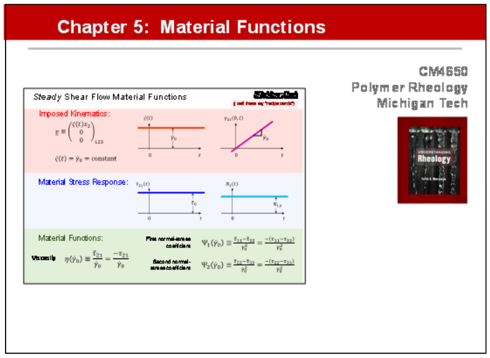
Done with Material Functions.



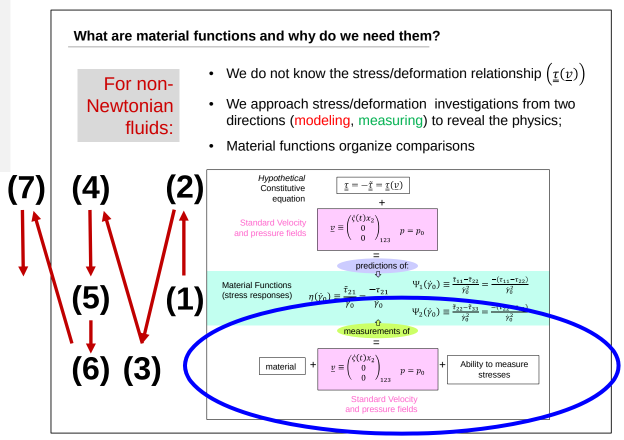
What now?

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

1

Investigating **Stress/Deformation** Relationships

(**Rheology**)



1. Choose a material function
2. Predict what Newtonian fluids would do
3. See what non-Newtonian fluids **do**
4. Hypothesize a $\underline{\underline{\tau}}(\underline{v})$
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

3

Chapter 6: Experimental Data

CM4650
Polymer Rheology
Michigan Tech

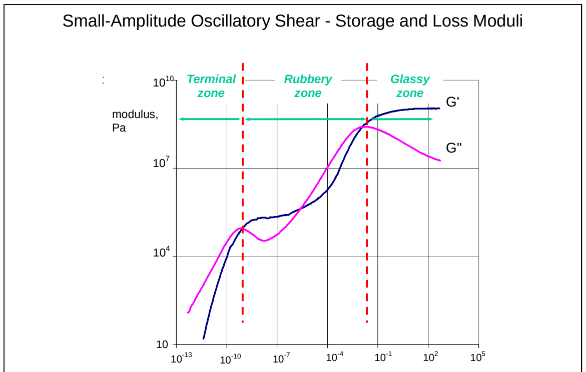


Figure 6.30, p. 192 Plazek and O'Rourke; PS

3

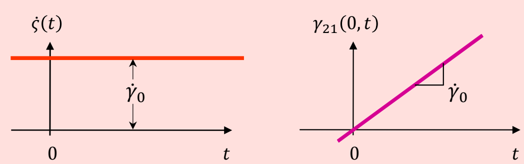
Steady Shear Flow Material Functions

Michigan Tech

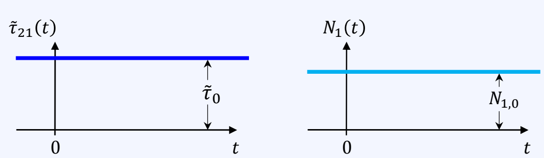
Imposed Kinematics:

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

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



Material Stress Response:



Material Functions:

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

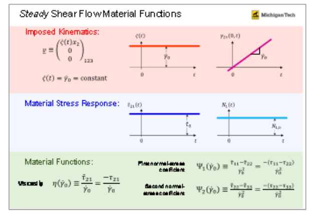
First normal-stress coefficient $\Psi_1(\dot{\gamma}_0) \equiv \frac{\tilde{\tau}_{11} - \tilde{\tau}_{22}}{\dot{\gamma}_0^2} = \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$

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

4

Material Behavior Catalog (in terms of material functions)

Experimental Data (Chapter 6)



First recipe card:

Steady shear flow

What do we observe for

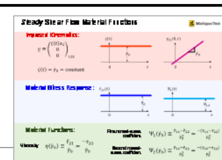
- Linear Polymers
- Limits on measurability
- Material effects - MW, MWD, branching, mixtures, copolymers
- Temperature and pressure

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

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

5

Material Behavior Catalog (in terms of material functions)



Steady shear viscosity and first normal stress coefficient

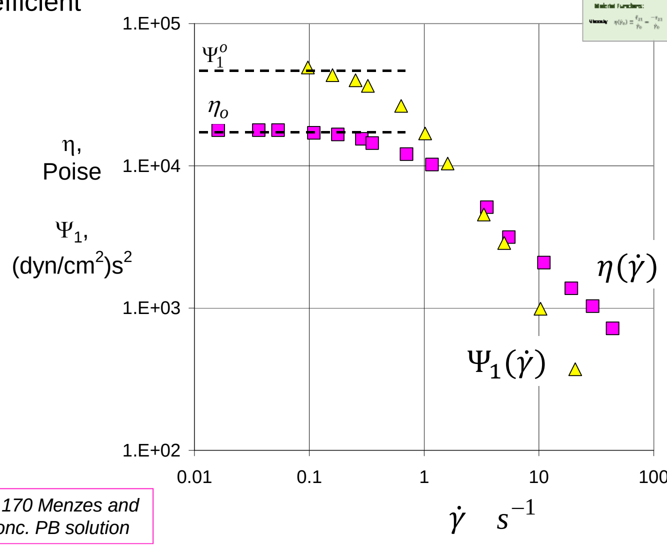


Figure 6.1, p. 170 Menzes and Graessley conc. PB solution

6

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity and first normal stress coefficient

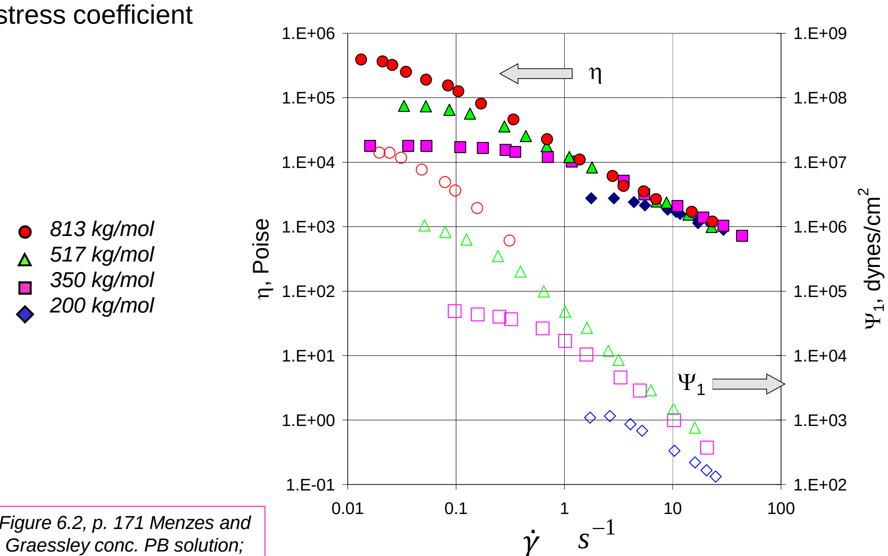


Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; c=0.0676 g/cm³

7

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity and first normal stress coefficient

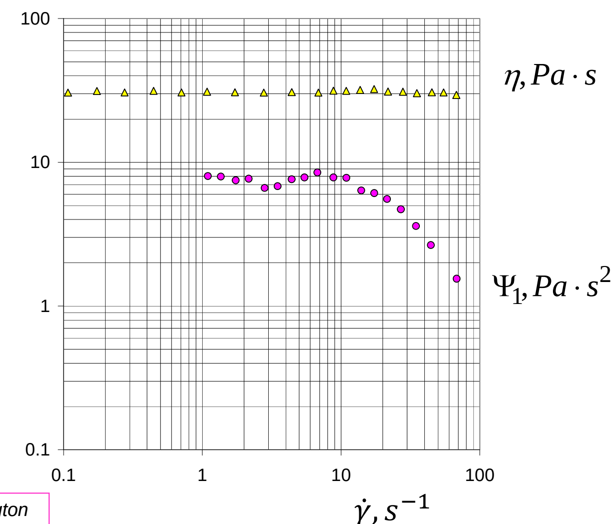
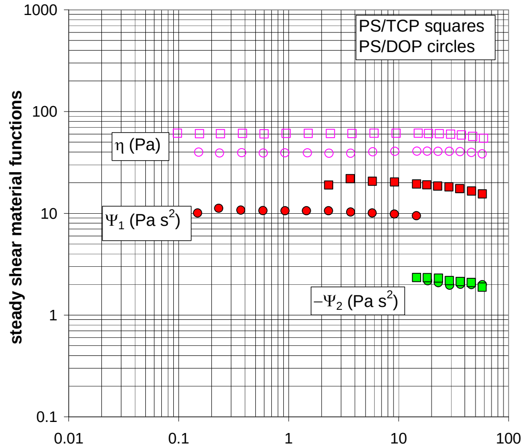


Figure 6.5, p. 173 Binnington and Boger; PIB soln

8

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity and first and ***second*** normal stress coefficient



$\dot{\gamma}, s^{-1}$

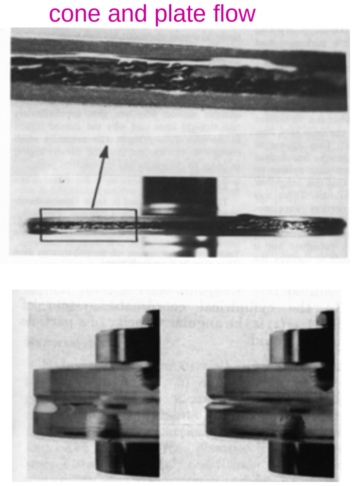
Figure 6.6, p. 174
Magda et al.; PS solns

9

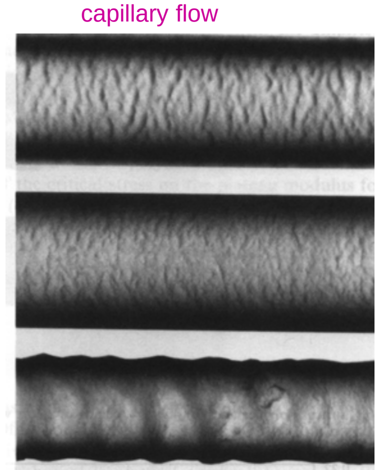
Material Behavior Catalog (in terms of material functions)

Limits on Measurements: Flow instabilities in rheology

cone and plate flow



capillary flow



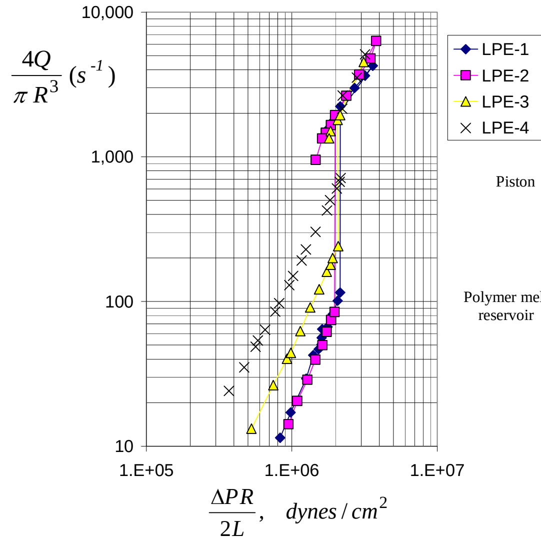
Figures 6.7 and 6.8, p. 175 Hutton; PDMS

Figure 6.9, p. 176
Pomar et al. LLDPE

10

Material Behavior Catalog (in terms of material functions)

Spurt instability



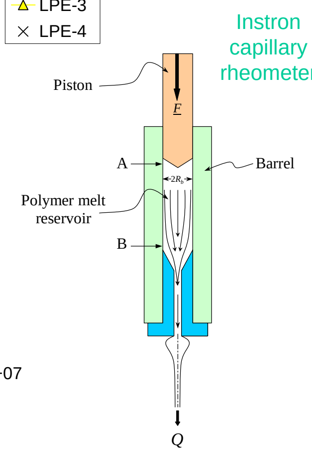


Figure 6.10, p. 177
Blyler and Hart; PE

11

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity and first normal stress coefficient - ***Molecular weight effects***

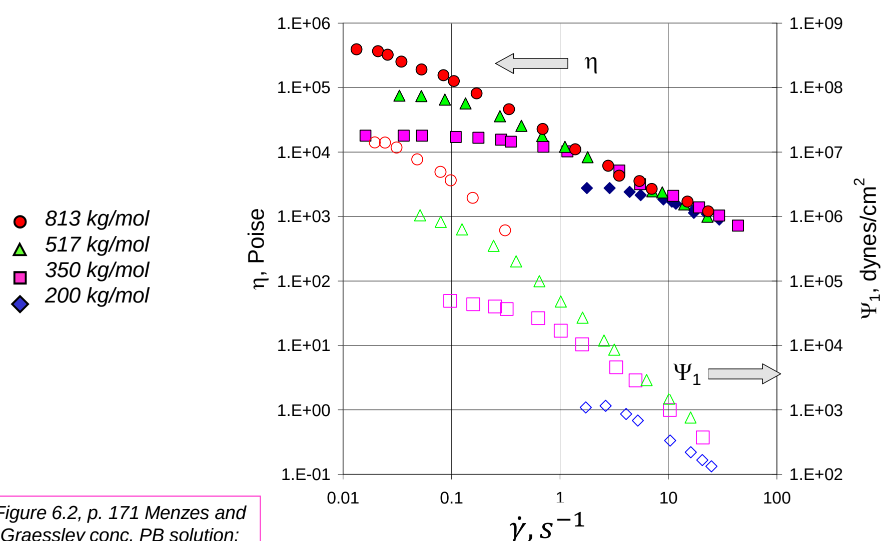


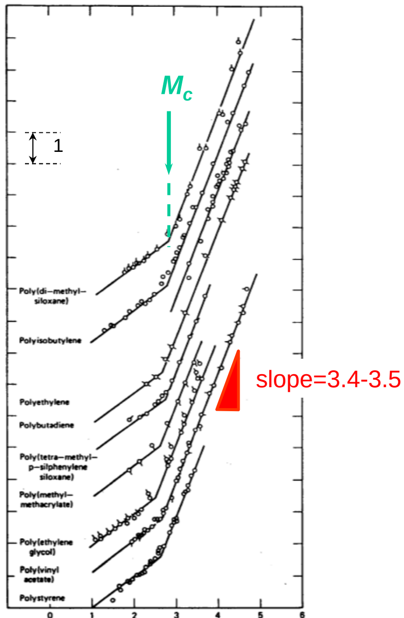
Figure 6.2, p. 171 Menzes and Graessley conc. PB solution; various MW

12

Material Behavior Catalog (in terms of material functions)

Variation of viscosity with molecular weight

$\log \eta_0$
+ constant



log M + constant

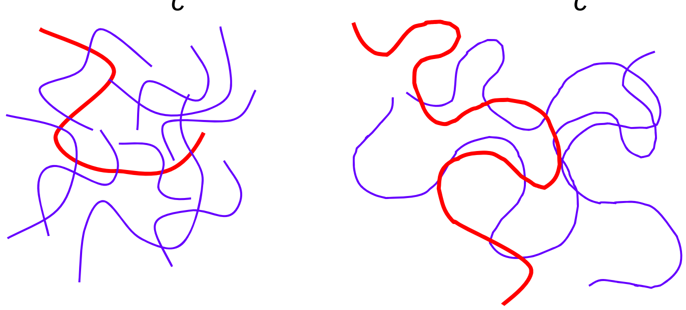
Figure 6.12, p. 178 Berry and Fox, 1968; various polymers

13

Material Behavior Catalog (in terms of material functions)

Entanglements strongly affect polymer relaxation

$M<M_c$ | $M>M_c$



Unentangled
relaxation is rapid

Entangled
relaxation is retarded

14

Material Behavior Catalog (in terms of material functions)

Effect of Distribution of Molecular Weight

A - M_w/M_n=1.09

B - M_w/M_n= 2.0

C - *branched*

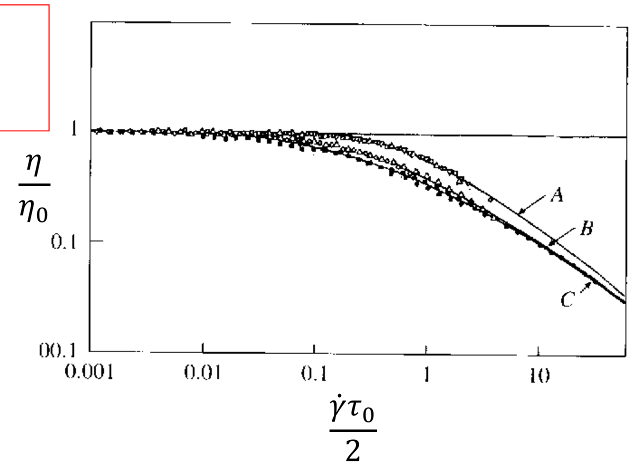
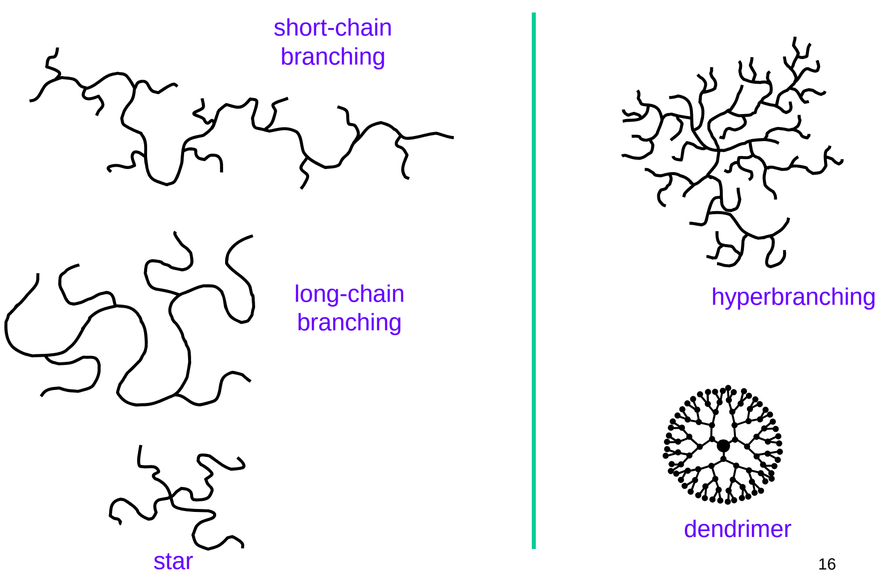


Figure 6.14, p. 179 Berry and Fox; PVA solns in DEP

15

Material Behavior Catalog (in terms of material functions)

Types of polymer architecture

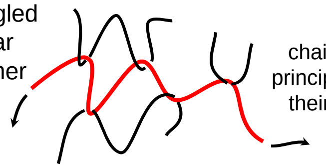


16

Material Behavior Catalog (in terms of material functions)

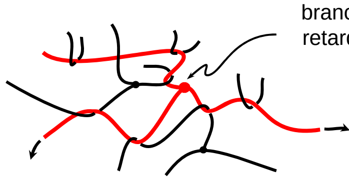
Motion of Branched Polymers

Entangled linear polymer

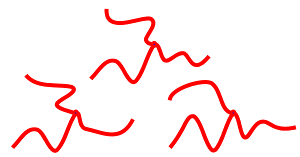


chains move principally along their contour

Entangled branched polymer



branch points retard motion

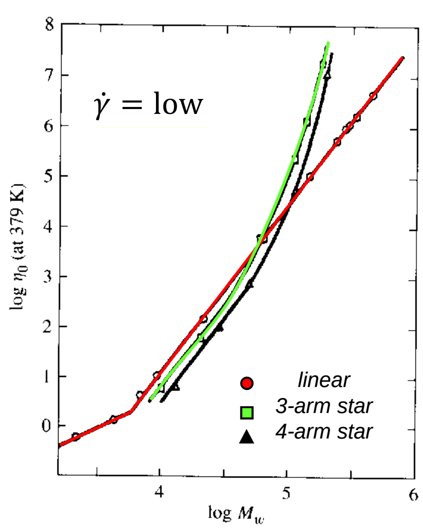


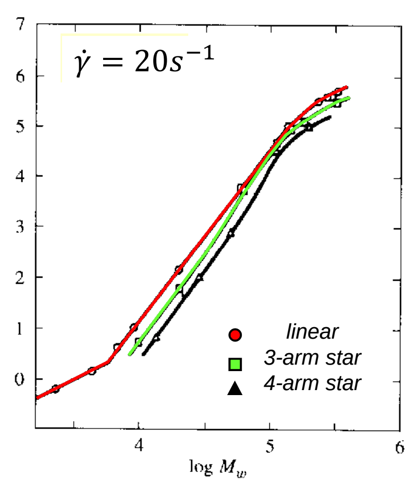
once disentangled (high shear rate), branched polymers flow more freely

17

Material Behavior Catalog (in terms of material functions)

Effect of Branching on $\eta(\dot{\gamma})$

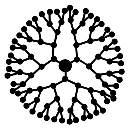




Figures 6.17, 6.18, pp. 181,3 Kraus & Gruver; PB

18

Material Behavior Catalog (in terms of material functions)



Steady shear rheology of PAMAM dendrimers

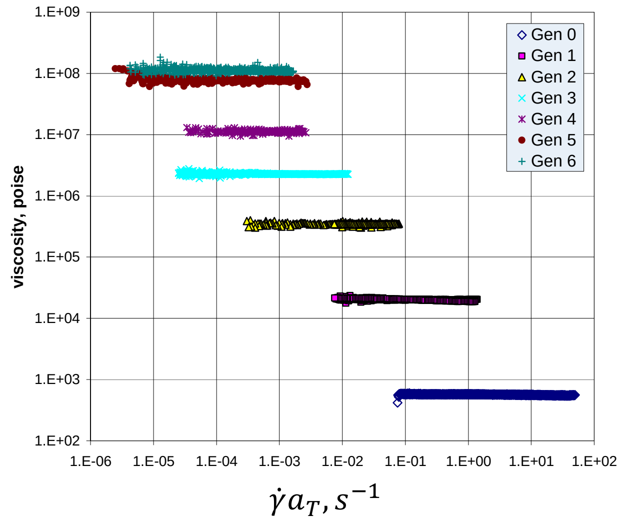


Figure 6.20 p. 183; from Uppuluri

19

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

20

Material Behavior Catalog (in terms of material functions)

Mixtures of Polymers with other materials - Filler Effect

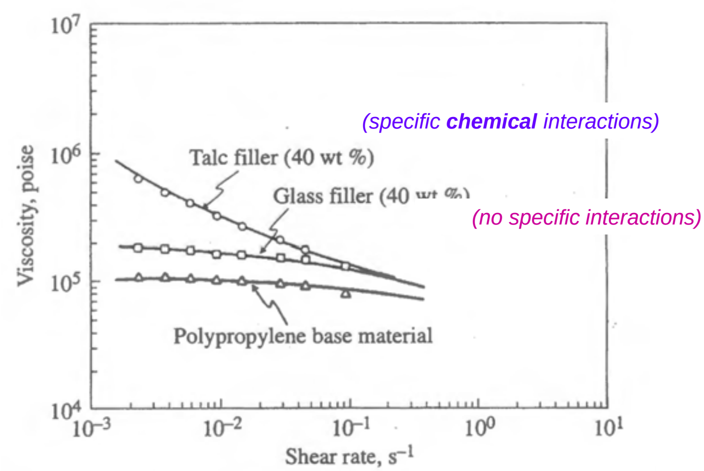


Figure 6.22, p. 184 Chapman and Lee; PP and filled PP

For more on filled systems, see Larson, *The Structure and Rheology of Complex Fluids*, Oxford, 1999.

21

Material Behavior Catalog (in terms of material functions)

Mixtures of Polymers with other materials - Filler Effect

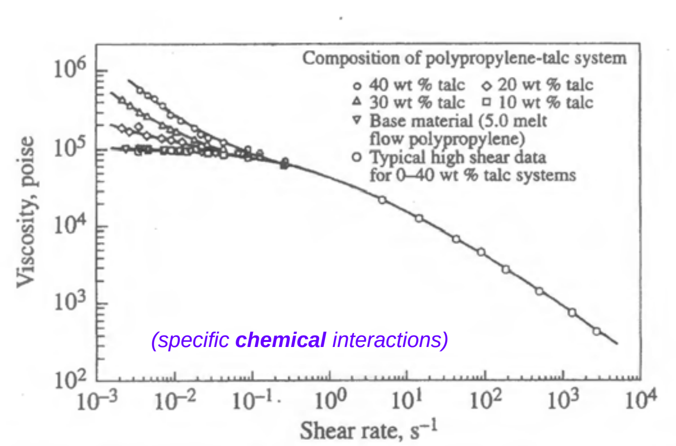


Figure 6.21, p. 184 Chapman and Lee; filled PP

For more on filled systems, see Larson, *The Structure and Rheology of Complex Fluids*, Oxford, 1999.

22

Material Behavior Catalog (in terms of material functions)

For discussion of causes of shear thickening, see Wagner and Brady, *Phys. Today*, October 2009

Steady shear viscosity - shear thickening

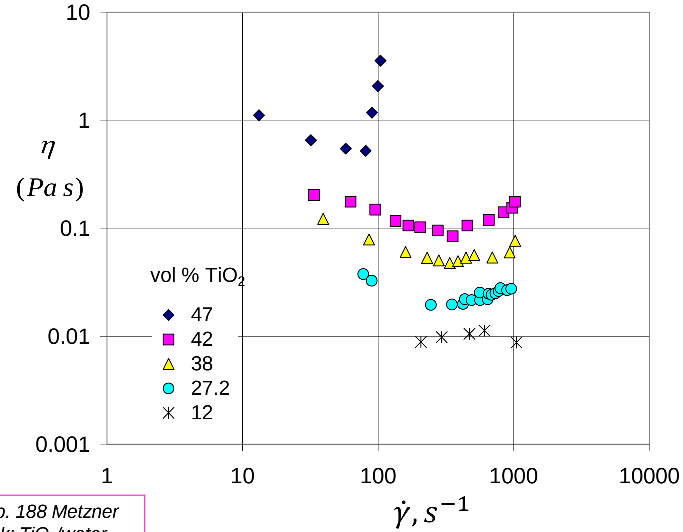


Figure 6.27, p. 188 Metzner and Whitlock; TiO_2/water suspensions

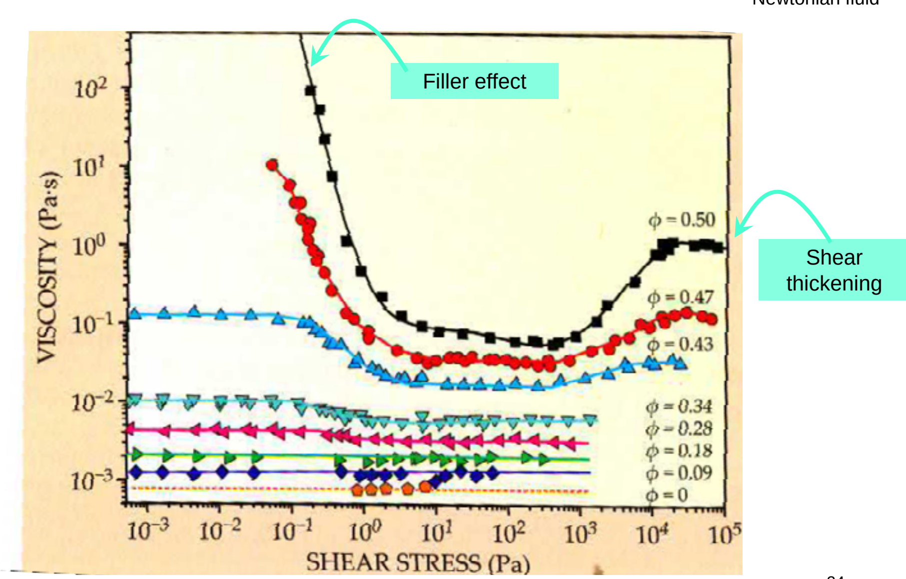
23

Material Behavior Catalog (in terms of material functions)

Wagner and Brady, *Phys. Today*, Oct 2009

Steady shear viscosity - shear thickening

Latex spheres in Newtonian fluid



24

Material Behavior Catalog (in terms of material functions)

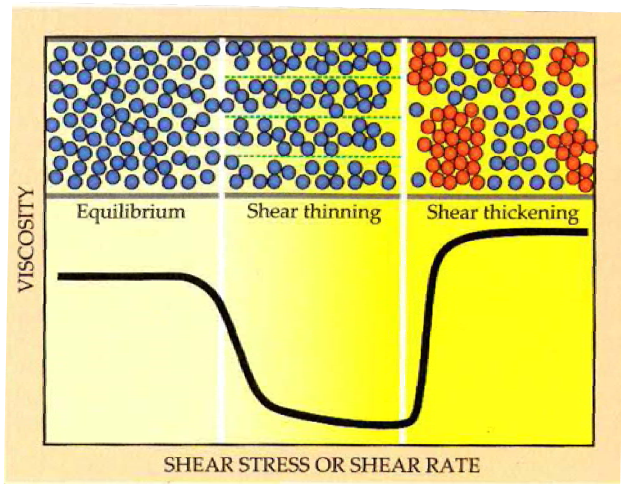
Wagner and Brady, *Phys. Today*, Oct 2009

Steady shear viscosity - shear thickening

Particles bump into each other

Layers of particles slide past each other

Clusters of particles bump into each other



Hydrodynamic interaction causes shear thickening:

The pressure distribution in the Newtonian suspending fluid exerts forces on the particles and causes them to form structures in flow.

25

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity - temperature dependence

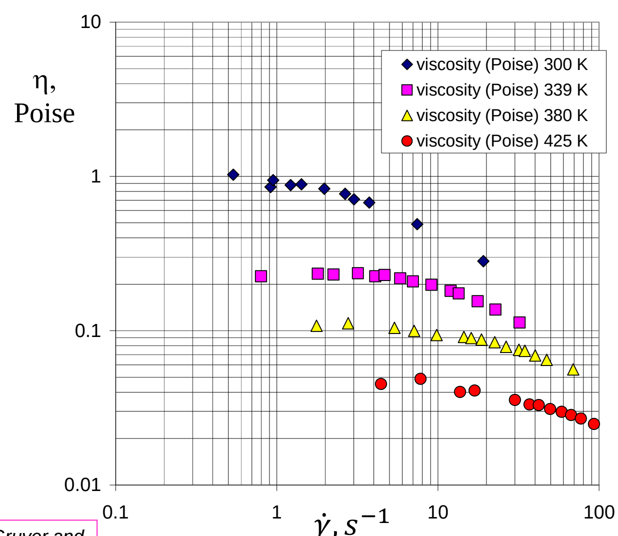


Figure 6.28, p. 189 Gruver and Kraus; PB melt

26

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity - pressure dependence

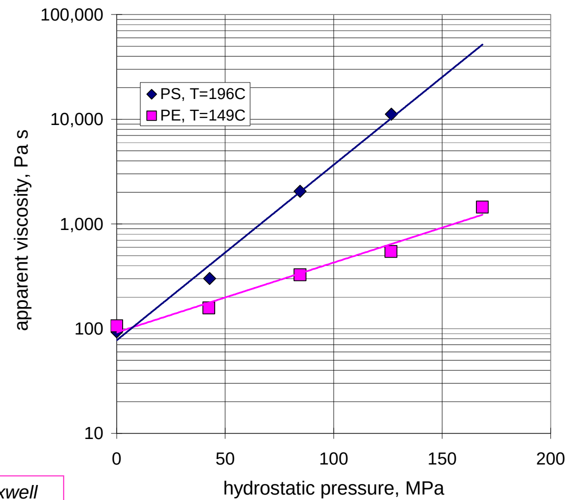


Figure 6.29, p. 189 Maxwell and Jung; PS and PE

27

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

28

Material Behavior Catalog (in terms of material functions)

Experimental Data (continues)

Next:

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

29

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - Storage and Loss Moduli

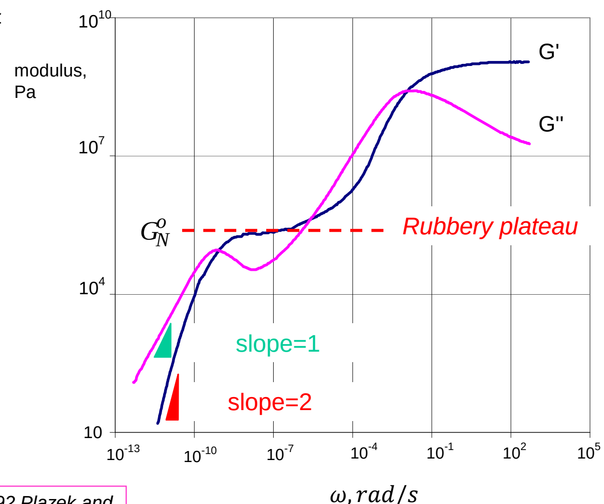


Figure 6.30, p. 192 Plazek and O'Rourke; PS

30

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - Storage and Loss Moduli

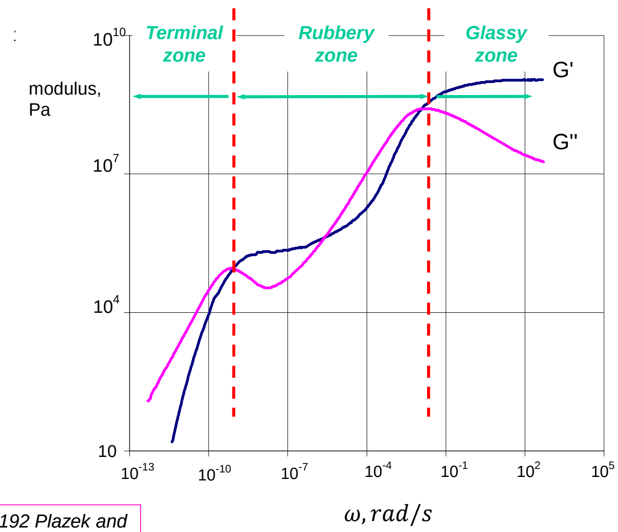


Figure 6.30, p. 192 Plazek and O'Rourke; PS

31

Material Behavior Catalog (in terms of material functions)

Step Shear Strain - Relaxation Modulus

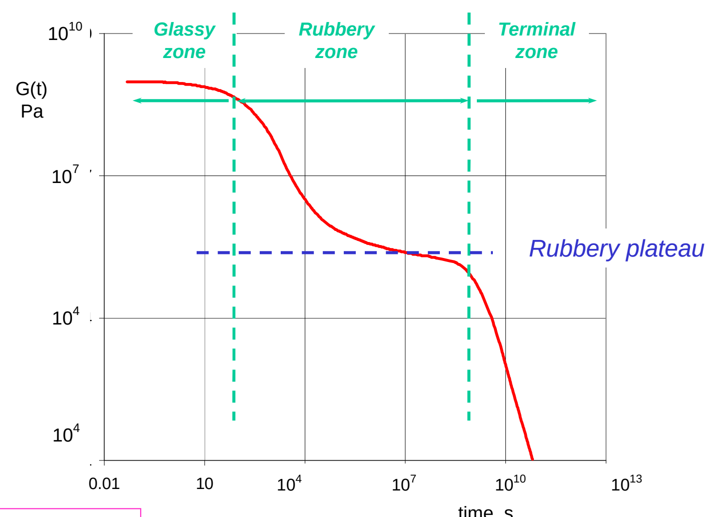


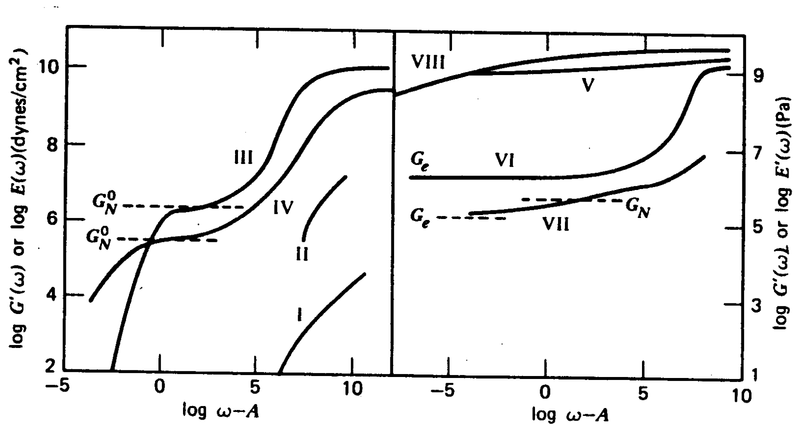
Figure 6.31, p. 192 Plazek and O'Rourke; PS

32

Material Behavior Catalog (in terms of material functions)

Ferry's Summary of Viscoelastic properties of several classes of polymers

Storage modulus



$\omega, rad/s$

Figure2-3 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980

33

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 x 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.

VII. **Highly crystalline polymer**: linear polyethylene.

34

Material Behavior Catalog (in terms of material functions)

Ferry's Summary of Viscoelastic properties of several classes of polymers

Loss modulus

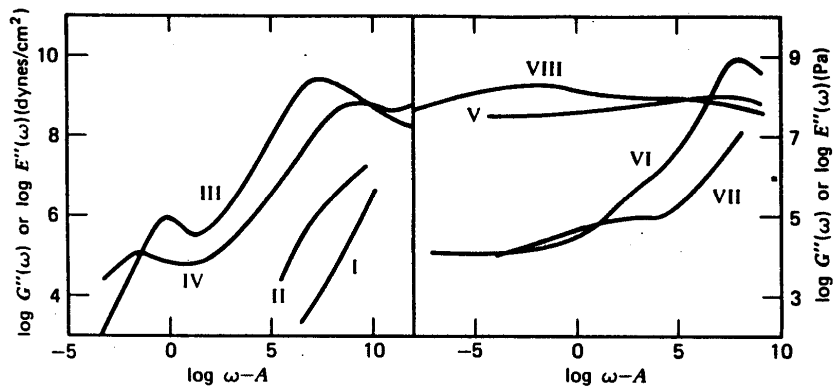


Figure2-4 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980

35

Material Behavior Catalog (in terms of material functions)

Ferry's Summary of Viscoelastic properties of several classes of polymers

Relaxation modulus

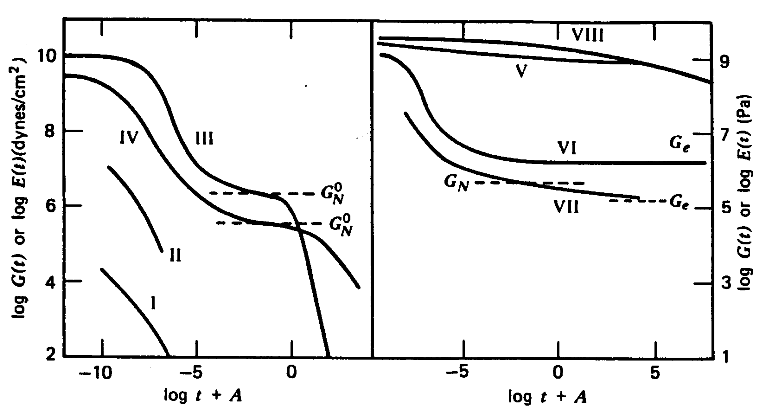


Figure2-2 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980

36

Material Behavior Catalog (in terms of material functions)

Ferry's Summary of Viscoelastic properties of several classes of polymers

Loss tangent

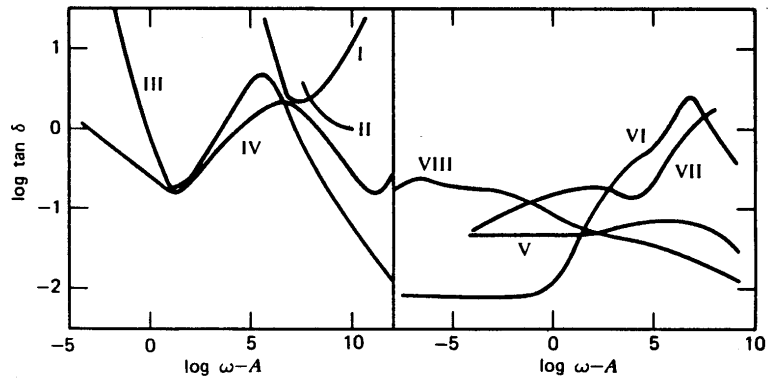


Figure2-8 from Ferry, Viscoelastic Properties of Polymers, Wiley, 1980

37

Material Behavior Catalog (in terms of material functions)

Cox-Merz Rule

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

An empirical way to infer steady shear data from SAOS data.

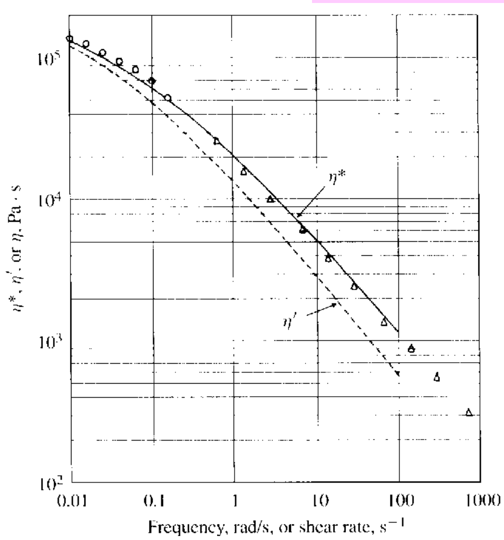


Figure 6.32, p. 193 Venkataraman et al.; LDPE

38

Material Behavior Catalog (in terms of material functions)

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

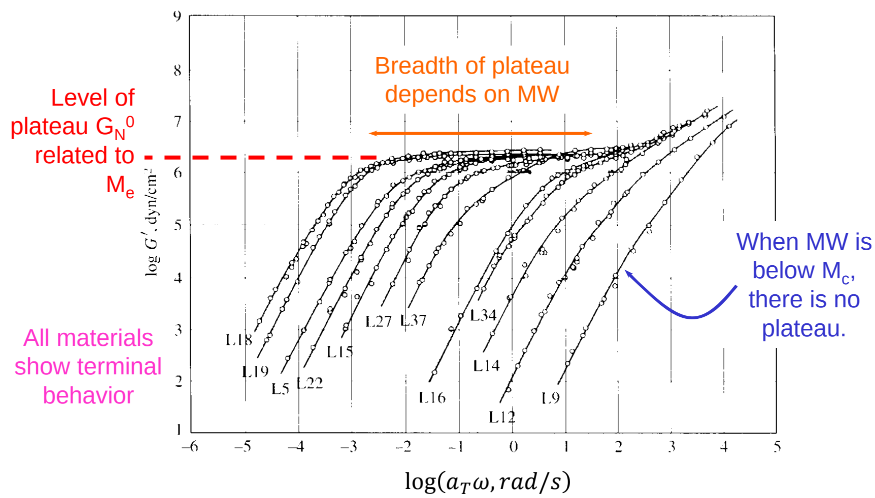
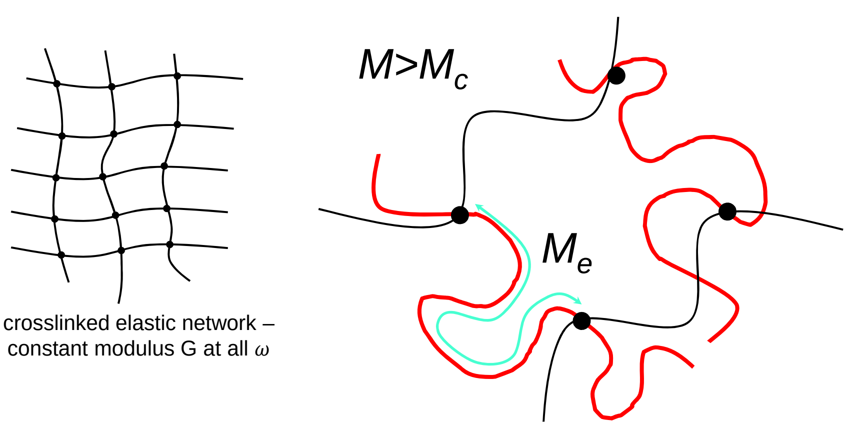


Figure 6.34, p. 195 Onogi et al; narrow MWD PS

39

Material Behavior Catalog (in terms of material functions)

Entanglements form a temporary network



crosslinked elastic network – constant modulus G at all ω

Entangled polymers – over a range of w when unable to disentangle, exhibit a constant modulus G_N^0

40

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)

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

n = density of effective cross links

n = cross links/volume

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

$$M_c \cong 2M_e$$

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

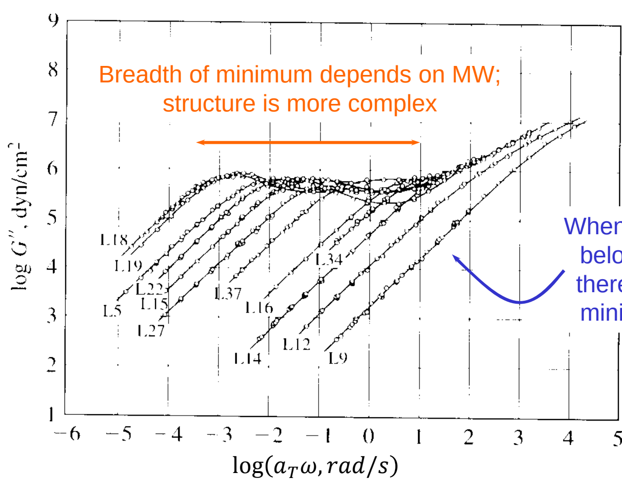
Larger the MW between entanglements, the softer the network

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

41

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - *G"* molecular weight dependence



All materials show terminal behavior

When MW is below M_c, there is no minimum.

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

42

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

43

Material Behavior Catalog (in terms of material functions)

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

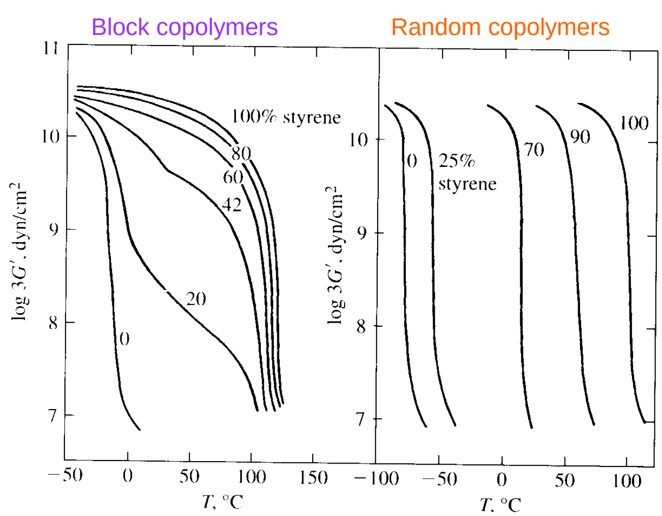


Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random

44

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - temperature dependence

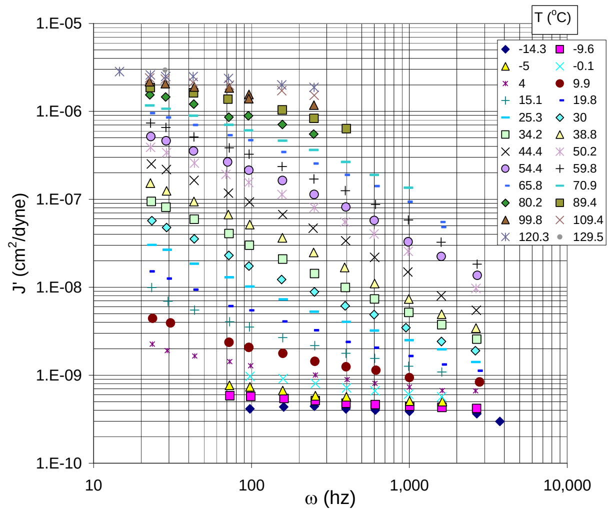


Figure 6.43, p. 202 Dannhauser et al.; P-OctylMethacrylate

45

Material Behavior Catalog (in terms of material functions)

Time-Temperature Superposition

Material functions depend on g_i, l_i

relaxation times

relaxation moduli

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

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

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

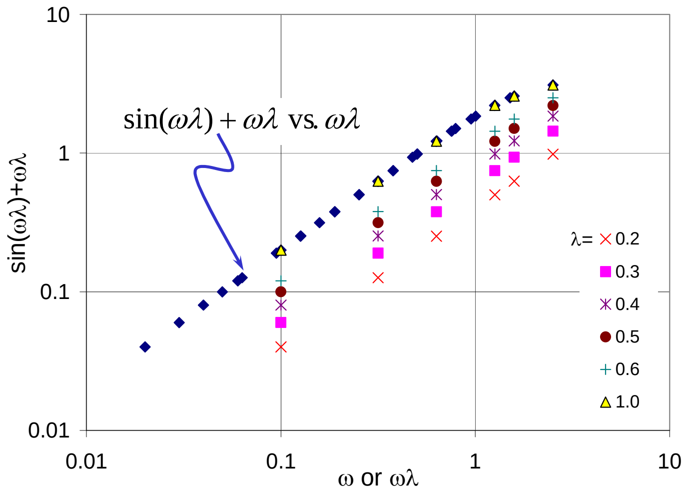
Theoretical result: in the linear-viscoelastic regime, material functions are a function of wl_i rather than of w and l_i individually.

46

Material Behavior Catalog (in terms of material functions)

Example: plot a simple function

$$f(\omega,\lambda)=\sin(\omega\lambda)+\omega\lambda$$



47

Material Behavior Catalog (in terms of material functions)

In general,

$$G' = G'(\omega\lambda_1(T),\ \omega\lambda_2(T),\ \omega\lambda_3(T),\ \mathrm{K}\quad)$$

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.

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

48

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 ($a_T(T)$)

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

temperature dependence of all moduli ($T\rho(T)$)

49

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 $\tilde{\lambda}_i$)

50

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - temperature dependence

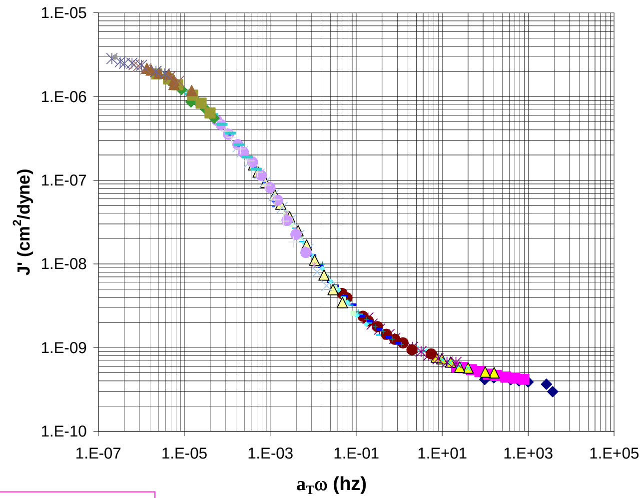


Figure 6.44, p. 202 Dannhauser et al.; P-OctylMethacrylate

51

Material Behavior Catalog (in terms of material functions)

Small-Amplitude Oscillatory Shear - temperature dependence

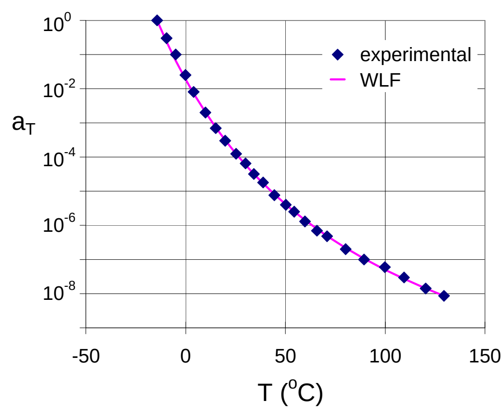


Figure 6.45, p. 203 Dannhauser et al.; P-OctylMethacrylate

52

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 $T > T_g + 100^o C$

Williams-Landel-Ferry (WLF) equation

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

found to be valid *w/in* $100^o C$ of T_g

53

Material Behavior Catalog (in terms of material functions)

Shifting other Material Functions

Other linear viscoelastic material functions:

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

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

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

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

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

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

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

Independent of temperature

54

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)

55

Material Behavior Catalog (in terms of material functions)

Steady shear viscosity - Temperature dependence

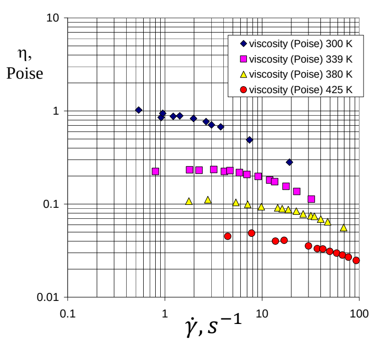
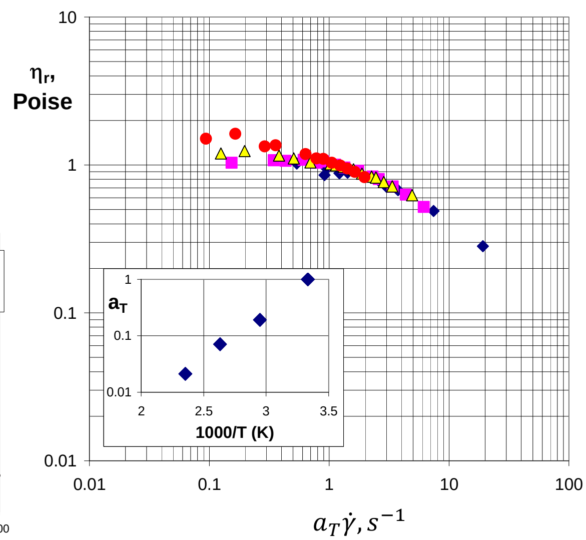


Figure 6.46, p. 204 Gruver and Kraus; PB melt



56

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 $\log G'(T)$.

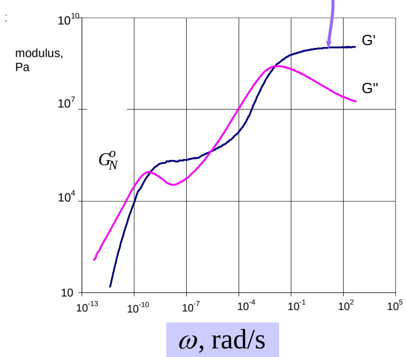


Figure 6.30, p. 192 Plazek and O'Rourke; PS

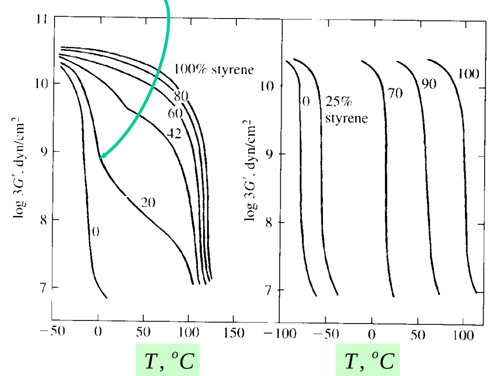


Figure 6.39, p. 198 Cooper and Tobolsky; SIS block and SBS random

Material Behavior Catalog (in terms of material functions)

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

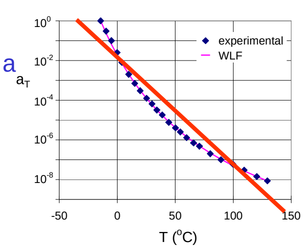
$$G'_r \equiv \frac{G'(T)T_{ref}\rho_{ref}}{T\rho} = f(a_T\omega, \tilde{\lambda}_i)$$

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 w resemble slightly skewed plots of log G' versus log $a_T w$. (mirror image)

Material Behavior Catalog (in terms of material functions)

Application of SAOS

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

○ 0 wt%
△ 30 wt%
□ 50 wt%
▽ 70 wt% tackifier

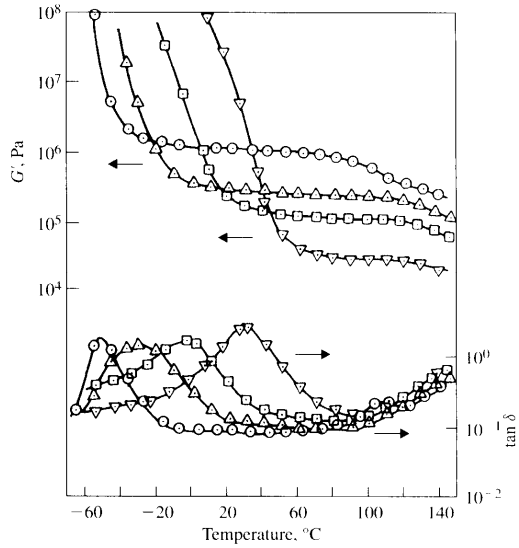
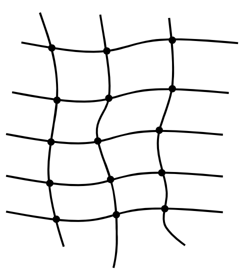


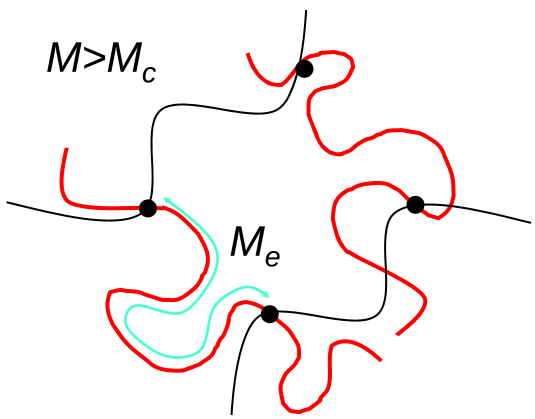
Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier

Material Behavior Catalog (in terms of material functions)

Entanglements form a temporary network



crosslinked elastic network – constant modulus G at all w



Entangled polymers – over a range of w when unable to disentangle, exhibit a constant modulus G_N^0

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

61

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

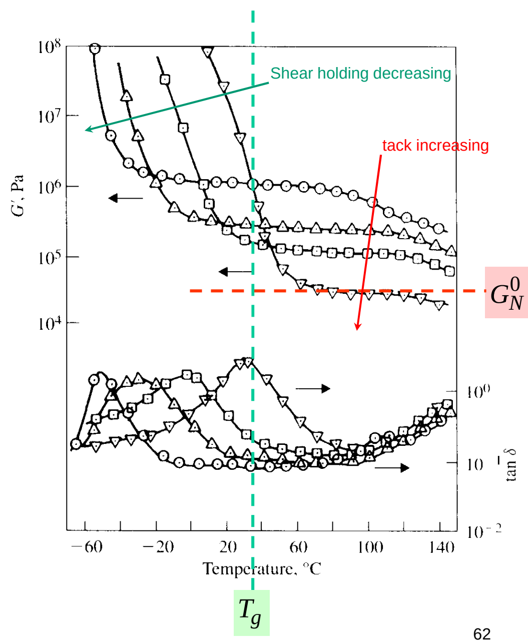


Figure 6.48, p. 207 Kim et al.; SIS block copolymer with tackifier

62

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

63

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

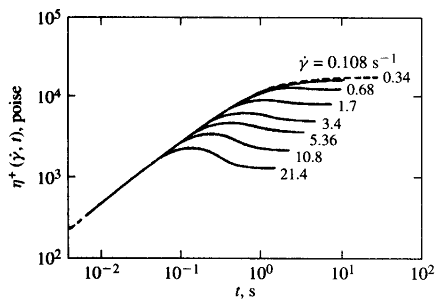
Unsteady elongation

64

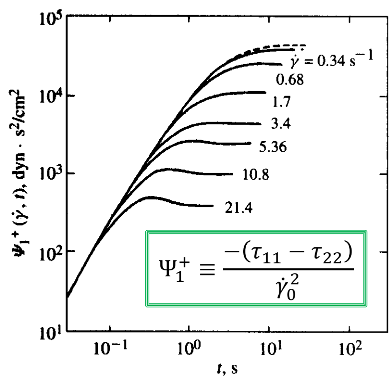
Material Behavior Catalog (in terms of material functions)

Startup of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} 0 & t < 0 \\ \dot{\gamma}_0 & t \geq 0 \end{cases}$$



$$\eta^+ \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$



$$\Psi_1^+ \equiv \frac{-(\tau_{11} - \tau_{22})}{\dot{\gamma}_0^2}$$

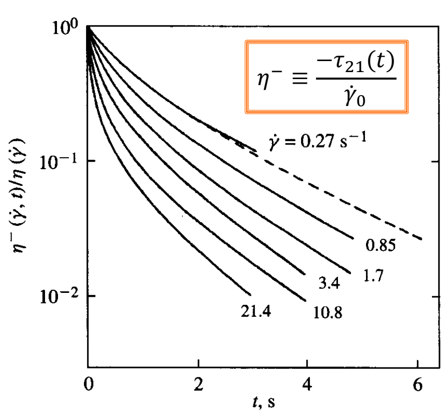
Figures 6.49, 6.50, p. 208 Menezes and Graessley, PB soln

65

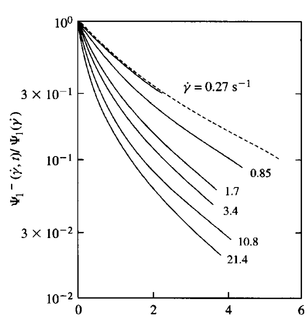
Material Behavior Catalog (in terms of material functions)

Cessation of Steady Shearing

$$\underline{v} \equiv \begin{pmatrix} \dot{\varsigma}(t) x_2 \\ 0 \\ 0 \end{pmatrix}_{123} \qquad \dot{\varsigma}(t) = \begin{cases} \dot{\gamma}_0 & t < 0 \\ 0 & t \geq 0 \end{cases}$$



$$\eta^- \equiv \frac{-\tau_{21}(t)}{\dot{\gamma}_0}$$



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

Figures 6.51, 6.52, p. 209 Menezes and Graessley, PB soln

66

Material Behavior Catalog (in terms of material functions)

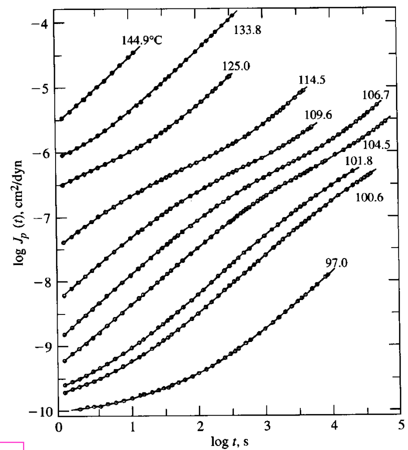
Shear Creep

$$\underline{v} \equiv \begin{pmatrix} \dot{\gamma}_{21}(t)x_2 \\ 0 \\ 0 \end{pmatrix}_{123}$$

$$\tau_{21}(t) = \begin{cases} 0 & t < 0 \\ \tau_0 & t \geq 0 \end{cases}$$

$$J_p = \frac{J(T)T\rho}{T_{ref}\rho_{ref}}$$

Data have been corrected for vertical shift.



$$J(t,\tau_0) \equiv \frac{\gamma_{21}(0,t)}{-\tau_0}$$

Figure 6.53, p. 210 Plazek; PS melt

67

Material Behavior Catalog (in terms of material functions)

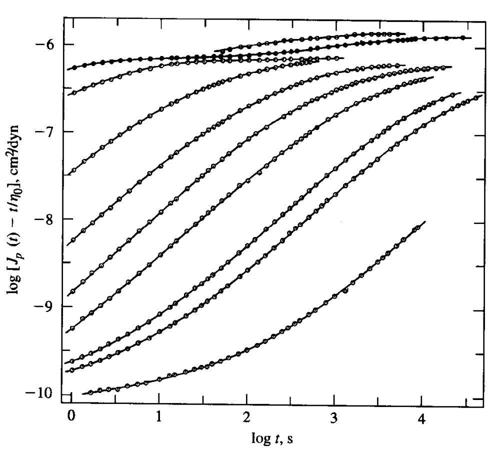
Shear Creep - Recoverable Compliance

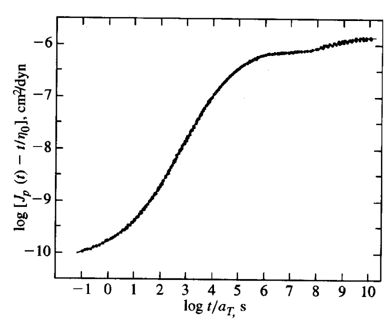
$$J(t) = R(t) + \frac{t}{\eta_0}$$

recoverable strain

$$\gamma(t) = \gamma_r(t) + t\dot{\gamma}_\infty$$

total strain; non-recoverable strain





Figures 6.54, 6.55, p. 211 Plazek; PS melt

68

Material Behavior Catalog (in terms of material functions)

Step shear strain - *strain dependence*

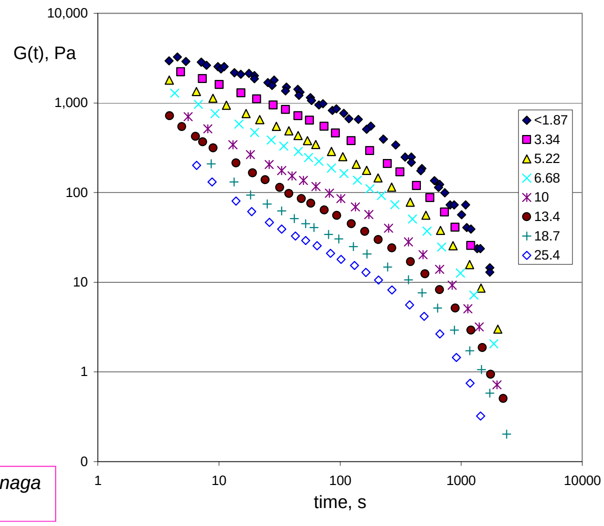


Figure 6.57, p. 212 Einaga et al.; PS soln

69

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.

Damping function

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

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

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

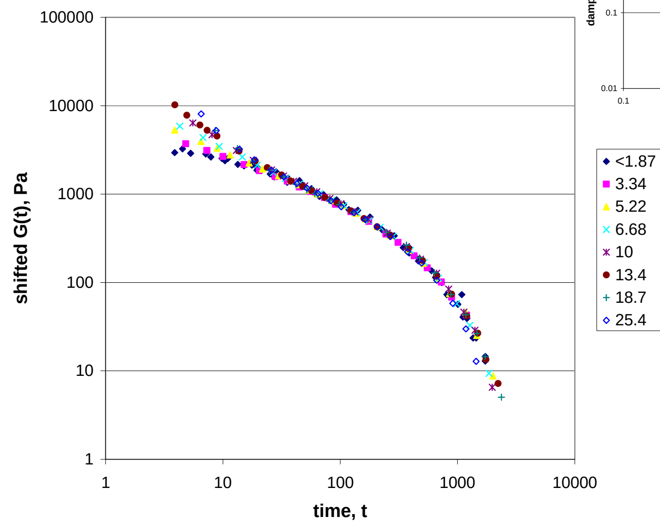
When $G(t,\gamma_0) = G(t)h(\gamma_0)$ the behavior is called time-strain separable.

This behavior is predicted by some advanced constitutive equations.

70

Material Behavior Catalog (in terms of material functions)

Step shear strain - **Damping Function**



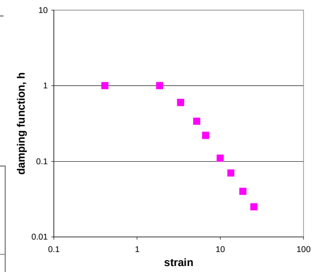


Figure 6.58, p. 213
Einaga et al.; PS soln

71

Material Behavior Catalog (in terms of material functions)

Large-Strain Unsteady Shear Summary:

1. General traits
2. Measurement issues

72

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

73

Material Behavior Catalog (in terms of material functions)

Steady State Elongation Viscosity

Both tension thinning and thickening are observed.

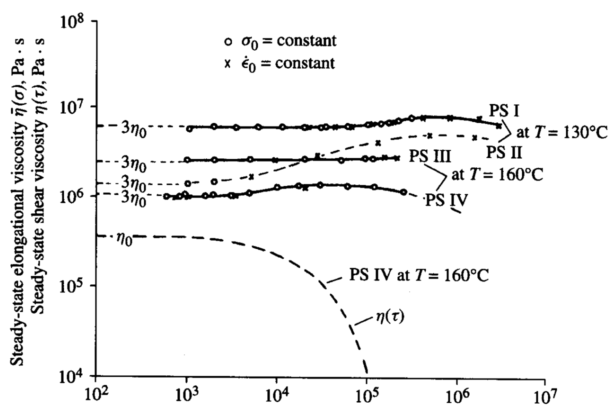


Figure 6.60, p. 215
Munstedt.; PS melt

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

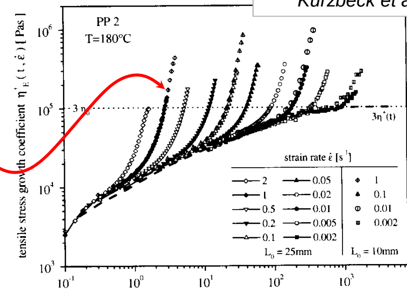
74

Material Behavior Catalog (in terms of material functions)

Start-up of Steady Elongation

Figure 6.64, p. 218 Kurzbeck et al.; PP

Strain-hardening



Fit to an advanced constitutive equation (12 mode pom-pom model)

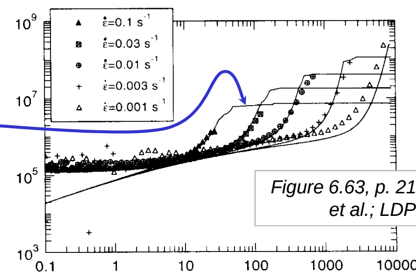
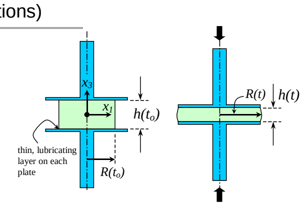


Figure 6.63, p. 217 Inkson et al.; LDPE

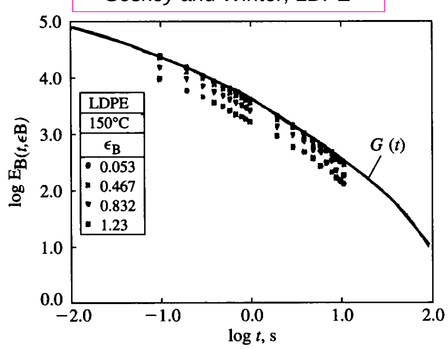
75

Material Behavior Catalog (in terms of material functions)

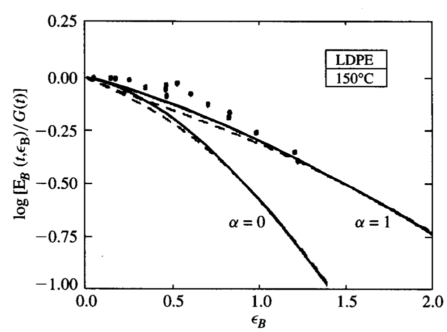
Elongation Step-Strain



Figures 6.68, 6.69, pp. 220-1 Soskey and Winter; LDPE



Relaxation function for step biaxial elongation



Damping function for step biaxial elongation

76

Material Behavior Catalog (in terms of material functions)

Elongational Flow Summary:

1. General traits
2. Measurement issues

77

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

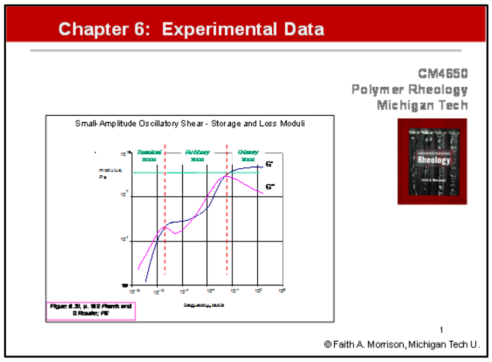
Mewis, Jan and Norm Wagner, *Colloidal Suspension* (Cambridge, 2012)

Journals

Journal of Rheology
Rheologica Acta
Macromolecules

78

Done with
Experimental Data.



Let's move on to
Generalized
Newtonian Fluids

Chapter 7: Generalized Newtonian fluids

CM4650
Polymer Rheology
Michigan Tech