

# Fluid Mechanics

Stress

Strain

Strain rate

Shear vs. Extension

Apparent Viscosity

Oversimplified Models:

Maxwell Model

Voigt Model

Continuity Equation

Navier-Stokes Equations

Boundary Conditions

Volumetric Flow Rate

## Linear Viscoelasticity

Boltzmann Superposition

Step Strain:

Relaxation Modulus

Generalized Maxwell Model

Viscosity

Creep/Recovery:

Creep Compliance

Recoverable Compliance

Steady State Compliance

Terminal Relaxation Time

Oscillatory Shear:

Storage Modulus

Loss Modulus

Phase Angle

Loss Tangent

Time-Temperature Superposition

# Molecular Structure Effects

Molecular Models:

Rouse Model (Unentangled)

Reptation Model (Entangled)

Viscosity

Recoverable Compliance

Diffusion Coefficient

Terminal Relaxation Time

Terminal Modulus

Plateau Modulus

Entanglement Molecular Weight

Glassy Modulus

Transition Zone

Apparent Viscosity

Polydispersity Effects

Branching Effects

Die Swell

# Nonlinear Viscoelasticity

Stress is an Odd Function of Strain and Strain Rate

Viscosity and Normal Stress are Even Functions of Strain and Strain Rate

Lodge-Meissner Relation

Nonlinear Step Strain

Extra Relaxation at Rouse Time

Damping Function

Steady Shear

Apparent Viscosity

Power Law Model

Cross Model

Carreau Model

Cox-Merz Empiricism

First Normal Stress Coefficient

Start-Up and Cessation of Steady Shear

Nonlinear Creep and Recovery

# Stress and Strain

## SHEAR

$$\text{Shear Stress} \quad \sigma \equiv \frac{F}{A}$$

$$\text{Shear Strain} \quad \gamma \equiv \frac{l}{h}$$

$$\text{Shear Rate} \quad \dot{\gamma} \equiv \frac{d\gamma}{dt}$$

$$\text{Hooke's Law} \quad \sigma = G\gamma$$

$$\text{Newton's Law} \quad \sigma = \eta\dot{\gamma}$$

## EXTENSION

$$\text{Tensile Stress} \quad \sigma \equiv \frac{F}{A}$$

$$\text{Extensional Strain} \quad \varepsilon \equiv \frac{\Delta l}{l}$$

$$\text{Extension Rate} \quad \dot{\varepsilon} \equiv \frac{d\varepsilon}{dt}$$

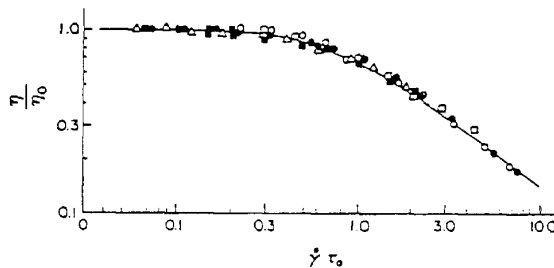
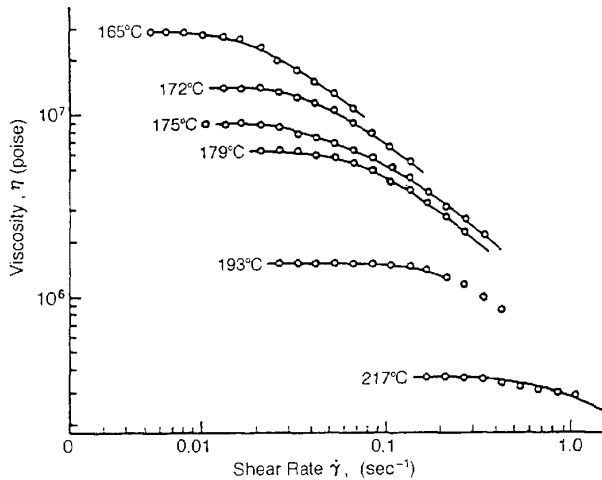
$$\text{Hooke's Law} \quad \sigma = 3G\varepsilon$$

$$\text{Newton's Law} \quad \sigma = 3\eta\dot{\varepsilon}$$

# Viscoelasticity

## APPARENT VISCOSITY

$$\eta \equiv \frac{\sigma}{\dot{\gamma}}$$



1. Apparent Viscosity of a Monodisperse Polystyrene.

# Oversimplified Models

## MAXWELL MODEL

Stress Relaxation  $\sigma(t) = \sigma_0 \exp(-t/\lambda)$

$$G(t) = G_0 \exp(-t/\lambda)$$

Creep  $\gamma(t) = \gamma_0(1 + t/\lambda)$

$$J(t) = J_s^0(1 + t/\lambda) = J_s^0 + t/\eta$$

Oscillatory Shear  $G'(\omega) = \omega\lambda G''(\omega) = \frac{G_0(\omega\lambda)^2}{1 + (\omega\lambda)^2}$

The Maxwell Model is the simplest model of a

VISCOELASTIC LIQUID.

## VOIGT MODEL

Creep  $\gamma(t) = \gamma_\infty[1 - \exp(-t/\lambda)]$

$$J(t) = J_\infty[1 - \exp(-t/\lambda)]$$

The Voigt Model is the simplest model of creep for a

VISCOELASTIC SOLID.

# Equations of Fluid Motion

## CONTINUITY

Incompressible  $\vec{\nabla} \cdot \vec{v} = 0$

Continuity is a differential equation describing conservation of mass.

## NAVIER-STOKES

Slow Flows (no inertia,  $Re < 1$ )  $\rho \frac{\partial \vec{v}}{\partial t} = -\vec{\nabla} P + \rho \vec{g} + \eta \nabla^2 \vec{v}$

The Navier-Stokes equations are force balances (per unit volume).

DO NOT MEMORIZE CONTINUITY OR N-S EQUATIONS. IF NEEDED, I WILL GIVE THEM TO YOU.

YOU DO NEED TO KNOW HOW TO USE THEM TO SOLVE FOR PRESSURE AND VELOCITY DISTRIBUTIONS.

## BOUNDARY CONDITIONS

1. NO SLIP at solid surfaces
2. No infinite velocities

## MAXIMUM VELOCITY

for  $v_x = v_x(y)$ ,  $\frac{\partial v_x}{\partial y} = 0$

## AVERAGE VELOCITY and VOLUMETRIC FLOW RATE

$$v_{ave} = \frac{Q}{A} = \frac{1}{A} \int v_x dA$$

# Linear Viscoelasticity

Stress Relaxation Modulus  $G(t) \equiv \frac{\sigma(t)}{\gamma_0}$

BOLTZMANN SUPERPOSITION: Add effects of many step strains to construct ANY linear viscoelastic deformation.

Viscosity  $\eta_0 = \int_0^{\infty} G(t) dt$

Creep Compliance  $J(t) \equiv \frac{\gamma(t)}{\sigma}$

Steady State Compliance  $J_s^0 = \lim_{t \rightarrow \infty} \left[ J(t) - \frac{t}{\eta_0} \right]$

$$J_s^0 = \frac{1}{\eta_0^2} \int_0^{\infty} G(t) t dt$$

Recoverable Compliance  $R(t) \equiv \frac{\gamma_r(t)}{\sigma} = J(t) - \frac{t}{\eta_0}$

$$J_s^0 = \lim_{t \rightarrow \infty} [R(t)]$$

Terminal Relaxation Time  $\lambda = \eta_0 J_s^0 = \frac{\int_0^{\infty} G(t) t dt}{\int_0^{\infty} G(t) dt}$



# Linear Viscoelasticity

## OSCILLATORY SHEAR

apply strain  $\gamma(t) = \gamma_0 \sin(\omega t)$

measure stress  $\sigma(t) = \gamma_0 [G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t)]$

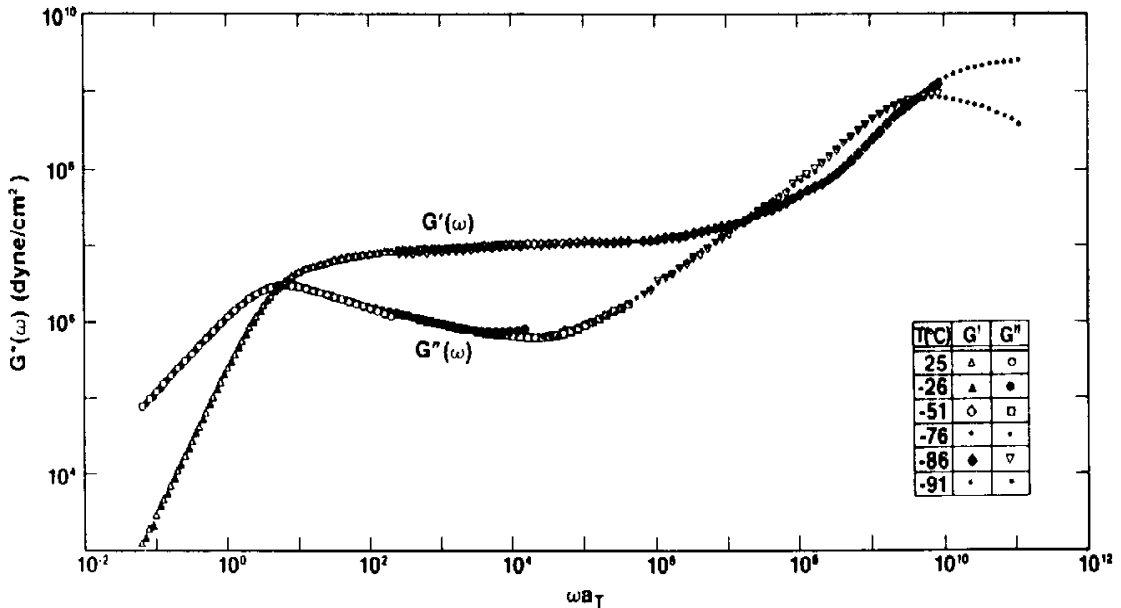
Loss Tangent  $\tan(\delta) = \frac{G''}{G'}$

Viscosity  $\eta_0 = \lim_{\omega \rightarrow 0} \left[ \frac{G''(\omega)}{\omega} \right]$

Steady State Compliance  $J_s^0 = \lim_{\omega \rightarrow 0} \left[ \frac{G'(\omega)}{[G''(\omega)]^2} \right]$

# Linear Viscoelasticity

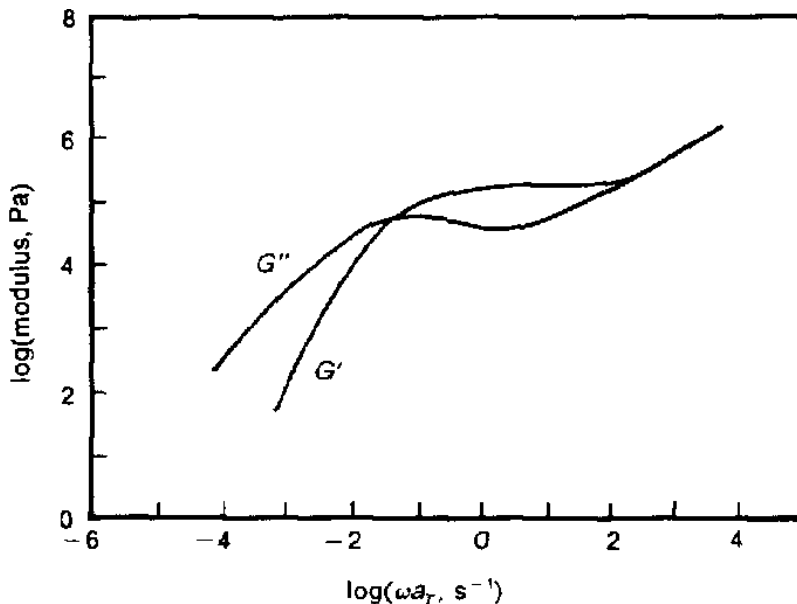
## OSCILLATORY SHEAR RESPONSE OF A LINEAR MONODISPERSE POLYMER



2. Storage and Loss Modulus Master Curves for Polybutadiene at Reference Temperature  $T_0 = 25^\circ\text{C}$ .

# Linear Viscoelasticity

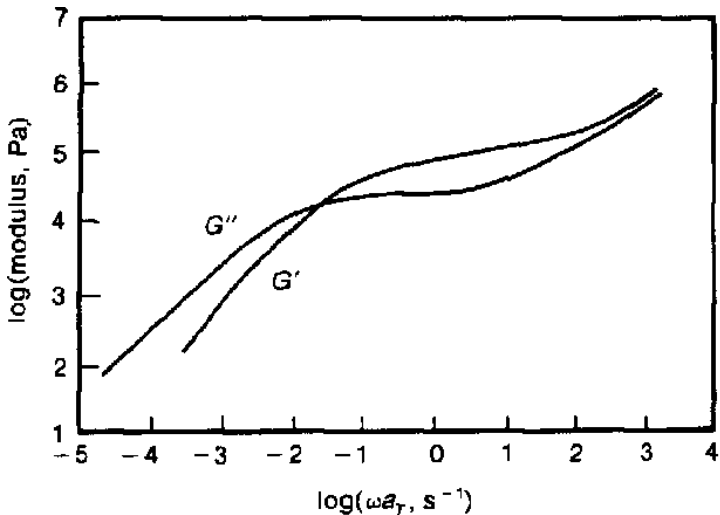
## EFFECTS OF MOLECULAR STRUCTURE



6. Storage and Loss Moduli for Polystyrene  $L15$  with  $M_w = 215000$ .

# Linear Viscoelasticity

## EFFECTS OF MOLECULAR STRUCTURE



7. Storage and Loss Moduli for Polystyrene with  $M_w = 315000$  and  $M_w/M_n = 1.8$ .

# MOLECULAR THEORIES

ROUSE MODEL:

$$D_R \sim \frac{1}{N} \quad \lambda_R \cong \frac{R^2}{D_R} \sim N^2 \quad G(\lambda_R) = \frac{\rho RT}{M} \quad \eta \cong \lambda_R G(\lambda_R) \sim N$$

$$G(t) \sim t^{1/2} \quad \text{for } \lambda_N < t < \lambda_R$$

REPTATION MODEL:

Relaxation is simple Rouse motion up to the Rouse relaxation time of an entanglement strand.

$$\lambda_e \sim N_e^2 \quad G(t) \sim t^{1/2} \quad \text{for } \lambda_N < t < \lambda_e$$

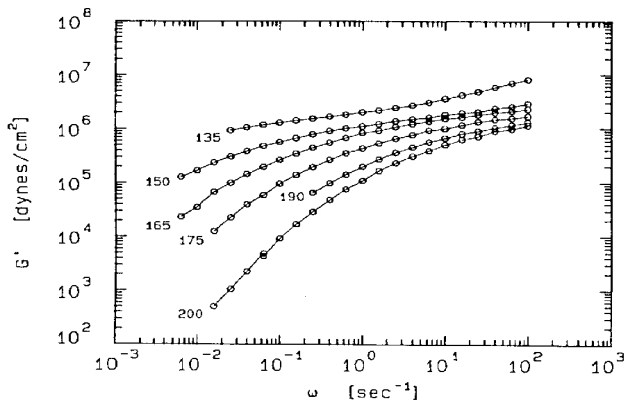
Plateau Modulus

$$G_N^0 = \frac{\rho RT}{M_e}$$

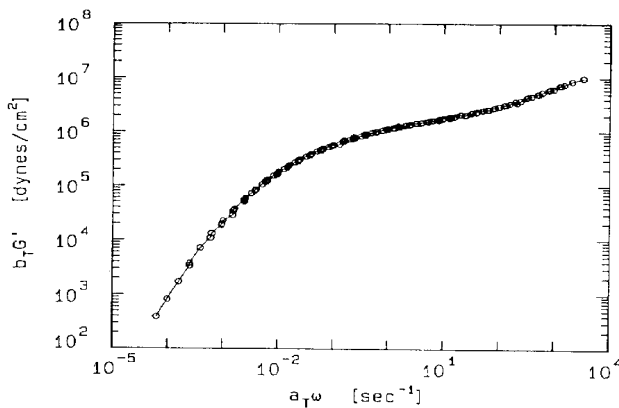
$$\lambda_d \cong \frac{L^2}{D_R} \sim N^3 \quad D \cong \frac{R^2}{\lambda_d} \sim \frac{1}{N^2} \quad \eta \cong \lambda_d G_N^0 \sim N^3$$

# Linear Viscoelasticity

## TIME-TEMPERATURE SUPERPOSITION



(A)



(B)

Figure 1: (A) Isothermal Storage Modulus  $G'(\omega)$  of a Polystyrene at Six Temperatures. (B) Storage Modulus Master Curve at Reference Temperature  $T_0 = 150$  °C.

# Nonlinear Stresses

Shear Stress is an odd function of shear strain and shear rate.

$$\sigma(\gamma) = G\gamma + A_1\gamma^3 + \dots$$

$$\sigma(\dot{\gamma}) = \eta_0\dot{\gamma} + A_2\dot{\gamma}^3 + \dots$$

Apparent viscosity is thus an even function of shear rate.

$$\eta(\dot{\gamma}) \equiv \frac{\sigma(\dot{\gamma})}{\dot{\gamma}} = \eta_0 + A_2\dot{\gamma}^2 + \dots$$

The first normal stress difference is an even function of shear strain and shear rate.

$$N_1(\gamma) = G\gamma^2 + B_1\gamma^4 + \dots$$

The first term comes from the Lodge-Meissner Relation

$$\frac{N_1}{\sigma} = \gamma$$

$$N_1(\dot{\gamma}) = \Psi_1^0\dot{\gamma}^2 + B_2\dot{\gamma}^4 + \dots$$

First Normal Stress Coefficient is thus an even function of shear rate.

$$\Psi_1 \equiv \frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} = \Psi_1^0 + B_2\dot{\gamma}^2 + \dots$$

# Nonlinear Step Strain SHORT-TIME RELAXATION PROCESSES

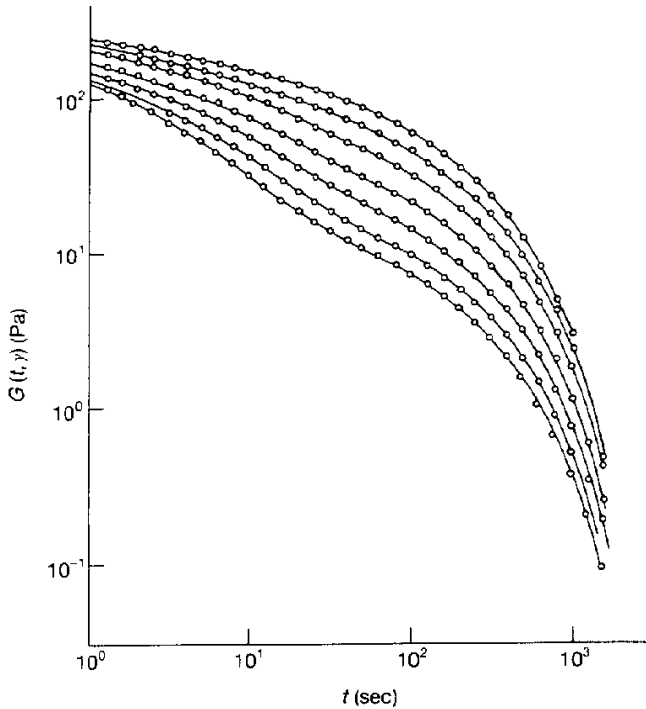


Figure 3: Nonlinear Relaxation Modulus  $G(t)$  for a 6% Polystyrene Solution at 30 °C.

## SEPARABILITY AT LONG TIMES

$$G(t, \gamma) = h(\gamma)G(t, 0)$$

$$N_1(t, \gamma) = \gamma^2 h(\gamma)G(t, 0)$$

$$h(\gamma) \leq 1$$



# Steady Shear

Apparent Viscosity

$$\eta \equiv \frac{\sigma}{\dot{\gamma}}$$

First Normal Stress Coefficient

$$\Psi_1 \equiv \frac{N_1}{\dot{\gamma}^2}$$

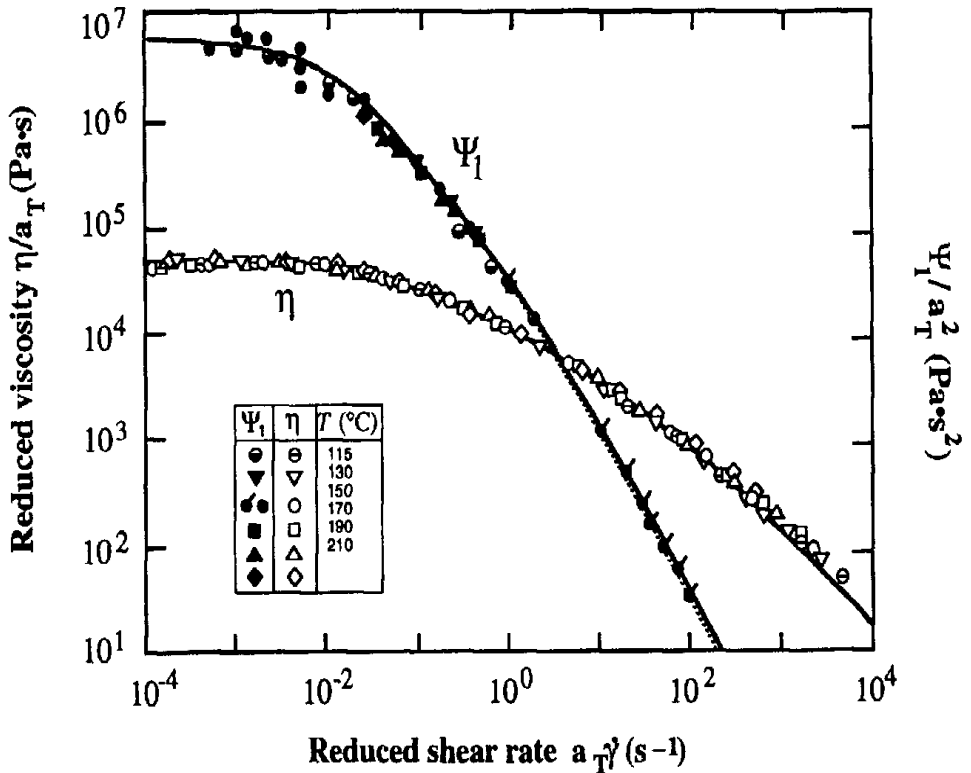


Figure 4: Shear Rate Dependence of Viscosity and First Normal Stress Coefficient for Low Density Polyethylene.

# Steady Shear APPARENT VISCOSITY MODELS

Power Law Model  $\eta = \eta_0 |\lambda \dot{\gamma}|^{n-1}$

Cross Model  $\eta = \eta_0 [1 + |\lambda \dot{\gamma}|^{1-n}]^{-1}$

Carreau Model  $\eta = \eta_0 [1 + (\lambda \dot{\gamma})^2]^{(n-1)/2}$

## MOLECULAR WEIGHT DEPENDENCES

$$\eta_0 = K M_w^{3.4}$$

$$\lambda = \frac{\eta_0}{G_N^0} \sim M_w^{3.4}$$

$$\Psi_{1,0} = 2\eta_0^2 J_s^0 \sim M_w^{6.8}$$

## THE COX-MERZ EMPIRICISM

$$\eta(\dot{\gamma}) = |\eta^*(\omega)| \quad (\omega = \dot{\gamma})$$

# Nonlinear Viscoelasticity START-UP OF STEADY SHEAR

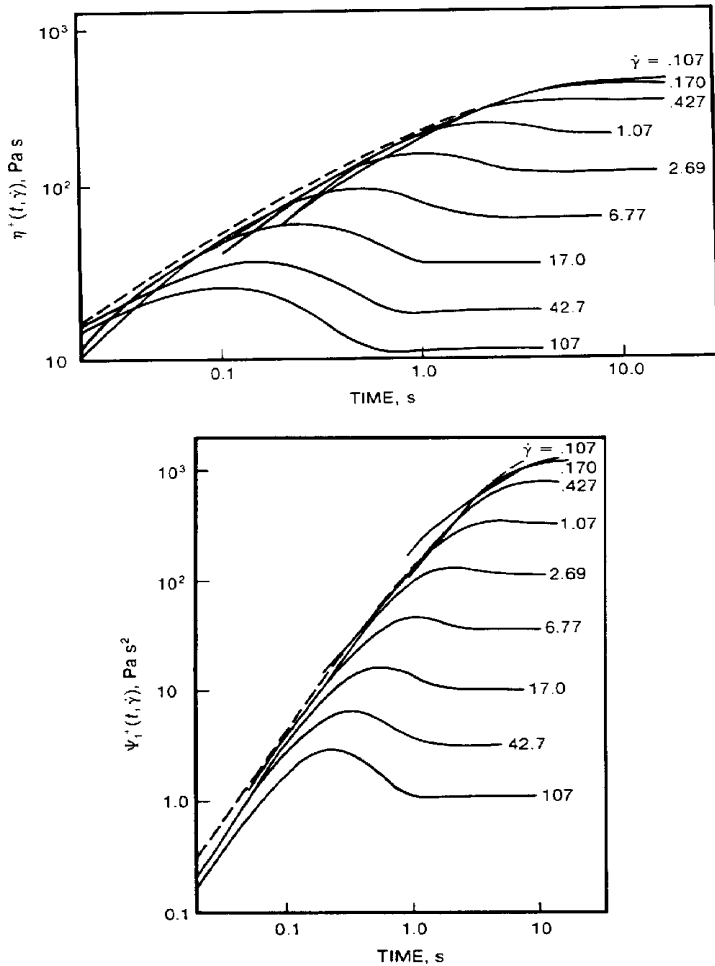


Figure 5: Shear Stress Growth and Normal Stress Growth Coefficients for the Start-Up of Steady Shear of a Polystyrene Solution.

Start-up of nonlinear steady shear shows maxima in shear and normal stress growth functions, indicating extra short-time relaxation processes induced by the large shear rate.

# Nonlinear Viscoelasticity CESSATION OF STEADY SHEAR

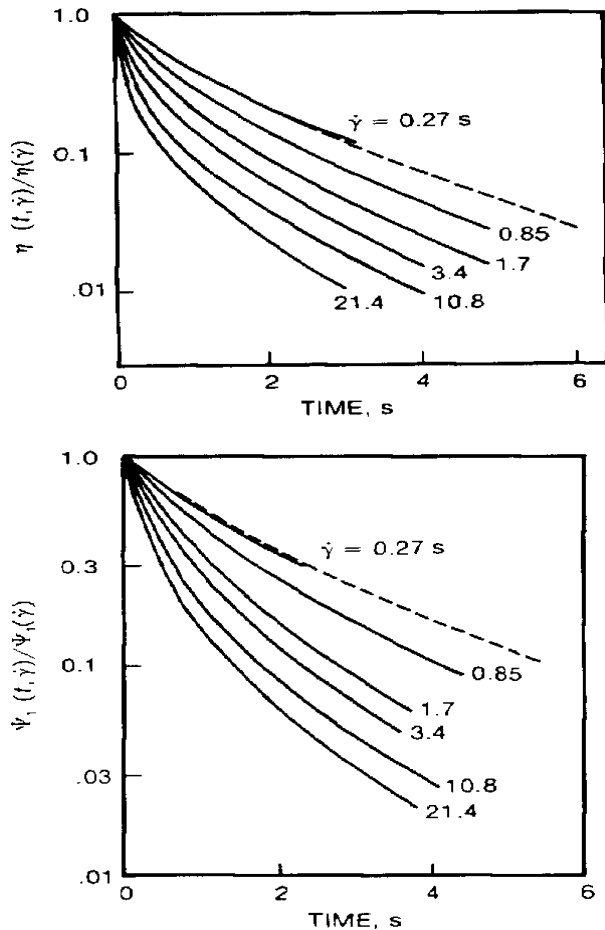


Figure 6: Shear Stress Decay and Normal Stress Decay Coefficients for Cessation of Steady Shear Flow of a Polyisobutylene Solution.

Shear and normal stresses both decay FASTER at larger shear rates, consistent with long relaxation modes being replaced by shorter-time relaxation processes that are activated in steady shear.

# Nonlinear Viscoelasticity

## NONLINEAR CREEP

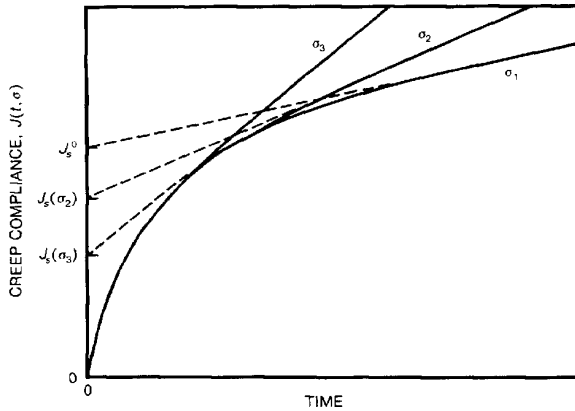


Figure 7: Creep Compliance at a Linear Viscoelastic Stress  $\sigma_1$  and two Nonlinear Stresses with  $\sigma_3 > \sigma_2 > \sigma_1$ .

As stress increases, the viscosity drops and the recoverable strain drops, consistent with large stresses inducing additional dissipation mechanisms.

## NONLINEAR RECOVERY

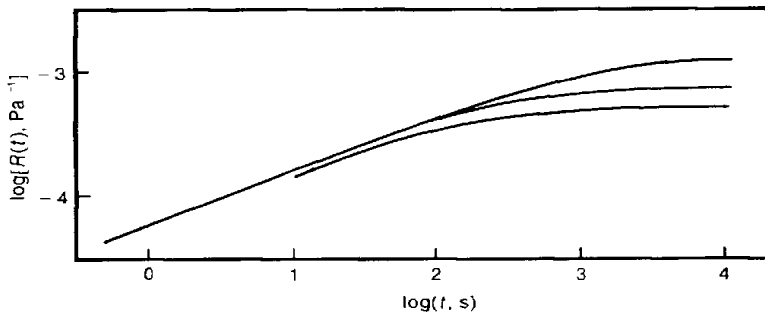


Figure 8: Recoverable Compliance after Creep at Three Stress Levels (Increasing Creep Stress from Top to Bottom).

# Rheometry

## Couette Devices:

- Gap Loading vs. Surface Loading
- Controlled Stress vs. Controlled Strain
- Transducer (and Instrument) Compliance
- Cone & Plate
- Parallel Plate
- Eccentric Rotating Disks
- Concentric Cylinder
- Sliding Plates

## Poiseuille Devices:

- Pressure Driven vs. Rate Driven
- Capillary Rheometer
  - Wall Shear Stress
  - Wall Shear Rate
  - Bagley End Correction
  - Cogswell Orifice Short-Cut
  - Rabinowitch Correction
- Slit Rheometer
- Melt Flow Index
- Die Swell
- Extrudate Distortion

# Rheometry

## ROTATIONAL AND SLIDING SURFACE RHEOMETERS

### GEOMETRIES OF GAP LOADING INSTRUMENTS:

#### 1. Cone and Plate

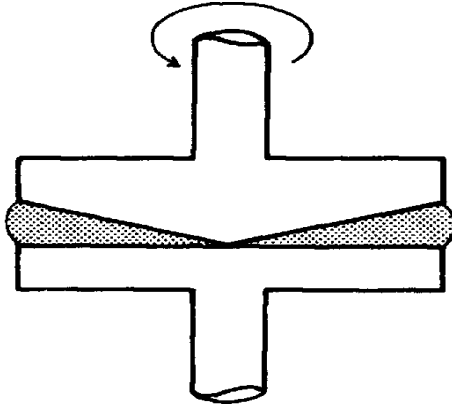


Figure 11: The Cone and Plate Rheometer.

#### 2. Parallel Disks

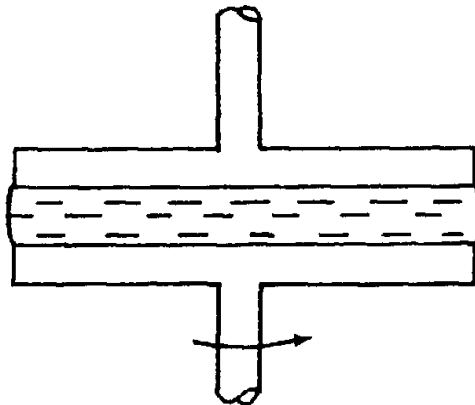


Figure 12: The Parallel Disk Rheometer.

# Rheometry

## CAPILLARY RHEOMETER

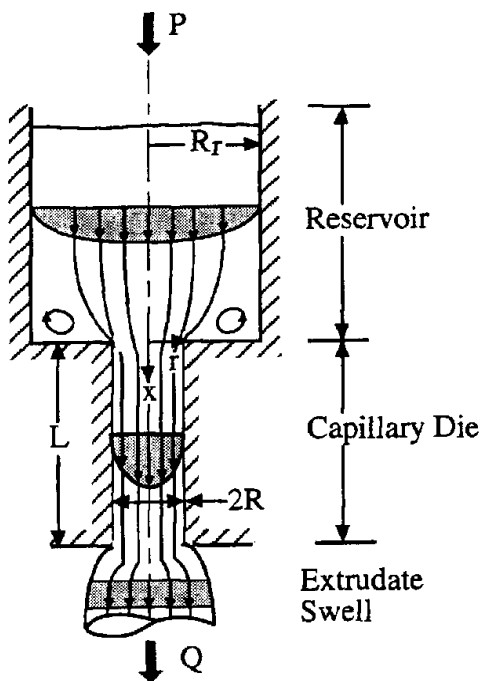


Figure 1: The Capillary Rheometer.

Wall Shear Stress

$$\sigma_w = \frac{R}{2} \left( -\frac{dP}{dz} \right)$$

Apparent Wall Shear Rate

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



# Rheometry

## SLIT AND CAPILLARY RHEOMETERS

### DIE SWELL

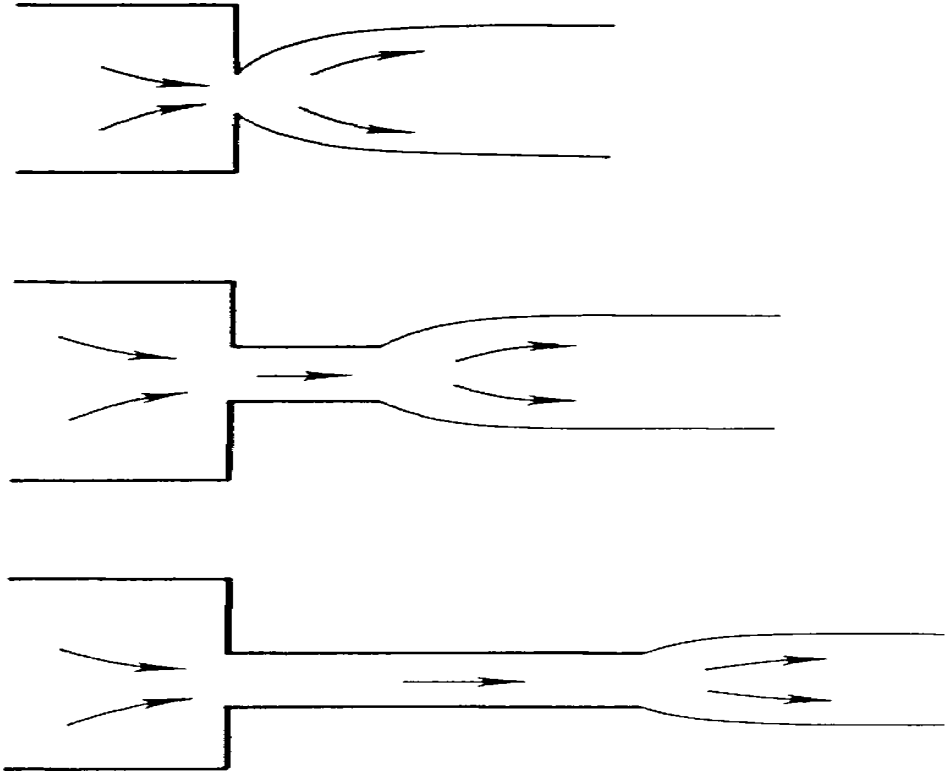


Figure 5: Extrudate Swell after Exiting the Die Diminishes as the Die is Made Longer because the Memory of the Flow Contraction at the Entrance is Reduced.

With a specific polymer and die, die swell increases with increasing shear stress.

Die swell increases as the die is shortened.

Die swell increases as the molecular weight increases.

Die swell increases as the molecular weight distribution is broadened, as it is particularly sensitive to the high molecular weight tail of the distribution.

# Molecular Structure Effects

## POLYDISPERSITY

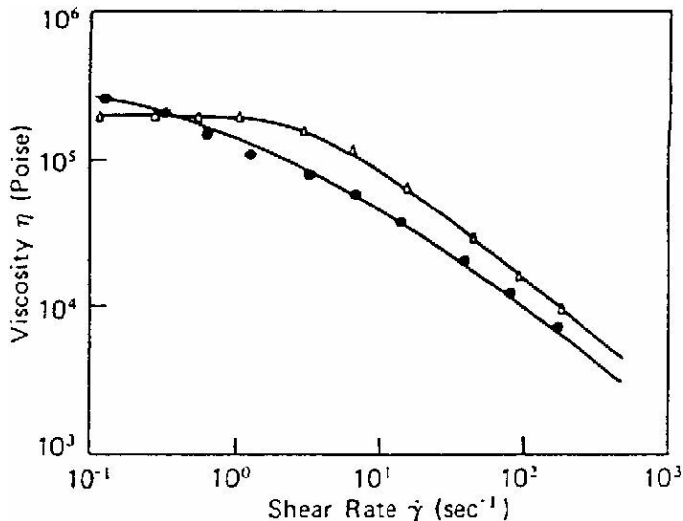


Figure 21: Apparent Viscosity in Steady Shear for Polystyrene. Filled symbols have  $M_w = 260000$  with  $M_w/M_n = 2.4$ . Open symbols have  $M_w = 160000$  with  $M_w/M_n < 1.1$ .

Zero shear viscosity is simply a function of weight-average molecular weight.

$$\eta_0 = \begin{cases} K_1 M_w & \text{for } M_w < M_c \text{ (unentangled)} \\ K_2 M_w^{3.4} & \text{for } M_w > M_c \text{ (entangled)} \end{cases}$$

Steady state compliance, and other measures of elasticity (such as first normal stress difference and die swell) are strong functions of polydispersity.

$$J_s^0 \sim \left( \frac{M_z}{M_w} \right)^a \quad \text{with } 2 < a < 3.7$$

# Molecular Structure Effects

## BRANCHING

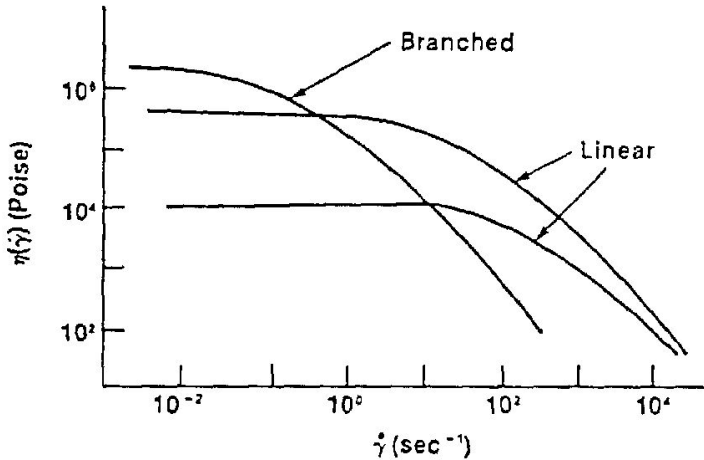


Figure 22: Apparent Viscosity of Randomly Branched Polymers Compared to Linear Polymers.

Monodisperse entangled branched polymers have a stronger dependence of viscosity on molecular weight than linear polymers.

$$\eta_0 \sim \exp\left(\frac{\nu M_b}{M_e}\right)$$

Monodisperse entangled branched polymers have steady state compliance increasing with molecular weight.

$$J_s^0 = \frac{0.6M_b}{cRT}$$

$M_b$  is the molecular weight of the star arm.

Randomly branched polymers have effects of **both** branching and polydispersity.

# Injection Molding

## Injection Molding Cycle

- Inject and pack mold

- Extrude next shot once gate solidifies

- Eject part once part solidifies

## Injection Molding Economics

- Only inexpensive if we make many parts

## Injection Molding Window

## Poiseuille Flow in Runners and Simple Cavities

- Calculate injection pressure to fill mold

- Balance runner systems

- Calculate clamping force

- Assumptions:

  - Isothermal

  - Newtonian

# Extrusion

Extruder Characteristic:

$$Q = \alpha N - \frac{\beta}{\mu} \Delta P$$

Die Characteristic:

$$Q = \frac{K}{\mu} \Delta P$$

together, they determine the Operating Point

Pumping vs. Mixing:

Compression Ratio and Flow Restrictions

Pressure Distribution

Residence Time Distribution

Twin Screw Extrusion