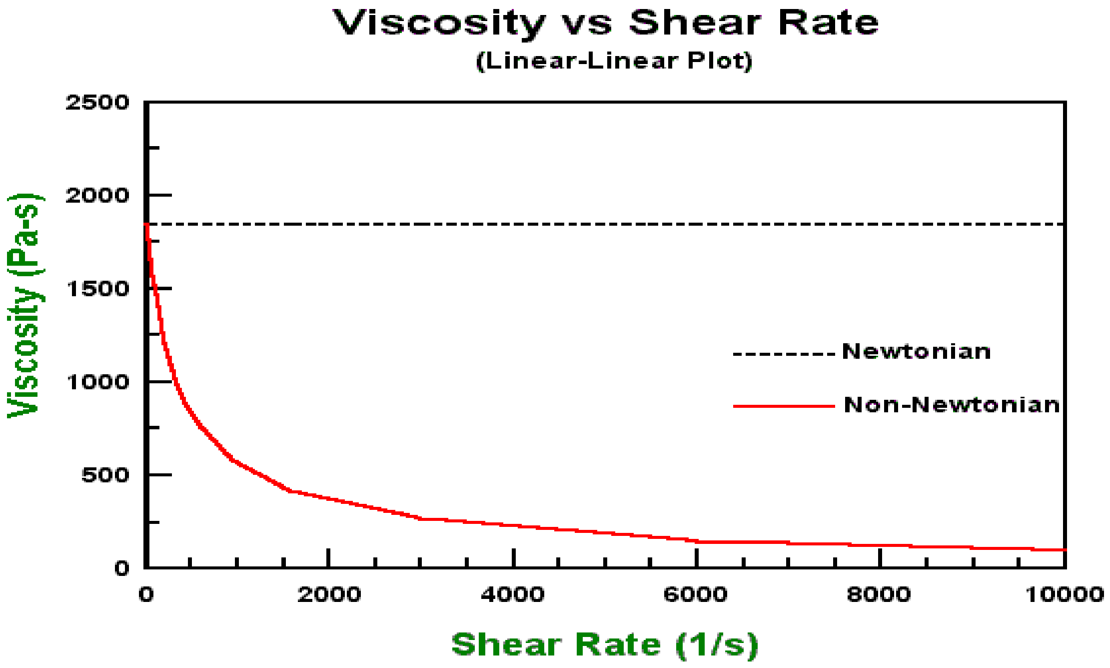
Diameter: 0.762 mm L/D: 40/1

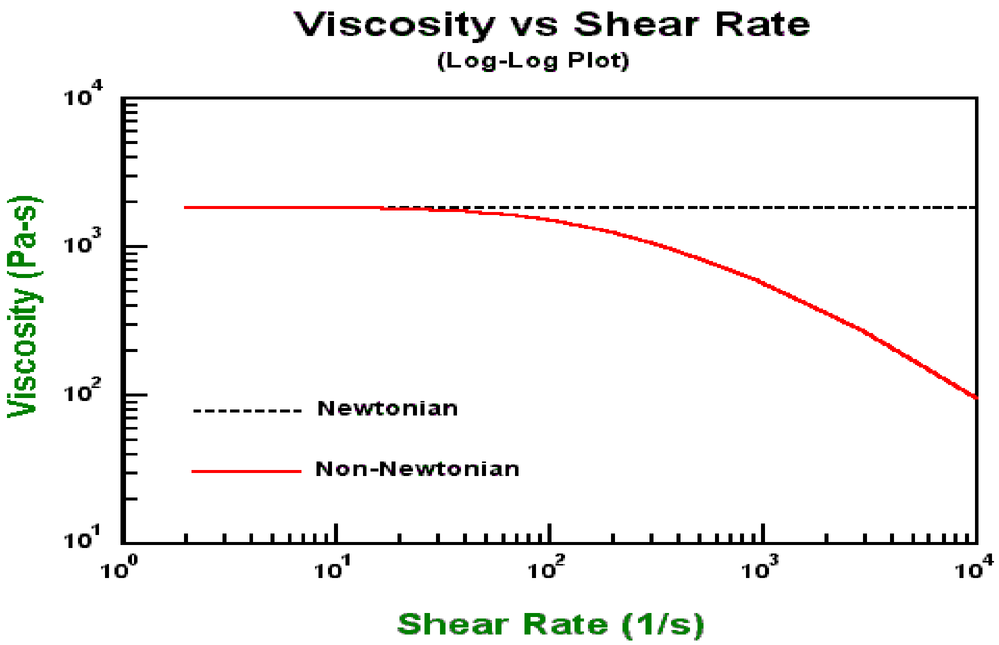


Other Possible Curve Shapes During a Stability Test on the LCR7000 Series



LCR7000 Series Shear Rate Sweeps


Viscosity vs Shear Rate
(Linear-Linear Plot)
2500
2000
1500
1000
500
0
Viscosity (Pa-s)
0
2000
4000
6000
8000
10000
Shear Rate (1/s)
Newtonian
Non-Newtonian


Viscosity vs Shear Rate
(Log-Log Plot)
Viscosity (Pa-s)
10^4
10^3
10^2
10^1
Newtonian
Non-Newtonian
10^0
10^1
10^2
10^3
10^4
Shear Rate (1/s)

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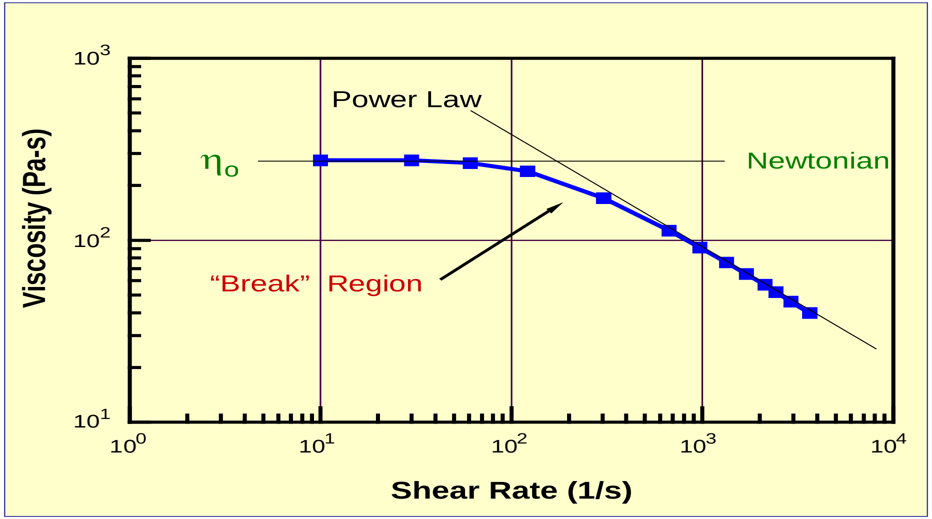
The Viscosity Curve



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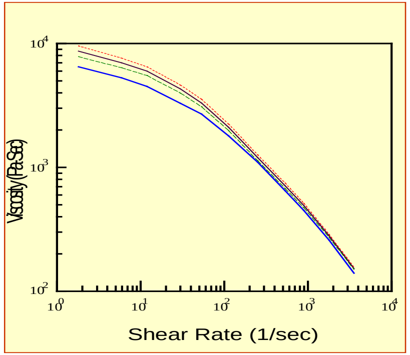
Effect of the Change in Molecular Structure on Melt Viscosity

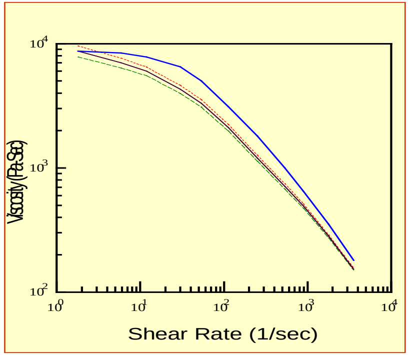
The Rheology "Tube"

Simulated

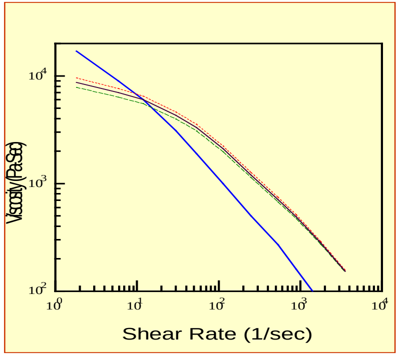
Molecular Weight



Molecular Weight Distribution



Branching



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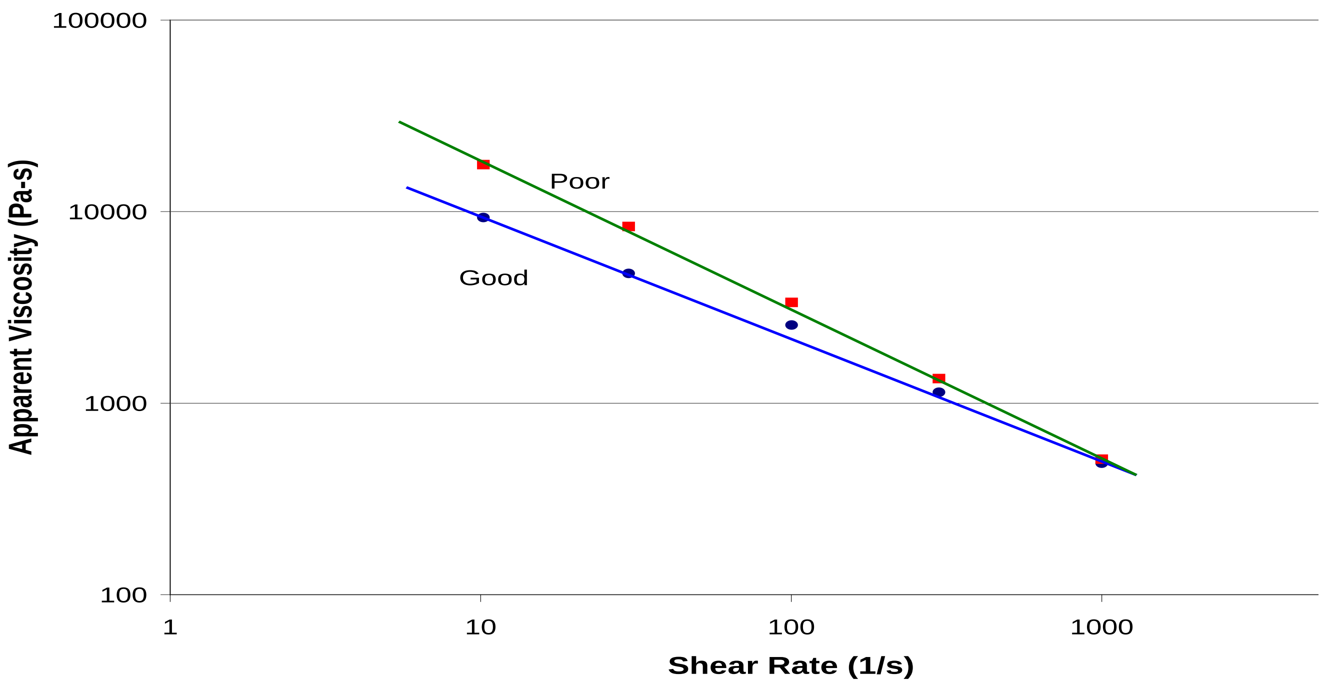
Some Materials Show a "Power Law" or Linear Relationship Between Log(Viscosity) and Log(Shear Rate)



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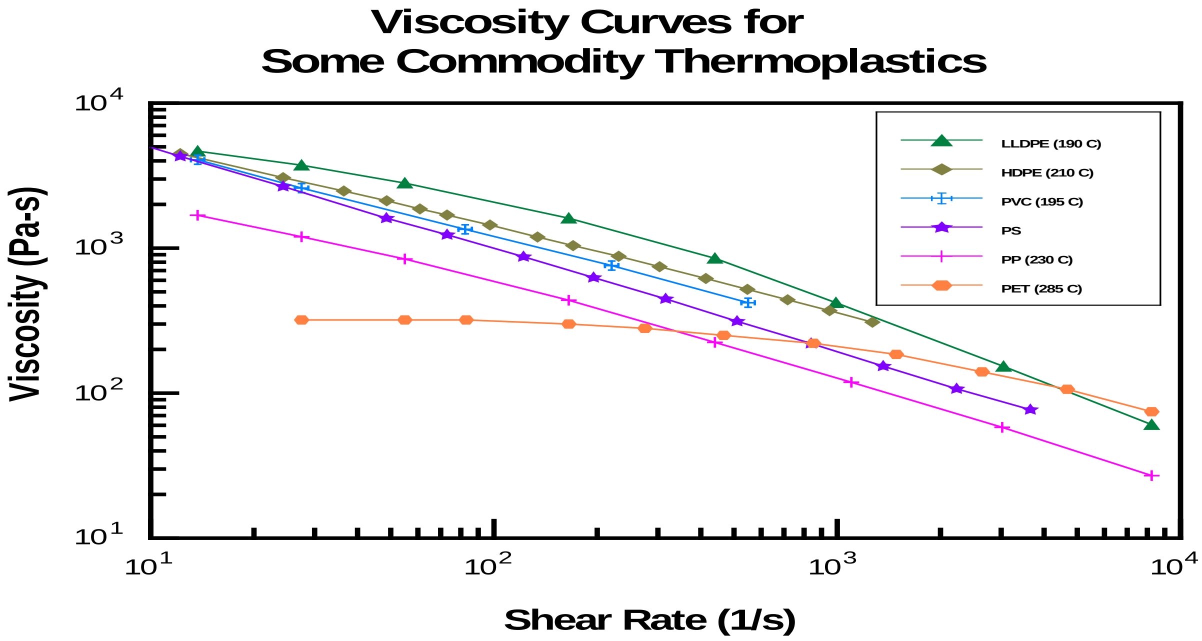
Plot Also Shows Need for Multi-Shear Rate Tests



Viscosity Curves for
Some Commodity Thermoplastics
Viscosity (Pa-s)
Shear Rate (1/s)
LLDPE (190 C)
HDPE (210 C)
PVC (195 C)
PS
PP (230 C)
PET (285 C)

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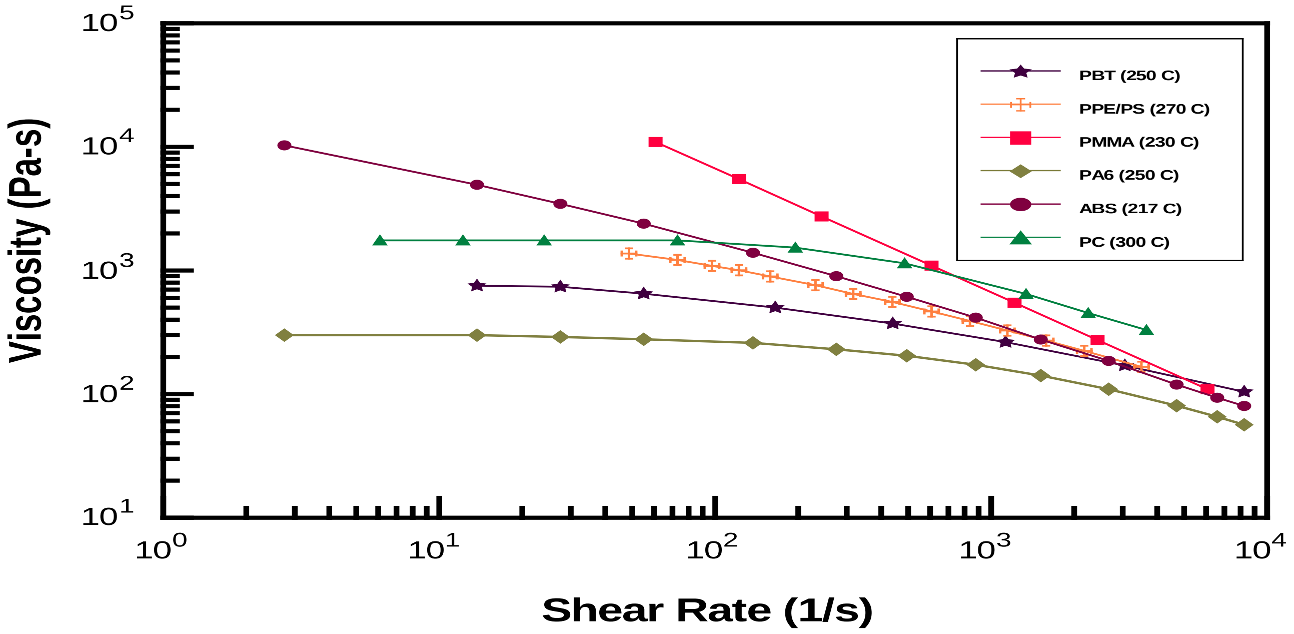
Viscosity Curves for Some Engineering Thermoplastics



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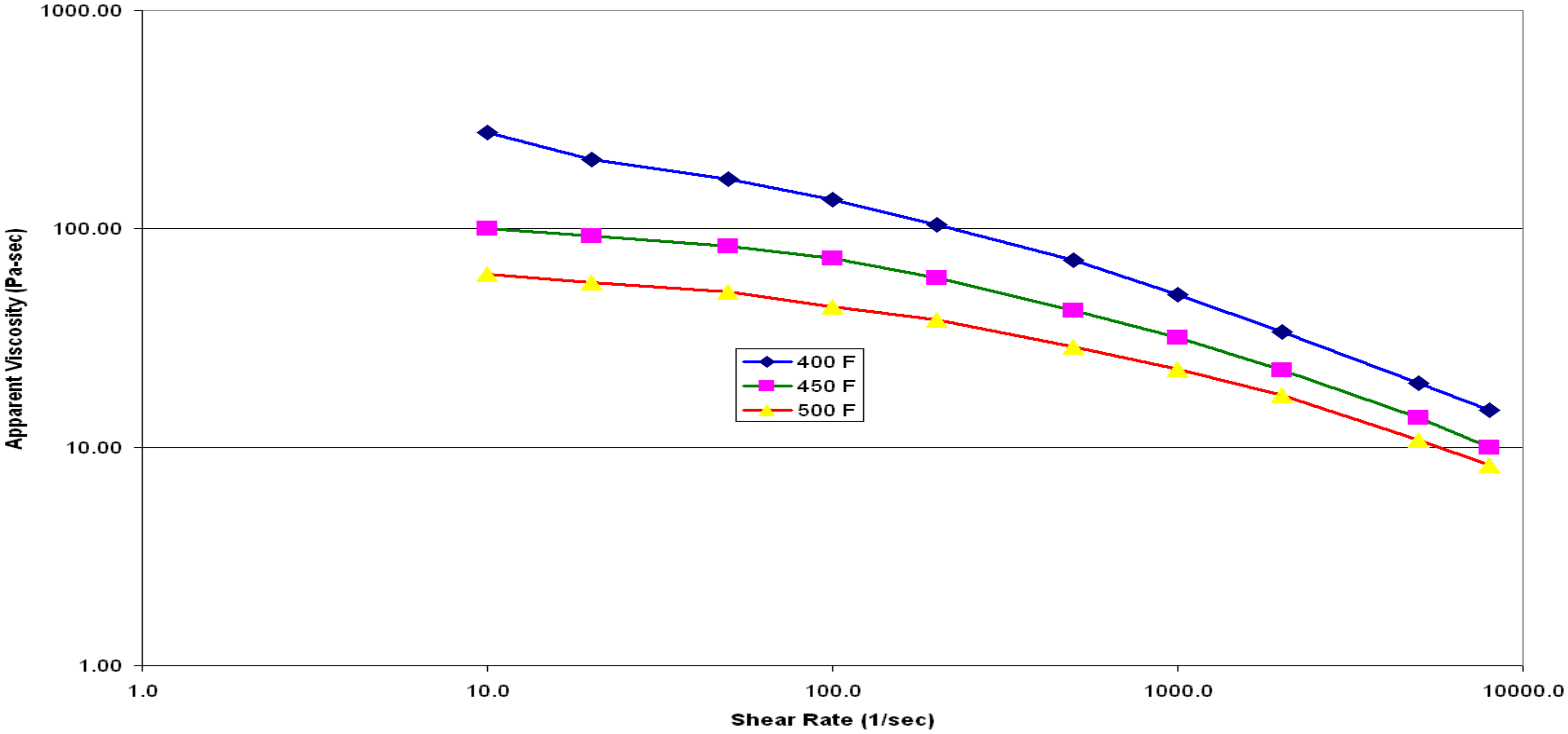
Effect of Temperature on Viscosity



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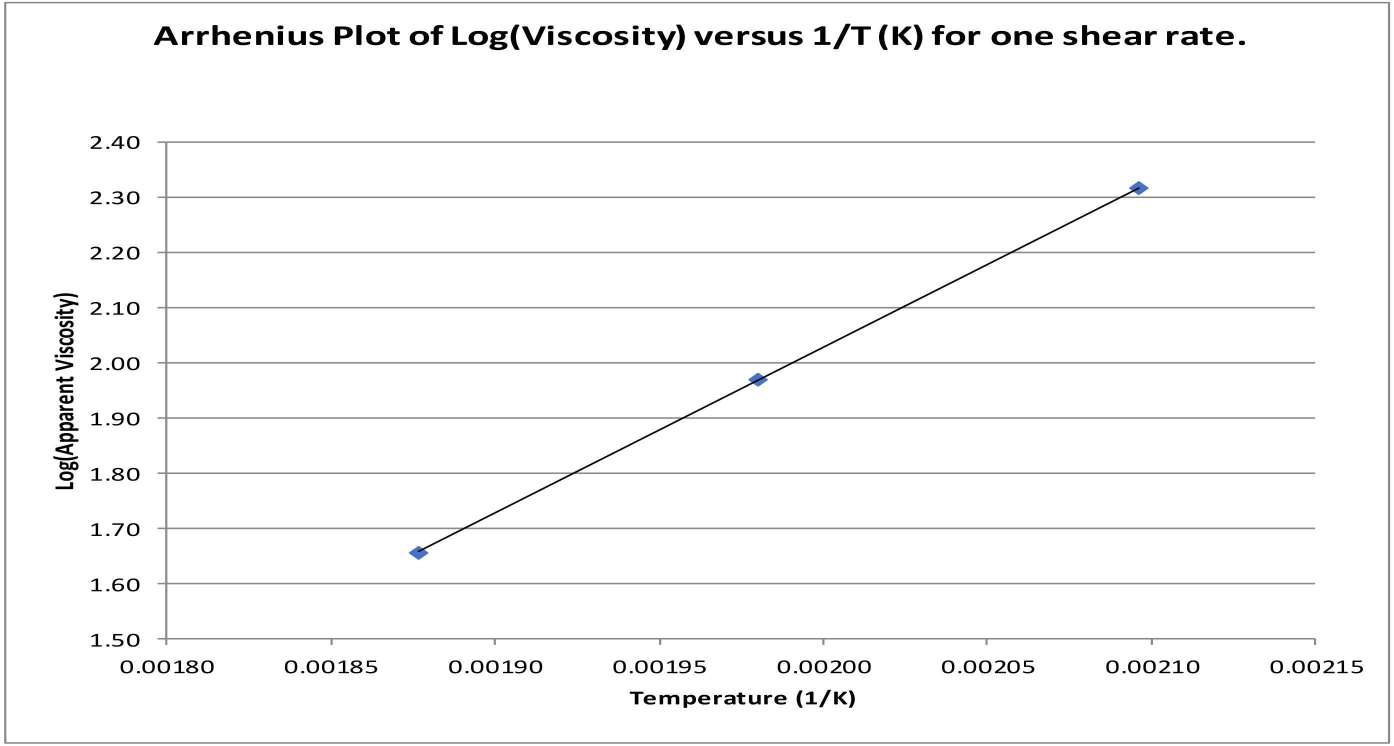
Use Arrhenius Plot to Predict Viscosity at Other Temperatures



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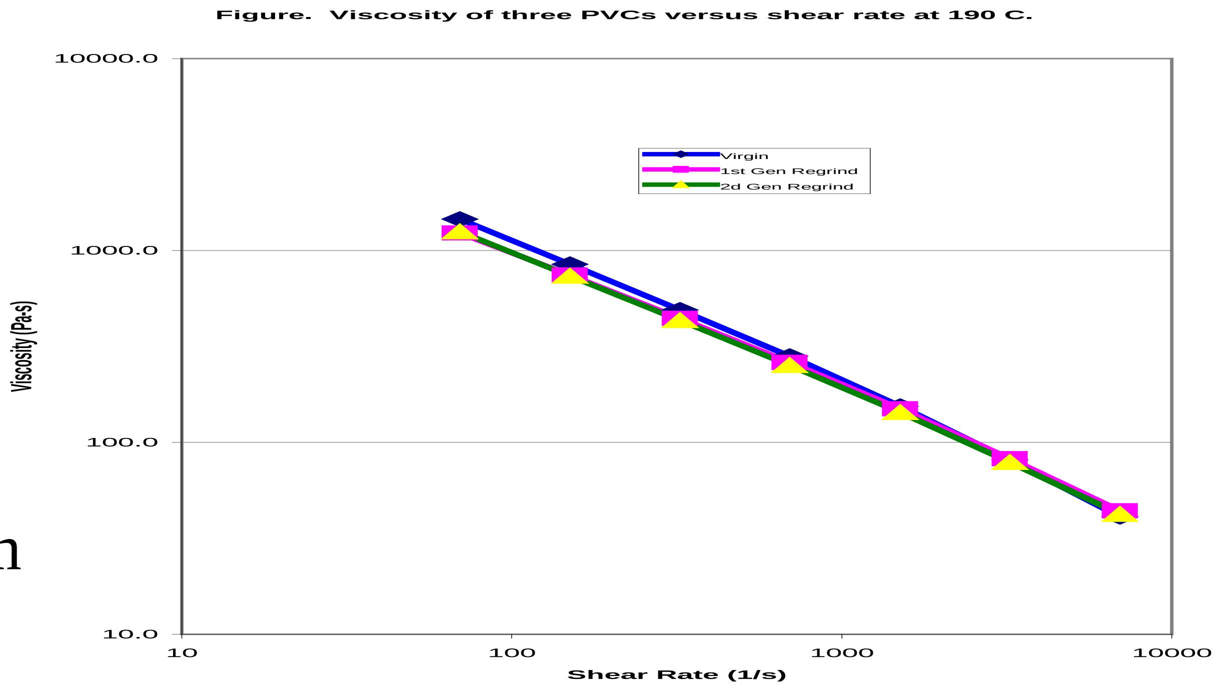
High Viscosity Materials Such as PVC are easier to test with the LCR



Diameter: 1.524 mm
L/D: 5/1

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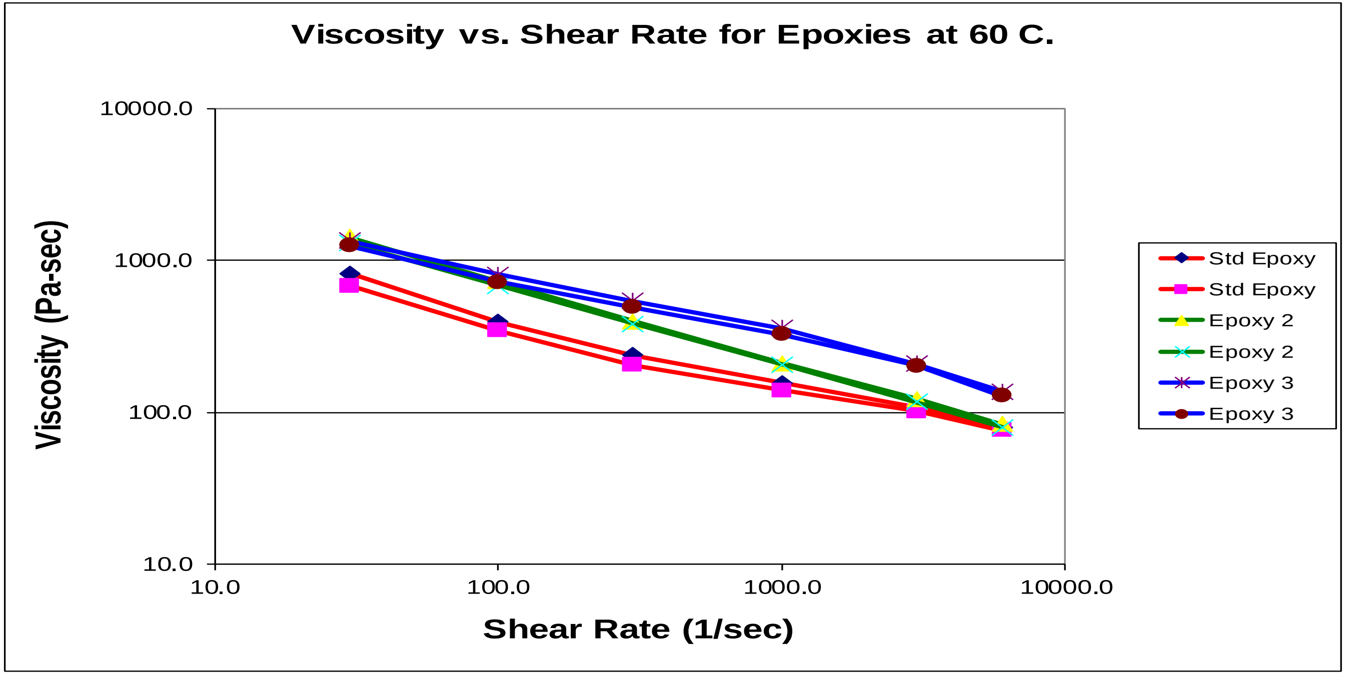
Measure Viscosity of Thermosets Before Cure



Diameter: 0.762 mm

L/D: 25/1

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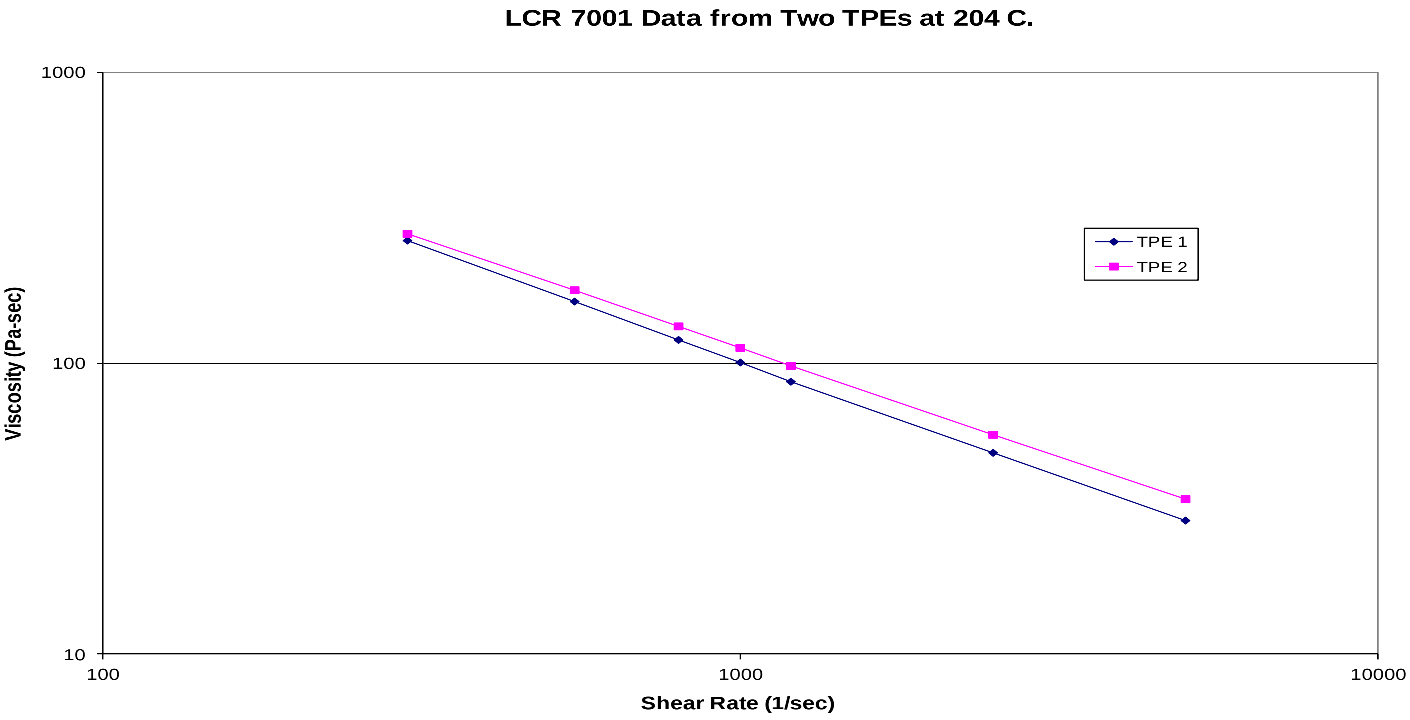
Diameter: 1 mm L/D: 30/1



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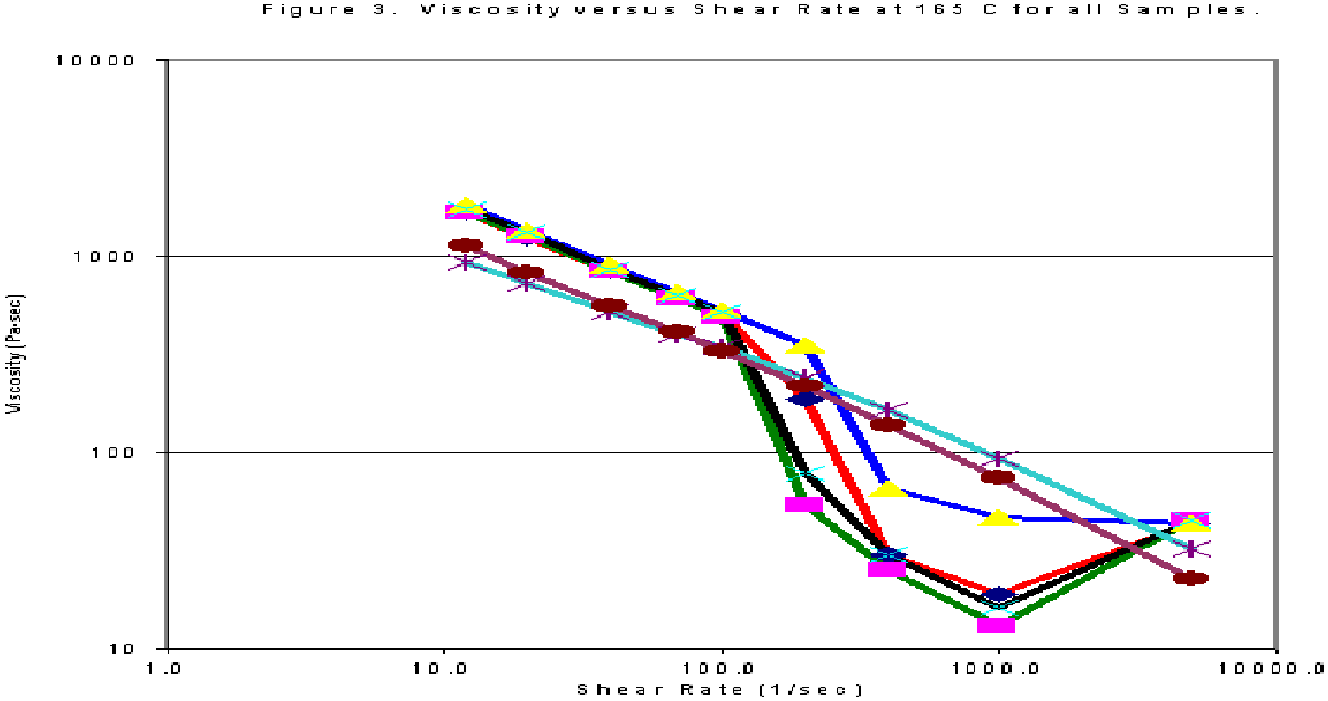
Diameter: 1 mm L/D: 20

Metal Filled Polymers



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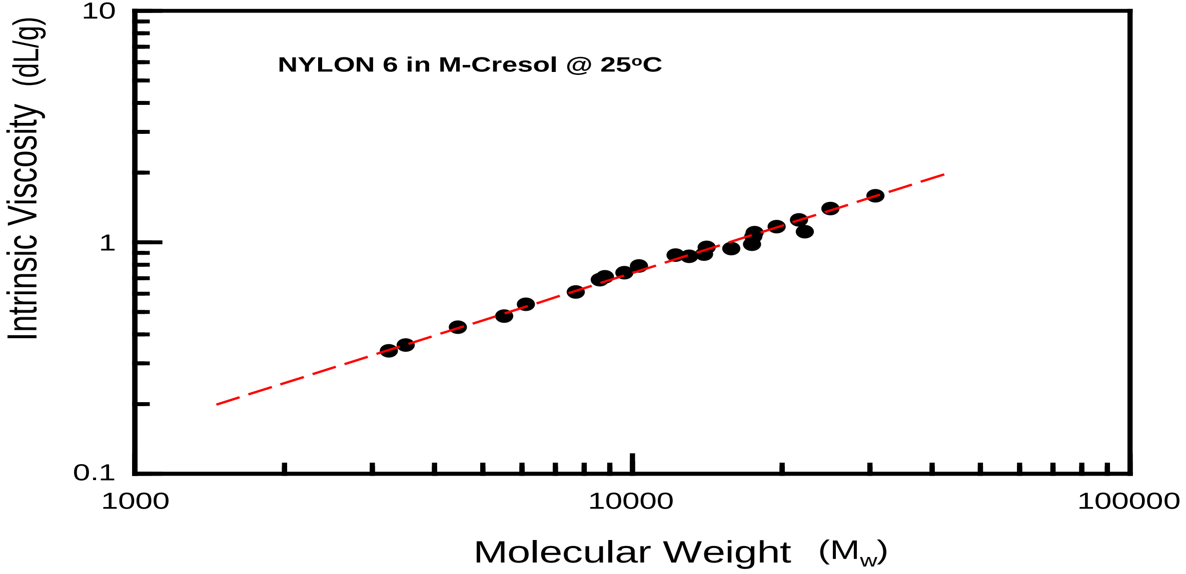
PET Intrinsic Viscosity (IV) by Melt Viscosity

Important Solution Viscosity Values

- Intrinsic Viscosity – The effect of PET on the viscosity of a solution of PET and a solvent. The result provides a measure of the Molecular Weight of the PET. A method without solvent can be done on either the LMI or the LCR to output a PET IV value when a test is run at 285 C.
- Inherent Viscosity – The effect of Nylon on the viscosity of a solution of Nylon and a solvent. The result provides a measure of the Molecular Weight of the Nylon. The LMI and LCR cannot output an Inherent Viscosity. Customers have to develop their own methodology.

Relationship of Intrinsic Viscosity to Molecular Weight



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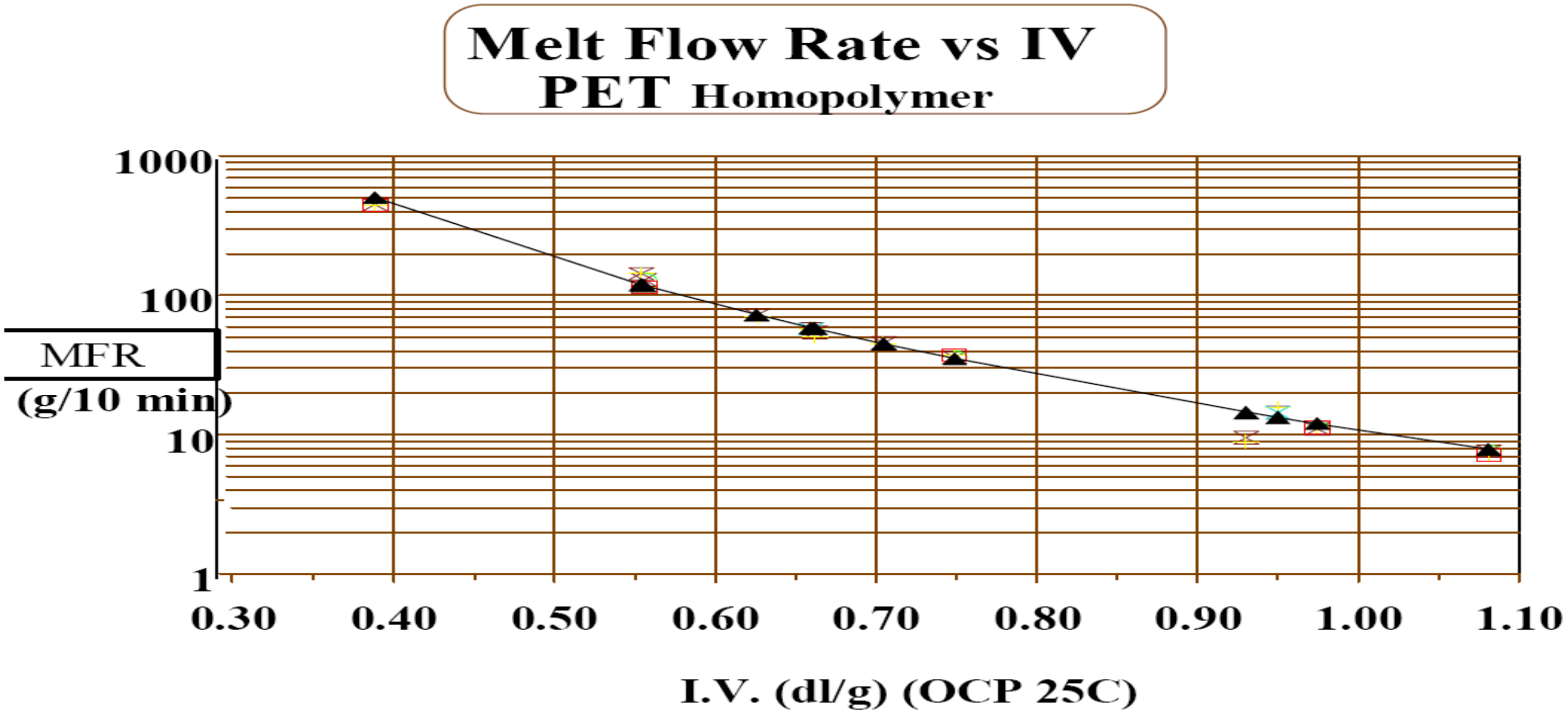
PET IV Value and Recommended Application

- 0.60 dl/g: Fiber
- 0.65 dl/g: Film
- 0.76-0.84 dl/g: Bottles
- 0.85 dl/g: Tire cord

LMI Correlation Developed by Dynisco



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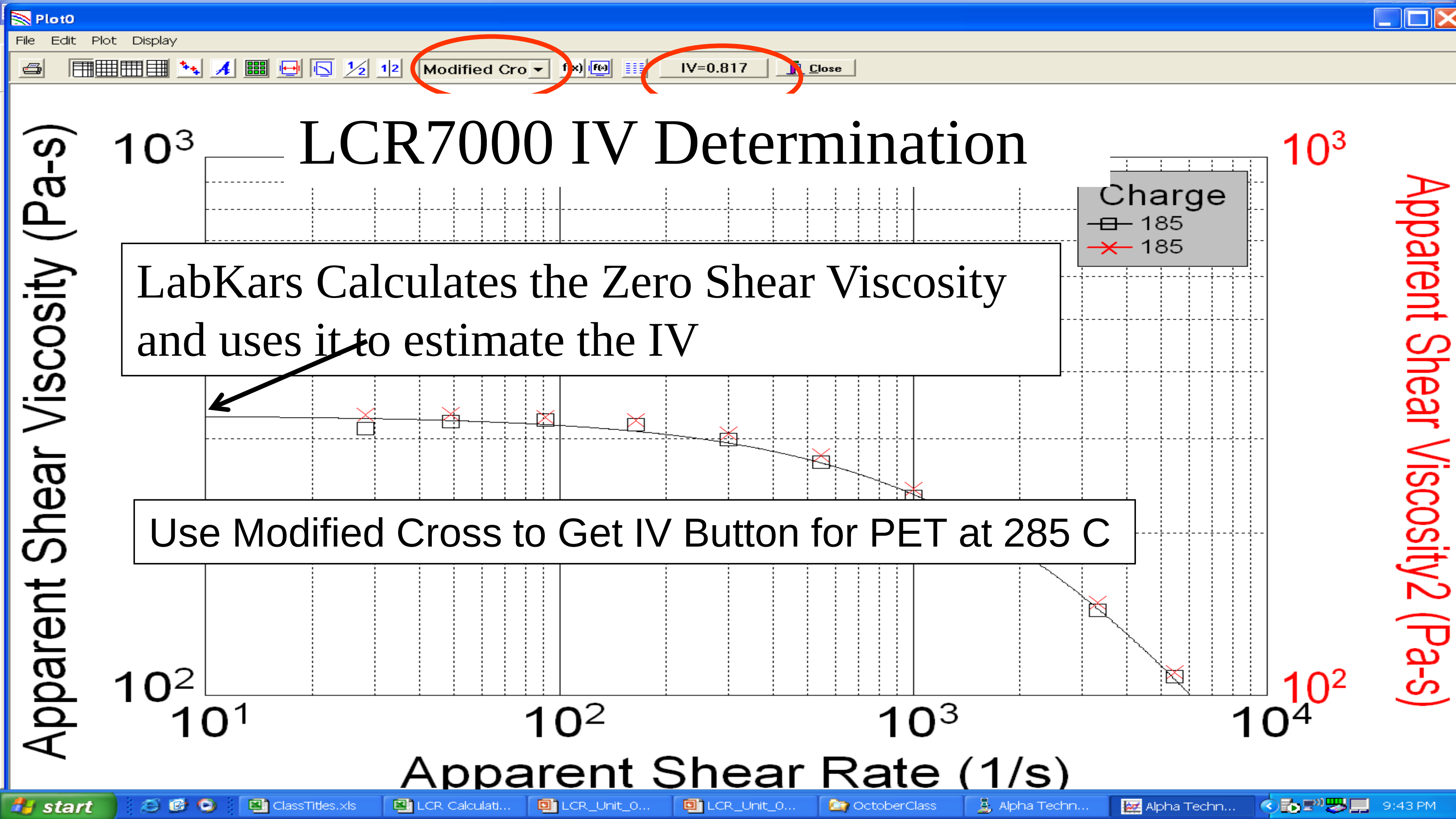
IV displayed on LMI after MFR test.

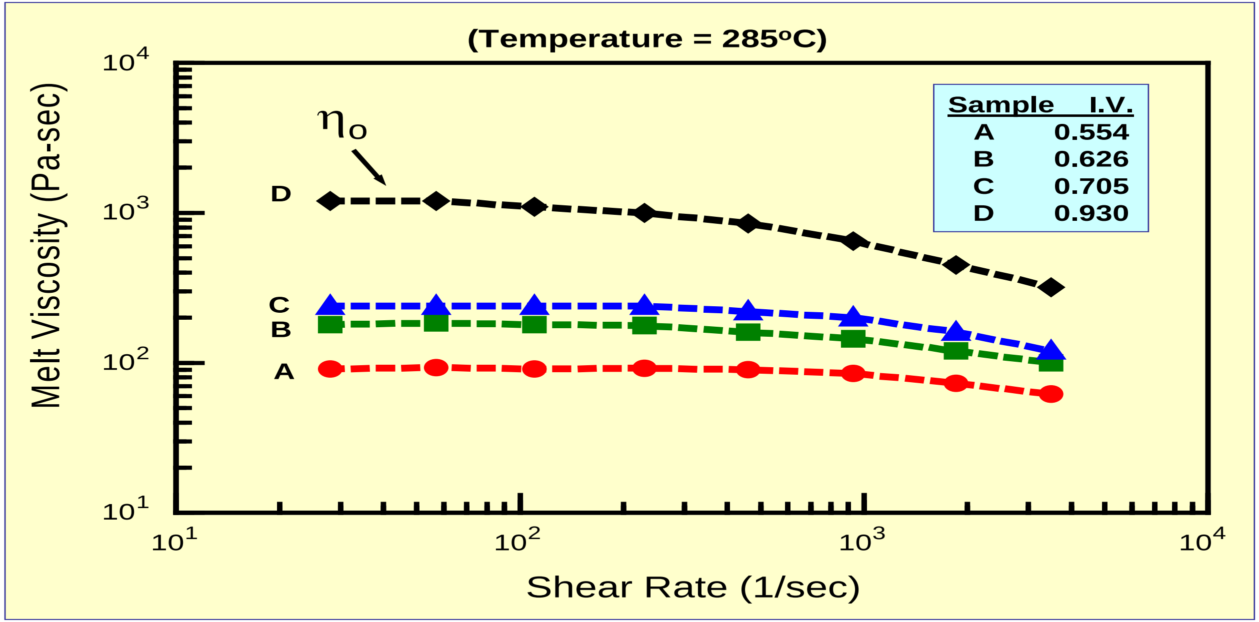
LCR7000 IV Determination

LabKars Calculates the Zero Shear Viscosity and uses it to estimate the IV

Use Modified Cross to Get IV Button for PET at 285 C



Melt Viscosities of PET Resins with Different IVs



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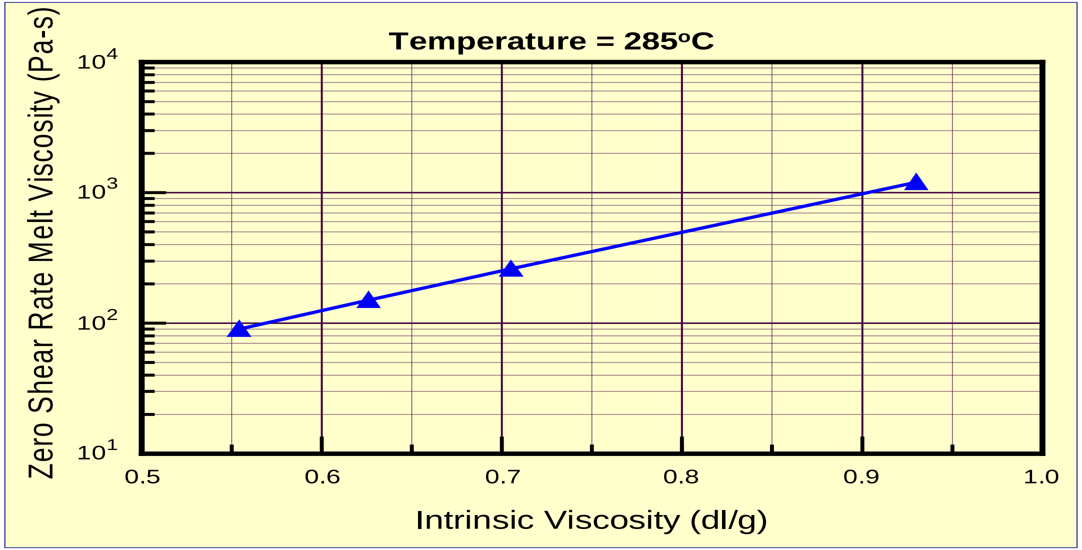
PET Melt Viscosity verses Intrinsic Viscosity



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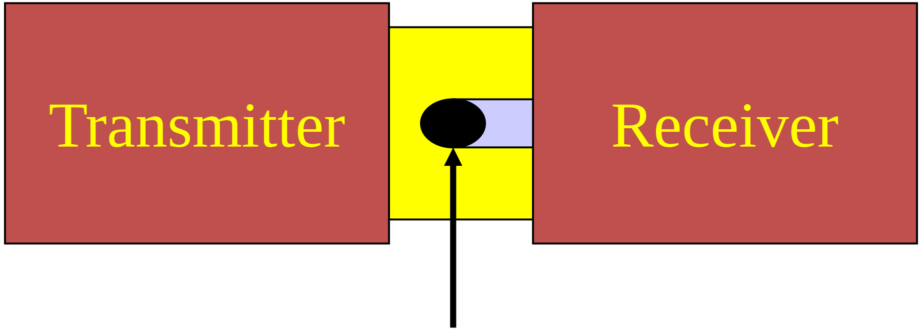
LCR7000 Series Die Swell Measurement

Laser Die Swell Measurement



Direct Measure of Extrudate to ±0.03 mm
or Percent Die Swell

- Running Die Swell – Piston moves during measurements

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Example of Percent Die Swell Calculation

$$Percent\_Die\_Swell = \frac{(100)(1.87 \quad -1.524)}{1.524} = 22.7\%$$

where

1.87 mm = Diameter of Extrudate Leaving Die
1.524 mm = Diameter of Die

Die Swell Analysis

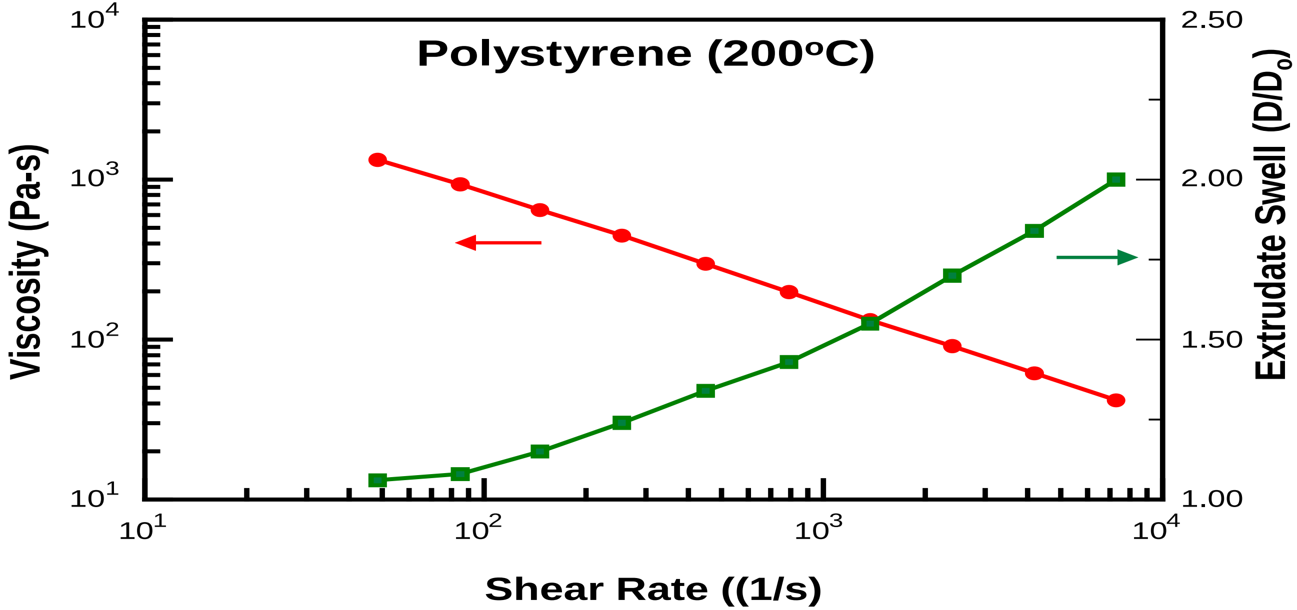
- Relaxed Die Swell
  - Predict Part Dimensions
- Running Die Swell
  - Productivity of extrusion / calendar
- Smoothness of Extrudate
  - Part finish

How to Control Die Swell.

Usually, lower die swell is preferred!

- Higher process speeds will increase die swell. Determine effect of speed on die swell to optimize process speed.
- Die Swell is reduced at higher temperature. Determine whether process speed can increase with temperature increase without degrading material.
- Determine effect of L/D on Die Swell. Making a die with a longer L/D can reduce die swell.

Viscosity and Extrudate Swell as a Function of Shear Rate



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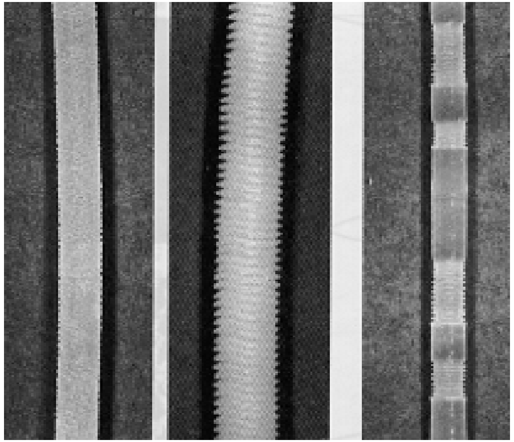
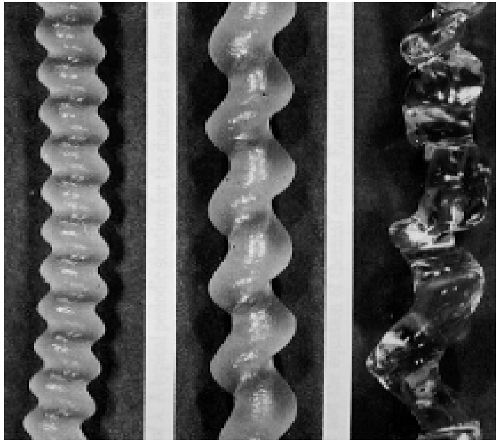
Melt Fracture

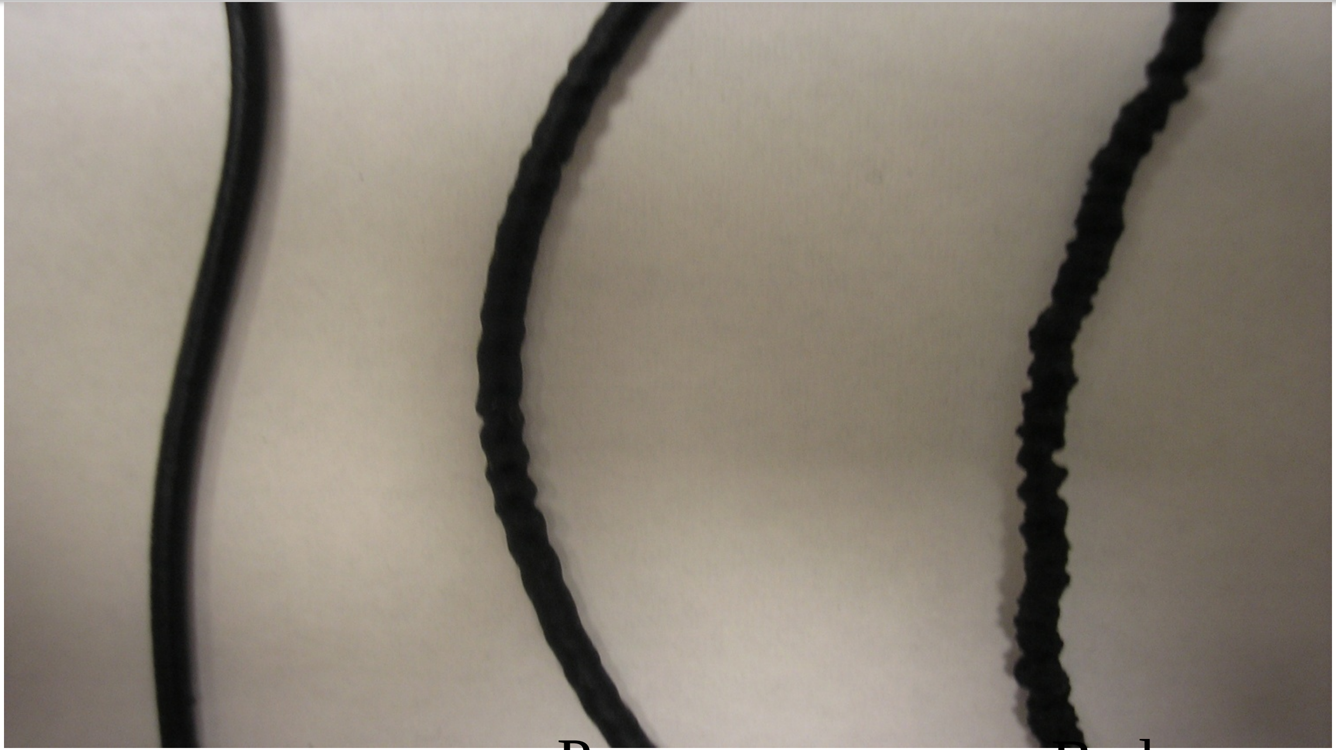
- If extrudate shows melt fracture, product quality will probably suffer if produced at the same shear rate.
- Longer L/Ds and tapered entrance to die may reduce Melt Fracture. Capillary Rheometer can help predict behavior as function of changes to die.

Melt Fracture

Melt fracture can produce a cyclical or noisy die swell measurement.

Comparison of Extrudate Appearance
Same Compound / Different Batch



Good Poor Bad

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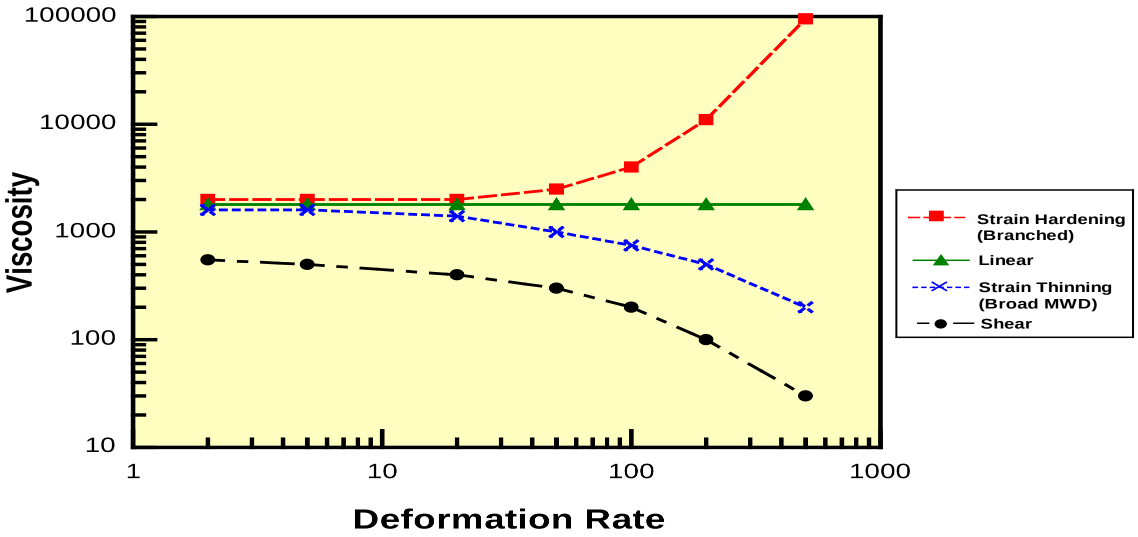
LCR7000 Series Extensional Viscosity from Cogswell Equations

LCR Method for Extensional Viscosity

- Uses Cogswell Equation
- Need to do Bagley Correction
  - Two Tests: Short Die and Long Die Test
  - Automatically calculated with LabKars
- Results are poor when extrudate is rough

Types of Extensional *Viscosities*



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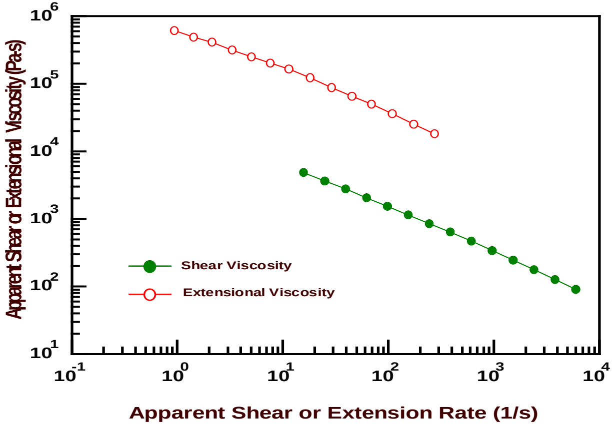
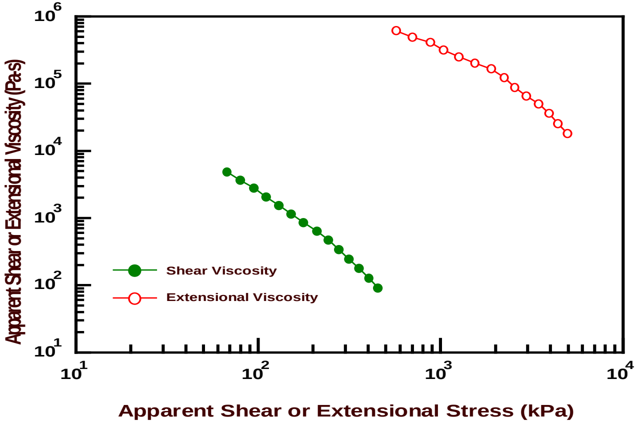
Measurement of Extensional Viscosities

Experimental results

LLDPE @ 190 °C





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Applications for Extensional Viscosity

- Film Blowing
- Fiber Drawing