Rheology with Application to Polyolefins

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DELIVERING SOLUTIONS
UNLOCKING OPPORTUNITIES

Outline

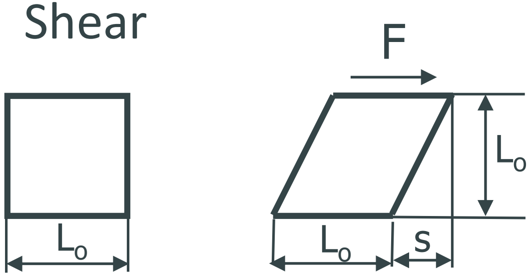
- Introduction
- Steady Shear Flow
- Oscillatory Shear Flow
- Extensional Rheology
- Concluding Remarks

Rheology

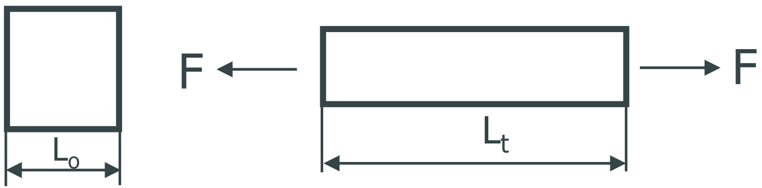
- Science dealing with deformation and flow of materials.
- Includes both molten and solid state behavior.
- Most commonly measured for materials such as polymers, polymer solutions, paint, food, and blood.
- Requires measuring the *deformation* resulting from a given *force* or measuring a force required to produce a given deformation.
- Importance for polymers:
  - Processing: extrusion, gear pumps, flow through pipes, pressure drops, etc.
  - Relation to molecular structure such as:
    - Molecular weight (M_w)
    - Molecular weight distribution (MWD)
    - Long chain branching (LCB)

Deformation

- Shear



- Elongation

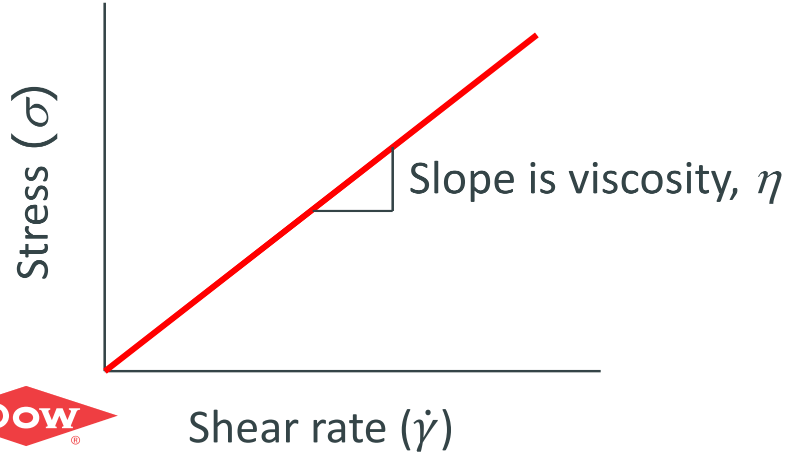


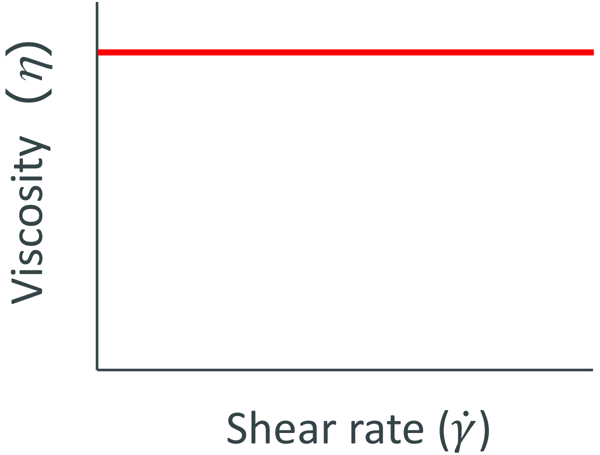
- Measurement and analysis
  - Single deformation modes
  - Straight-forward description
  - Measure material properties

- Flow in applications
  - Mixed deformation modes
  - Complex analysis

Viscosity (Newtonian Fluid)

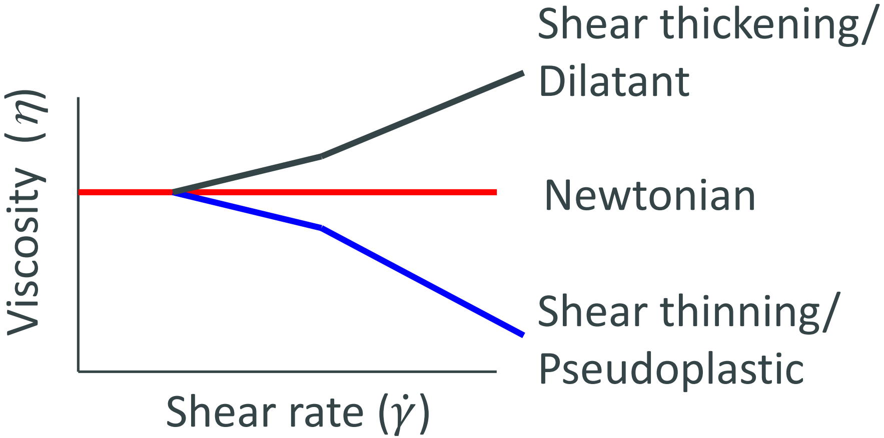
- Viscosity relates to the resistance of a material to flow.
- Linear relationship between shear stress and shear rate: $\sigma = \eta \dot{\gamma}$.
    - For simple shear, the constant of proportionality is the viscosity, η .
- A material that behaves in this way is a *Newtonian* fluid.
    - The viscosity does not depend on the shear rate.





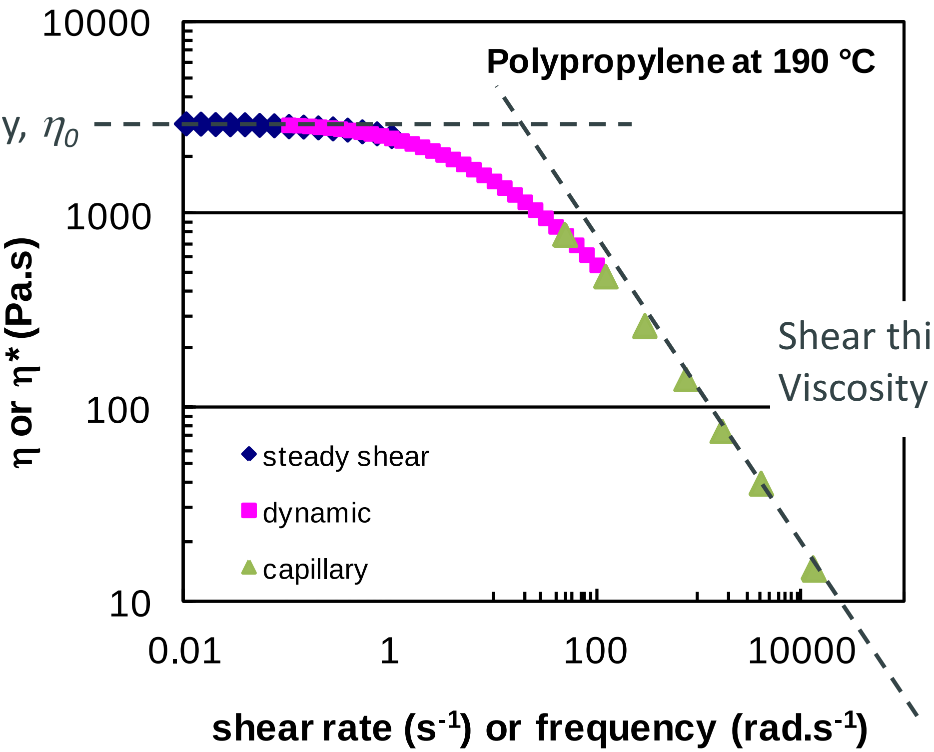
Viscoelasticity and Non-Newtonian Behavior

- The majority of materials are neither purely elastic or viscous, but are considered viscoelastic (exhibit viscous resistance and elasticity).
- In this case, the relationship between the stress and strain rate is no longer linear and cannot be described in terms of a single constant, η.
- Generalized equation for steady simple shear: $\eta(\dot{\gamma}) = \sigma / \dot{\gamma}$ in which the η is function of $\dot{\gamma}$.



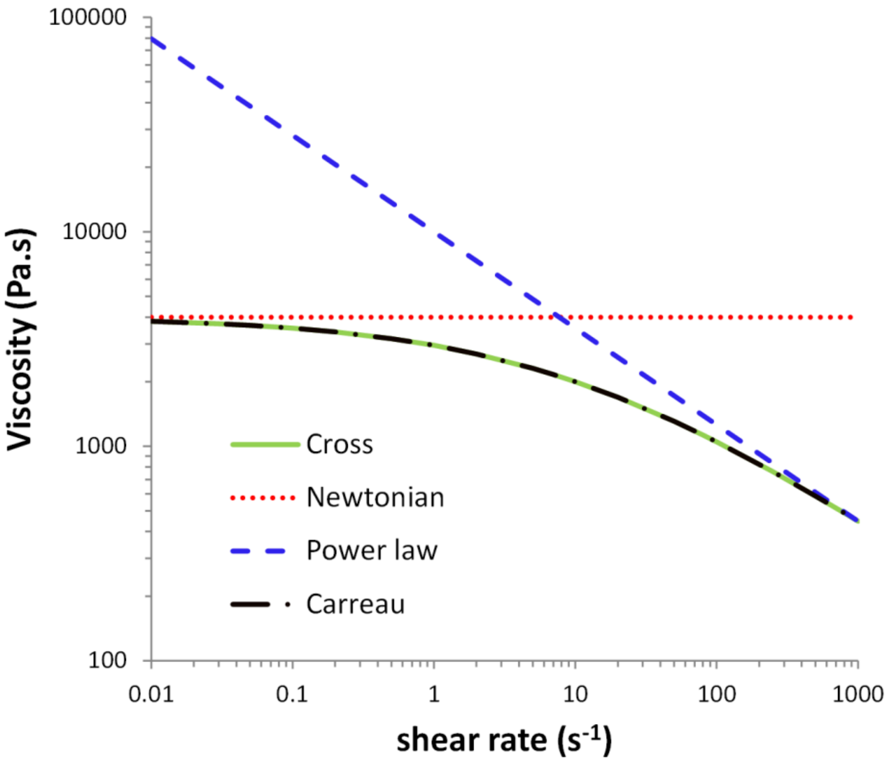
Non-Newtonian Behavior: Typical Polymer Flow Curve

Plateau region
Viscosity constant
→ Zero-shear viscosity, η_0



Shear thinning region
Viscosity ↓ with ↑ shear rate

Non-Newtonian Behavior: Viscosity Models



Power law

$$\sigma = K\dot{\gamma}^{n}$$
$$\eta = K\dot{\gamma}^{n-1}$$

n-1 < 0: shear-thinning
n-1 > 0: shear-thickening
n = 1: Newtonian fluid

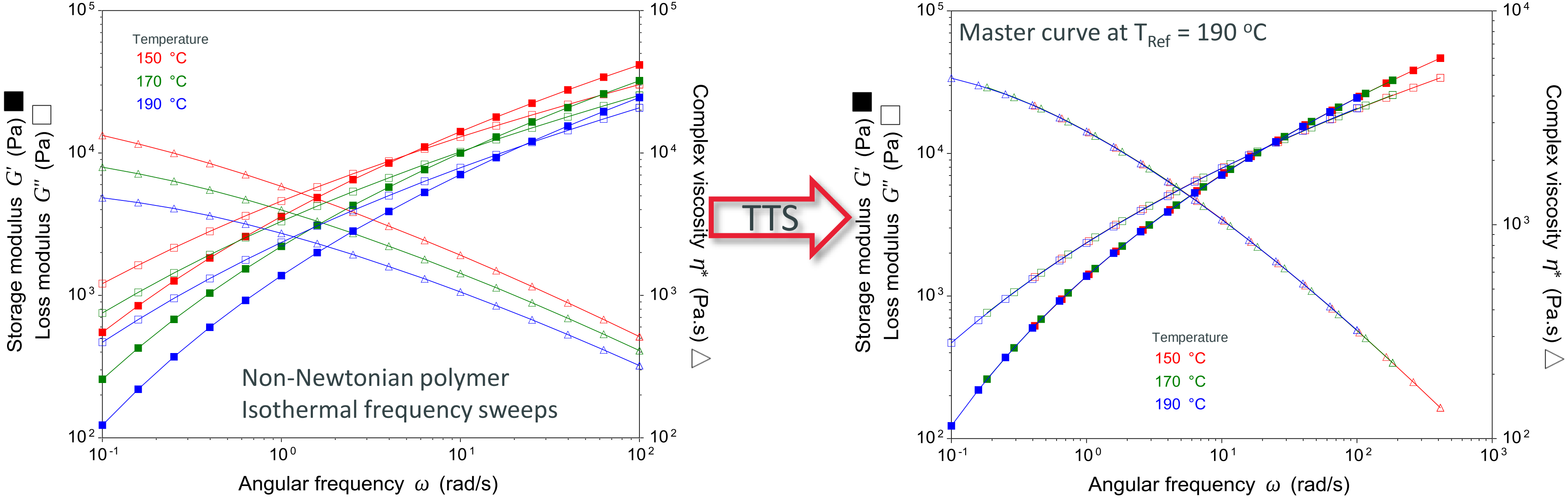
$$Cross: \frac{\eta}{\eta_0} = \frac{1}{1+(\lambda\dot{\gamma})^{(1-n)}}$$

$$Carreau: \frac{\eta}{\eta_o} = \frac{1}{[(1+(\lambda\dot{\gamma})^2]^{(1-n)/2}}$$

η = viscosity, $\dot{\gamma}$ = shear rate
η_o = zero shear viscosity
λ = relaxation time
n = high shear rate fitting parameter

[T.A. Plumley *et al.*, *SPE ANTEC Proceedings*, p. 1221 (1994)]

Temperature Dependency of Viscosity (Activation Energy)



- Viscosity ↓ with ↑ temperature
- *G′* and *G″* ↓ with ↑ temperature

$$\text{Arrhenius: } a_T = \frac{\eta_0(T)}{\eta_0(T_{Ref})} = exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{Ref}}\right)\right],$$

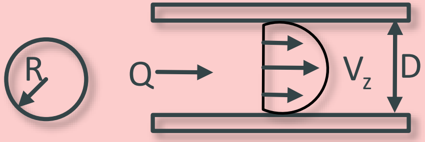
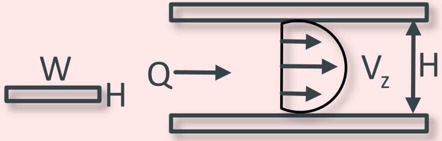
E_a flow activation energy

Viscometric Flows

- With these flow geometries, the viscosity, as well as fluid velocities, shear rates, and pressure distributions can be determined analytically.

Viscometric flow	Flow example
Steady tube flow	Capillary flow
Steady slit flow	Cast die
Annular pressure flow	Blown film die
Steady concentric flow	Brookfield viscosity
Steady parallel disk flow	DMS
Steady cone and plate flow	DMS
Steady sliding cylinder flow	Wire coating
Steady helical flow	Spiral die
Combined drag/P flow	Extrusion

Useful Equations for Steady Flow Through a Capillary and Slit

Flow Geometry	Shear Rate, $\dot{\gamma}$	Shear Stress, τ or σ	Depiction of Flow
Capillary	$\dot{\gamma} = \frac{32Q}{\pi D^3} = \frac{4Q}{\pi R^3}$	$\tau = \frac{\Delta P}{4\left(\frac{L}{D}\right)} = \frac{\Delta P}{2\left(\frac{L}{R}\right)}$	
Slit	$\dot{\gamma} = \frac{6Q}{WH^2}$	$\tau = \frac{\Delta P}{2\left(\frac{L}{H}\right)}$	

$\dot{\gamma}$ = shear rate
Q = volumetric flow rate
ΔP = pressure drop
V = velocity

R = radius of capillary
L = length of capillary
D = diameter of capillary

W = width of slit
H = height of slit

Typical Shear Rates in Common Processes

Process	Shear rate (s^{-1})	Application
Extrusion	10^0 - 10^3	Polymer melts, food
Mixing	10^1 - 10^3	Liquid manufacturing
Spraying, brushing	10^3 - 10^4	Spray-drying, paints
Rubbing	10^4 - 10^5	Creams & lotions
Injection molding	10^2 - 10^5	Polymer melts
Coating flows	10^5 - 10^6	Paper

Steady Shear Flow

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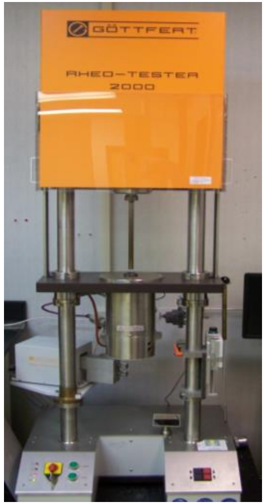
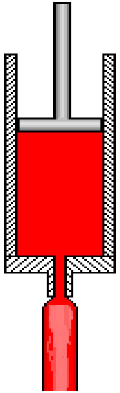
Shear Flow: Measurement Methods

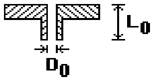
Rotational rheometer

- Uniform simple shear flow
- Steady, oscillatory or creep flow
- Rates: low (creep) to moderate
- Variety of tools

Capillary rheometer



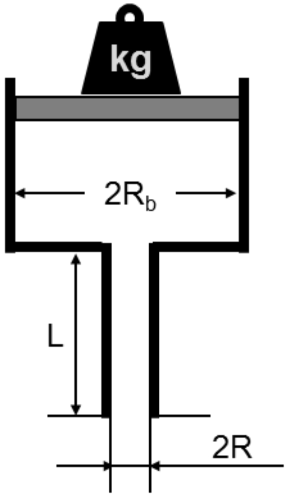




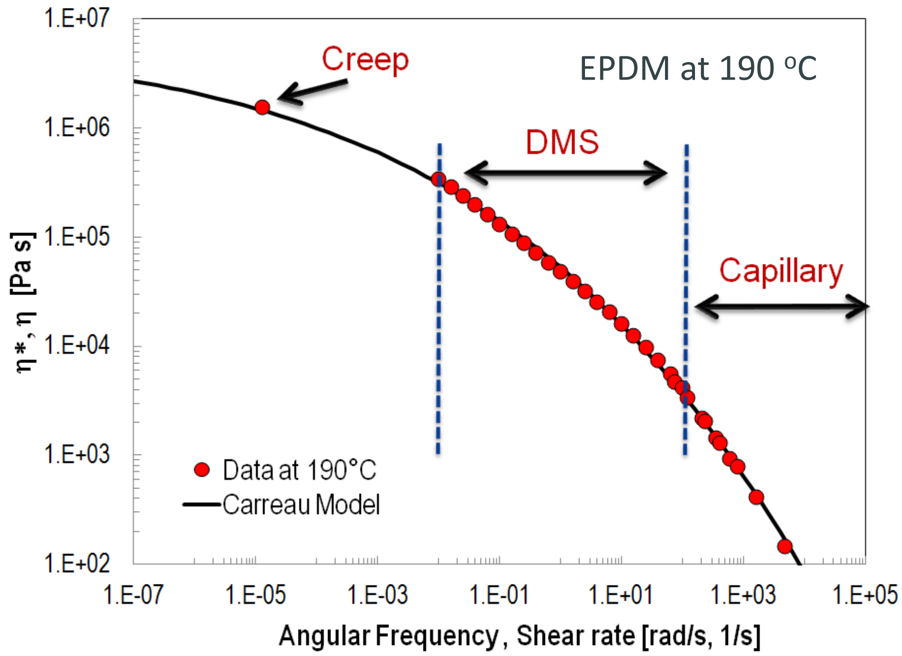
- Steady tube flow in capillary die
- Steady shear flow
- Entry/exit effects → *Apparent* viscosity
- Rates: moderate to high
- Variety of dies

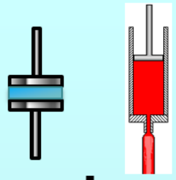
Melt Index (ASTM D-1238, ISO 1133)

- Industry standard.
- Similar to capillary rheology except use load instead of instrumented crosshead and short die.
- Single-point measurement of flow rate:
  - Melt index: g/10 min
  - Melt index ↑, viscosity ↓
- For Polyethylene:
  - T = 190 °C
  - Load = 2.16 kg (I_2); 10 kg (I_{10}); 21.16 (I_{21})
  - $2R_b$=0.376”
  - 2R=0.0825”
  - L/D=3.818”



Combining Different Methods Gives Broad Flow Curves





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Cox-Merz Rule

Cox & Merz. JPolymSci (1958)

$$\eta\left(\dot{\gamma}\right) = \left|\eta^{*}(\omega)\right|_{\dot{\gamma}=\omega}$$

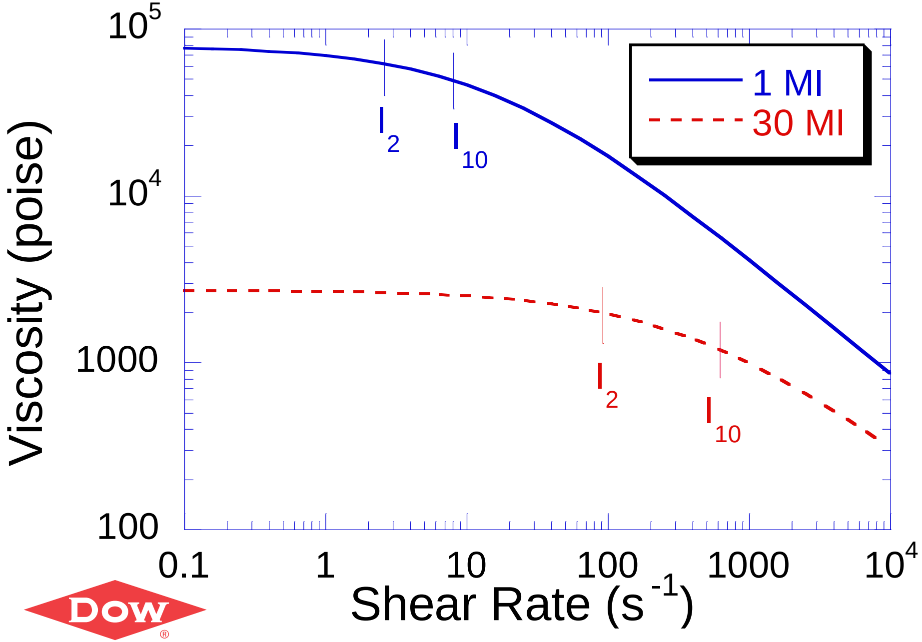
$$\dot{\gamma}(s^{-1}) = \omega(rad/s)$$

=

Flow curve

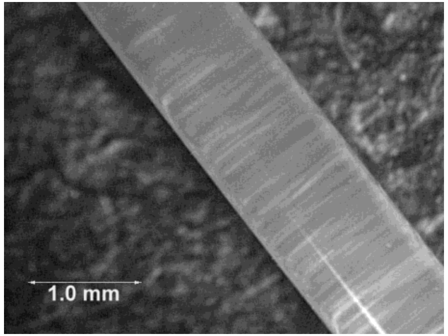
Melt Index Correlations

- Based upon modeling a melt indexer as capillary flow: $\dot{\gamma} \sim 2.5 I_2$
- Thus, the shear rate at which higher melt indexes are measured is greater. The stress correspondingly increases with the MI load.

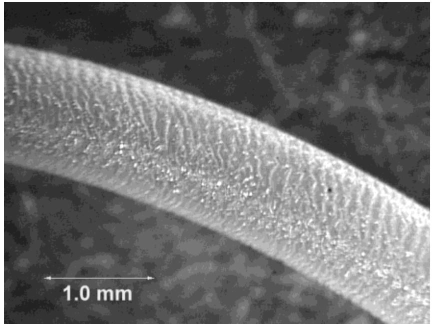


Melt Index	Weight (kg)	Shear Stress (dyn/cm²)	Pressure (Psi)	Pressure (MPa)
I_2	2.16	1.93×10^5	43	0.296
I_5	5	4.47×10^5	99	0.683
I_{10}	10	8.94×10^5	198	1.37
I_{21}	21.6	1.93×10^6	429	2.96

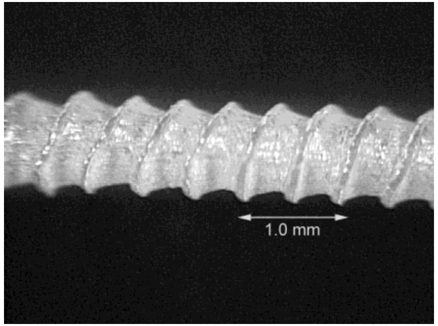
Shear Flow: Melt Fracture at High Shear Rates, Capillary Flow



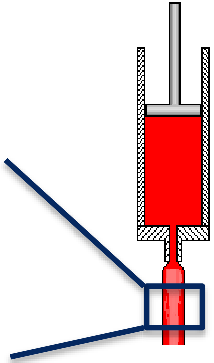
Smooth

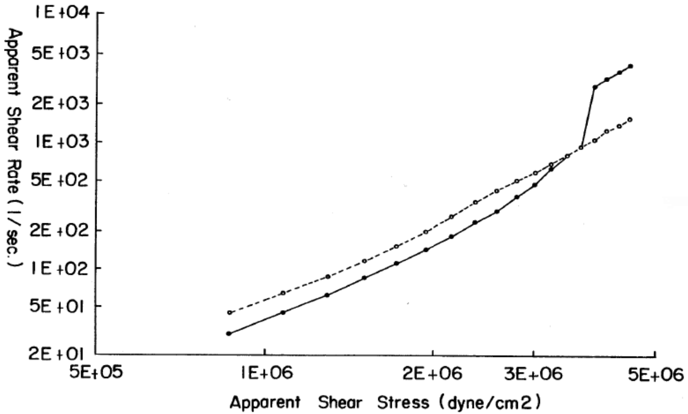


Surface Melt Fracture

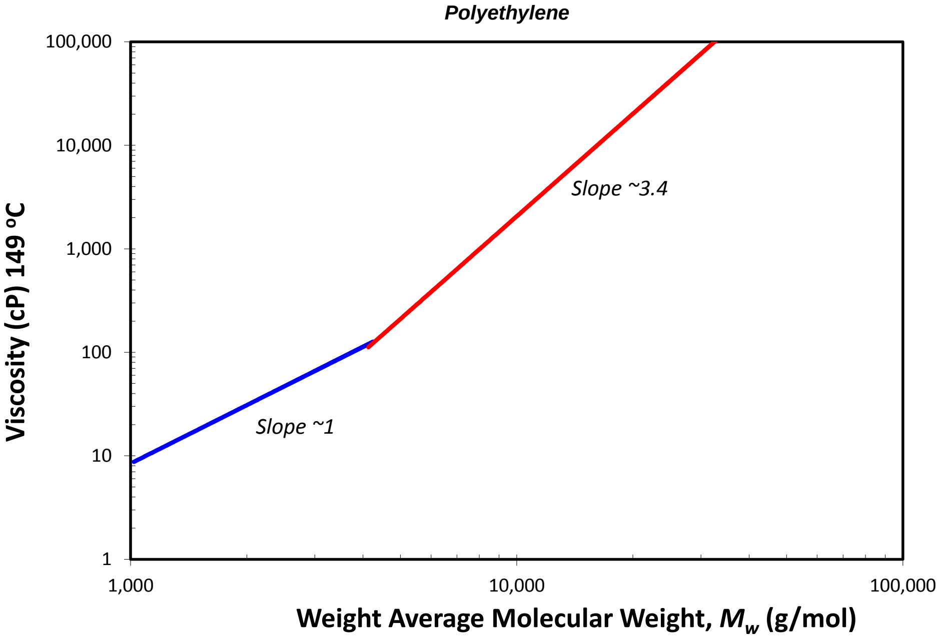


Gross Melt Fracture





Effect of Molecular Weight on Zero Shear Viscosity



M_w dependency

- η_0 ↗ as M_w ↗
- Above $M_{w,cr}$: $\eta_0 = kM_w^{3.4}$

  k = f(T)

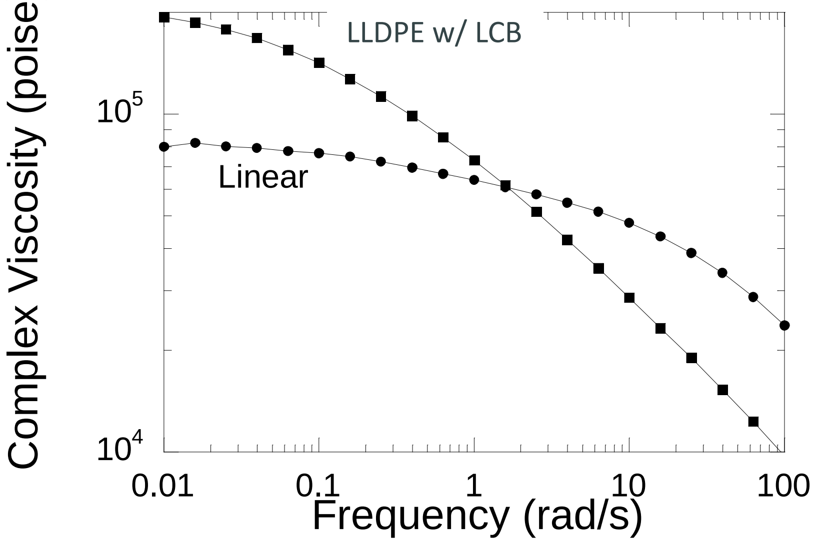
  $M_{w,cr}$ depends on polymer type

- Below $M_{w,cr}$: $\eta_0 = kM_w$

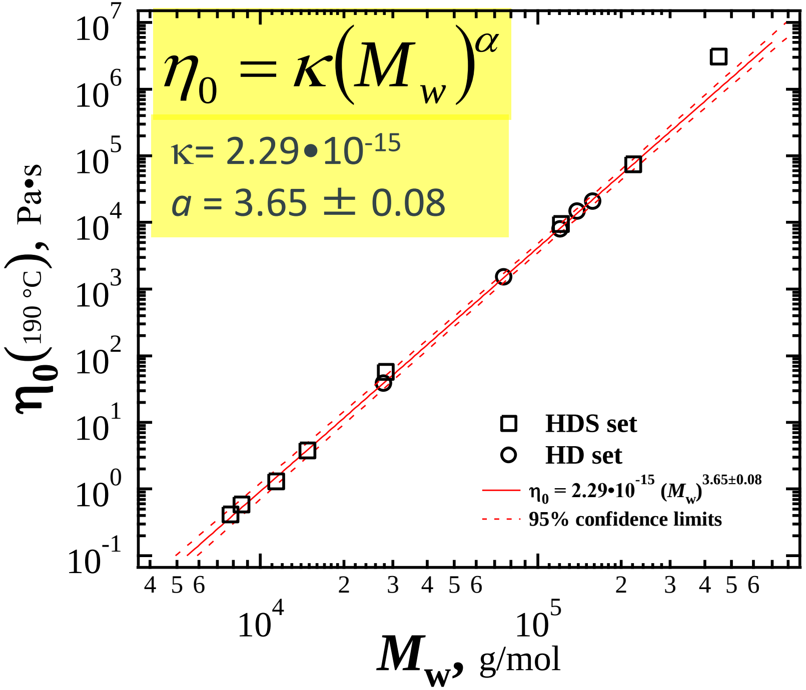
Shear Flow: Effect of Polymer Properties

Polymer architecture and η

1. η_0 increases with LCB
2. Shear thinning increases with LCB



Molecular Weight and η_0



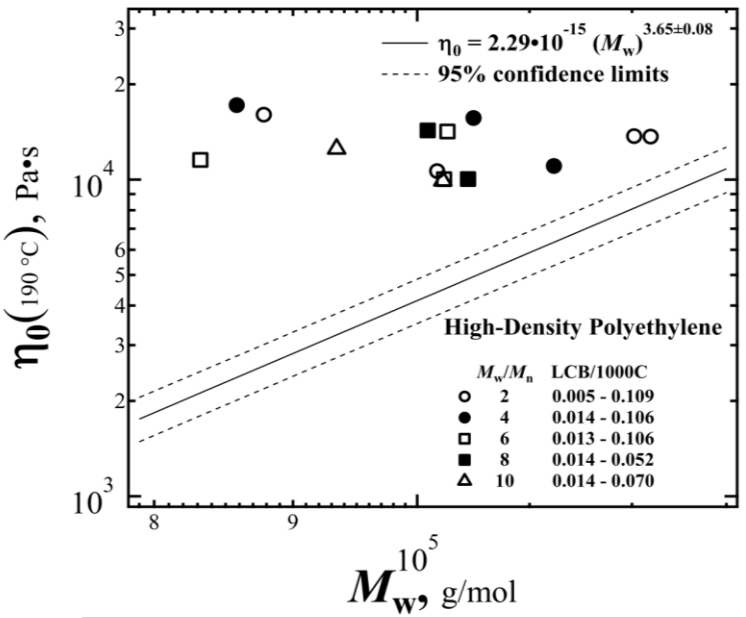
$$\eta_0 = \kappa(M_w)^{\alpha}$$

$\kappa = 2.29 \bullet 10^{-15}$

$a = 3.65 \pm 0.08$

[Karjala *et al.*, *J. Appl. Polym. Sci.*, 119, 636-646 (2011)]

Shear Flow: Effect of Polymer Properties



LCB as low as 0.005 is easily detected for resins with M_w=110,000 g/mol

$$ZSVR = \frac{\eta_0}{2.29x10^{-15} M_w^{3.65}}$$

ZSVR : zero shear viscosity ratio
η_0 : zero shear viscosity from creep
M_w : molecular weight by GPC

Resin	NMR LCB /1000C	GPC M_w g/mol	GPC M_w/M_n	η_0 (creep), Pa•s 190 °C	ZSVR
B0P2	0	121,200	2.03	9,569	1.16
B1P2	0.005	121,900	2.11	13,670	1.63
B2P2	0.01	120,200	2.17	13,720	1.72
B3P2	0.056	101,700	2.58	10,640	2.46
B4P2	0.109	87,800	2.18	16,040	6.33
B0P4	0	122,100	4.14	10,790	1.28
B1P4	0.014	112,300	4.47	11,040	1.78
B2P4	0.052	104,900	3.96	15,640	3.23
B3P4	0.106	85,800	3.81	17,190	7.38

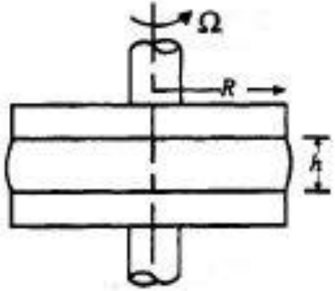
ZSVR → Sensitive to identify LCB

[Karjala *et al., J. Appl. Polym. Sci.*, 119, 636-646 (2011)]

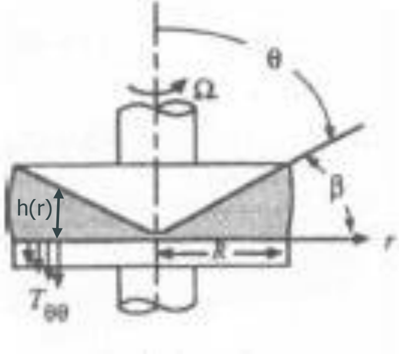
Oscillatory Shear Flow

Shear Flow Rheometers

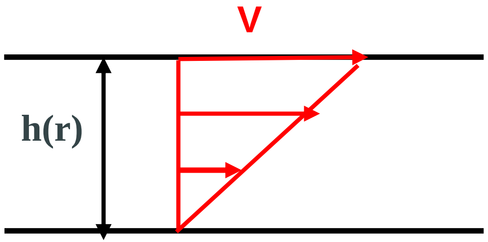
Parallel plates



Cone and plate



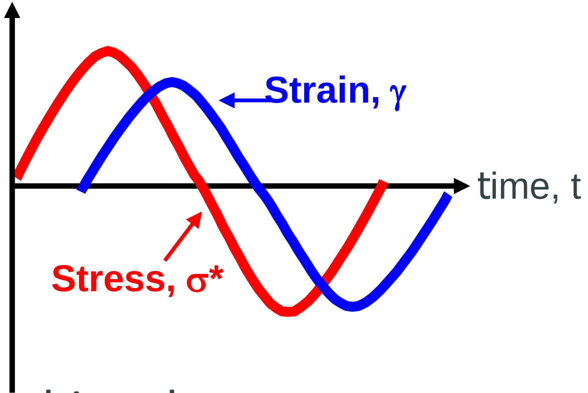
- One part rotating at Ω rad/s, torque M
- Steady or oscillatory shear flow
- *Small amplitude* oscillatory flow



Small Amplitude Oscillatory Shear Flow

- Oscillatory (dynamic, sinusoidal) deformation (γ_0, ω)
  - γ_0: maximum amplitude, typically a small deformation
  - ω: angular frequency
- Response: sinusoidal stress (σ_0, ω) at a radial distance δ
  - δ: phase angle
  - Measure for viscoelasticity

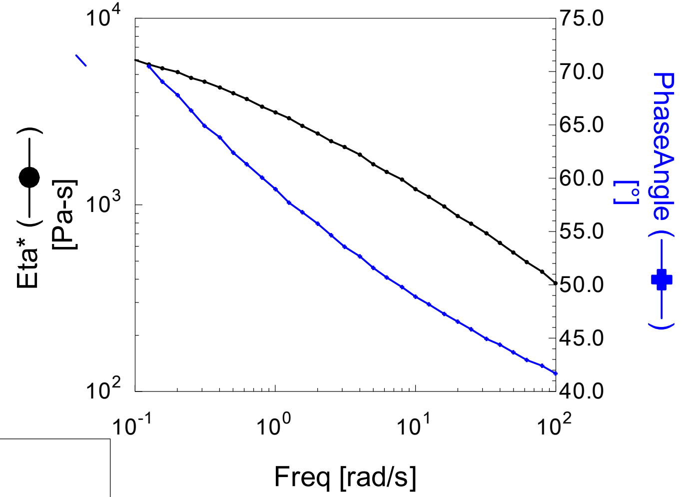
    90 °: viscous liquid
    0 °: elastic solid

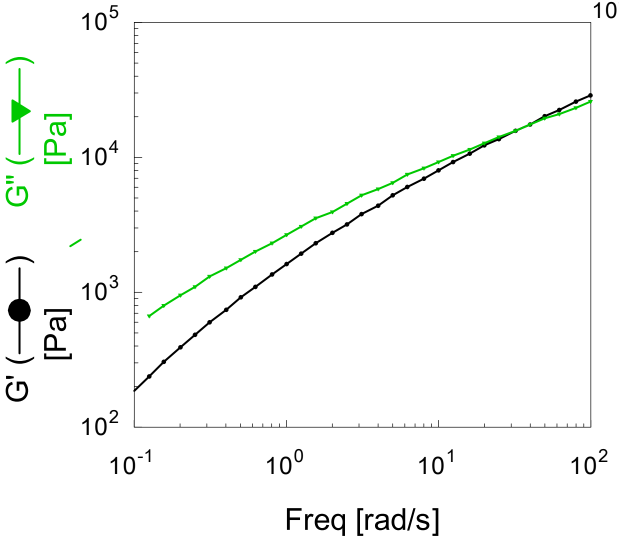


- Use:
  - to study structured materials without disturbing the structure
  - proxy for steady shear flow (Cox-Merz rule)

Oscillatory Shear Flow

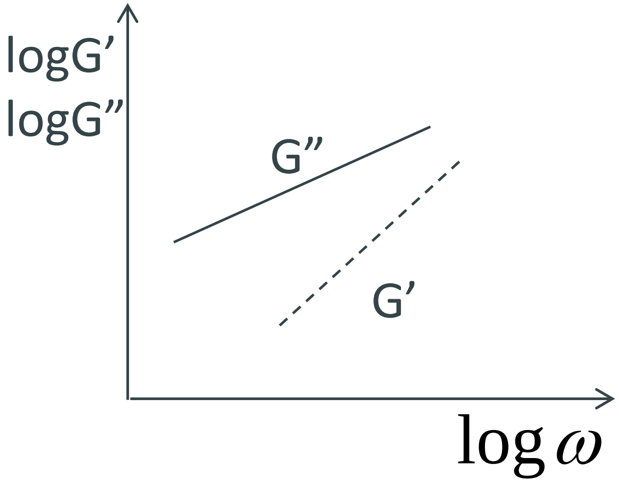
- Properties measured:
  - η*: complex viscosity
  - G’: Storage modulus (elastic)
  - G”: Loss modulus (viscous)
  - δ → tan δ = G”/G: damping factor

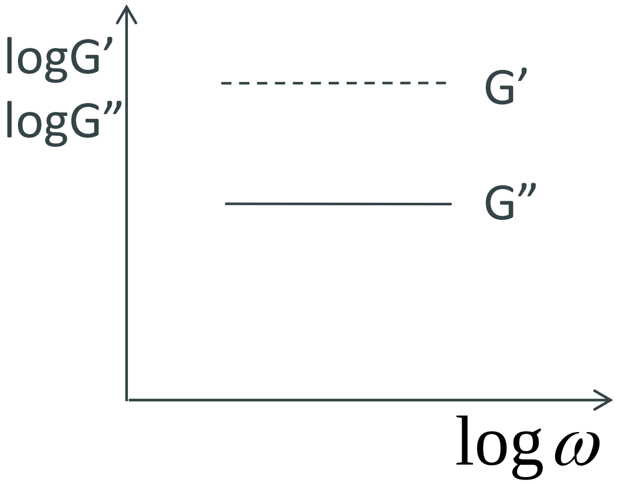




- Typical use:
  - Polymer melts
  - Viscoelastic materials
  - Structured materials

Oscillatory Shear Flow





Typical liquid

- Frequency dependent

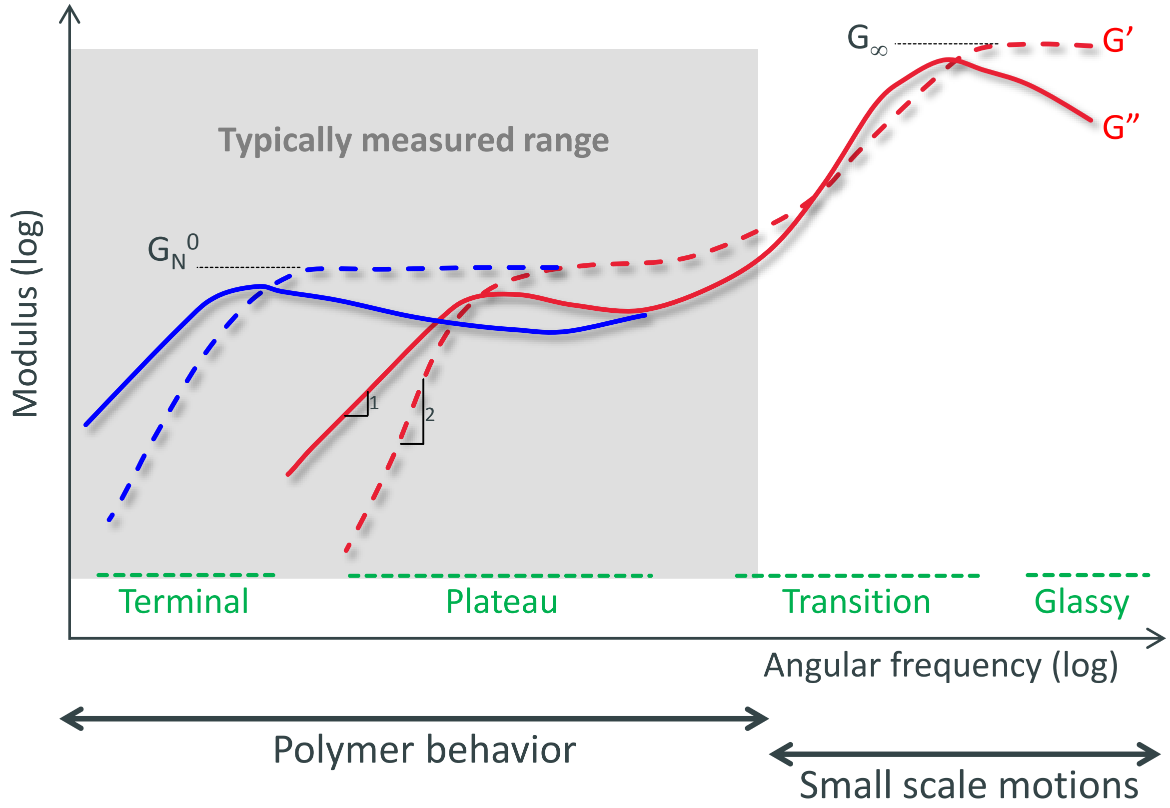
- G' < G''

Typical solid

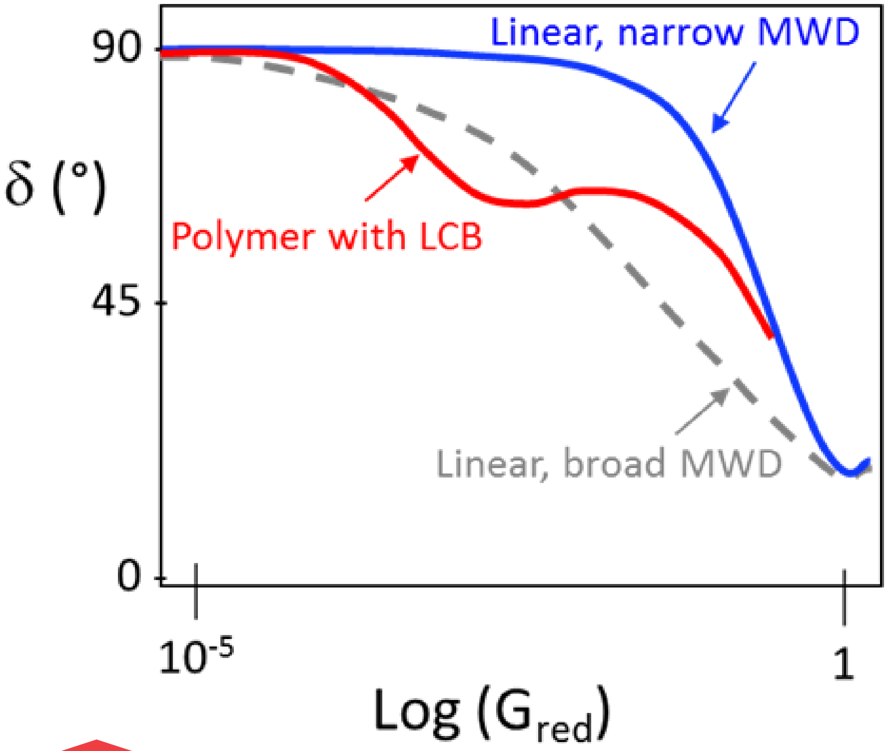
- Frequency independent

- G' > G''

Oscillatory Shear Flow



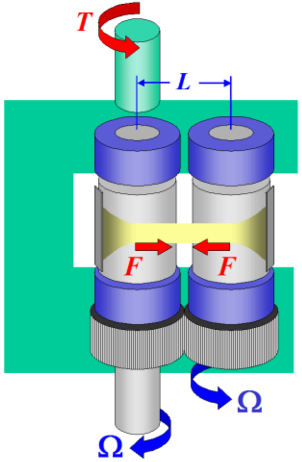
van Gurp - Palmen (vGP) Plot



- $\delta(|G^*|)$
  - Impression of sample topology / morphology
  - Verify TTS
- Reduced vGP plot $\delta(|G^*|/G_N^0)$
  - Polymer topology
  - Across chemistries

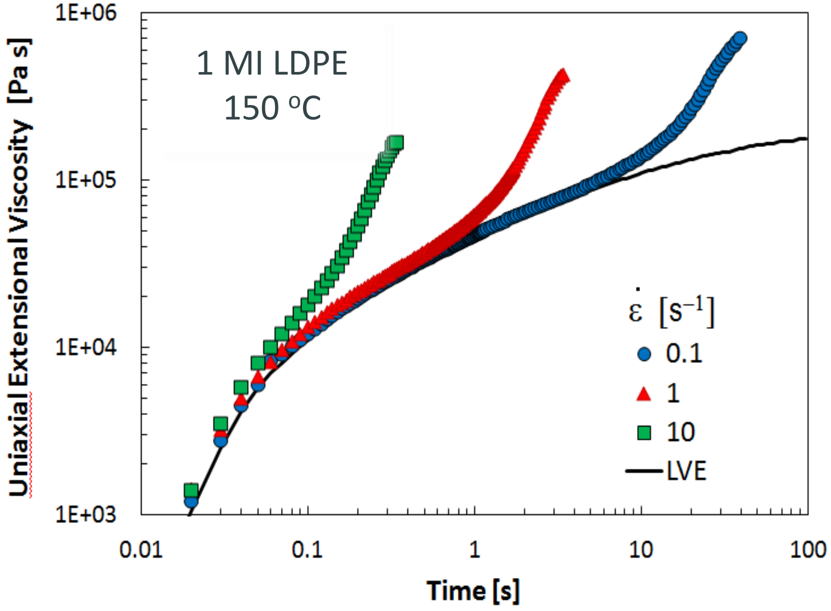
Extensional Rheology

Uniaxial Elongational Flow Devices

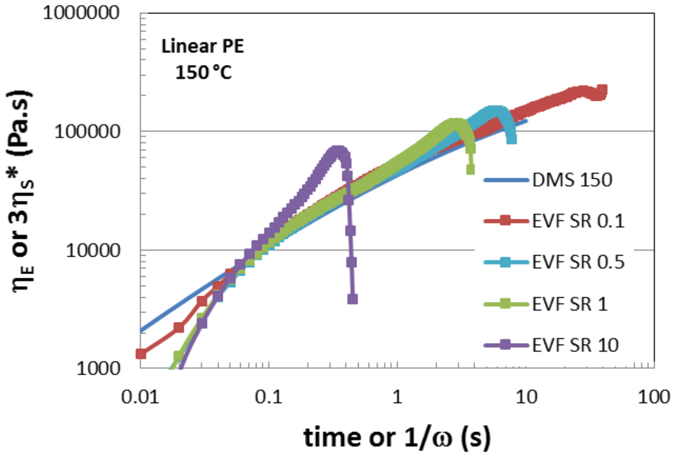


- Rotating drums on rotational rheometers
- Different vendors, different names
  - EVF, SER, UXF,…
- Homogeneous deformation
- Only for high viscosity materials
  - sample should not sag
- Limited to relatively low elongation rates
- Max. $\varepsilon_H = 4$
- Sources of error: slip, necking, sagging

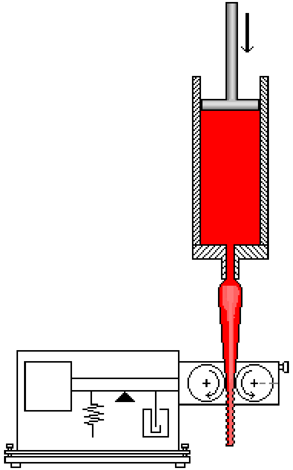
Extensional Flow: Strain Hardening

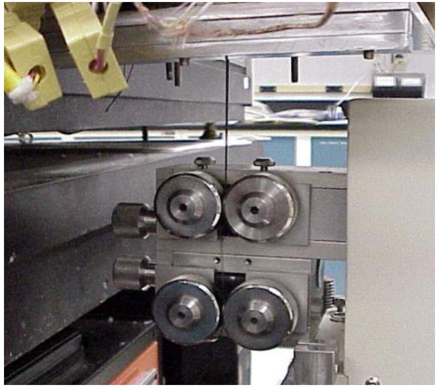


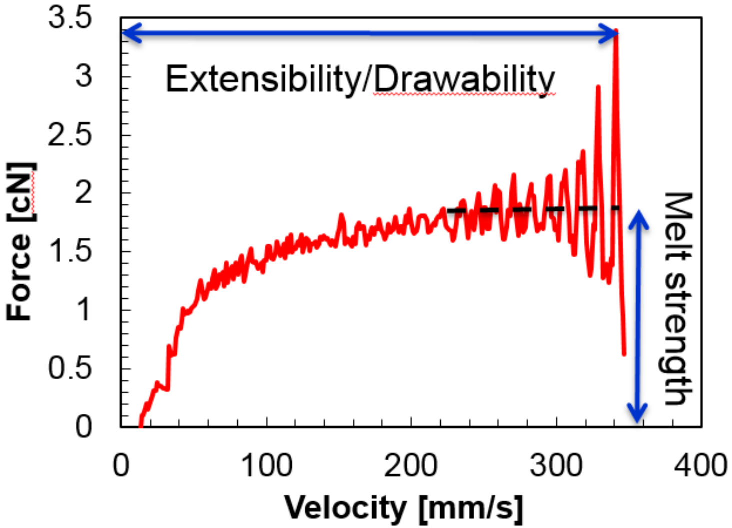
- Strain-hardening if η_E > LVE envelope
- Strain-hardening factor $SHF = \frac{\eta_E}{3\eta_S}$
- Strain-hardening required to withstand flow in stretching processes
- LCB contributes heavily



Extensional Flow: Melt Strength by Rheotens



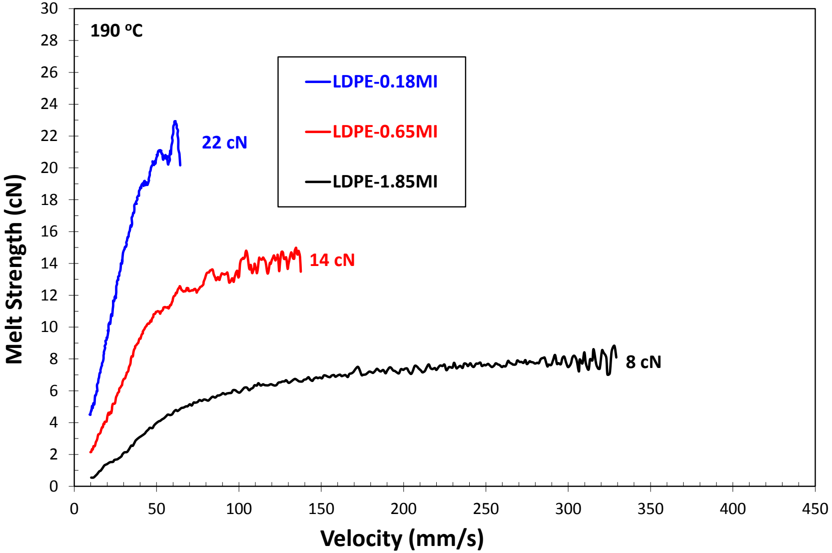


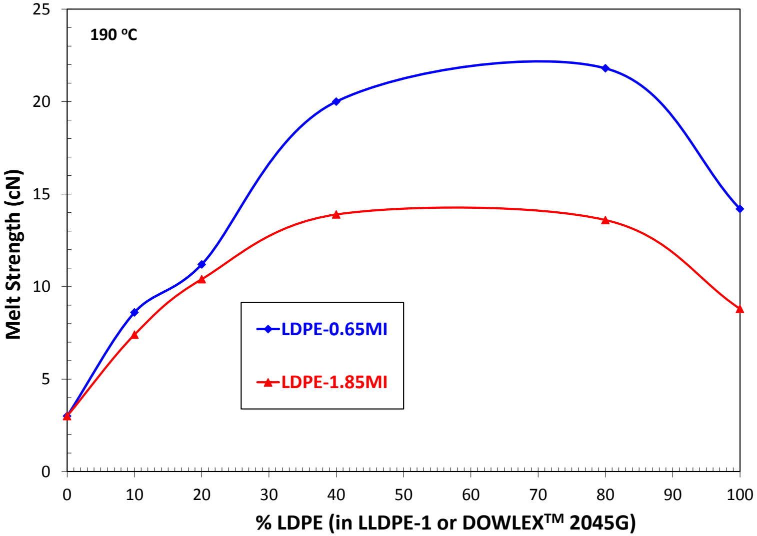


- Fiber is drawn from a die at increasing pull-off velocity (increasing force) until filament breaks
- Can reach high stretch rates, ~processing
- Transient, non-uniform stretching

- Melt strength
- Drawability
- Draw resonance

Extensional Flow: Melt Strength





[Karjala *et al., SPE ANTEC Proceedings* (2016)]

- Effect of Mw (MI)
- Effect of polymer structure

Concluding Remarks

DELIVERING SOLUTIONS
UNLOCKING OPPORTUNITIES

Summary

Rheology

- Shear
  - Creep
  - DMS
  - Capillary
  - Flow curve/Viscosity
  - Relaxation modulus
  - Oxidative/Thermal stability
  - Effect of polymer architecture
  - Instabilities
- Extensional
  - Uniaxial extension
  - Shrink
  - Melt strength/Extensibility
  - Strain hardening
  - Shrink tension
  - Effect of polymer architecture

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