

Done with Material Functions.

What now?

Chapter 5: Material Functions

CM4650
Polymer Rheology
Michigan Tech

Steady Shear Flow Material Functions

Imposed Kinematics:

$$\underline{\dot{\gamma}} = \begin{pmatrix} \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

$$\dot{\gamma}(t) = \dot{\gamma}_0 = \text{constant}$$

Material Stress Response:

$$\underline{\tau}(t) = \begin{pmatrix} \tau_{11}(t) & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Material Functions:

First normal stress coefficient: $\Psi_1(\dot{\gamma}_0) = \frac{\tau_{11} - \tau_{22}}{2\dot{\gamma}_0^2} = -\frac{\tau_{11} - \tau_{22}}{2\dot{\gamma}_0^2}$

Second normal stress coefficient: $\Psi_2(\dot{\gamma}_0) = \frac{\tau_{22} - \tau_{33}}{2\dot{\gamma}_0^2} = -\frac{\tau_{22} - \tau_{33}}{2\dot{\gamma}_0^2}$

Viscosity: $\eta(\dot{\gamma}_0) = \frac{\tau_{11}}{\dot{\gamma}_0} = -\frac{\tau_{22}}{\dot{\gamma}_0}$

1. Intro
2. Vectors/tensors
3. Newtonian
4. Standard Flows
5. Material Functions
6. **Experimental Behavior**
7. Inelastic effects
8. Memory effects
9. Advanced
10. Rheometry



Investigating Stress/Deformation Relationships (Rheology)

What are material functions and why do we need them?

For non-Newtonian fluids:

- We do not know the stress/deformation relationship ($\underline{\tau}(\underline{\dot{\gamma}})$)
- We approach stress/deformation investigations from two directions (**modeling**, **measuring**) to reveal the physics;
- Material functions organize comparisons

Diagram:

Hypothetical Constitutive equation: $\underline{\tau} = \underline{\tau}(\underline{\dot{\gamma}})$

Standard Velocity and pressure fields: $\underline{\dot{\gamma}} = \begin{pmatrix} \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, $p = p_0$

predictions of: $\Psi_1(\dot{\gamma}_0) = \frac{\tau_{11} - \tau_{22}}{2\dot{\gamma}_0^2} = -\frac{\tau_{11} - \tau_{22}}{2\dot{\gamma}_0^2}$

Material Functions (stress responses): $\eta(\dot{\gamma}_0) = \frac{\tau_{11}}{\dot{\gamma}_0} = -\frac{\tau_{22}}{\dot{\gamma}_0}$, $\Psi_2(\dot{\gamma}_0) = \frac{\tau_{22} - \tau_{33}}{2\dot{\gamma}_0^2} = -\frac{\tau_{22} - \tau_{33}}{2\dot{\gamma}_0^2}$

measurements of: $\underline{\dot{\gamma}} = \begin{pmatrix} \dot{\gamma}_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$, $p = p_0$

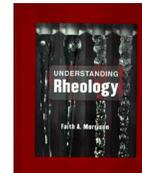
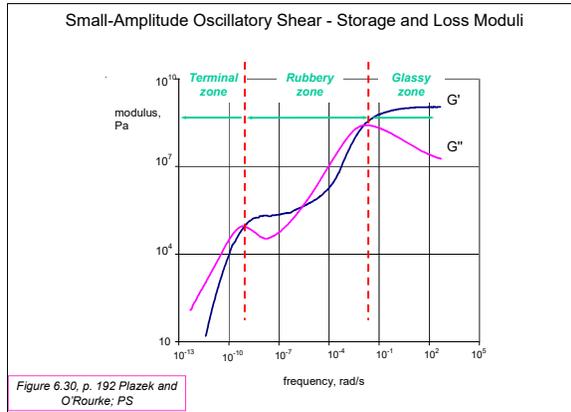
material + Ability to measure stresses

1. Choose a material function
2. Predict what Newtonian fluids would do
3. See what non-Newtonian fluids **do**
4. Hypothesize a $\underline{\tau}(\underline{\dot{\gamma}})$
5. Predict the material function
6. Compare with what non-Newtonian fluids **do**
7. Reflect, **learn**, revise model, repeat.

Let's focus more on material observations

Chapter 6: Experimental Data

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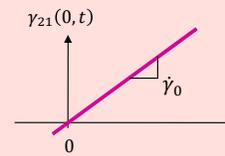
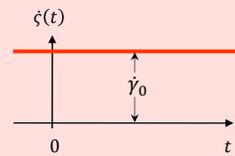
Steady Shear Flow Material Functions



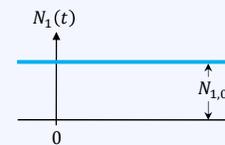
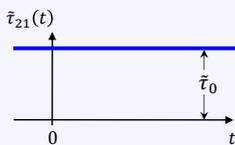
Imposed Kinematics:

$$\underline{v} \equiv \begin{pmatrix} \dot{\zeta}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

$$\dot{\zeta}(t) = \dot{\gamma}_0 = \text{constant}$$



Material Stress Response:



Material Functions:

Viscosity $\eta(\dot{\gamma}_0) \equiv \frac{\bar{\tau}_{21}}{\dot{\gamma}_0} = \frac{-\tau_{21}}{\dot{\gamma}_0}$

First normal-stress coefficient

$$\Psi_1(\dot{\gamma}_0) \equiv \frac{\bar{\tau}_{11} - \bar{\tau}_{22}}{\dot{\gamma}_0^2} = \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

Second normal-stress coefficient

$$\Psi_2(\dot{\gamma}_0) \equiv \frac{\bar{\tau}_{22} - \bar{\tau}_{33}}{\dot{\gamma}_0^2} = \frac{-(\tau_{22} - \tau_{33})}{\dot{\gamma}_0^2}$$

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Material Behavior Catalog (in terms of material functions)

Experimental Data (Chapter 6)

First recipe card: **Steady shear flow** →

What do we observe for

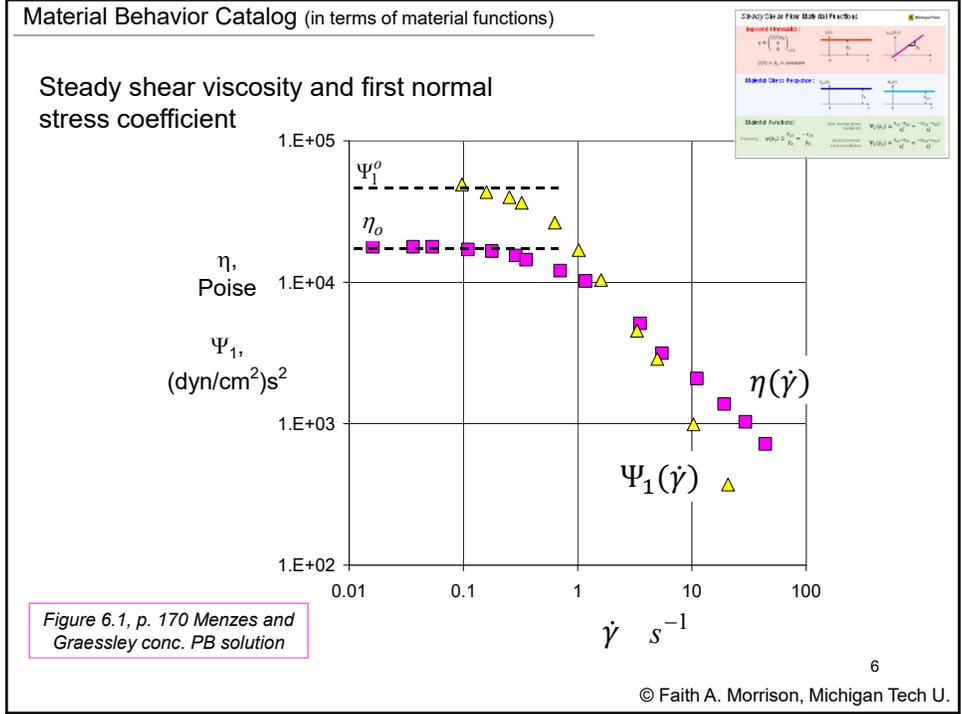
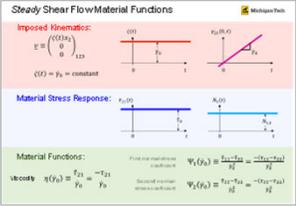
- Linear Polymers
- Limits on measurability
- Material effects - MW, MWD, branching, mixtures, copolymers
- Temperature and pressure

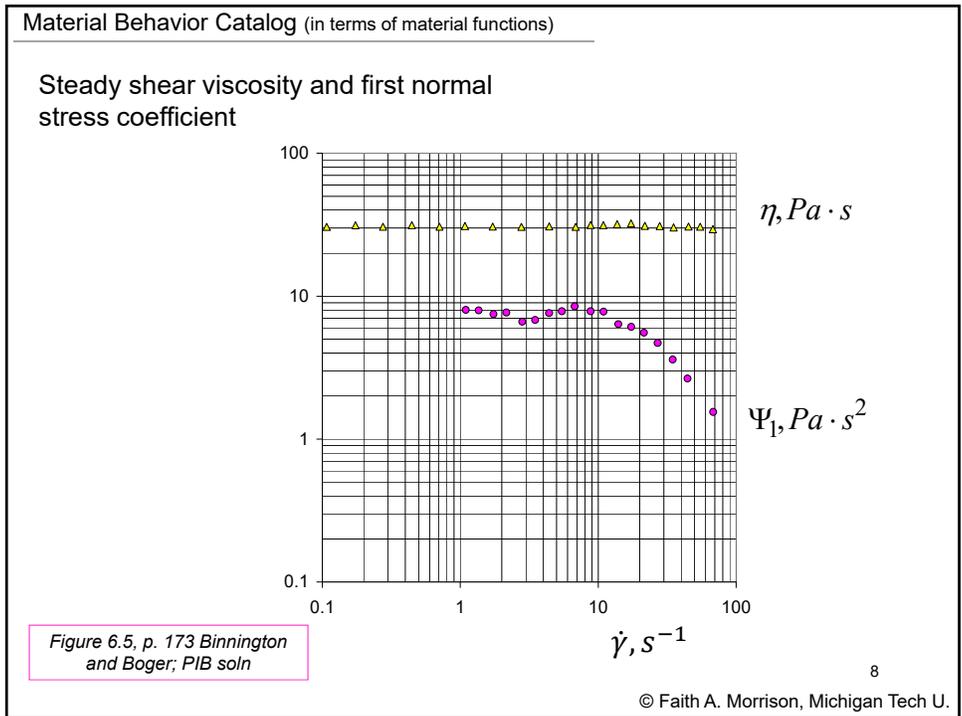
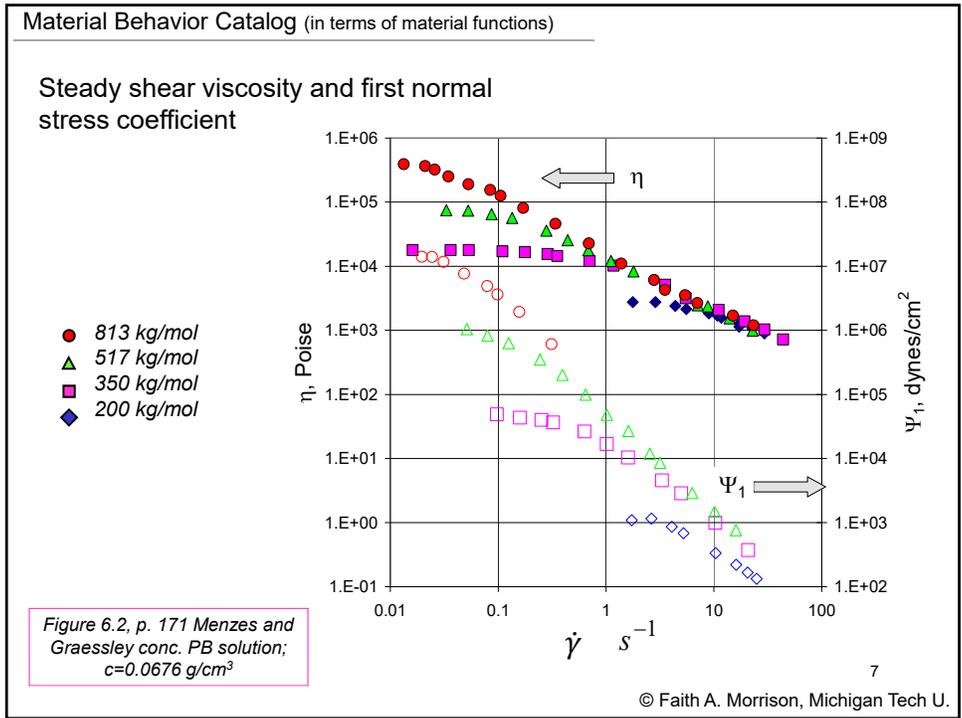
later ... (the rest of the recipe cards)

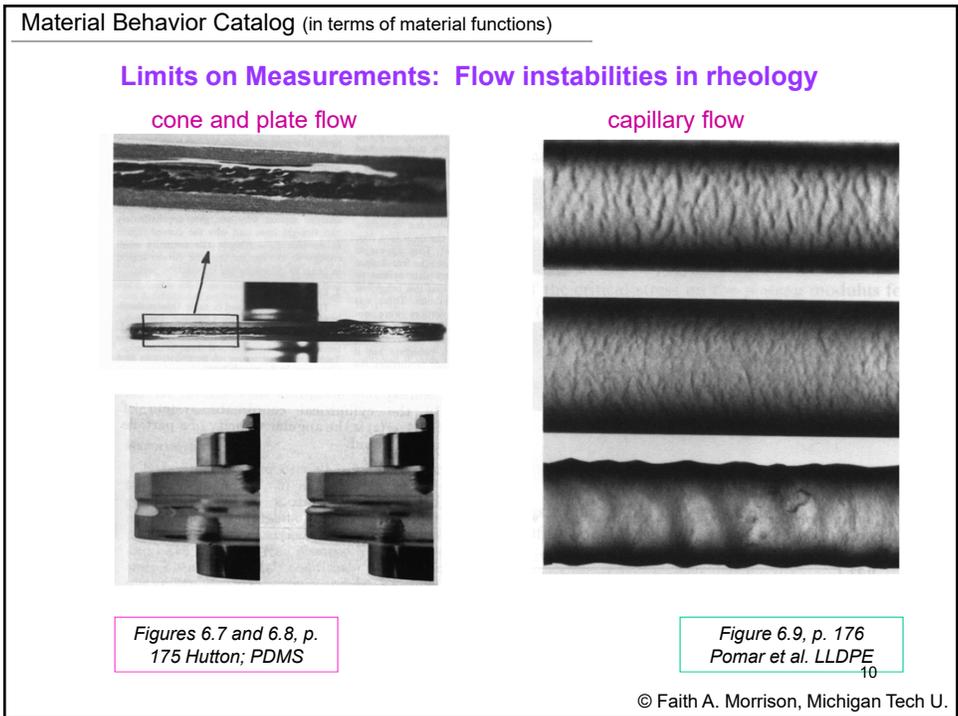
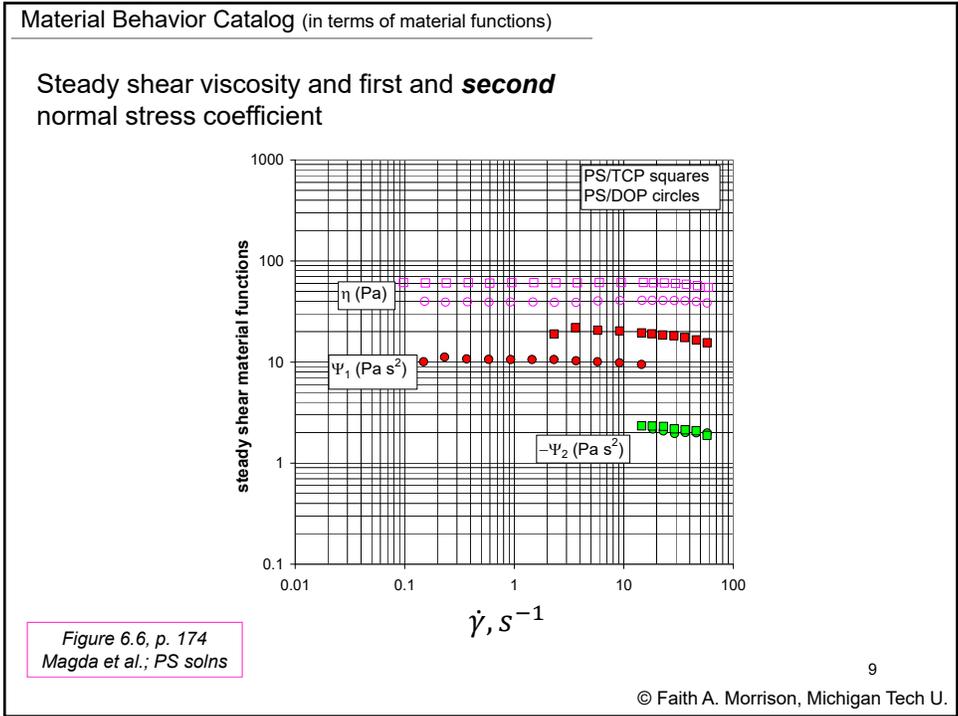
Unsteady shear flow (SAOS, step strain, start up, cessation)
Steady elongation
Unsteady elongation

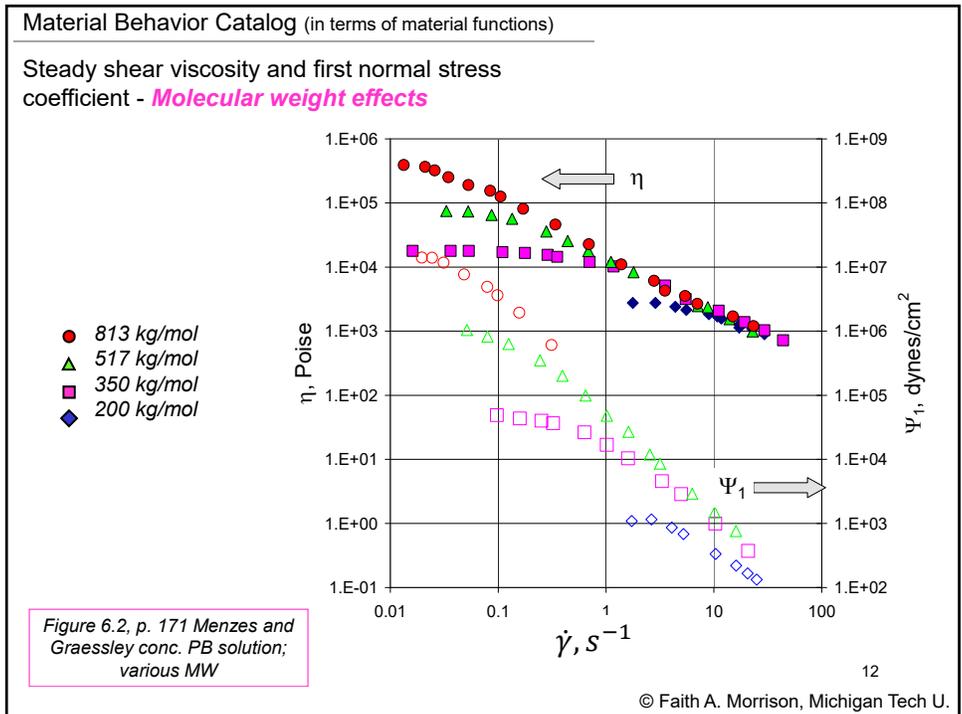
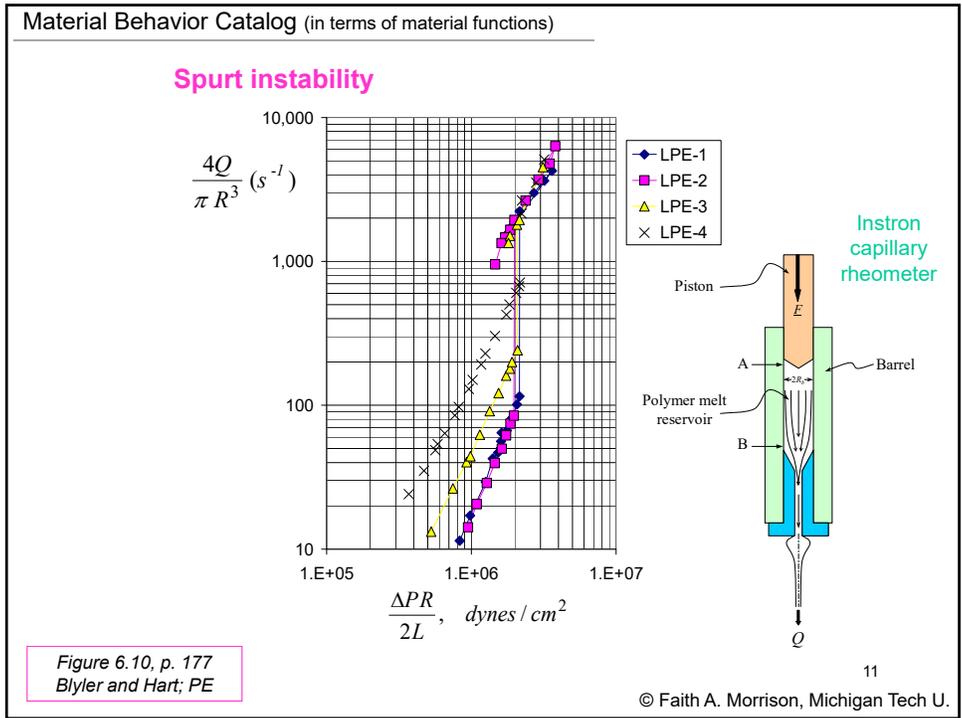
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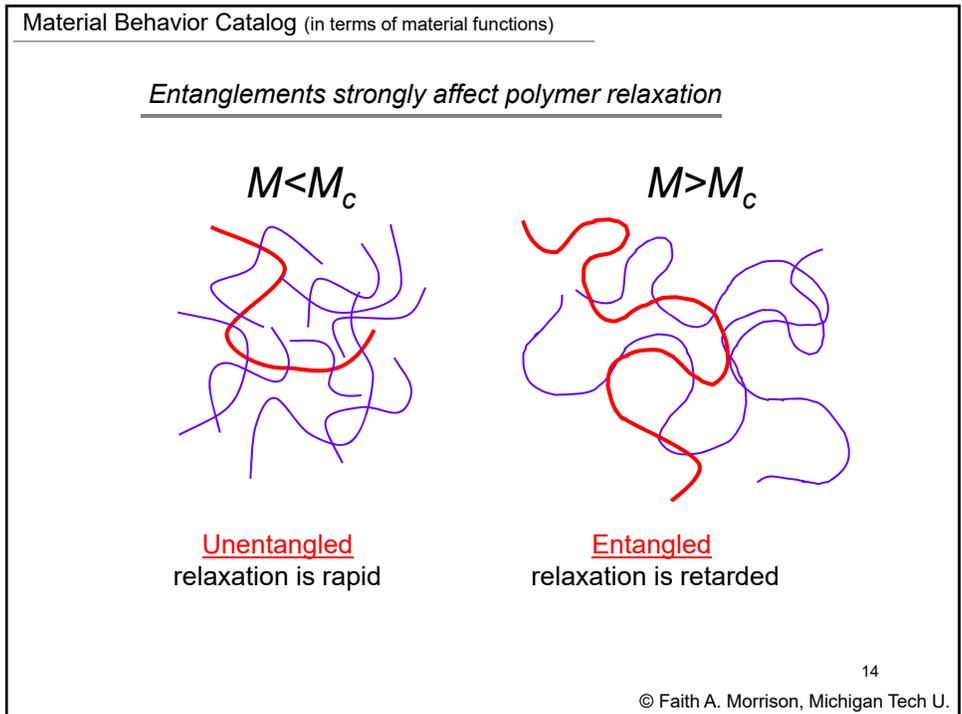
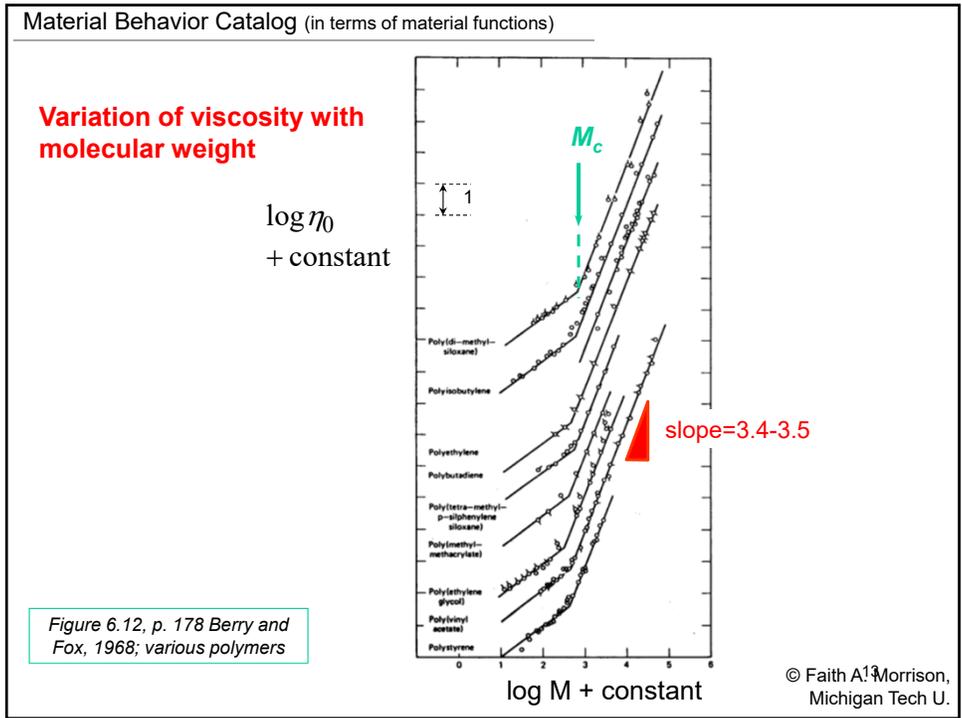
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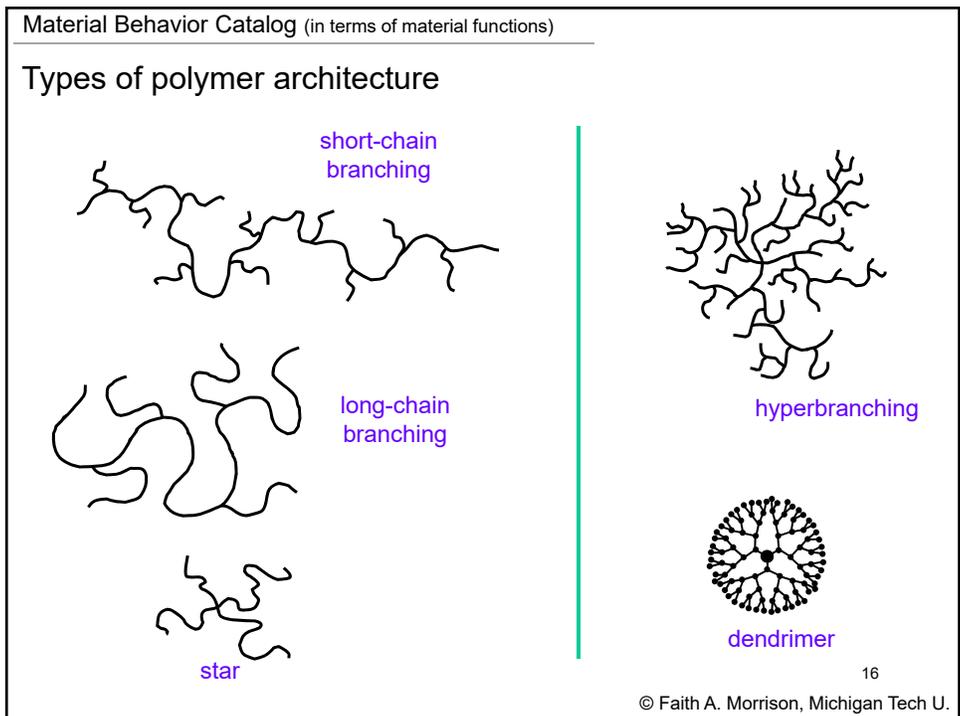
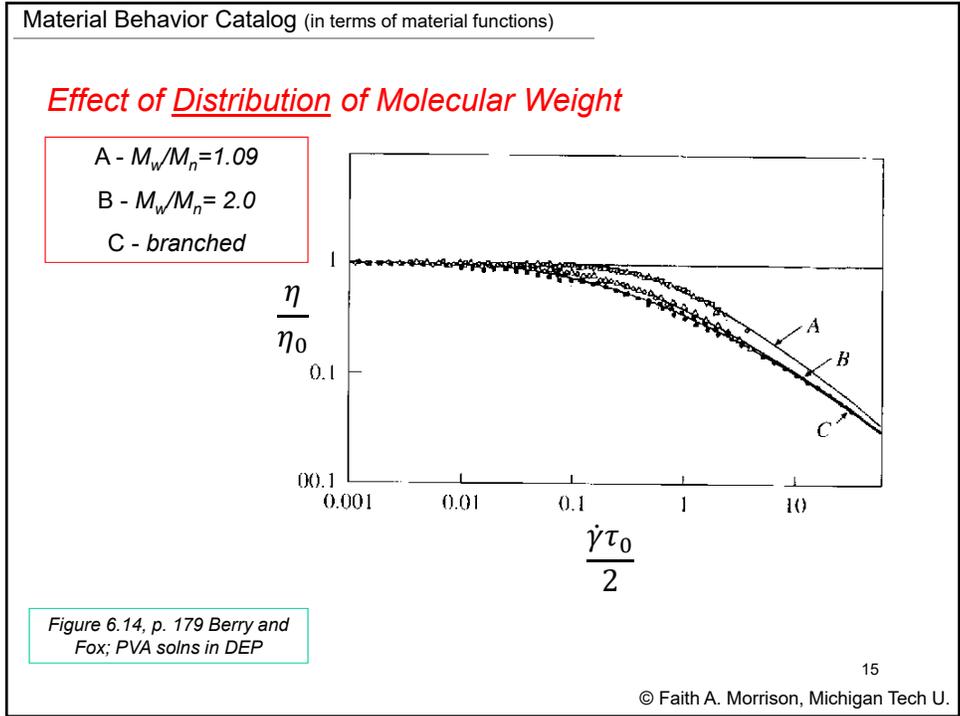


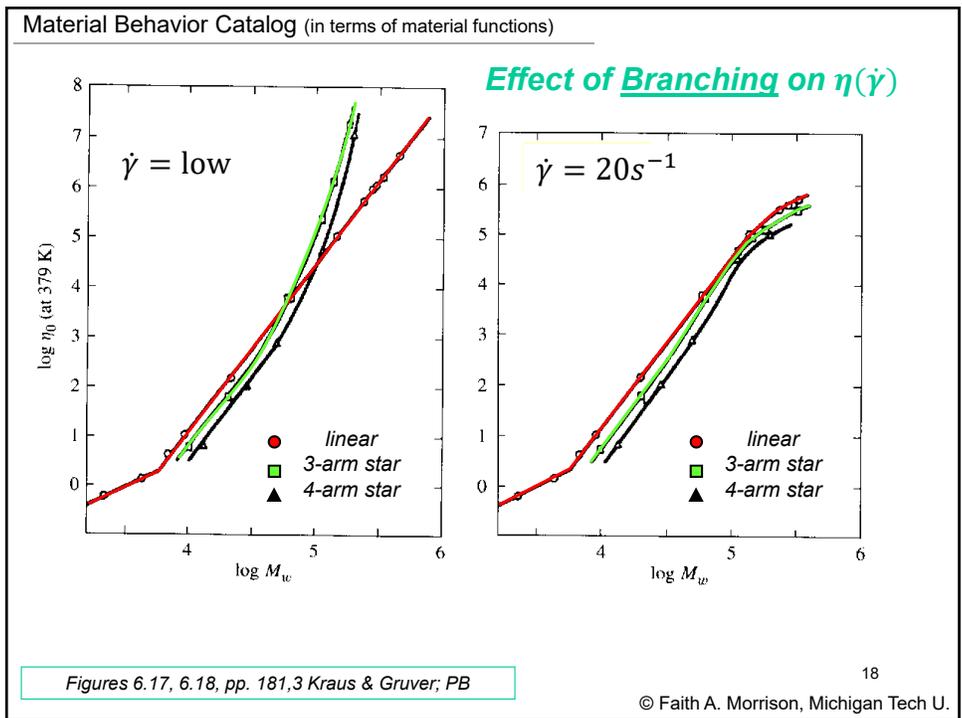
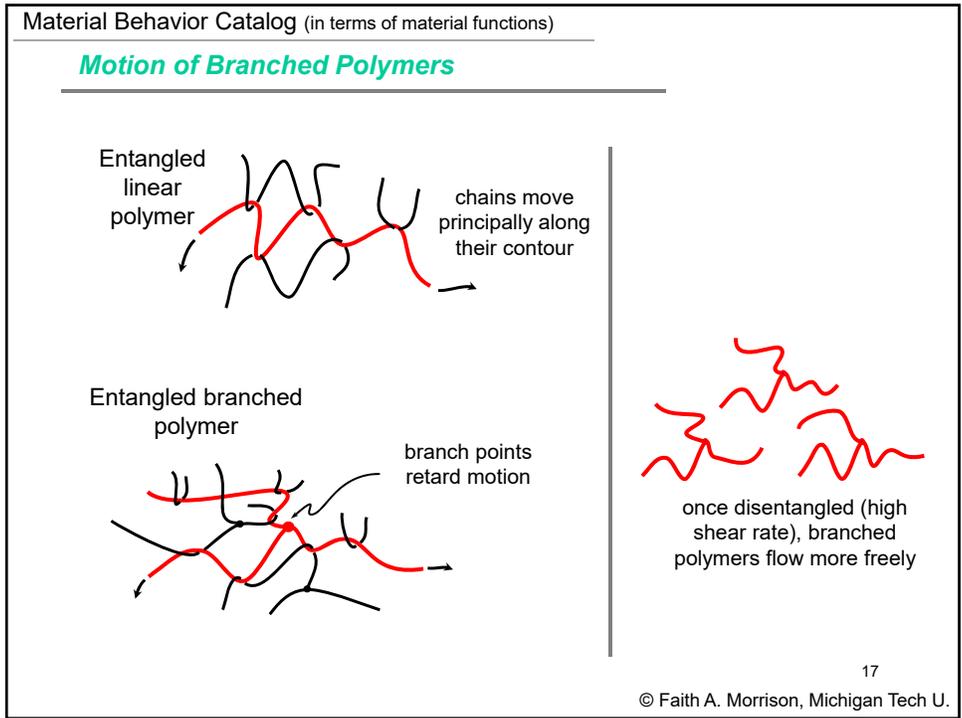


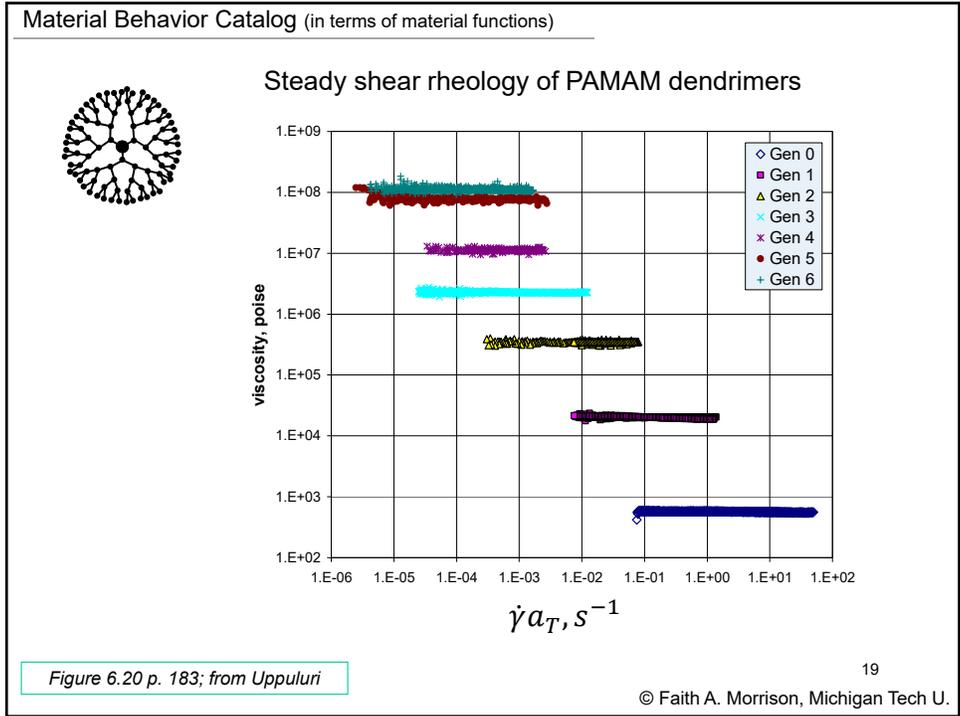




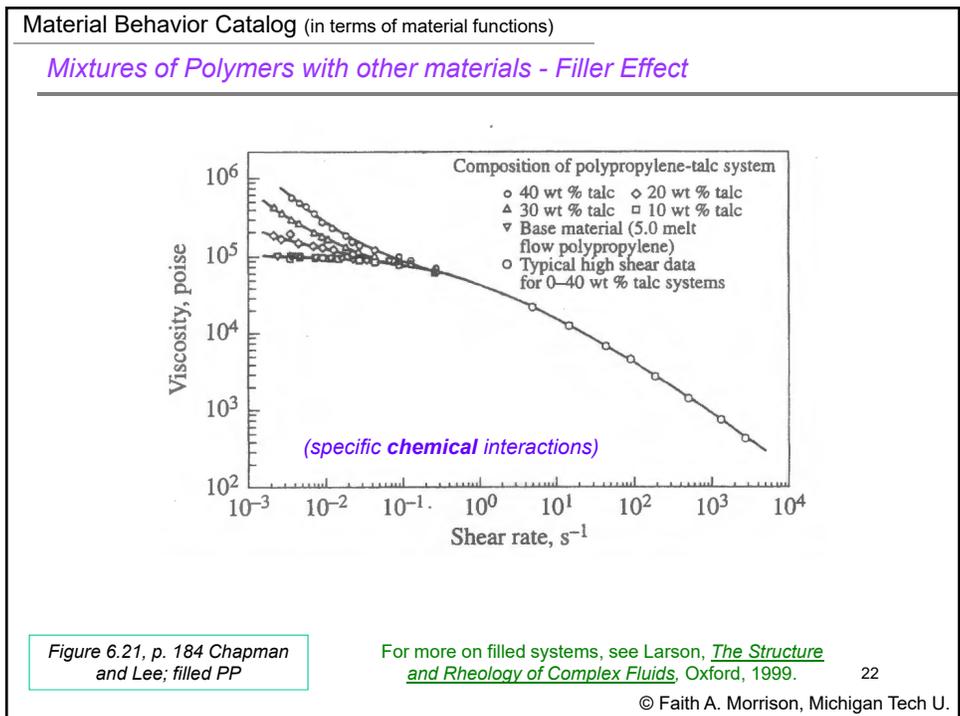
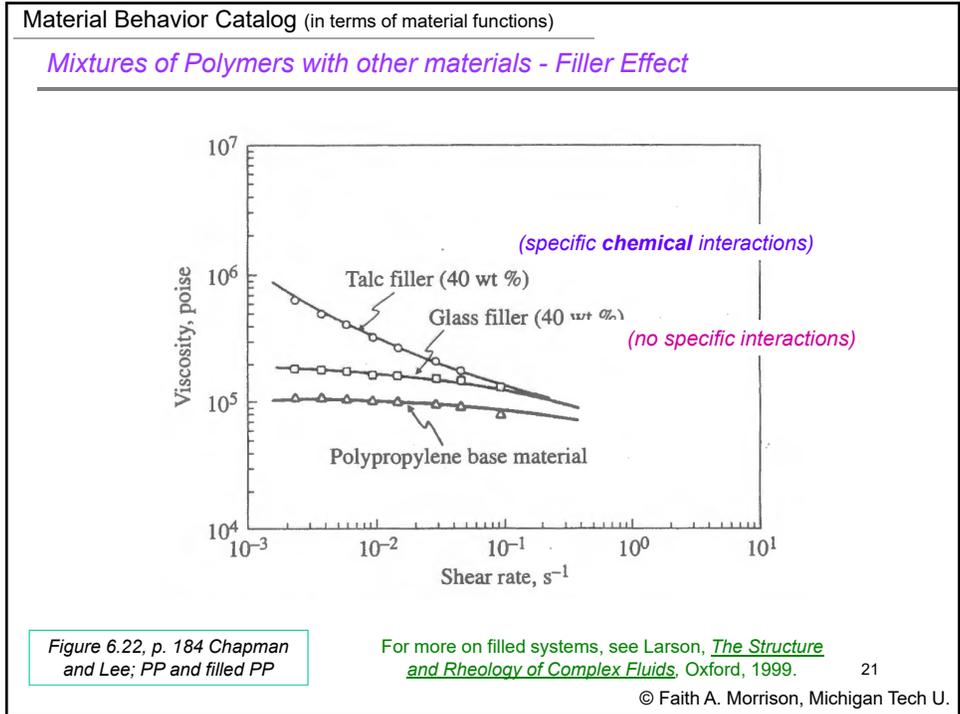


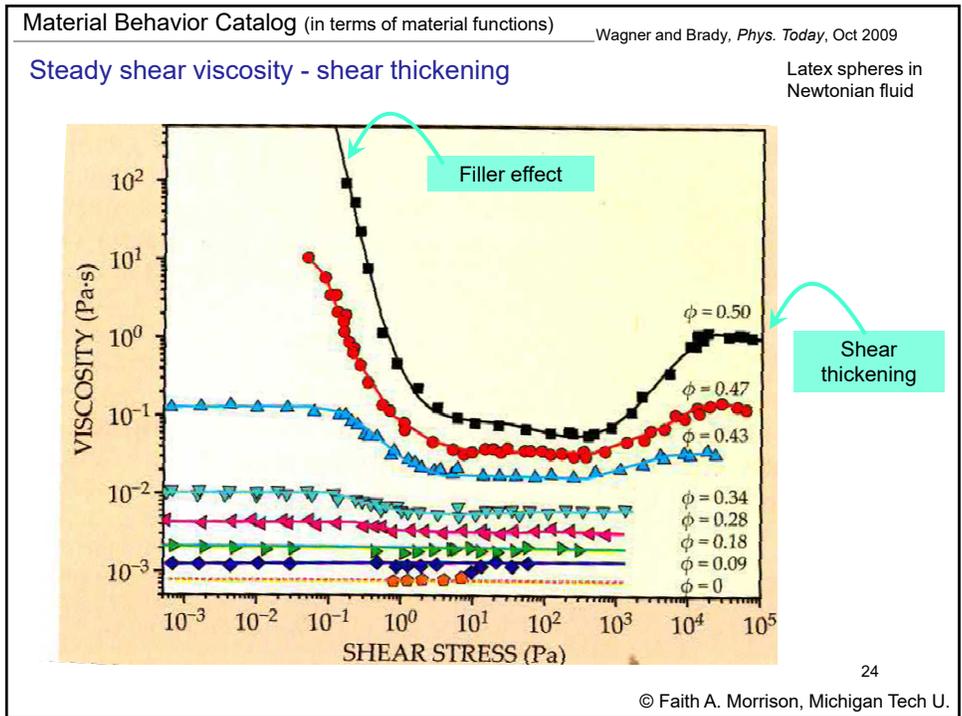
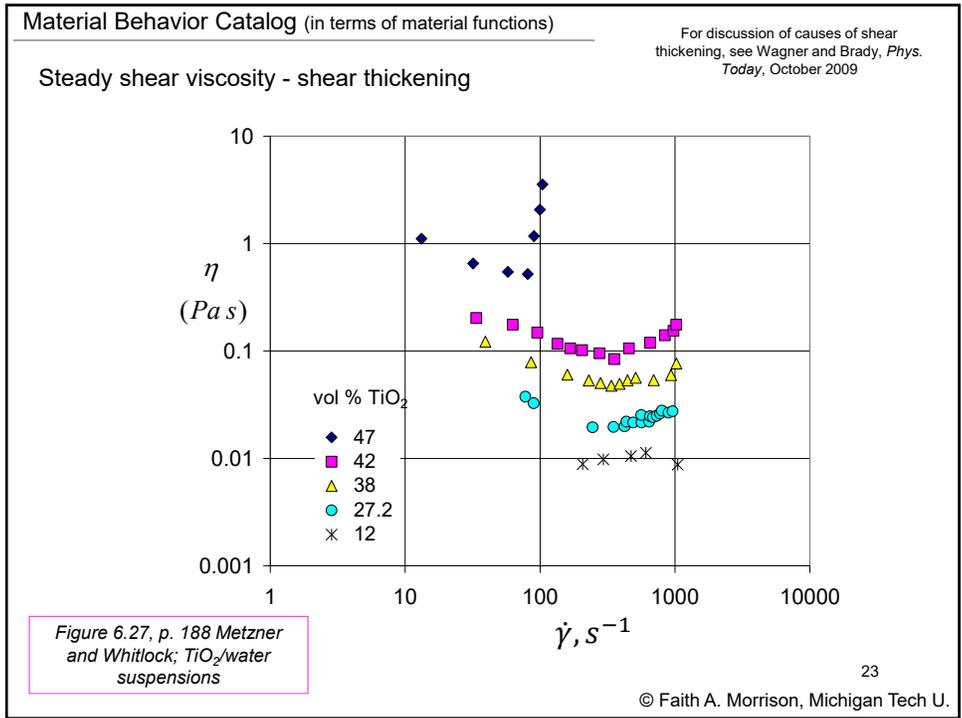


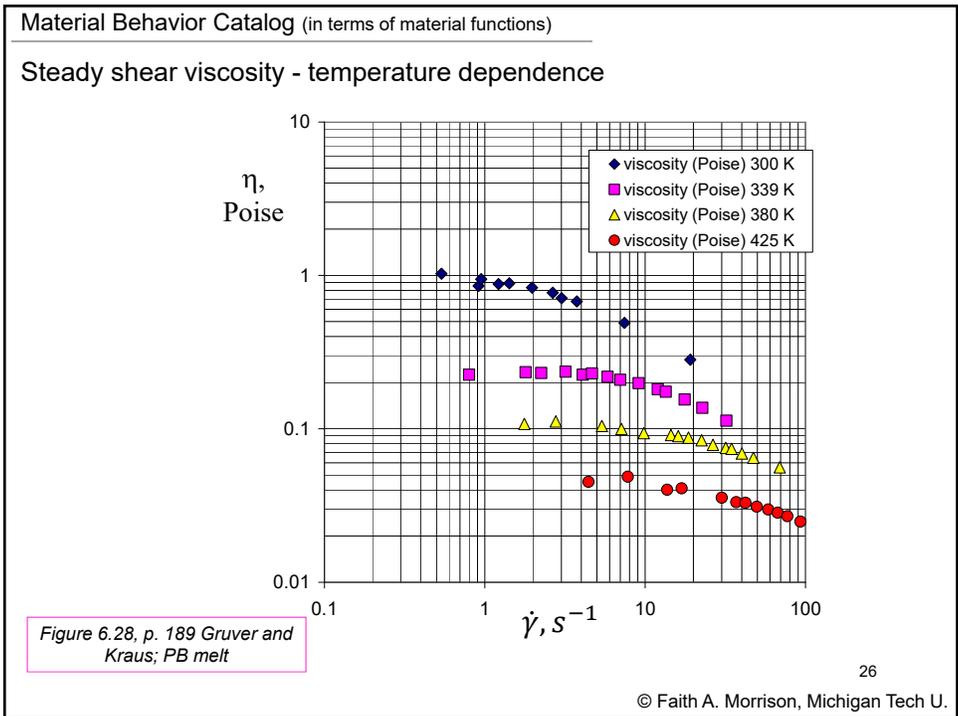
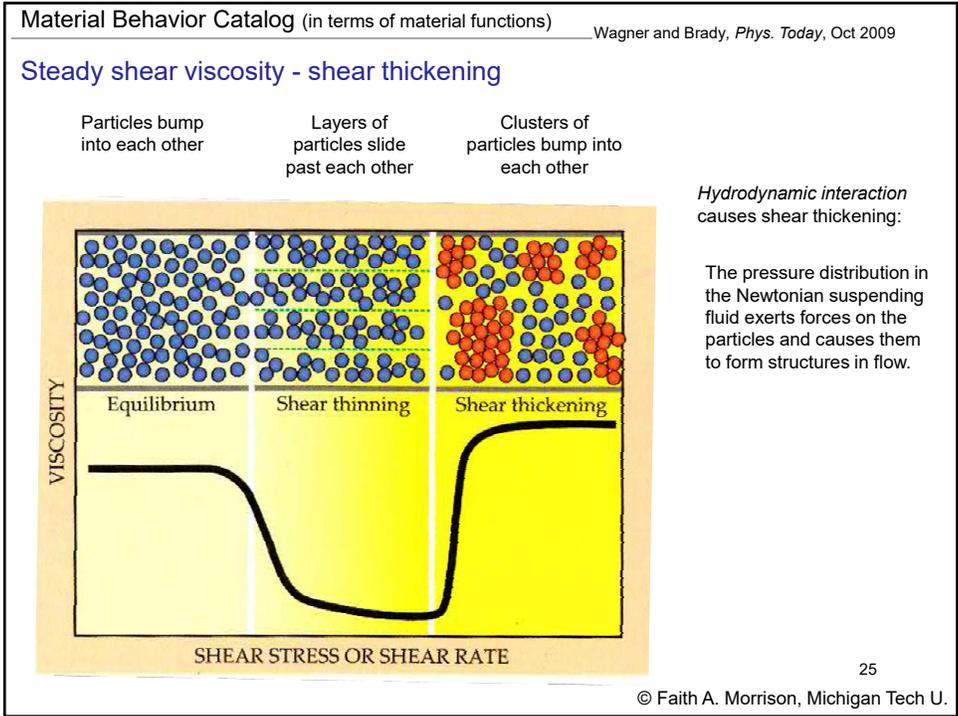


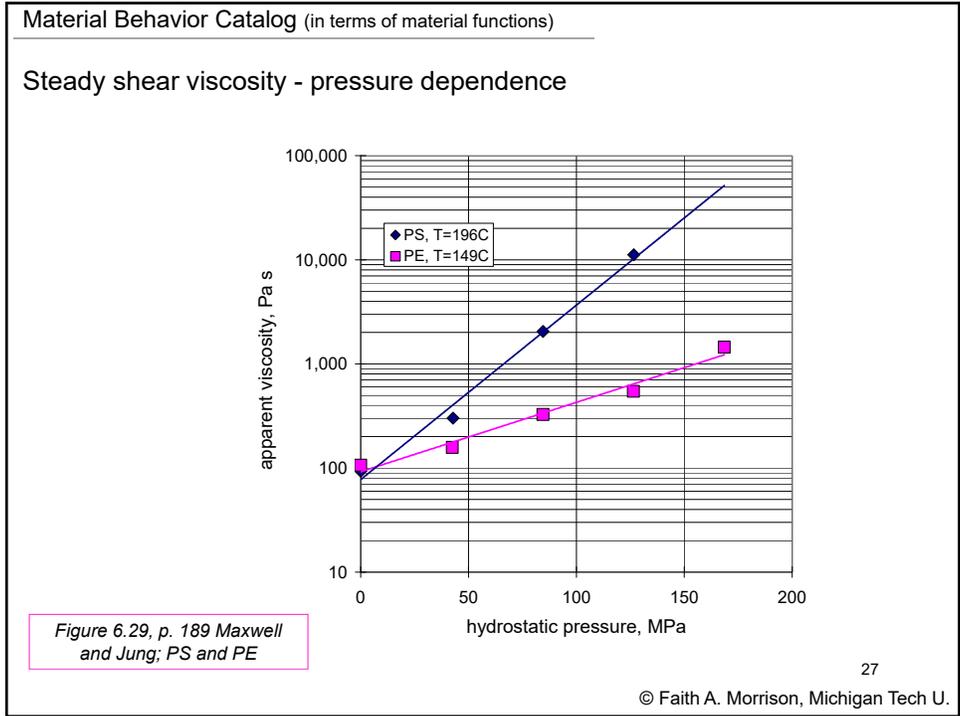


- Material Behavior Catalog (in terms of material functions)
- ### Steady Shear Summary:
1. General traits
 2. Effect of MW on linear polymers
 3. Effect of architecture
 4. Measurement issues
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- Material Behavior Catalog (in terms of material functions)
- Steady Shear Summary:
-
1. General traits
 2. Effect of MW (linear polymers)
 3. Effect of architecture
 4. Measurement issues
 5. Effect of chemical composition
 6. Effect of temperature
 7. Effect of pressure
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Material Behavior Catalog (in terms of material functions)

Experimental Data (continues)

Next:

Unsteady shear flows (small and large strain)
Steady elongation
Unsteady elongation

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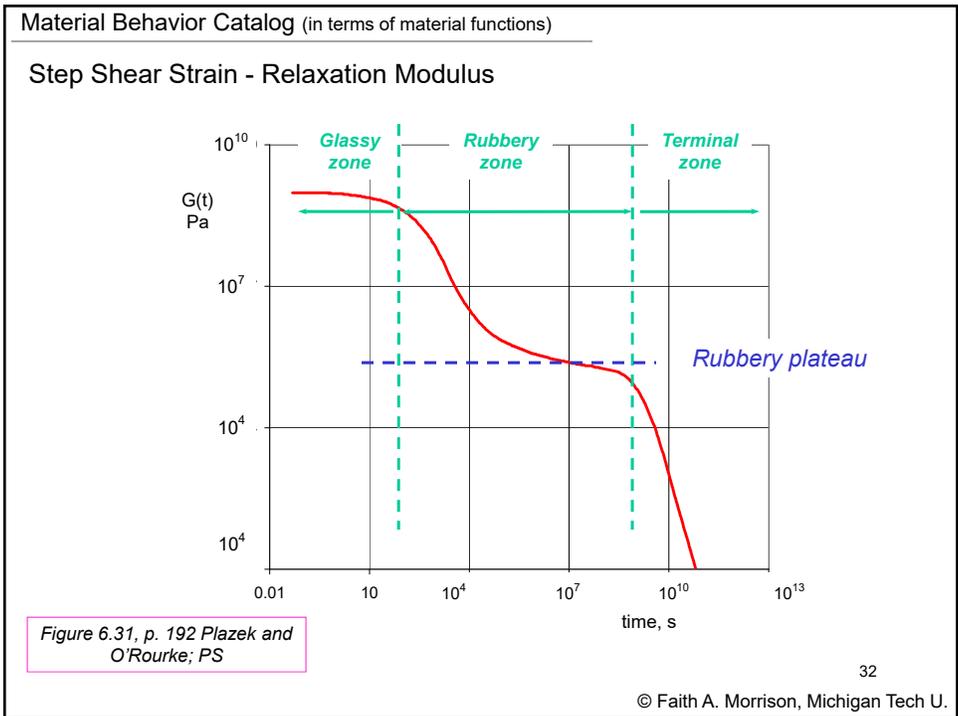
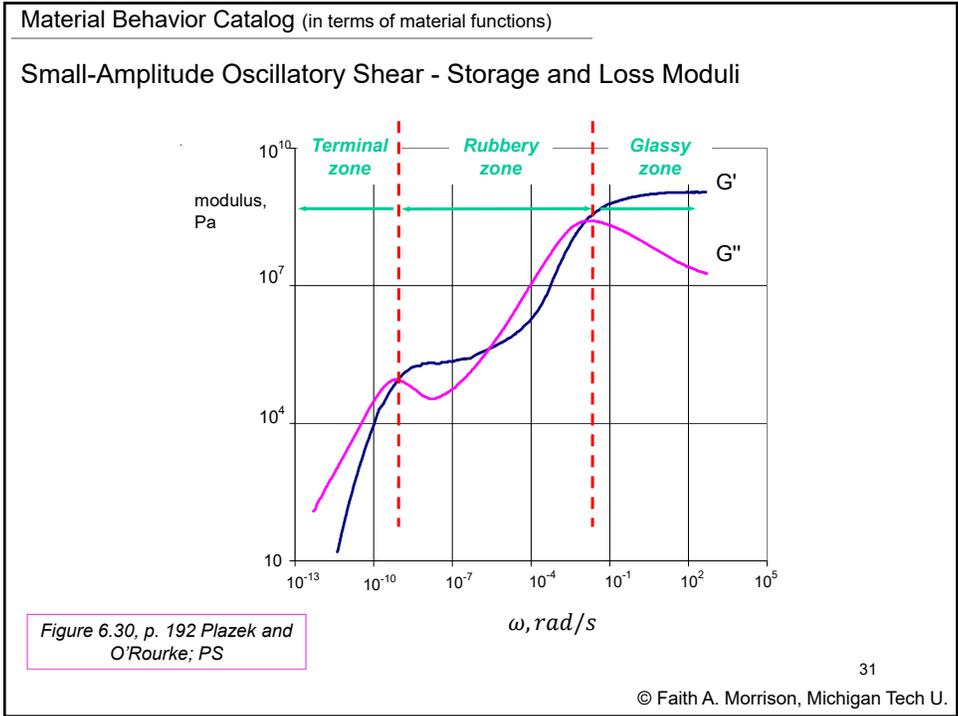
Material Behavior Catalog (in terms of material functions)

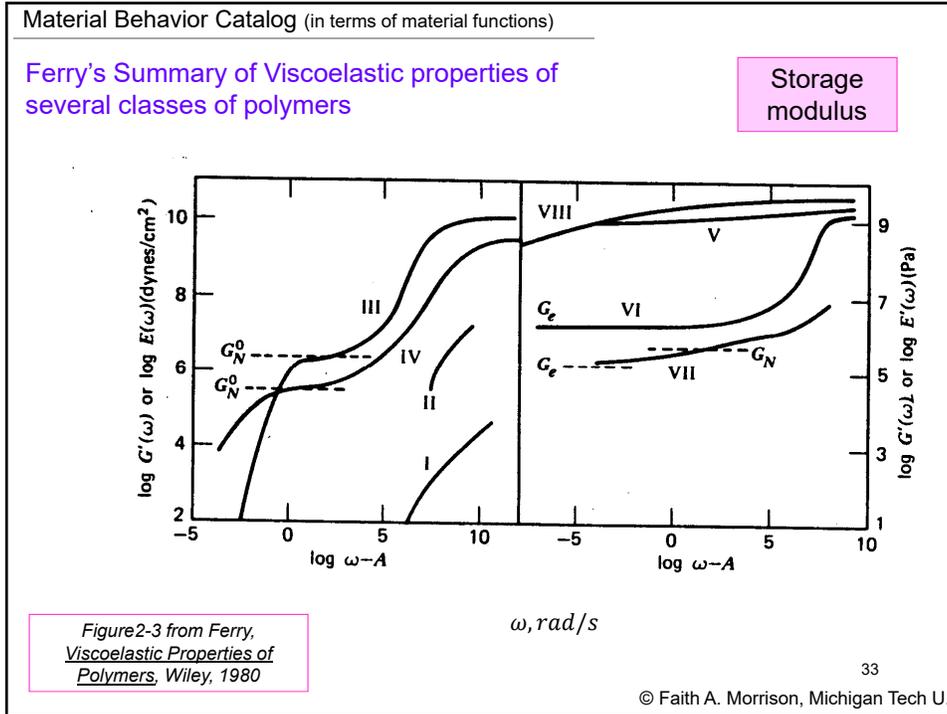
Small-Amplitude Oscillatory Shear - Storage and Loss Moduli

$\omega, \text{rad/s}$

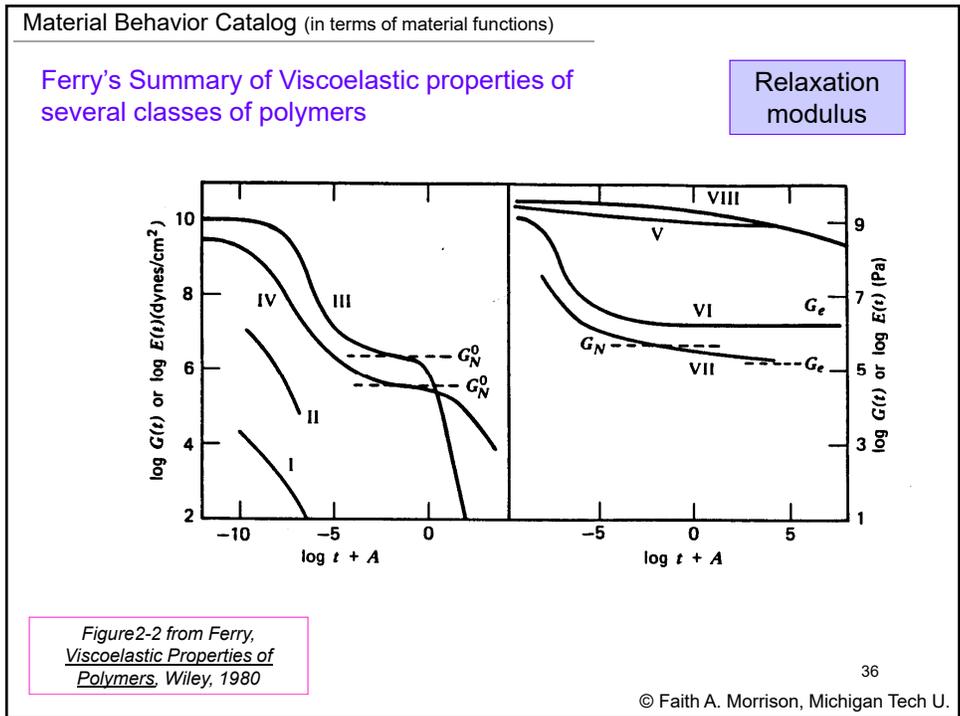
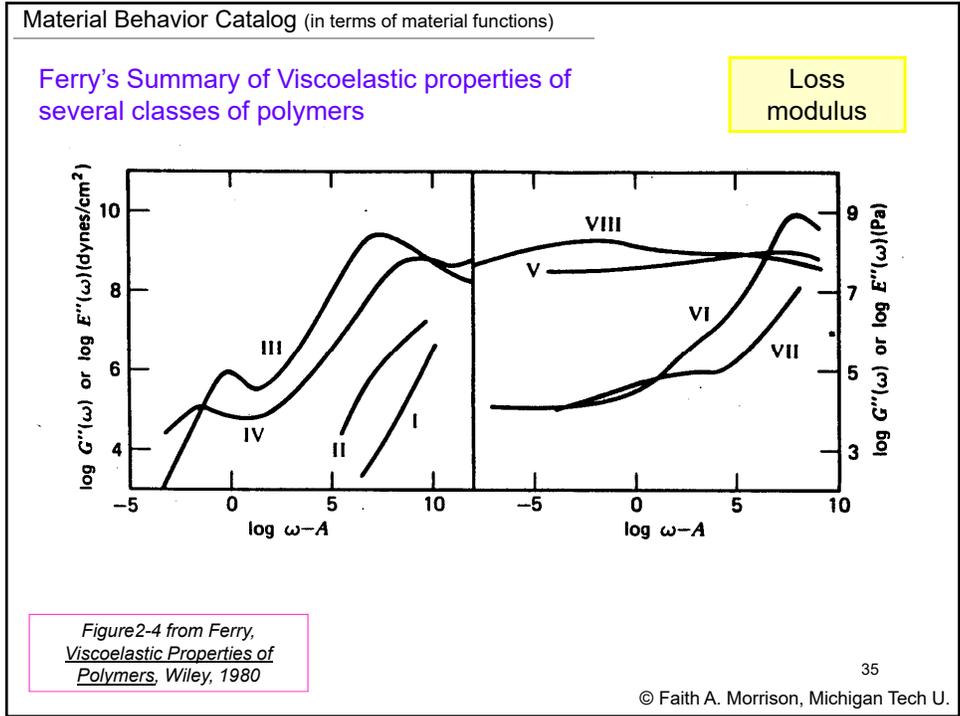
Figure 6.30, p. 192 Plazek and O'Rourke; PS

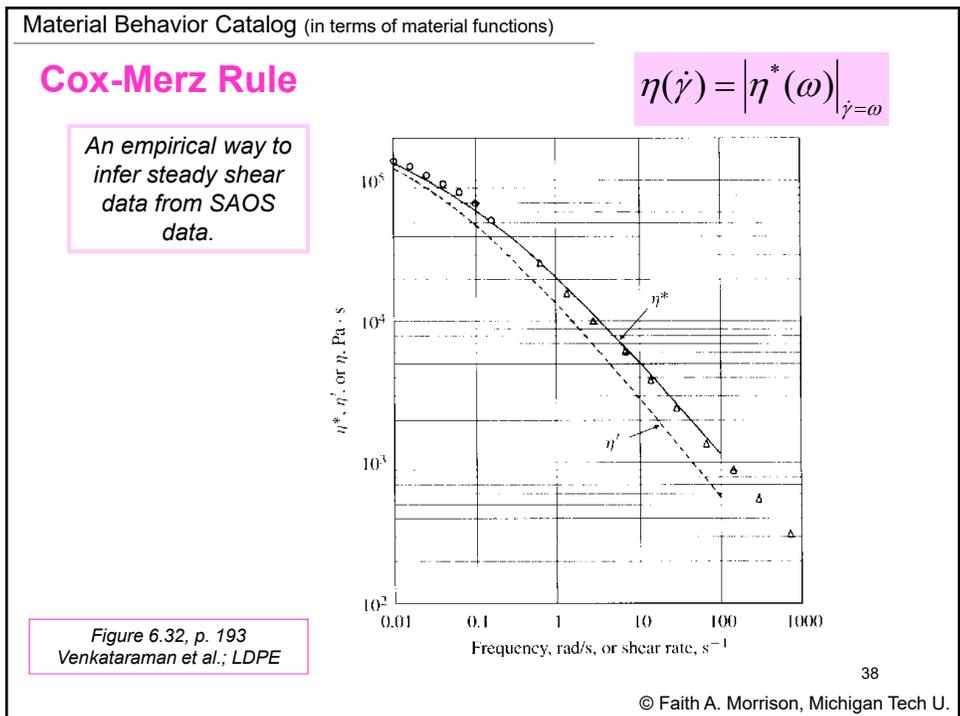
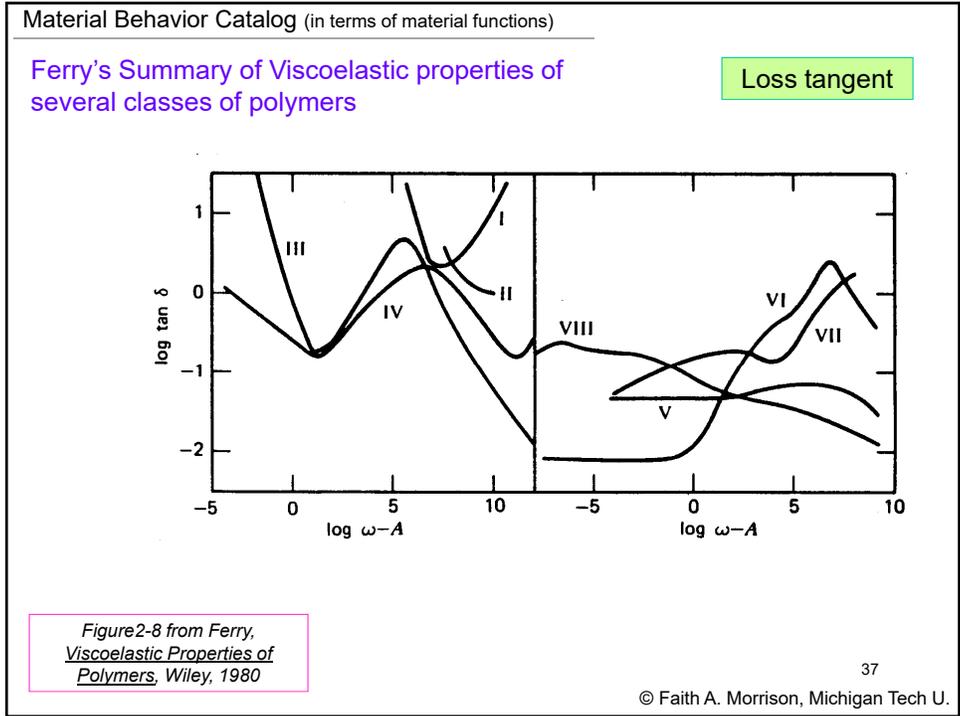
30
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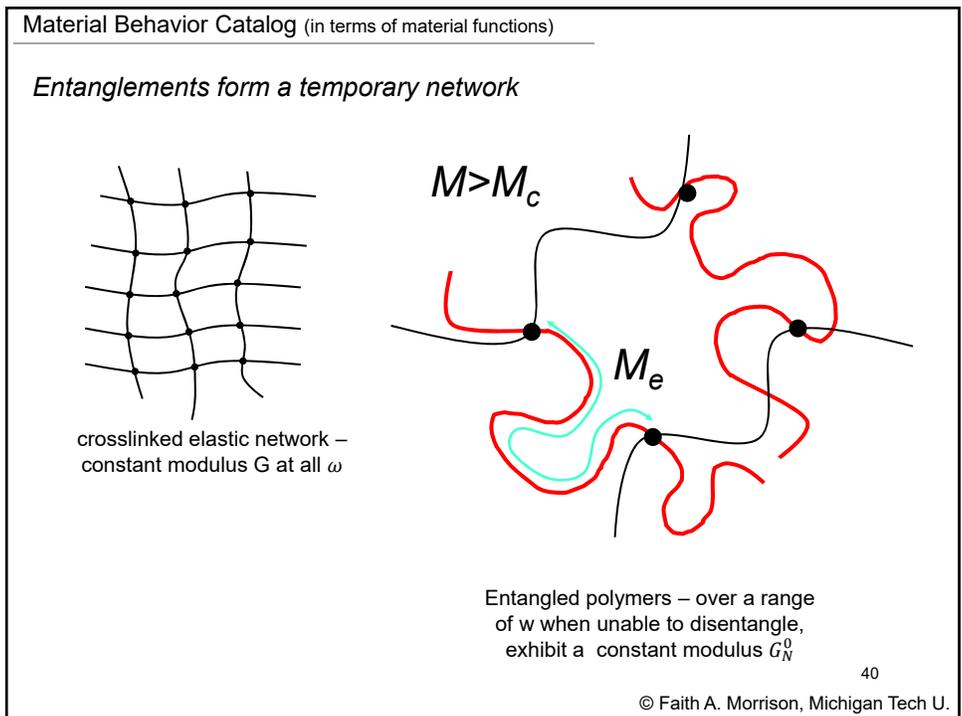
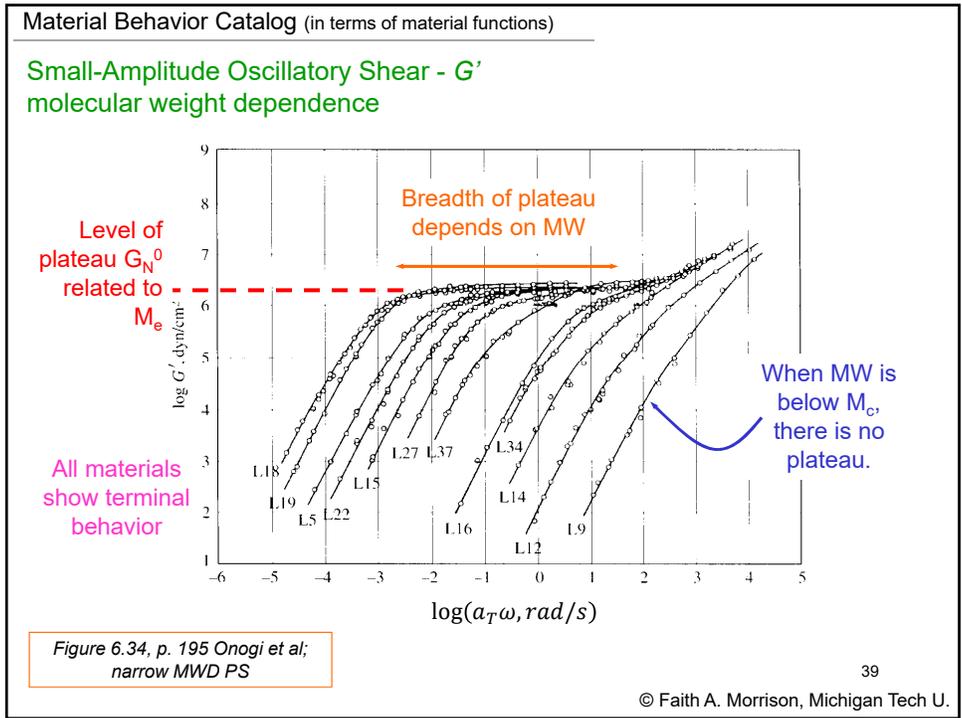




- Material Behavior Catalog (in terms of material functions)
- Key to Ferry's plots
- I. **Dilute polymer solutions: atactic polystyrene**, 0.015 g/ml in Aroclor 1248, a chlorinated diphenyl with viscosity 2.47 poise at 25°C. $M_w=86,000$, M_w/M_n near 1.
 - II. **Amorphous polymer of low molecular weight**: poly(vinyl acetate), $M=10,500$, fractionated.
 - III. **Amorphous polymer of high molecular weight**: atactic polystyrene, narrow MW distribution, $M_w=600,000$.
 - IV. **Amorphous polymer of high molecular weight with long side groups**: fractionated poly(n-octyl methacrylate), $M_w=3.62 \times 10^6$.
 - V. **Amorphous polymer of high molecular weight below its glass transition temperature**: poly(methyl methacrylate).
 - VI. **Lightly cross-linked amorphous polymer**: lightly vulcanized Hevea rubber.
 - VII. **Very lightly cross-linked amorphous polymer**: styrene butadiene random copolymer, 23.5% styrene by weight.
 - VIII. **Highly crystalline polymer**: linear polyethylene.
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Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - G'
molecular weight dependence

Level of plateau G_N^0 is related to M_e
(molecular theory for temporary networks)

$$G_N^0 = \frac{4}{5} \nu k_B T$$

ν = density of effective cross links
 ν = cross links/volume

$$M_e = \frac{\left(\frac{\text{mass}}{\text{volume}}\right) \left(\frac{\text{crosslinks}}{\text{mole}}\right)}{\left(\frac{\text{crosslinks}}{\text{volume}}\right)} = \frac{\rho N_A}{\nu}$$

$$M_c \cong 2M_e$$

$$G_N^0 = \frac{4}{5} \frac{\rho N_A k_B T}{M_e}$$

Larger the MW between entanglements, the softer the network

See Larson, *The Structure and Rheology of Complex Fluids*, Oxford, 1999

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Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - G''
molecular weight dependence

Breadth of minimum depends on MW; structure is more complex

When MW is below M_c , there is no minimum.

All materials show terminal behavior

Figure 6.36, p. 196 Onogi et al; narrow MWD PS

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Material Behavior Catalog (in terms of material functions)

Small-Strain Unsteady Shear Summary:

1. General traits
2. Effect of MW (linear polymers)
3. Effect of architecture
4. Relationship to steady flow material functions
5. Measurement issues
6. Effect of chemical composition

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Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - G' as a function of temperature for copolymers

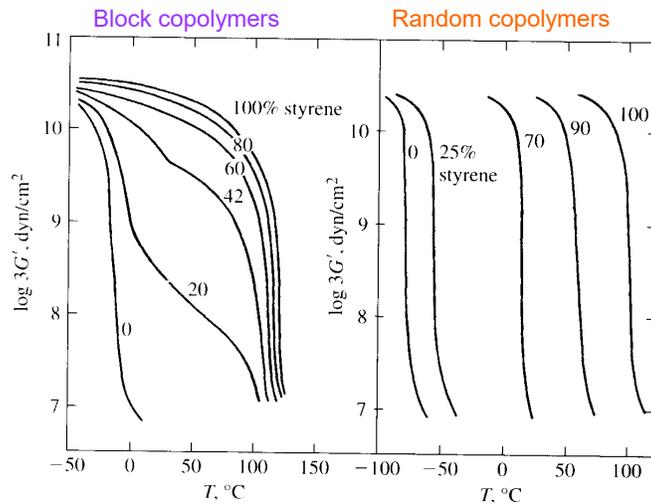
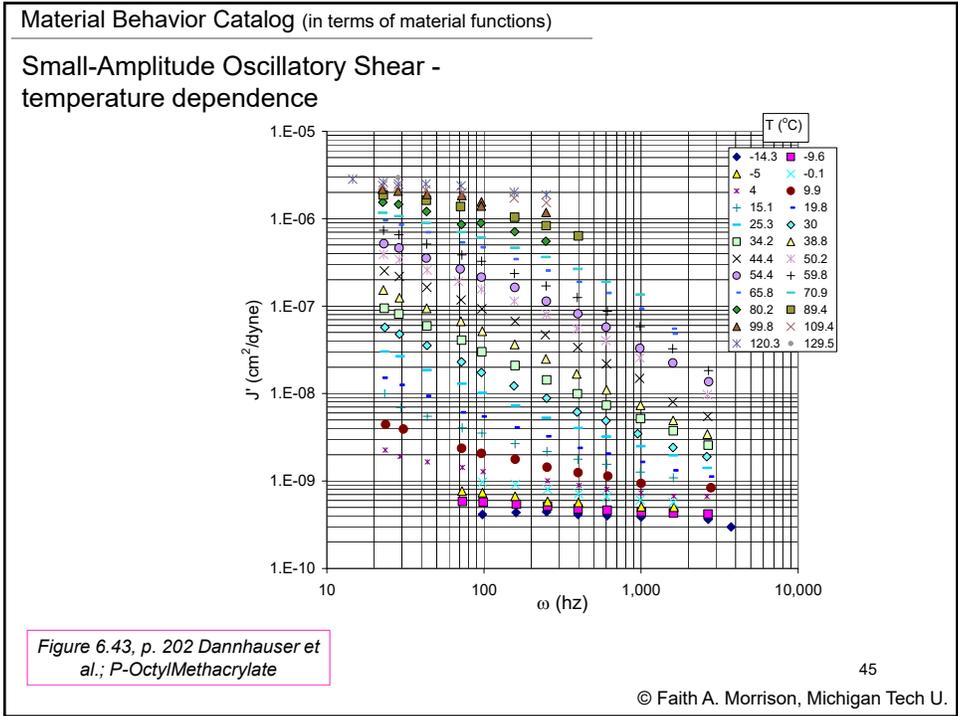


Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random

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Material Behavior Catalog (in terms of material functions)

Time-Temperature Superposition

Material functions depend on g_i, l_i

$$G' = G'(\omega, \lambda_i, g_i)$$

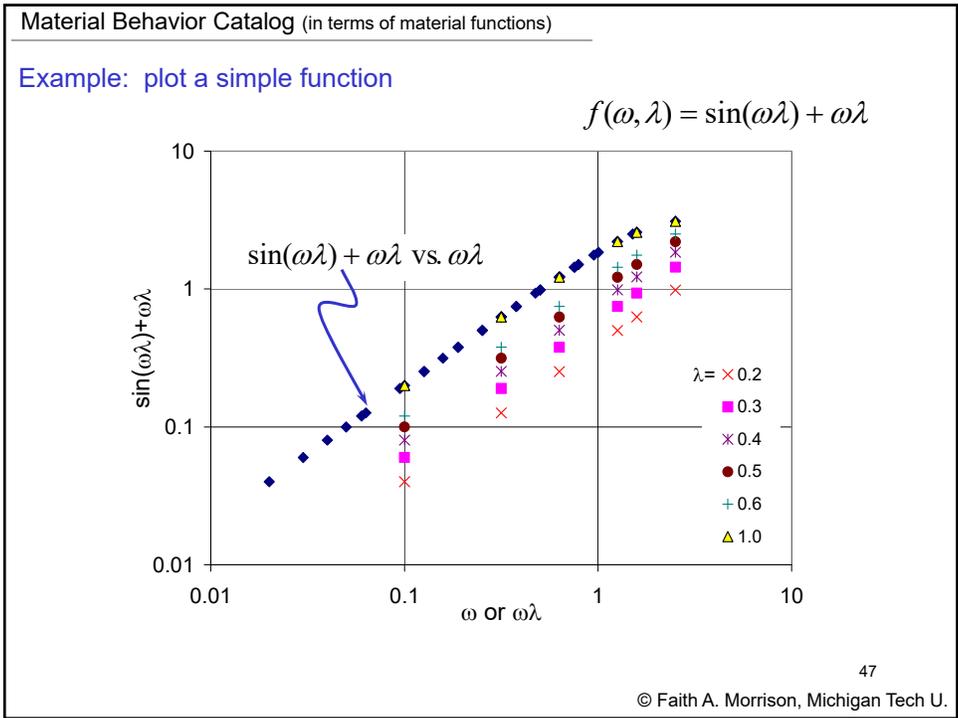
$$G'' = G''(\omega, \lambda_i, g_i)$$

g_i, l_i are in turn functions of temperature and material properties

Theoretical result: in the linear-viscoelastic regime, material functions are a function of w/l_i rather than of w and l_i individually.

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Material Behavior Catalog (in terms of material functions)

In general,

$$G' = G'(\omega\lambda_1(T), \omega\lambda_2(T), \omega\lambda_3(T), \dots)$$

Suppose that the temperature-dependence of l_i could be factored out. Let $a_{Ti}(T)$ be the temperature-dependence of l_i .

$$\lambda_i(T) = a_{Ti}(T)\tilde{\lambda}_i$$

not a function of temperature

Then we could group the temperature-dependence function with the frequency.

$$G' = G'(a_{T1}\omega\tilde{\lambda}_1, a_{T2}\omega\tilde{\lambda}_2, a_{T3}\omega\tilde{\lambda}_3, \dots)$$

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Material Behavior Catalog (in terms of material functions)

Time-Temperature Superposition

- Relaxation times decrease strongly as temperature increases
- Moduli associated with relaxations are proportional to absolute temperature; depend on density

Empirical observation: for many materials, all the relaxation times and moduli have the same functional dependence on temperature

(for the i^{th} relaxation mode)

$$\lambda_i(T) = \tilde{\lambda}_i a_T(T)$$


temperature dependence of all relaxation times

$$g_i(T) = \tilde{g}_i T \rho(T)$$


temperature dependence of all moduli

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Material Behavior Catalog (in terms of material functions)

Second theoretical result: the g_i enter into the functions for G' , G'' such that $T\rho$ can be factored out of the function

$$\frac{G'}{T\rho} = \tilde{f}(a_T \omega, \tilde{\lambda}_i)$$

$$\frac{G''}{T\rho} = \tilde{h}(a_T \omega, \tilde{\lambda}_i)$$

Therefore if we plot reduced variables, we can suppress all of the temperature dependence of the moduli.

$$G'_r \equiv \frac{G'(T) T_{ref} \rho_{ref}}{T\rho} = f(a_T \omega, \tilde{\lambda}_i) T_{ref} \rho_{ref} = G'(T_{ref})$$

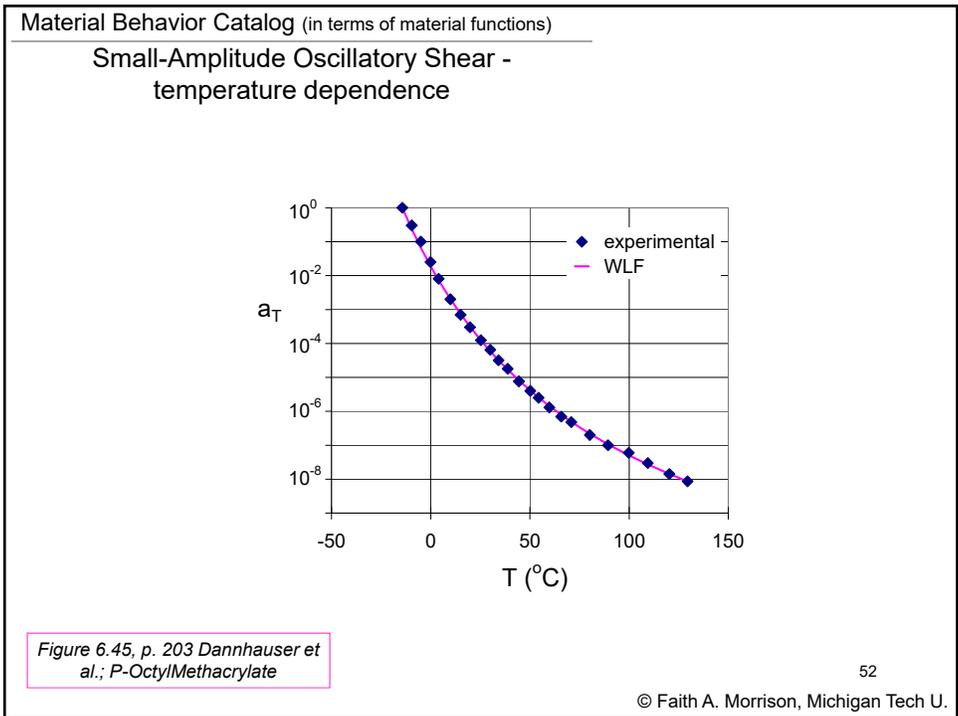
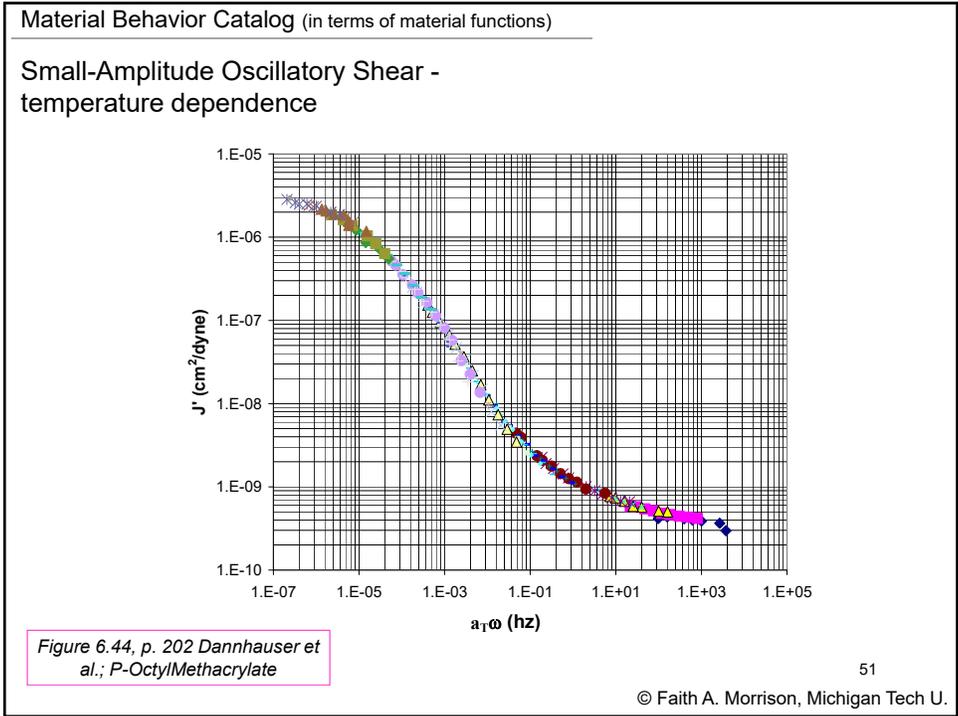
$$G''_r \equiv \frac{G''(T) T_{ref} \rho_{ref}}{T\rho} = h(a_T \omega, \tilde{\lambda}_i) T_{ref} \rho_{ref} = G''(T_{ref})$$

Plots of G'_r, G''_r versus $a_T \omega$ will therefore be independent of temperature.

(will still depend on the material through the $\tilde{\lambda}_i$)

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Material Behavior Catalog (in terms of material functions)

Shift Factors

Arrhenius equation

$$a_T = \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

found to be valid for $T > T_g + 100^\circ C$

Williams-Landel-Ferry (WLF) equation

$$\log a_T = \frac{-c_1^0(T - T_{ref})}{c_2^0 + (T - T_{ref})}$$

found to be valid w/in $100^\circ C$ of T_g

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Material Behavior Catalog (in terms of material functions)

Shifting other Material Functions

Other linear viscoelastic material functions:

$$\eta' \equiv \frac{G''(T)}{\omega}$$

$$\eta'' \equiv \frac{G'(T)}{\omega}$$

$$\tan \delta = \frac{G''}{G'}$$

$$J' = \frac{1/G'}{1 + \tan^2 \delta}$$

$$J'' = \frac{1/G''}{1 + (\tan^2 \delta)^{-1}}$$

$$G'_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T, \omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G'(T_{ref})$$

$$G''_r \equiv \frac{G''(T)T_{ref}\rho_{ref}}{T\rho} = h(a_T, \omega, \tilde{\lambda}_i)T_{ref}\rho_{ref} = G''(T_{ref})$$

Independent of temperature

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Material Behavior Catalog (in terms of material functions)

Shifting other Material Functions

linear viscoelastic

$$\eta'_r \equiv \frac{G''(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$\eta''_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{a_T\omega T\rho} = \frac{\eta'' T_{ref}\rho_{ref}}{a_T T\rho}$$

$$J'_r \equiv \frac{J'(T)T\rho}{T_{ref}\rho_{ref}}$$

$$J''_r \equiv \frac{J''(T)T\rho}{T_{ref}\rho_{ref}}$$

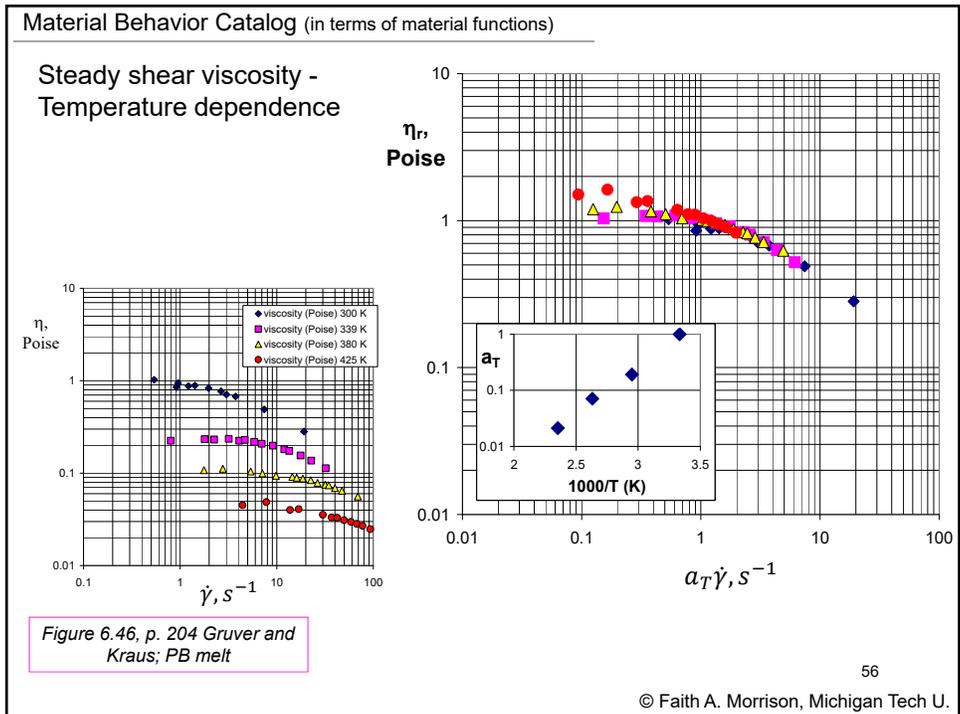
steady shear

$$\eta_r(a_T\dot{\gamma}) = \frac{\eta(T)T_{ref}\rho_{ref}}{a_T T\rho}$$

$$\tan \delta = \frac{G''}{G'}$$

= independent of temperature when plotted versus reduced frequency

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Material Behavior Catalog (in terms of material functions)

Another consequence of $\lambda_i(T) = \tilde{\lambda}_i a_T(T)$ is the similarity between $\log G'(\omega)$ and $\log G'(T)$.

Figure 6.30, p. 192 Plazek and O'Rourke; PS

Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random

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Material Behavior Catalog (in terms of material functions)

Take data for G' , G'' at a fixed ω for a variety of T .

$$G'_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)$$

but, what is $a_T(T)$?
We do not know.

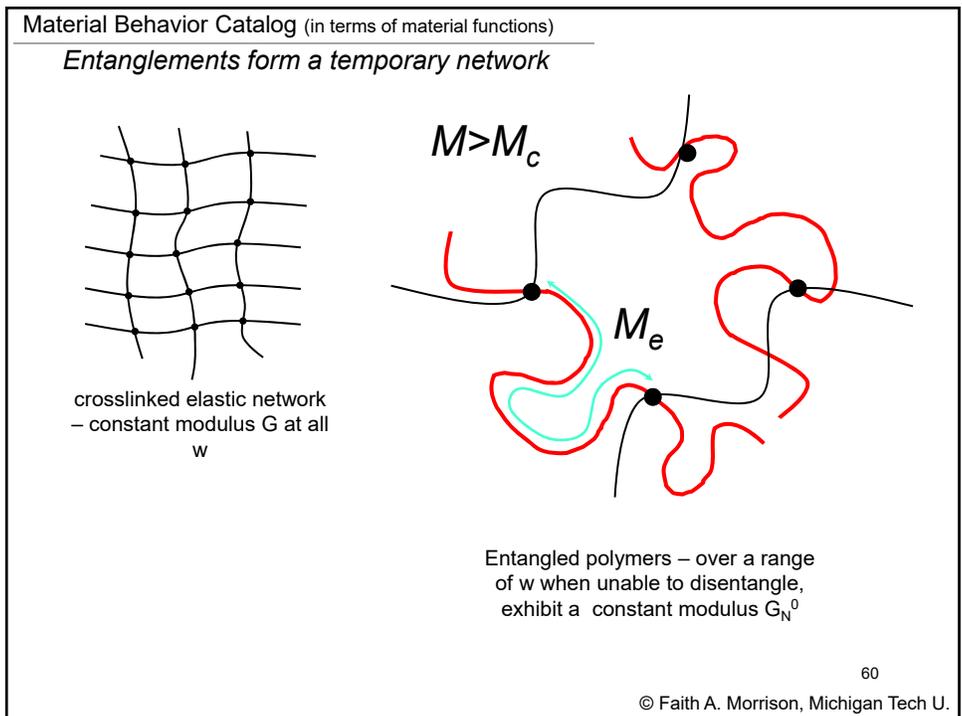
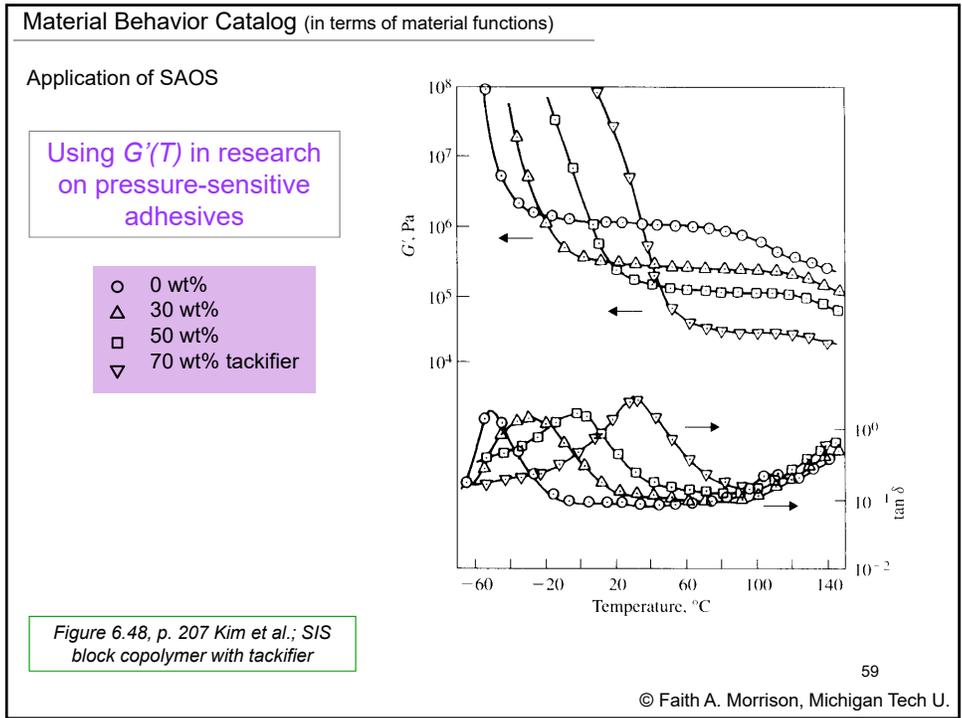
$$G''_r \equiv \frac{G''(T)T_{ref}\rho_{ref}}{T\rho} = h(a_T\omega, \tilde{\lambda}_i)$$

But since $\log a_T$ is approximately a linear function of T ,

curves of $\log G'$ versus T (not $\log T$) at constant ω resemble slightly skewed plots of $\log G'$ versus $\log a_T\omega$.
(mirror image)

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Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - G'
molecular weight dependence

Level of plateau G_N^0
is related to M_e
(molecular theory for temporary networks)

$$G_N^0 = \frac{4}{5} \frac{\rho N_A k_B T}{M_e}$$

Larger the MW between entanglements, the softer the network

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Material Behavior Catalog (in terms of material functions)

Using $G'(T)$ in research on pressure-sensitive adhesives

Height of plateau modulus and temperature of glass transition are key performance factors for PSAs.

Tack – if not tacky, will not produce bond
Shear holding – if too fluid, will slide under shear

Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier

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Material Behavior Catalog (in terms of material functions)

Small-Strain Unsteady Shear Summary:

1. General traits
2. Effect of MW (linear polymers)
3. Effect of architecture
4. Relationship to steady flow material functions
5. Measurement issues
6. Effect of chemical composition
7. Effect of temperature

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Material Behavior Catalog (in terms of material functions)

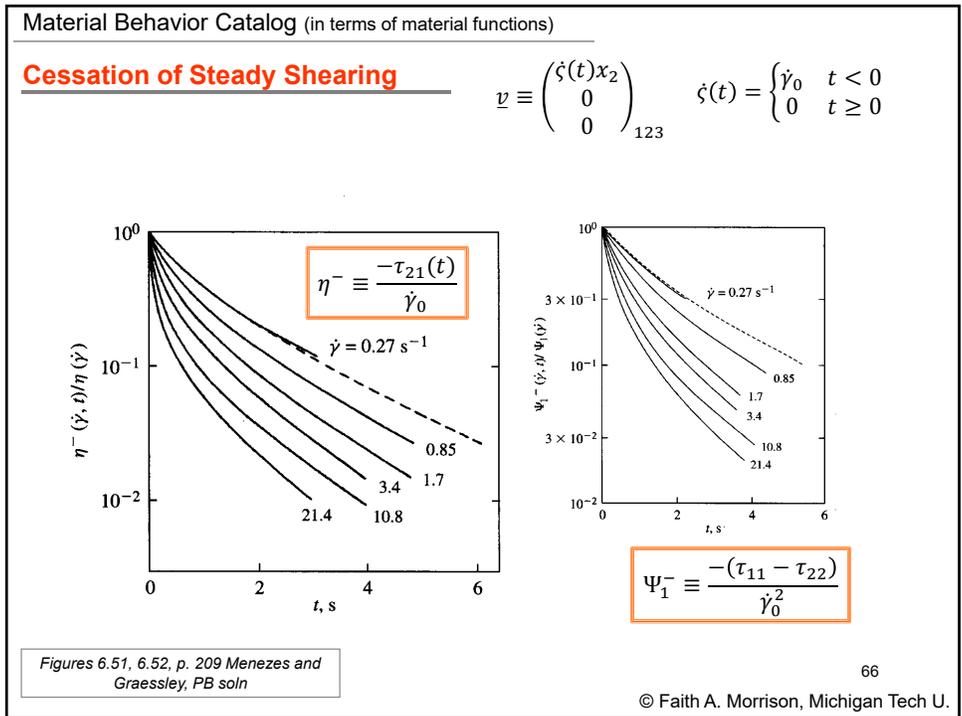
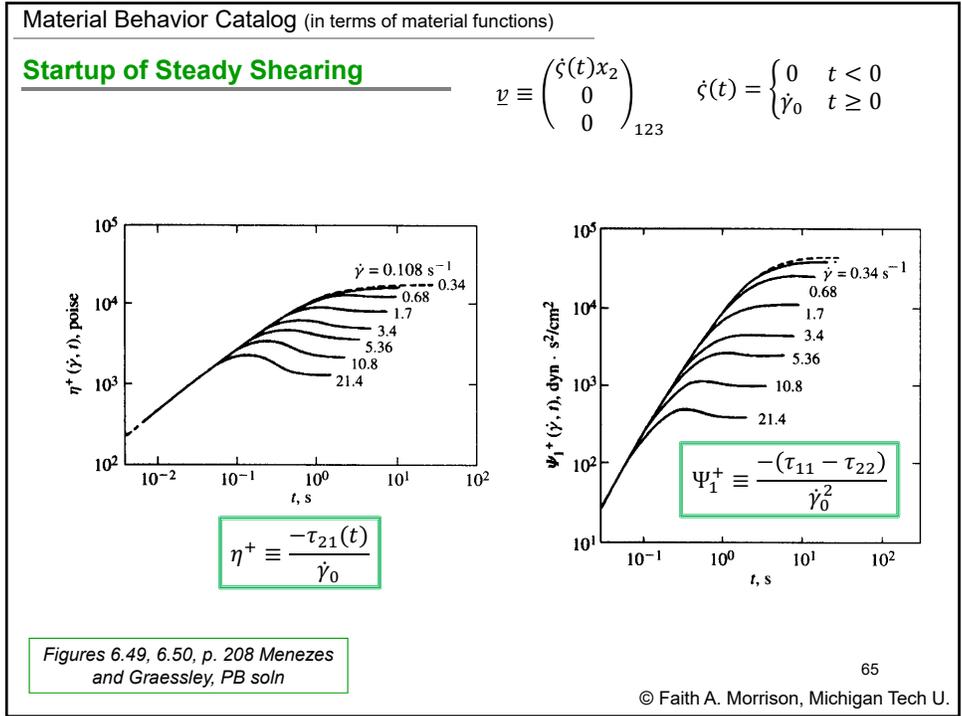
Experimental Data (continued)

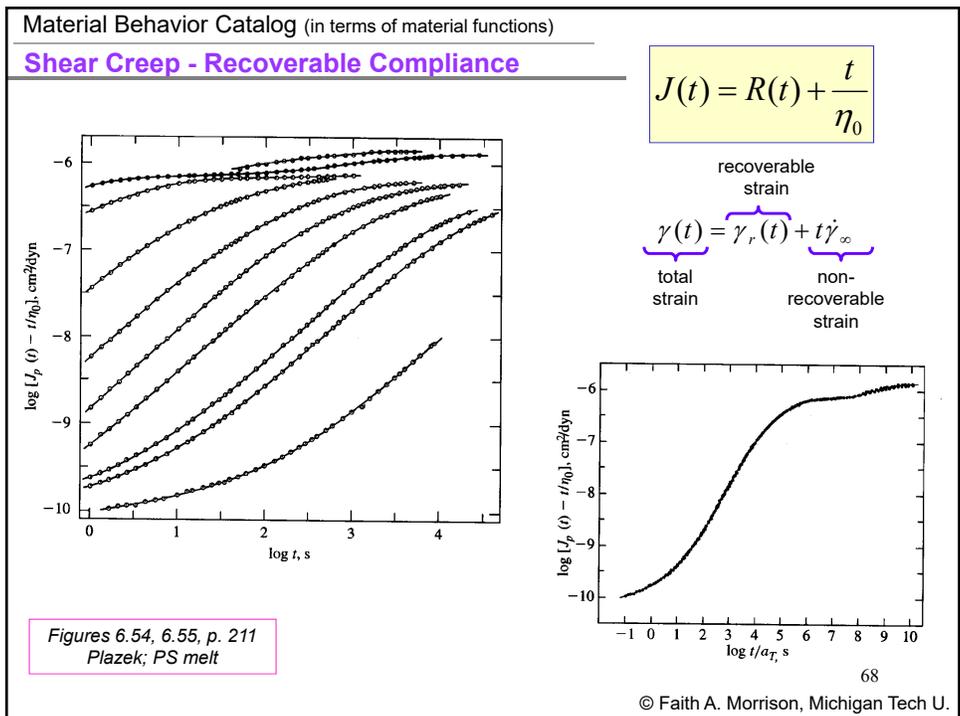
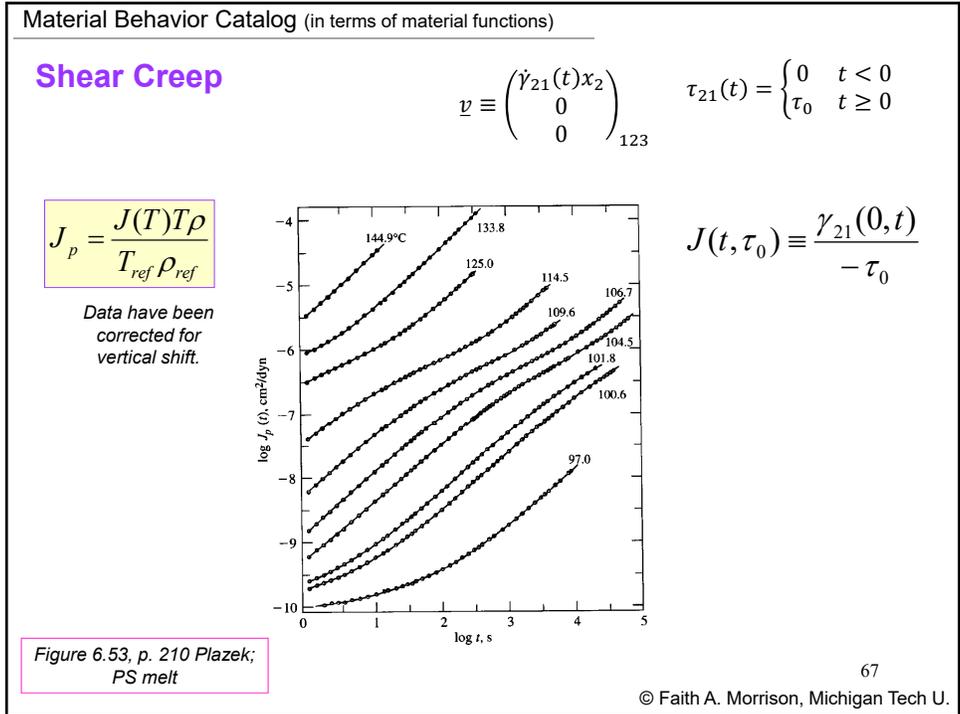
Unsteady shear flow

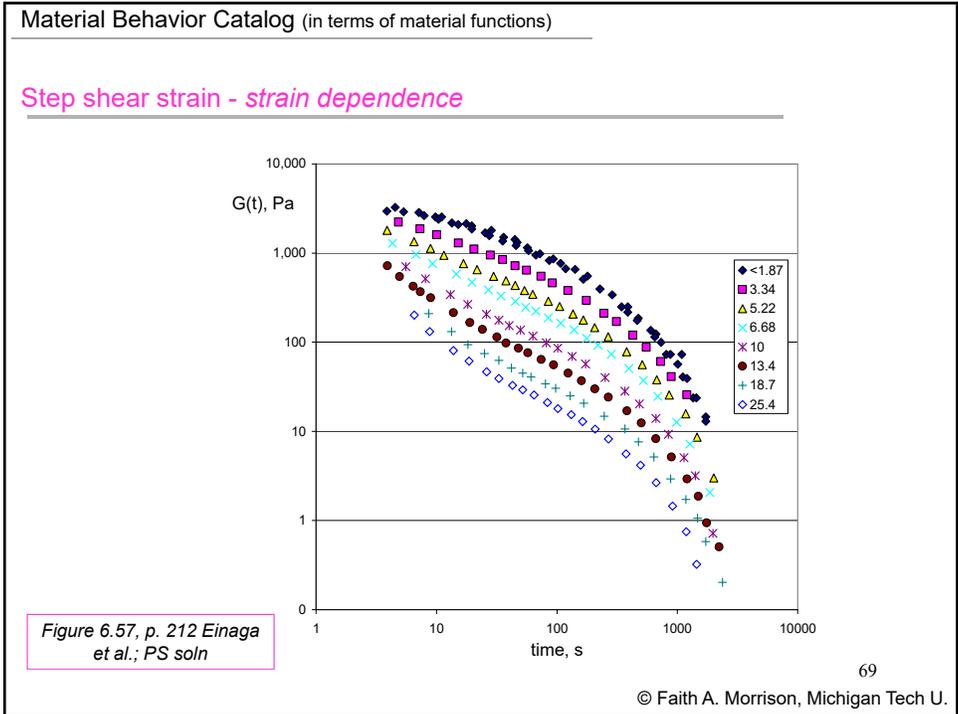
- ✓ •Small strain - SAOS, step strain
linear polymers, material effects, temperature effects
- ➔ •Large strain - start-up, cessation, creep, large-amplitude step strain

lastly ...
Steady elongation
Unsteady elongation

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Material Behavior Catalog (in terms of material functions)

Shear Damping Function

Observation: step-strain moduli curves have similar shapes and appear to be shifted down with strain.

$$G(t, \gamma_0) = G(t)h(\gamma_0)$$

Damping function

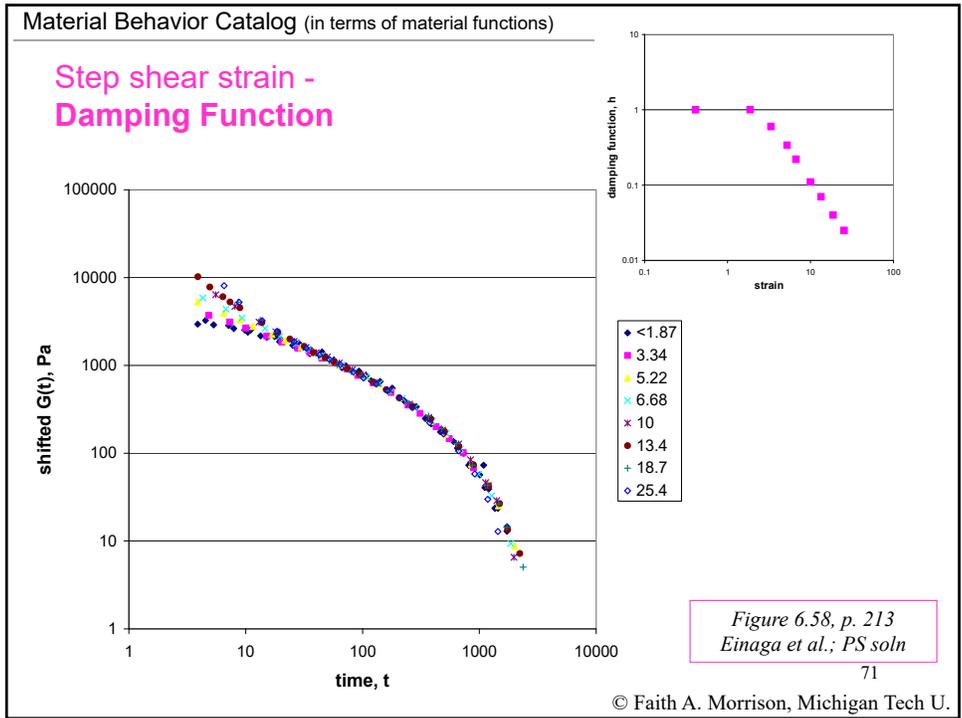
$$\log G(t, \gamma_0) = \log G(t) + \log h(\gamma_0)$$

The damping function gives the strain-dependence of the step-strain relaxation modulus.

When $G(t, \gamma_0) = G(t)h(\gamma_0)$ the behavior is called time-strain separable.

This behavior is predicted by some advanced constitutive equations.

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Material Behavior Catalog (in terms of material functions)

Large-Strain Unsteady Shear Summary:

1. General traits
2. Measurement issues

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Material Behavior Catalog (in terms of material functions)

Experimental Data (continued)

Unsteady shear flow

- ✓ • Small strain - SAOS, step strain
linear polymers, material effects, temperature effects
- ✓ • Large strain - start-up, cessation, creep, large-amplitude step strain

➔ *lastly ...*
Steady elongation
Unsteady elongation

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Material Behavior Catalog (in terms of material functions)

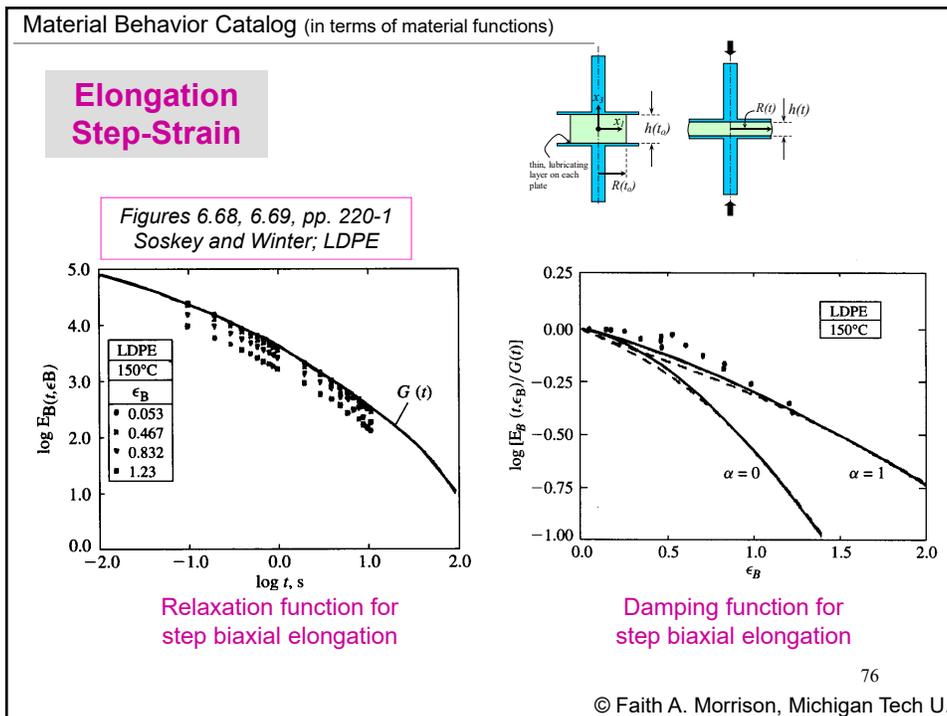
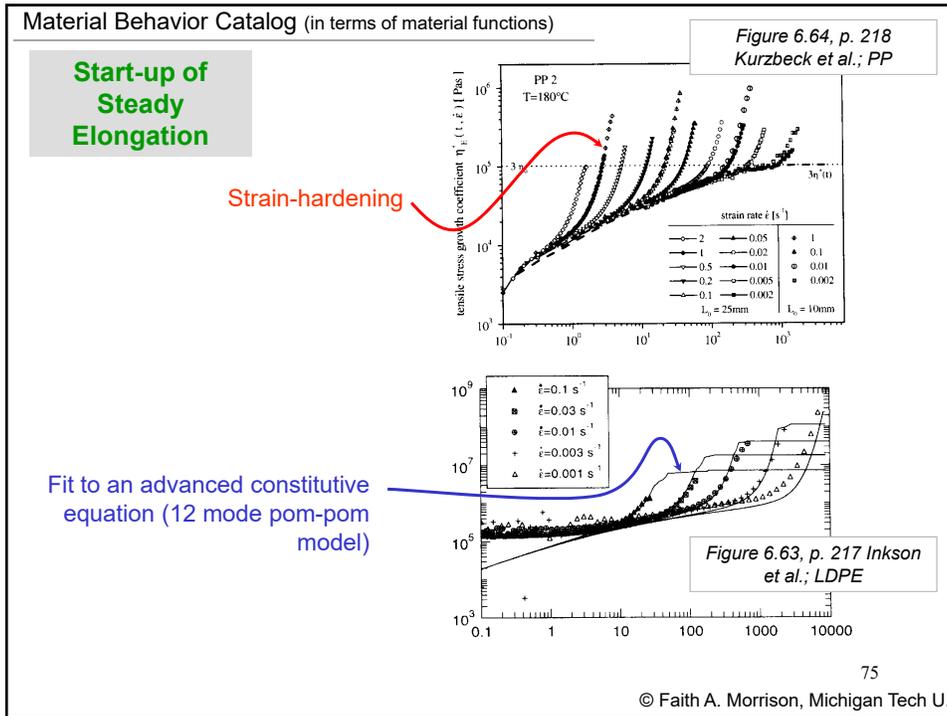
Steady State Elongation Viscosity

Both tension thinning and thickening are observed.

Trouton ratio: $Tr \equiv \frac{\bar{\eta}}{\eta_0}$

Figure 6.60, p. 215
Munstedt.; PS melt

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Material Behavior Catalog (in terms of material functions)

Elongational Flow Summary:

1. General traits
2. Measurement issues

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Material Behavior Catalog (in terms of material functions)

[More on Material Behavior](#)

Polymer Behavior

Larson, Ron, *The Structure and Rheology of Complex Fluids* (Oxford, 1999)
Ferry, John, *Viscoelastic Properties of Polymers* (Wiley, 1980)

Suspension Behavior

Mewis, Jan and Norm Wagner, *Colloidal Suspension* (Cambridge, 2012)

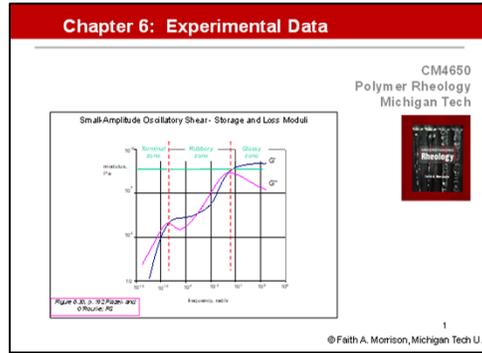
Journals

Journal of Rheology
Rheologica Acta
Macromolecules

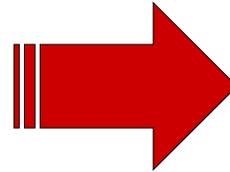
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Done with
Experimental Data.



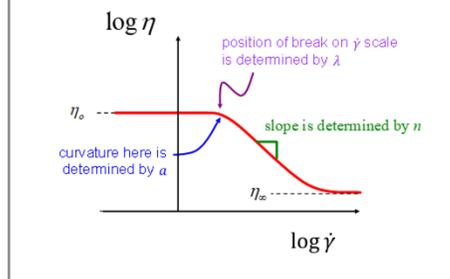
Let's move on to
Generalized
Newtonian Fluids



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Chapter 7: Generalized Newtonian fluids

Carreau-Yassuda GNF



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Polymer Rheology
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