

Rheology

Purely Viscous Flow

Viscometric Measurements

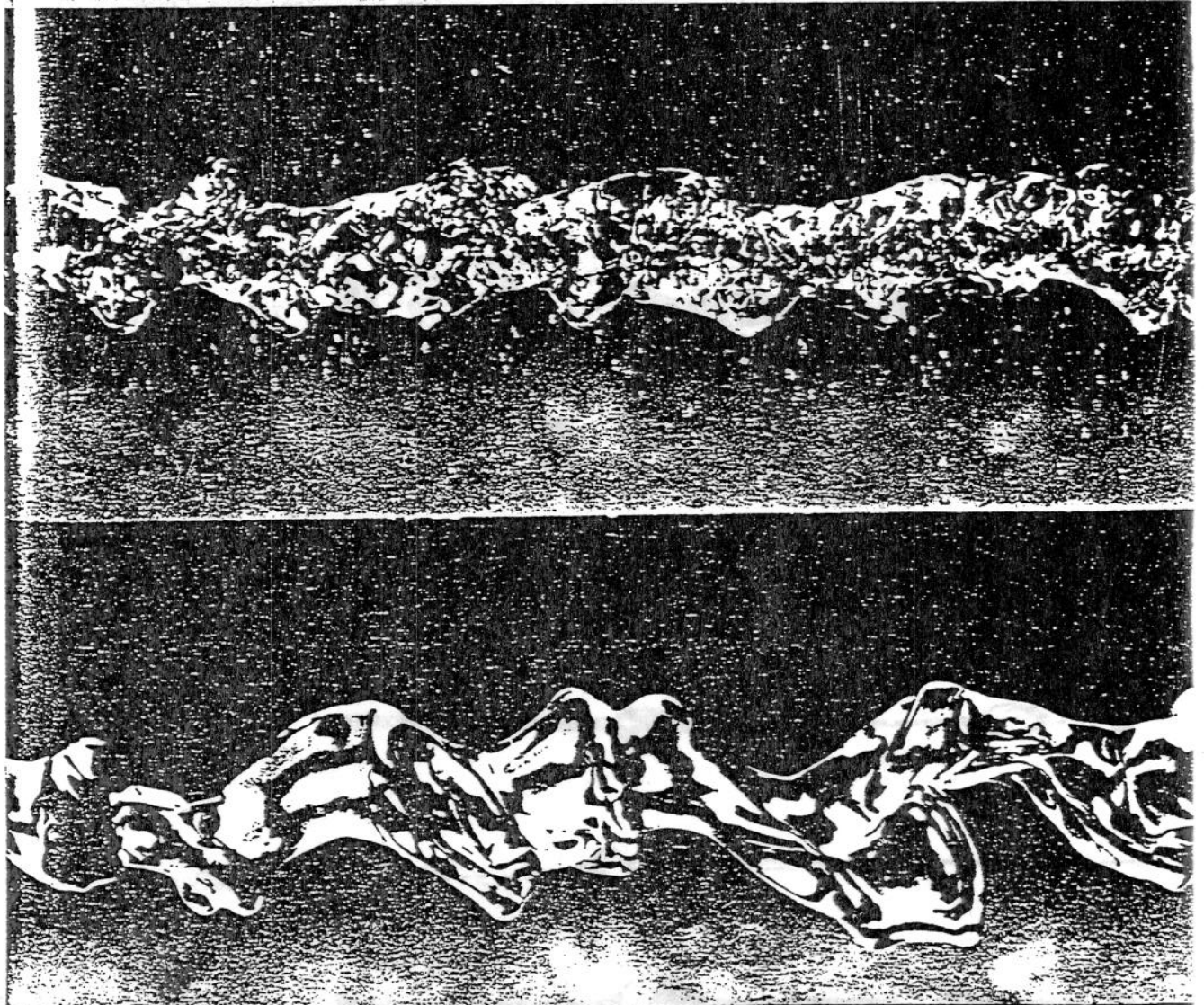
Linear Viscoelasticity

Polymer Physics: Reptation

*Rosen Chapters XV, XVI, XVII,
XVIII*

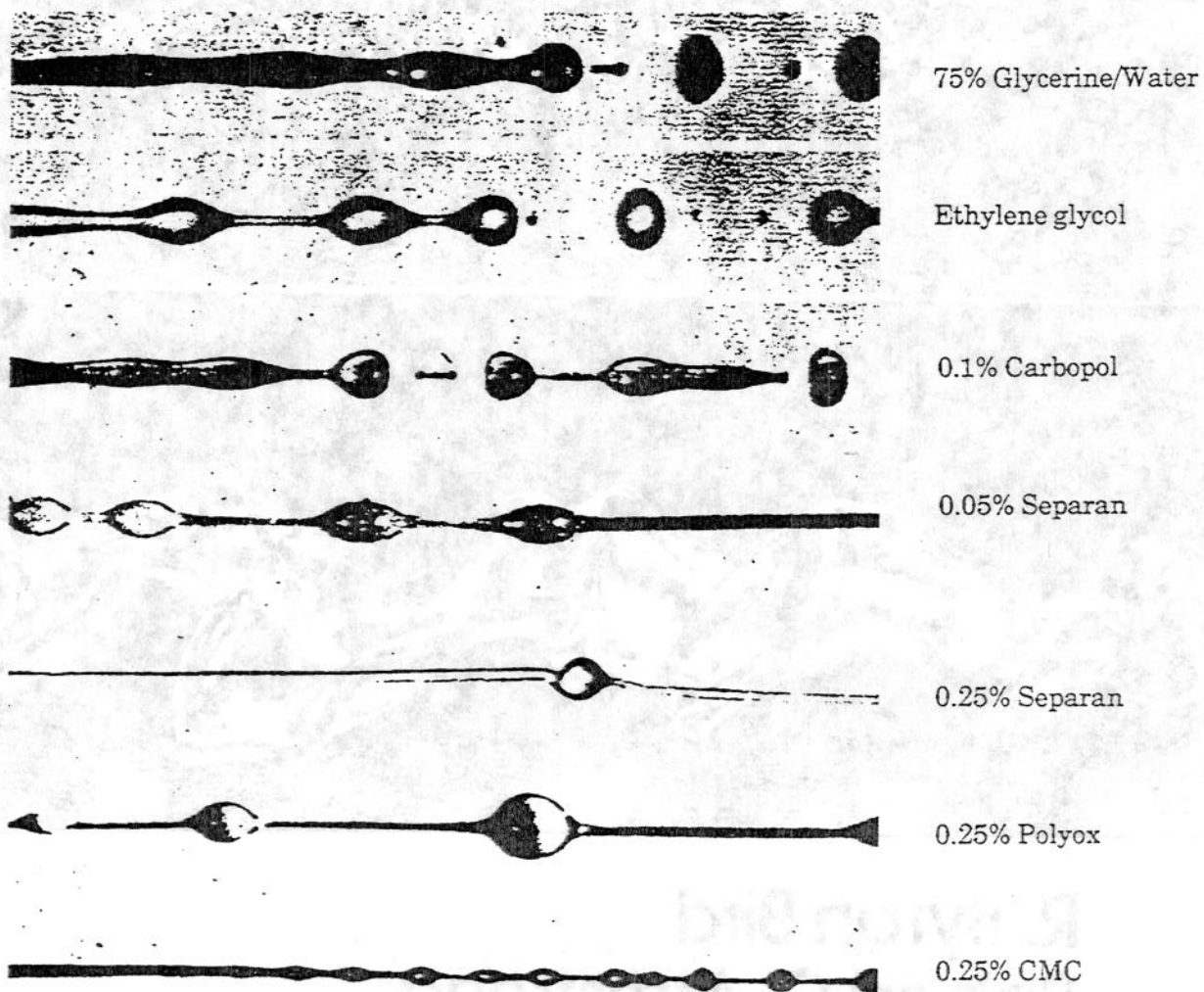
DYNAMICS OF POLYMERIC LIQUIDS

SECOND EDITION
Volume 1: Fluid Mechanics



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Robert C. Armstrong
Ole Hassager

▼ Fig. 6.1. Jet breakup. From the top down in the sequence of photographs is illustrated the typical appearance of two Newtonian fluids (75% glycerine-water and ethylene glycol), an inelastic non-Newtonian fluid (0.1% Carbopol solution); and four examples for viscoelastic fluids (0.05% and 0.25% polyacrylamide (Separan) solutions, a 0.25% polyethylene oxide (Polyox) solution and a 0.25% carboxy-methyl cellulose solution). The fluid jet is photographed using high speed photography as it emerges from a capillary exit into air at high Reynolds number. In the Newtonian jets a disturbance from within the capillary tube is propagated as an exponentially growing wave; the breakup length is reproducible and measurable from the photographs. The inelastic non-Newtonian Carbopol solution appears to have characteristics similar to the Newtonian jets. In contrast, the initial wave growth is retarded in the viscoelastic fluid jets and a string of droplets connected by thin threads is formed. (From M. Golding, J. Yerushalmi, R. Pfeffer and R. Shinnar, *J. Fluid Mechanics*, 38, 1969, 689.)



out of the fluid, the
siphoned.

f the exit, and then

the cross section of

Newtonian and non-
Newtonian fluids
siphoned out of
a reservoir (see Fig.
the container. We
Newtonian fluid as the
non-Newtonian fluid

shown in Figs. 2.5-3
large molecules along
the siphon work.
arising in the fluid

bubbles in a flow
regime¹¹ that when the
small tube diameter, a
large entrance to the
reservoir before finally

experiments on the Dead Sea
reservoir (see also
Gottlieb), The Modern
Science, which seems to be
Moshe Gottlieb.

of Dr. J. V. Sengers, Newark

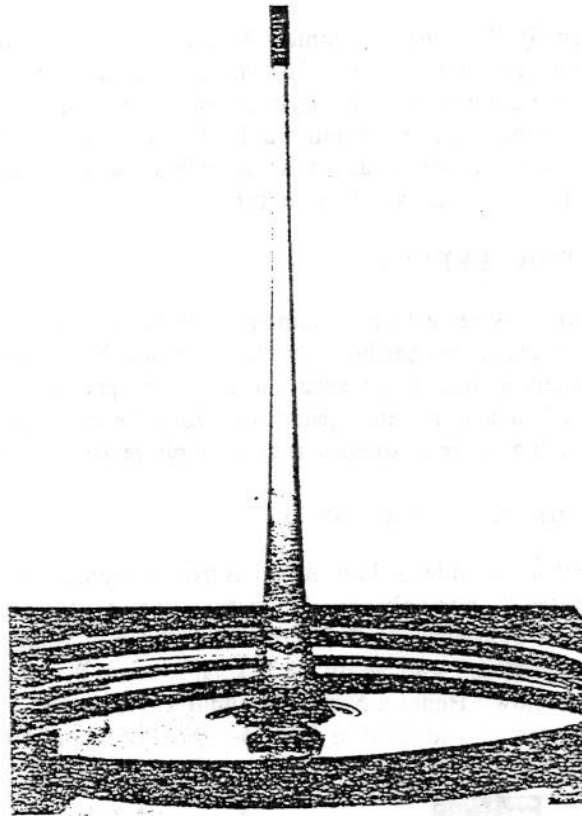


FIGURE 2.5-3. Fluid column in tubeless siphon experiment with a high molecular weight hydrocarbon polymer, AM-1 in JP-8 aviation fuel. [Reproduced from S. T. J. Peng and R. F. Landel, *J. Appl. Phys.* 47, 4255 (1976)].

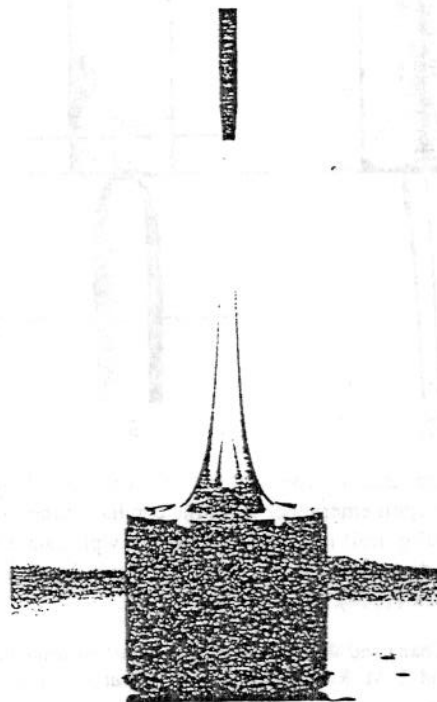


FIGURE 2.5-4. Fluid column in tubeless siphon experiment with the same polymer as in Fig. 2.5-3. Note the stable trapped bubble at the bottom of the column. [Reproduced from S. T. J. Peng and R. F. Landel in G. Astarita, G. Marrucci, and L. Nicolais, eds., *Rheology*, Vol. 2, Plenum Press, New York (1980), p. 388.]

polyacrylamide solution (P). For the Newtonian fluid the streaming motion is directly toward the oscillating cylinder along the axis of oscillation in an inner region, and opposite in an outer region. For the polymer solution, by contrast, there is only one region and the direction is toward the cylinder along the entire axis of oscillation.³ Thus there is a flow reversal in most of the fluid, but we see also that the rule about the competing effects of inertia and elasticity is no more than a rule of thumb.

§2.5 OTHER ELASTIC EFFECTS

In this section we consider a further number of effects that are all in one way or another manifestations of elastic properties of polymeric fluids. However the experiments are more difficult to analyze than those encountered in the previous two sections. In addition the experiments form a more heterogeneous group in the sense that there is not one well-defined property, such as normal stresses, that is simply related to them all.

a. Extrudate Swell (also called "die swell")

In this experiment we consider a fluid that exits from a capillary of diameter D into air forming a jet of diameter D_e . For polymeric fluids it is customary to refer to the material in the jet as the *extrudate*. For Newtonian fluids D_e will be about 13% larger than D in the limit of small Reynolds number¹ and about 13% smaller than D in the limit of large Reynolds number laminar flow.² Hence a Newtonian fluid leaves the capillary without any dramatic change in diameter, as evidenced in Fig. 2.5-1 (N). The contrasting behavior of a

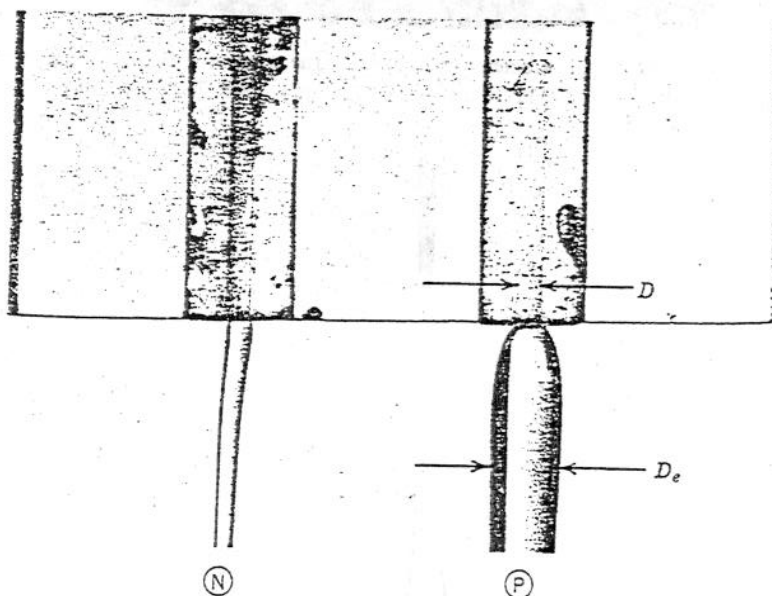


FIGURE 2.5-1. Behavior of fluids issuing from orifices. (N) A stream of Newtonian fluid (silicone fluid) shows no diameter increase upon emergence from the capillary tube; (P) a solution of 2.44 g of polymethylmethacrylate ($\bar{M}_n = 10^6$ g/mol) in 100 cm³ of dimethylphthalate shows an increase by a factor of 3 in diameter as it flows downward out of the tube. [Reproduced from A. S. Lodge, *Elastic Liquids*, Academic Press, New York (1964), p. 242.]

³ A detailed analysis is given by C. F. Chang and W. R. Schowalter, *J. Non-Newtonian Fluid Mech.*, 6, 47-67 (1979).

¹ R. I. Tanner in J. R. A. Pearson and S. M. Richardson, eds., *Computational Analysis of Polymer Processing*, Applied Science, London (1983), p. 66.

² See Problem 1B.4.

polymer:
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polymers, and

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where the subs
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in Example 2.3
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heating produ
demonstrated⁵
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"silly putty" wa
the tube extrude

In some
increased flow

³ R. I. Tanner, *J. Po*
(1985), pp. 321-329.

⁴ J. Vlachopoulos, N

⁵ H. B. Phuoc and F

⁶ R. I. Tanner, *J. N*

⁷ A. S. Lodge, *Elast*

⁸ H. Giesekus, *Rheo*

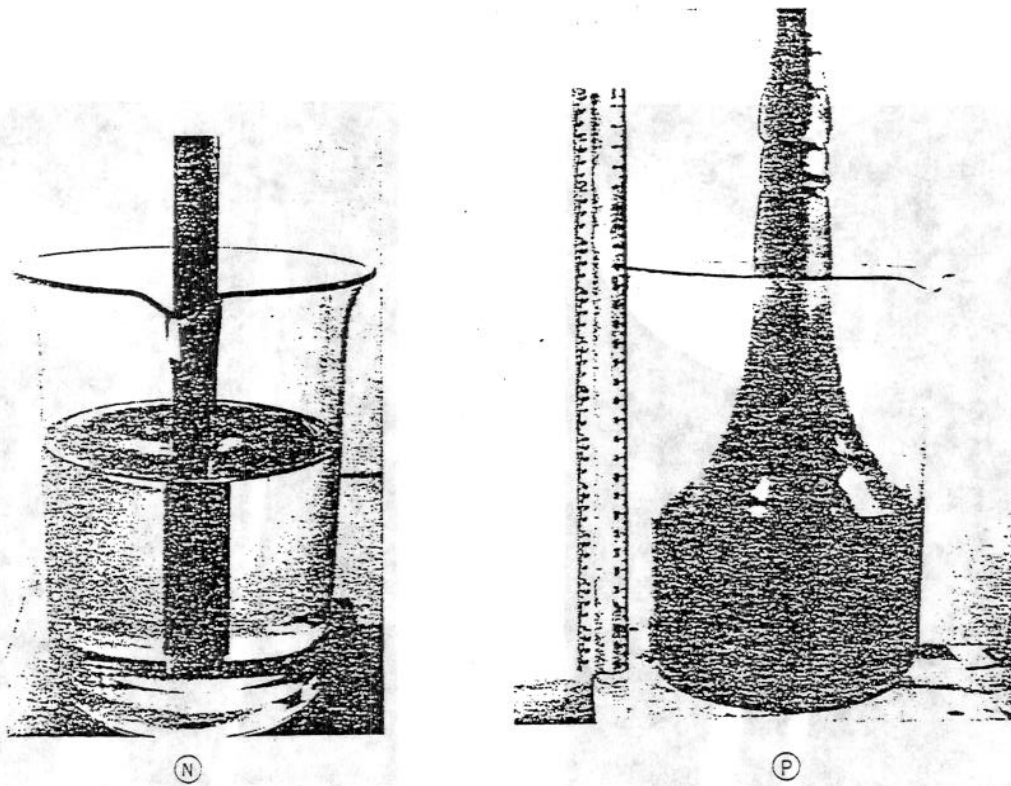


FIGURE 2.3-1. Fixed cylinder with rotating rod. (N) The Newtonian liquid, glycerin, shows a vortex: (P) the polymer solution, polyacrylamide in glycerin, climbs the rod. The rod is rotated much faster in the glycerin than in the polyacrylamide solution. At comparable low rates of rotation of the shaft, the glycerin will climb whereas the free surface of the Newtonian liquid will remain flat. [Photographs courtesy of Dr. F. Nazem, Rheology Research Center, University of Wisconsin-Madison.]

This phenomenon was first described by Garner and Nissan² and by Russel³ but seems to have been known in the paint industry prior to its description in the scientific literature. The phenomenon may be interpreted in a rather simple fashion with the use of the notion¹ of an extra tension along the streamlines. In the rod-climbing experiment the streamlines are closed circles and the extra tension along these lines "strangulates" the fluid and forces it inwards against the centrifugal force and upwards against the gravitational force.

The above simple argument takes no account of the second normal stress difference. In Example 2.3-1 we present an analysis of the experiment based on the equations of motion, which shows that both normal stress differences actually contribute to the effect.

Finally we mention the interesting *Quelleffect*⁴. If instead of having a rotating rod in

² F. H. Garner and A. H. Nissan, *Nature*, 158, 634-635 (1946).

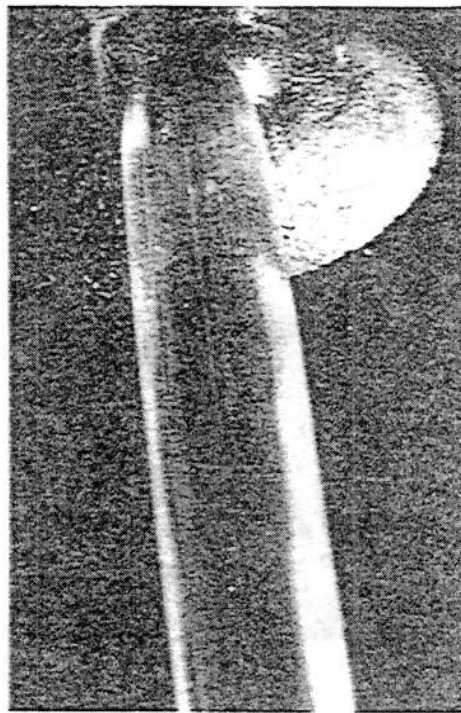
³ R. J. Russel, Ph.D. Thesis, Imperial College, University of London (1946) (unpublished), p. 58.

⁴ K. Kirschke, *Polymères et Lubrification*, Colloques Internationaux du CNRS, No. 233, Éditions du CNRS, Paris (1974), pp. 137-144; G. Böhme, *Strömungsmechanik nicht-Newtonischer Fluide*, Teubner, Stuttgart (1981), pp. 127-128; G. R. Böhme and W. Warnecke, *Rheol. Acta*, 24, 22-34 (1985).

▼ Fig. 2.15. Extrudate of a linear silicone oil at the exit of a cylindrical profiled orifice. The pressure is progressively increased in moving from (a) through (d). Sharkskin was not observed in this sequence. (From J.M. Piau, N. El Kissi and B. Tremblay, *J. Non-Newtonian Fluid Mechanics*, 34, 1990, 145.)



(a)



(b)



(c)



(d)

Rheology

"rheo" - Greek word meaning "to flow"

* Rheology: study of the deformation and flow of all matter.

* word coined by Professor Bingham (yes, the same guy!) of Lafayette College (Easton, PA).

• American Society of Rheology founded in 1929.

* Aside

QWERTY - standard letter arrangement on keyboard.

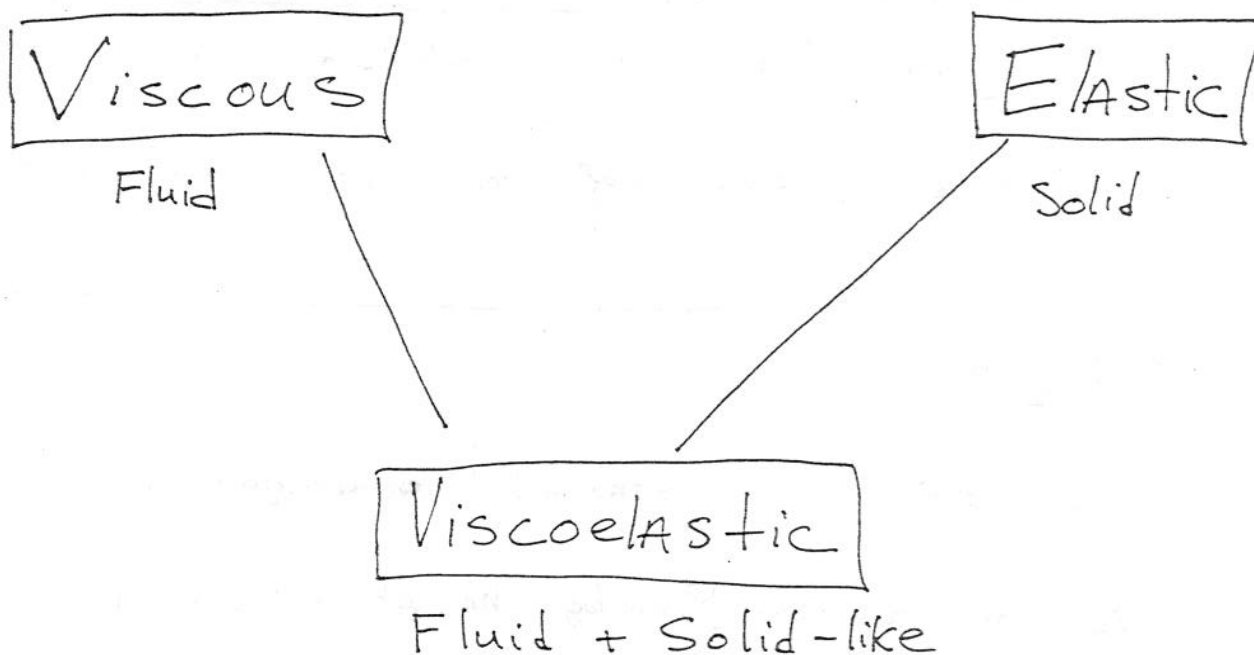
∞ Any book on Rheology has at least one incorrect reference to Theology.

Q. How is Rheology like Theology?

A. The theoreticians have the upper hand due to a lack of good experimental data.

Polymer Solutions

What makes a macromolecule different from a molecule in solution?



- the combination of viscous flow and an elastic restoring force is what gives polymer solutions their unusual behavior — and keeps Rheologists employed!!

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What do the following have in common?

- ① Stained Glass Windows @ Notre Dame (Paris).
- ② California Wildflower Honey
- ③ Balloons
- ④ Frisbee
- ⑤ STP Motor Oil (the "Racer's Edge")
- ⑥ Silly Putty
- ⑦ Perrier Water
- ⑧ Breast Implants
- ⑨ Mac Donald's Shakes
- ⑩ The Rocky Mountains

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Viscosity of Various Fluids

Note: 1 milli Pa-s = 1 centipoise

Material	η (cp)	Consistency
Air	10^{-2}	gas
Water	1.0	fluid
Olive Oil	100	liquid
Glycerine	10^3	liquid
Molasses	10^5	thick liquid
Polymer Melts	$10^5 - 10^9$	viscous liquid
Pitch	10^{12}	stiff
Glass	10^{24}	rigid

SUBJECT

Shear Viscosity

JOB NO.

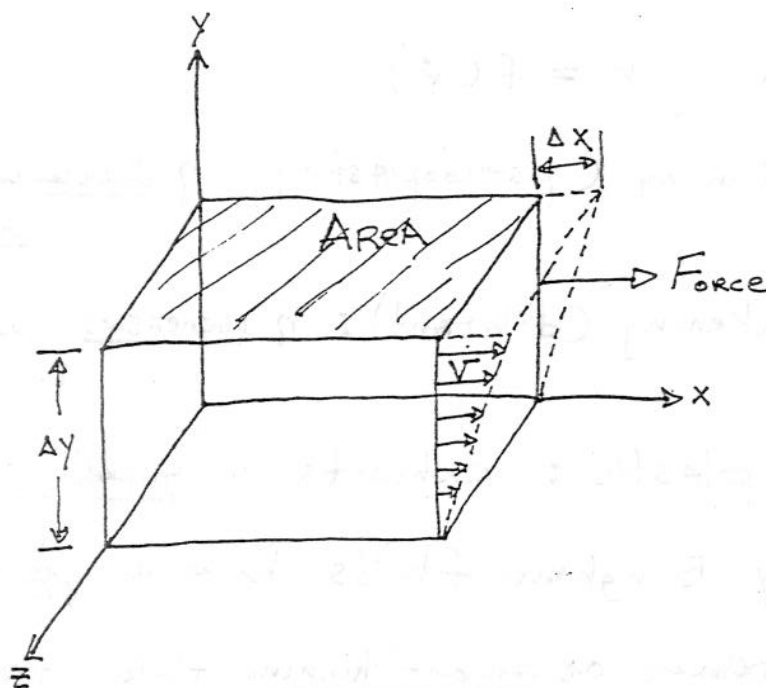
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$$\text{Stress} = \frac{\text{Force}}{\text{AREA}} \quad \sigma = F/A \quad [] \frac{\text{dynes}}{\text{cm}^2}$$

$$\text{Shear Strain} = \frac{\Delta x}{\Delta y} = \gamma \quad \text{Velocity} = \frac{d(\Delta x)}{dt} = v \quad [] \text{cm/sec}$$

$$\text{Shear Rate} = \frac{\Delta v}{\Delta y} = \dot{\gamma} \quad [] \text{sec}^{-1}$$

Newton's Law of Viscosity:

$$\sigma = \eta \frac{dv}{dy} = \eta \dot{\gamma} \quad \text{Newtonian Fluid}$$

- $\eta = \text{shear viscosity} \quad [] \frac{\text{dynes}}{\text{cm}^2 \cdot \text{sec}} = \text{Poise}$
 $= \text{Pa} \cdot \text{sec}$

Material Classification / Definitions

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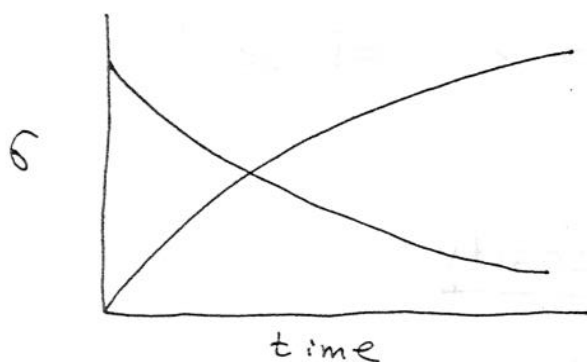
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Definitions:

- Newtonian: $\eta \neq f(\dot{\gamma})$
- Shear-thinning (pseudoplastic): η decreases with increasing $\dot{\gamma}$
- Shear-thickening (dilatant): η increases with increasing $\dot{\gamma}$
- Bingham plastic: exhibits a yield stress
 → typically Bingham fluids have a yield stress
 and behave as shear-thinning fluids thereafter
 i.e. $\sigma = \sigma_0 + K \dot{\gamma}^n$ ($n=1$ Newtonian Binghamlike)

Time-dependent fluids.



Rheopectic: viscosity increases with increasing time at constant $\dot{\gamma}$

Thixotropic: viscosity decreases with time at constant $\dot{\gamma}$

Units.

stress (σ)CGSdynes/cm²SINewton/m² = Pascalviscosity (η)
 dynes-sec/cm²
 = poise (P)
 = 100 cp

 PA-sec
 10 poise

SUBJECT

SHEAR Flow Behavior

JOB NO.

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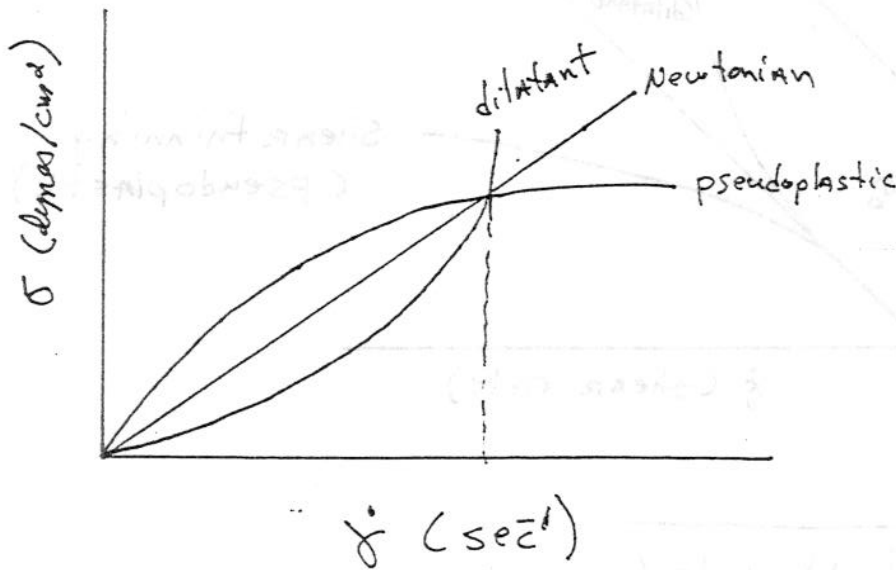
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How can three different fluids look the same under given flow conditions?



For Polymer Solutions specification of the shear rate is essential for fluid characterization.

Shear Flow Behavior of Various Fluids

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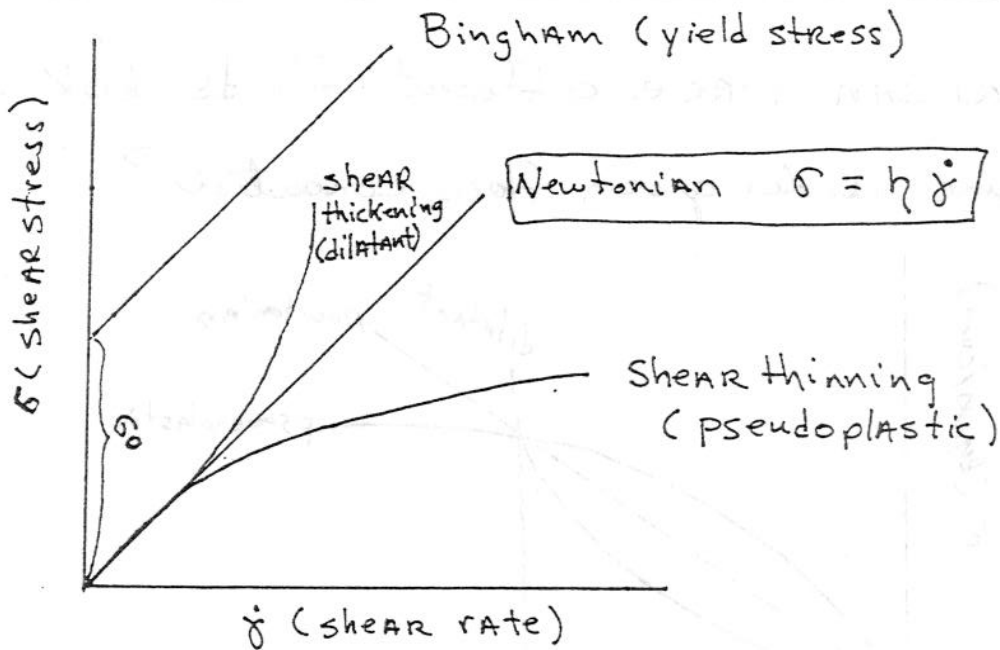
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Fluid Models

Newtonian

$$\sigma = \eta \dot{\gamma}$$

Bingham

$$\sigma = \sigma_0 + \eta \dot{\gamma}$$

↳ yield stress

Power-LAW

$$\sigma = K (\dot{\gamma})^n \quad \text{or} \quad \sigma = (K \dot{\gamma}) |\dot{\gamma}|^{n-1}$$

↳ viscosity units

$$n = 1$$

(Newtonian)

$$n < 1$$

shear thinning (pseudoplastic)

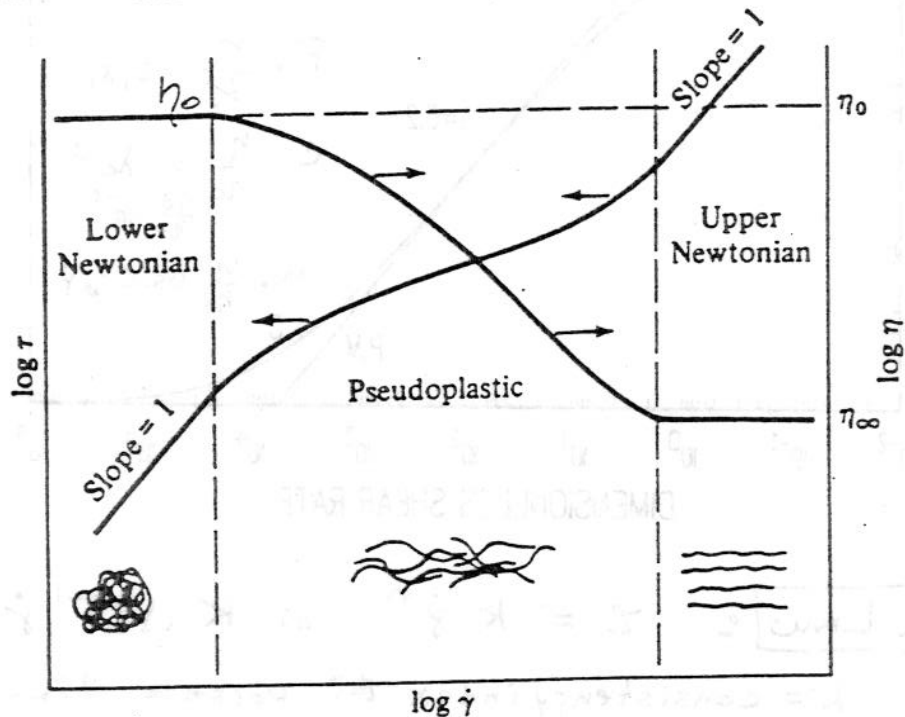
$$n > 1$$

shear thickening (dilatant)

Polymer Melts and Concentrated Solutions.

[Entangled Systems]

Generalized Flow Curve.



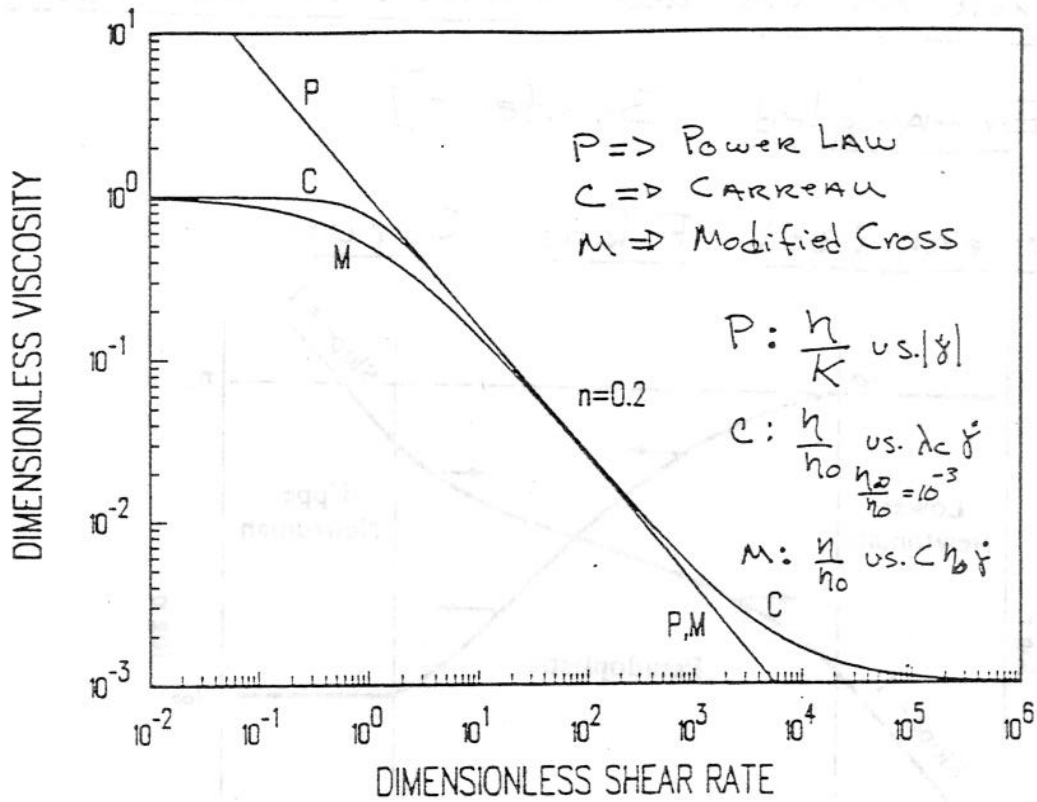
$\eta_0 \equiv$ zero-shear viscosity (lower Newtonian plateau)
 $\tau = \eta \dot{\gamma}$ (Newton's Law)

$\eta_\infty \equiv$ upper Newtonian plateau (rarely achieved for melts)

- Flow Properties governed by Entanglements.
- low shear \rightarrow high entanglement density
- entanglement density $\stackrel{(ED)}{=} f(\dot{\gamma})$.
 - ED decreases with increasing $\dot{\gamma}$.

Q. How large (Mw) does a molecule have to be to entangle?

Constitutive Equations for Viscosity



• **Power Law**: $\tau = k \dot{\gamma}^n$ or $K |\dot{\gamma}|^{n-1} \dot{\gamma}$

k = consistency index [3] poise = g/cm-sec
 n = flow index ($n=1$ Newtonian)

* does not predict zero-shear viscosity

• **Carreau Model**: $\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \left[1 + (\lambda_c \dot{\gamma})^2 \right]^{\frac{n-1}{2}}$

* four parameter model which has all features of melt flow curve

λ_c = characteristic time (sec)

$\lambda_c \dot{\gamma}$ = Weissenberg #

$\lambda_c \dot{\gamma} \ll 1.0 \Rightarrow \eta \rightarrow \eta_0$

• **Modified Cross Model**: $\eta(T, \dot{\gamma}) = \frac{\eta_0(T)}{1 + [C \eta_0(T) \dot{\gamma}]^{1-n}}$

C [3] area/force

$C \eta_0$ = characteristic time (sec)

$C \eta_0 \dot{\gamma}$ = Weissenberg # $\ll 1.0 \Rightarrow \eta \rightarrow \eta_0$

Note: This model can account for temperature effects.

Shear Flow Behavior.

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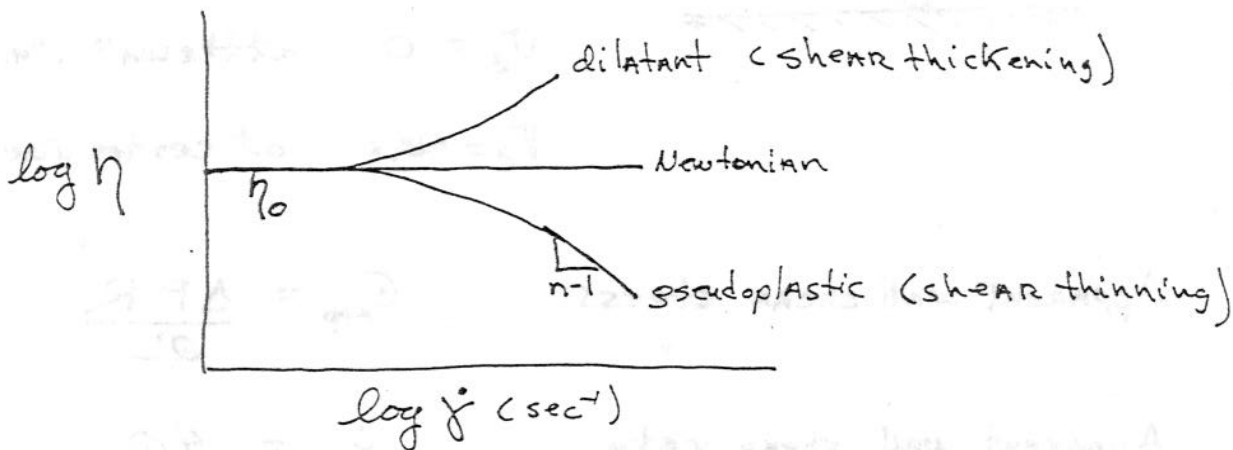
Power-LAW Fluids

$$\sigma = K \dot{\gamma}^n$$

divide both sides by $\dot{\gamma}$

$$\sigma/\dot{\gamma} = \eta = K \dot{\gamma}^{n-1} \quad (\text{or } \eta = K' \dot{\gamma}^m)$$

Log-Log Plot of Viscosity vs. Shear Rate.



$$\log \eta = \log K + (n-1) \log \dot{\gamma}$$

$$\left\{ \begin{array}{l} \text{intercept} = K \text{ (viscosity units)} \\ \text{slope} = n-1 \end{array} \right.$$

Polymer Solutions: Newtonian plateau = η_0 zero-shear viscosity
 linear region = "power-law" region

SUBJECT

Capillary Flow - Polymer Melts

JOB NO.

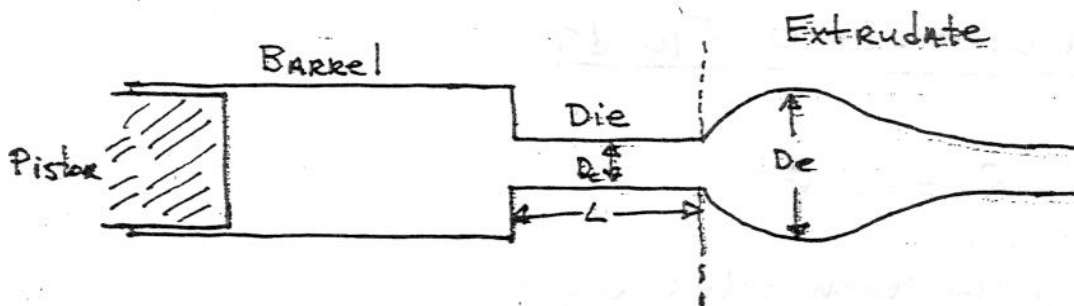
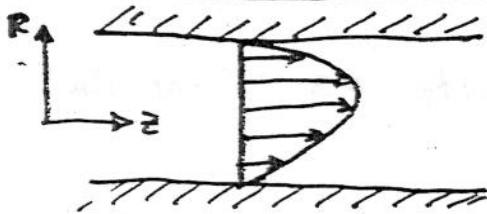
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Poiseuille Law for Capillary Flow

PARABOLIC velocity distribution
(Newtonian fluid)

$V_z = 0$ at the wall ("no slip")

$V_z = \text{MAX}$ at centerline

Apparent wall shear stress

$$\sigma_{\text{APP}} = \frac{\Delta P R}{2L}$$

Apparent wall shear rate

$$\dot{\gamma}_{\text{APP}} = \frac{4Q}{\pi R^3}$$

Apparent shear viscosity

$$\eta_{\text{APP}} = \sigma / \dot{\gamma}$$

Extrudate Swell (Die Swell) = Elasticity

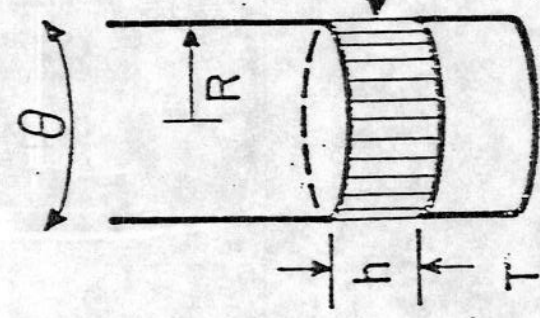
$$D_e/D \propto \text{NORMAL STRESS}$$

$$D_e/D = f(L/D)$$

RHEOLOGY: THE STUDY OF THE DEFORMATION OF MATTER IN RESPONSE TO AN IMPOSED STRESS

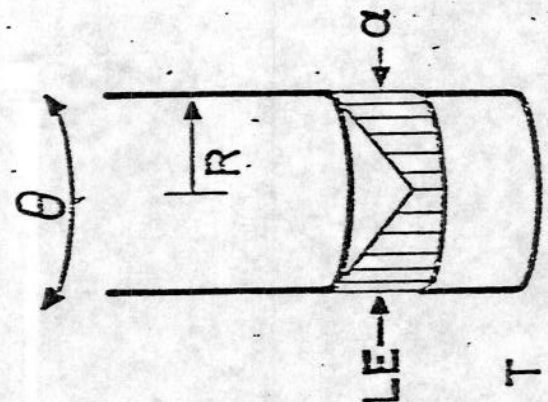
TESTING OF POLYMERIC LIQUIDS

PARALLEL PLATE



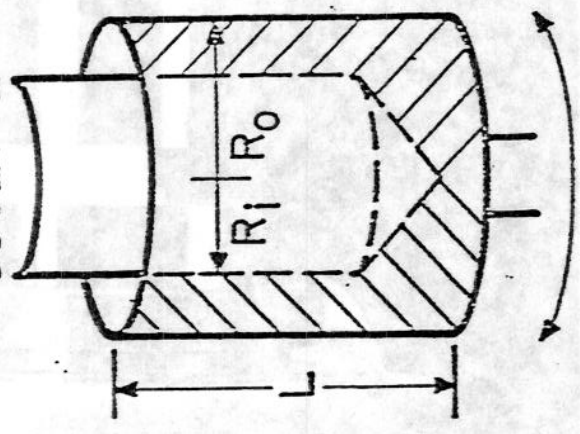
STRAIN $\gamma = \frac{R\theta}{h}$
 STRESS $\sigma = \frac{2T}{\pi R^3}$

CONE AND PLATE



$\gamma = \frac{\theta}{\alpha}$
 $\sigma = \frac{3T}{2\pi R^3}$

COUETTE




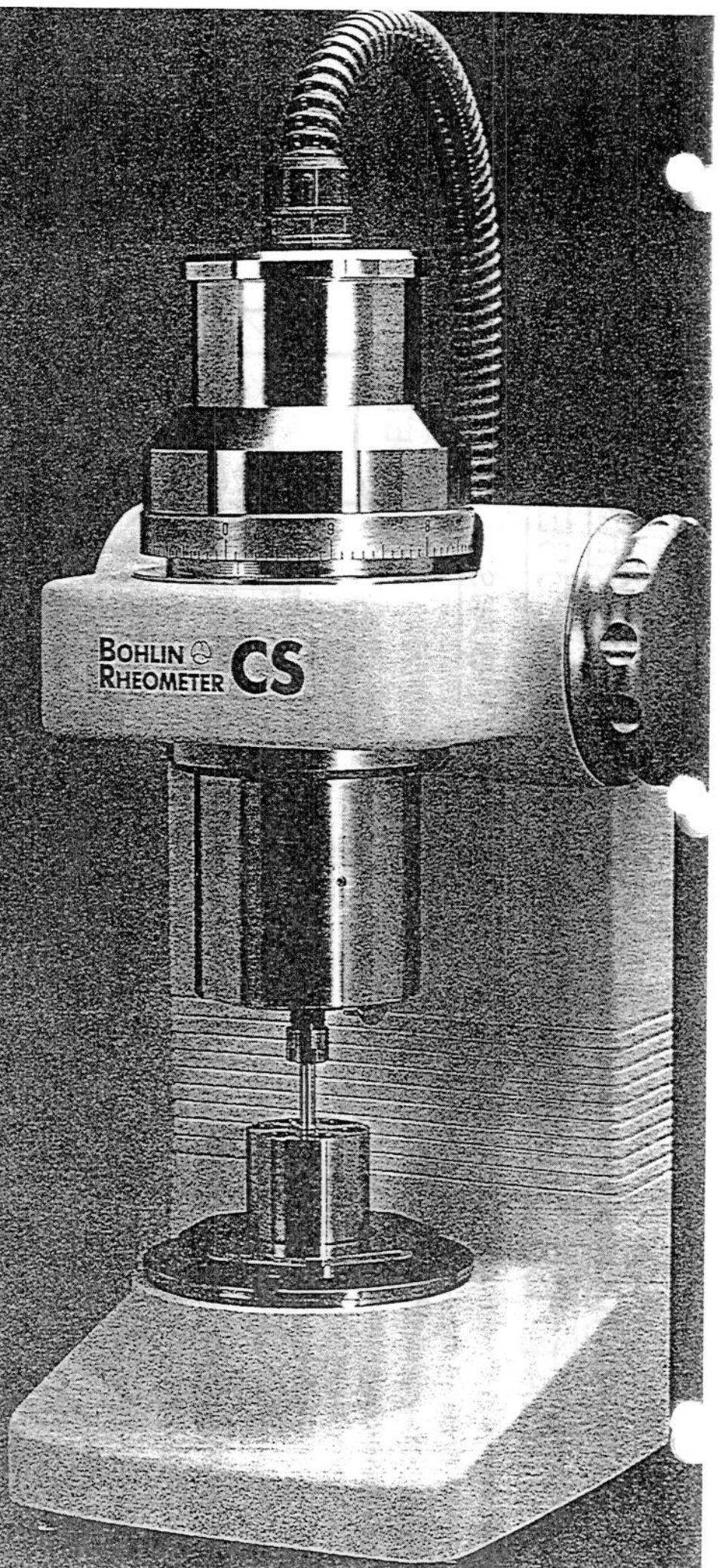
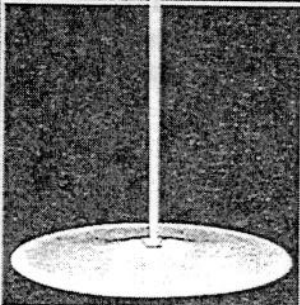
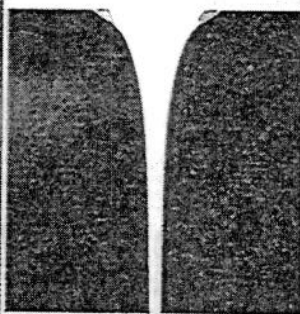
$\gamma = \frac{2\theta R_0^2}{R_0^2 - R_1^2}$
 $\sigma = \frac{T}{2\pi L R^2}$

Steady Shear: replace Θ with ω_0 to get $\dot{\gamma}$.
 $\dot{\gamma}_{(0)}$ = steady rotation rate



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PARTNER
IN
RHEOLOGY**

 **BOHLIN INSTRUMENTS**



BOHLIN  **CS**
RHEOMETER

SUBJECT

Viscometers : Shear Rate Profiles

JOB NO.

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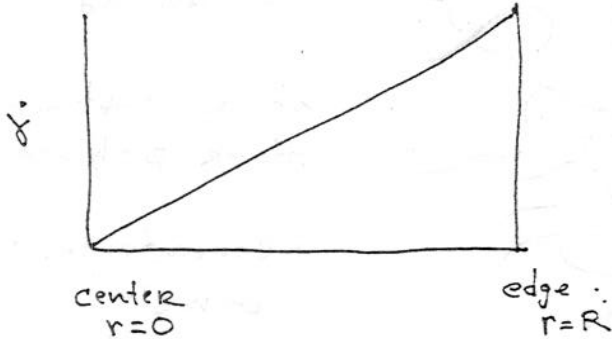
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① Parallel - Plate

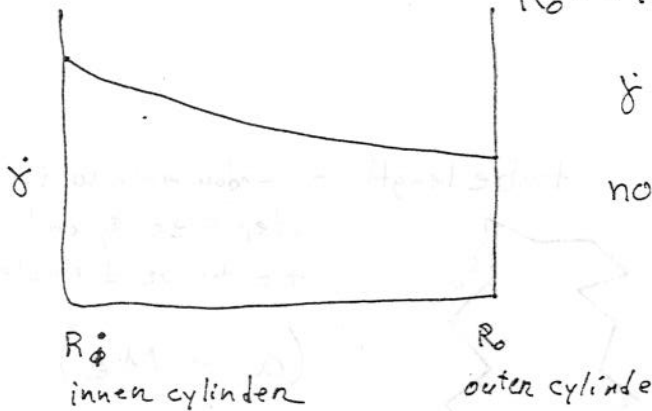
$$\dot{\gamma}_{Avg} = \frac{R \omega_0}{H}$$



$$\dot{\gamma} = f(\text{radial position})$$

② Couette

$$\dot{\gamma} = \frac{2 \omega_0 R_o^2}{R_o^2 - R_i^2}$$

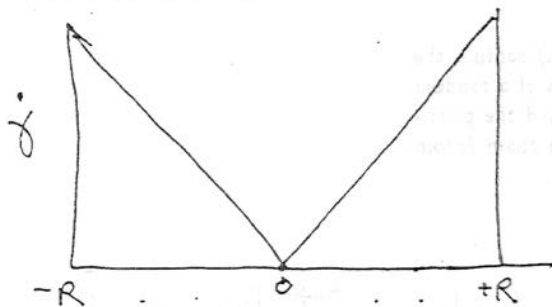


$$\dot{\gamma} = f(\text{gap position})$$

note: if $R_o - R_i \ll 1.0$ (small) then $\dot{\gamma} \approx \text{constant}$.

③ Capillary

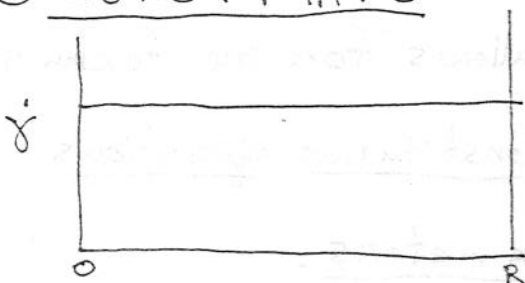
$$\dot{\gamma} = \frac{dV_z}{dr}$$



$\dot{\gamma} = f(\text{radial position})$
 $\dot{\gamma} = 0$ (center)
 $\dot{\gamma} = \text{maximum at the wall}$

④ Cone : Plate

$$\dot{\gamma} = \frac{\omega_0}{\alpha} \quad (\alpha = \text{cone angle})$$



$\dot{\gamma} = \text{constant for small } \alpha \quad (\alpha \leq 1^\circ)$

Reptation

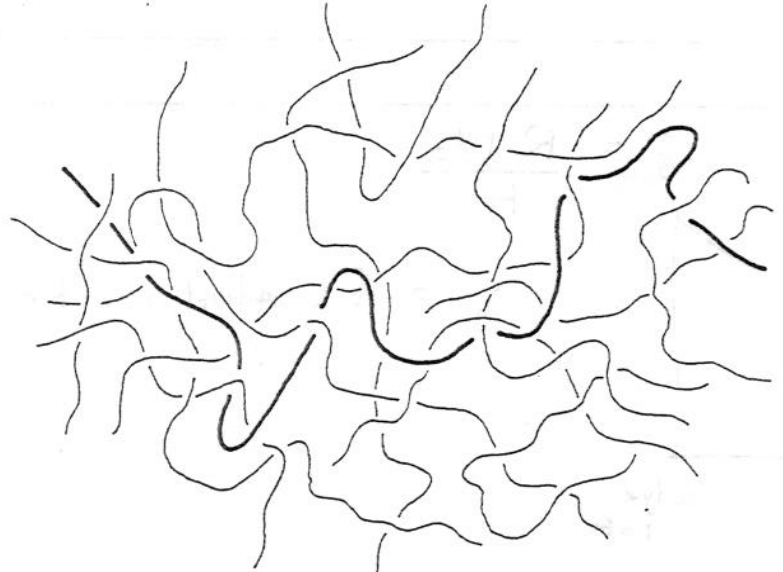


Fig. 4-6 Polymer molecule entangled in a mesh of other polymer chains (from Graessley,¹⁸ reprinted with permission from Advances in Polymer Science).

Polymer molecule
 "entangled"
 in a matrix of
 other polymer chains

- concentrated solution or melt
- $M > M_c$
 (high molecular weight)

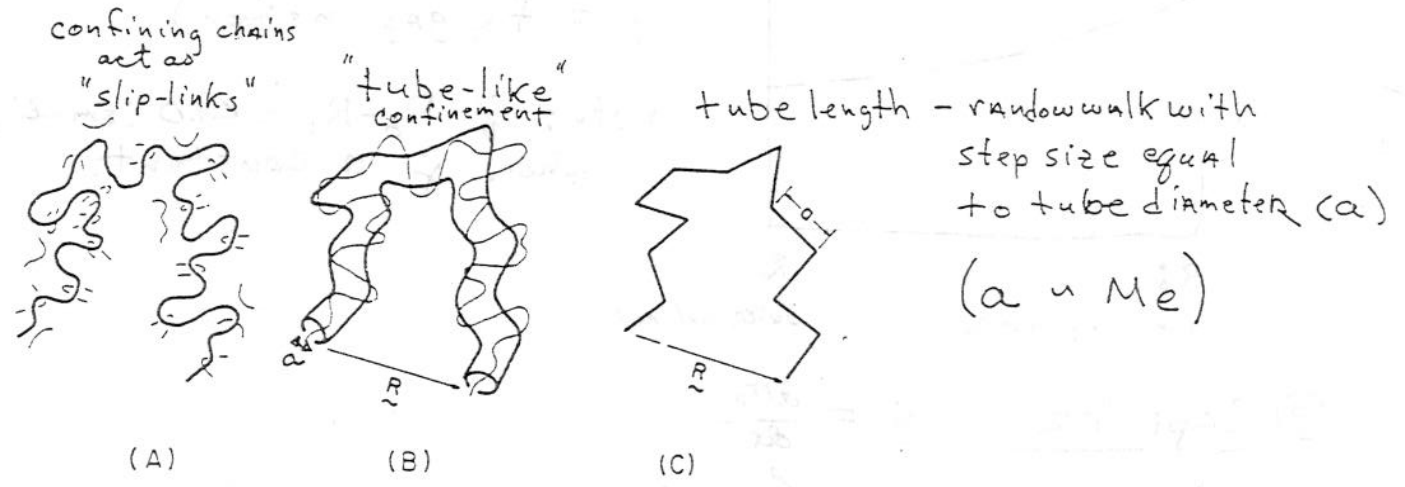


Fig. 4-7 Polymer molecules with which a given molecule is entangled (A) confine the given chain to a tube-like region (B). The tube contour (C) is roughly that of a random walk with step size equal to the tube diameter a . This random walk is called the primitive path; its contour length is much less than the contour length of the chain (From Graessley,¹⁸ reprinted with permission from Advances in Polymer Science).

Q. What is the appeal of Reptation Theory?

A. It is the first theory that allows for the formulation of predictive flow models (constitutive equations) based on Molecular Parameters.

Reptation Theory

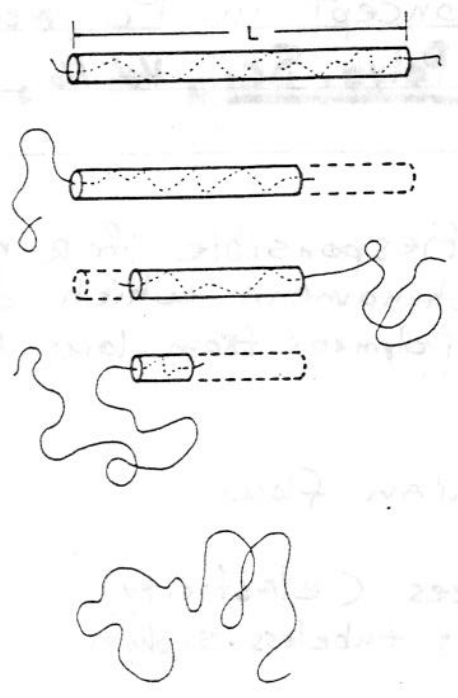


Fig. 4-8 Reptative diffusion of a polymer molecule out of its tube. For simplicity of visualization, the tube of Fig. 4-7 has been straightened out (From Graessley¹⁸).

Predictions

Diffusivity

$$D \propto M^{-2}$$

Maximum Relaxation
time

$$\tau_R \propto M^3$$

Zero-shear Viscosity

$$\eta_0 \propto M^3 \quad (\eta_0 \propto M^{3.4} \text{ observed})$$

Plateau Modulus

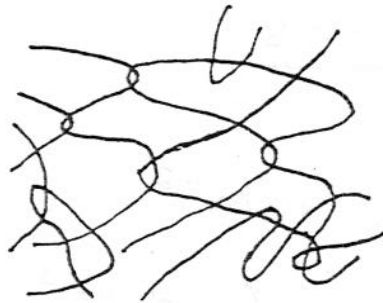
$$G_N^0 \propto M^0 \quad (\text{observed})$$

SUBJECT

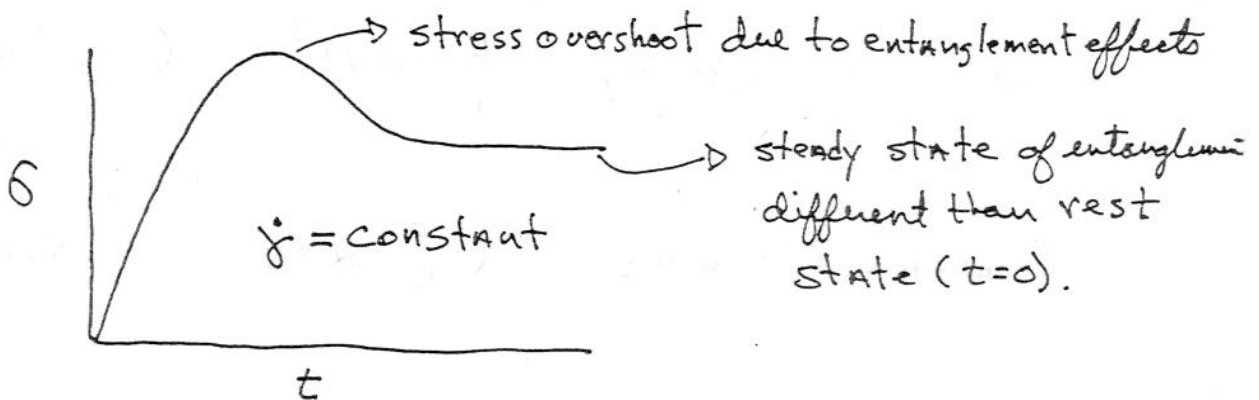
Entanglement Concept in Polymer Rheology
 W.W. Graessley, Adv. Polym. Sci., Vol. 16, 1974 (Springer-Verlag)

Entanglements: Responsible for many of the phenomena which distinguish polymers from low Mw fluids.

- ① Non-newtonian flow
- ② Normal Forces (elasticity)
 - recoil; tubeless siphon
- ③ Elasticity (Rubber and Viscoelastic)



Entangled \rightarrow non-permanent crosslinks

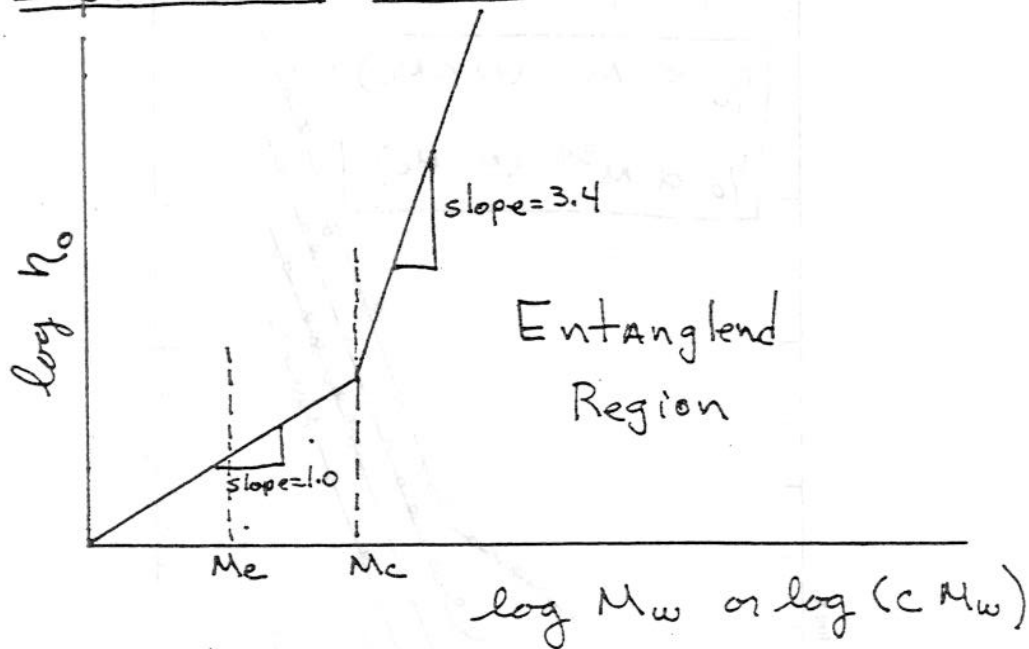


Influence of Molecular Weight on Viscosity

OR

Critical Molecular Weight for Entanglement.

Experimental Observation.



$\eta_0 \propto M_w$ for $M_w < M_{wc}$

$\eta_0 \propto M_w^{3.4}$ for $M_w > M_{wc}$

(M_{wc} = critical molecular weight for entanglements)

Note: For concentrated solutions substitute $\underline{c} M_{wc}$ for M_{wc}

- M_e = molecular weight between entanglements
(obtained from plateau modulus)

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

$M_e = f(\text{polymer type and temperature})$ remember

$M_e \sim 300 - 700$ backbone carbon units

• $M_e : M_c = 1 : 2-3$

Solution Viscometry
 $c[\eta] > 1.0$ (entangled)

molecular weight of
the viscosity average

(3.6-14)

roughly as $c[\eta]_0 <$
concentrations they
we can combine
approximately
relations. Because c
molecular weight and
estimate of the
sometimes called
of the number of
one concentration
at high and low

viscosity can be
zero-shear-rate
 $\propto \eta - 1$ (see
way to present
rate $\lambda \dot{\gamma}$ where λ is
 λ suggested by
rate $\beta \equiv \lambda \dot{\gamma} =$
initiation becomes
in which intrinsic
different tempera-
r weight on η_0 ,

understood. At low
solidate data for
and molecular

(3.6-15)

is obtained by
is close to the

striking feature
is seen that η_0
molecular weight M_c

(3.6-16)

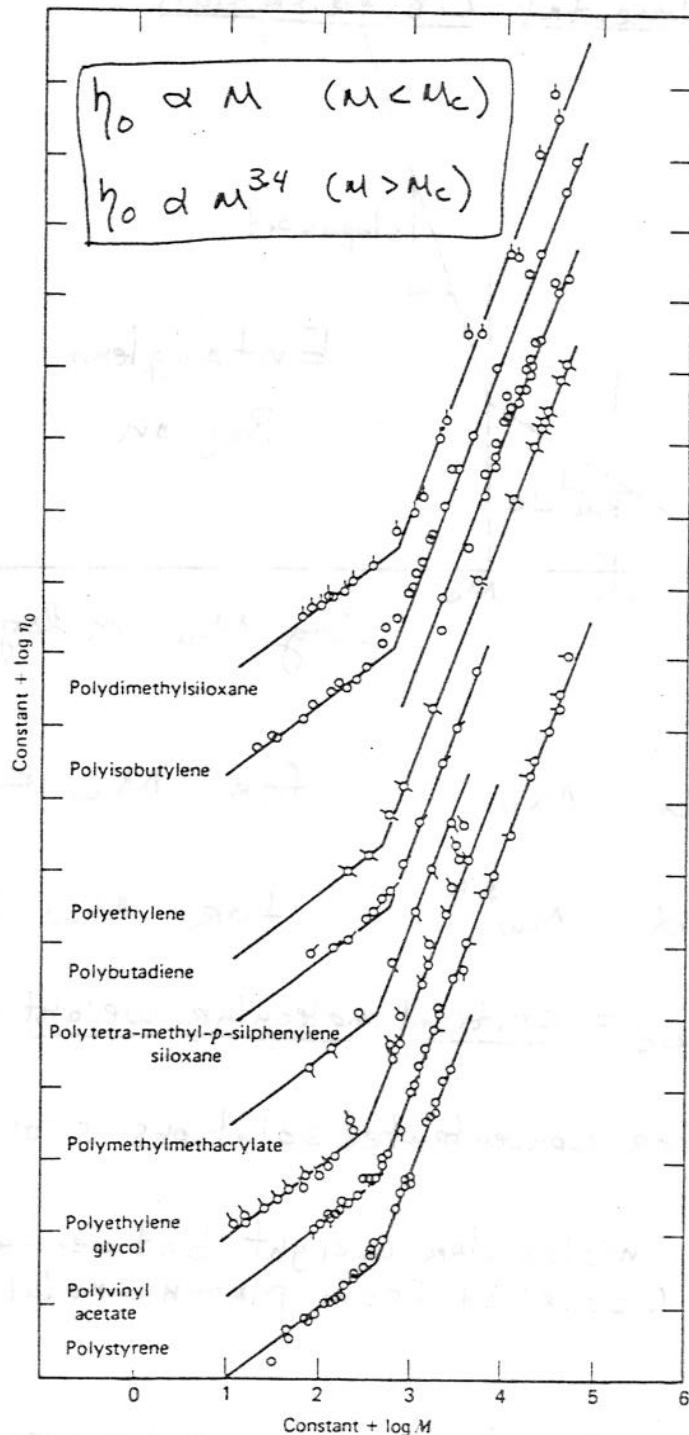


FIGURE 3.6-4. Plots of constant + $\log \eta_0$ vs. constant + $\log M$ for nine different polymers. The two constants are different for each of the polymers, and the one appearing in the abscissa is proportional to concentration, which is constant for a given undiluted polymer. For each polymer the slopes of the left and right straight line regions are 1.0 and 3.4, respectively. [G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*, 5, 261-357 (1968).]

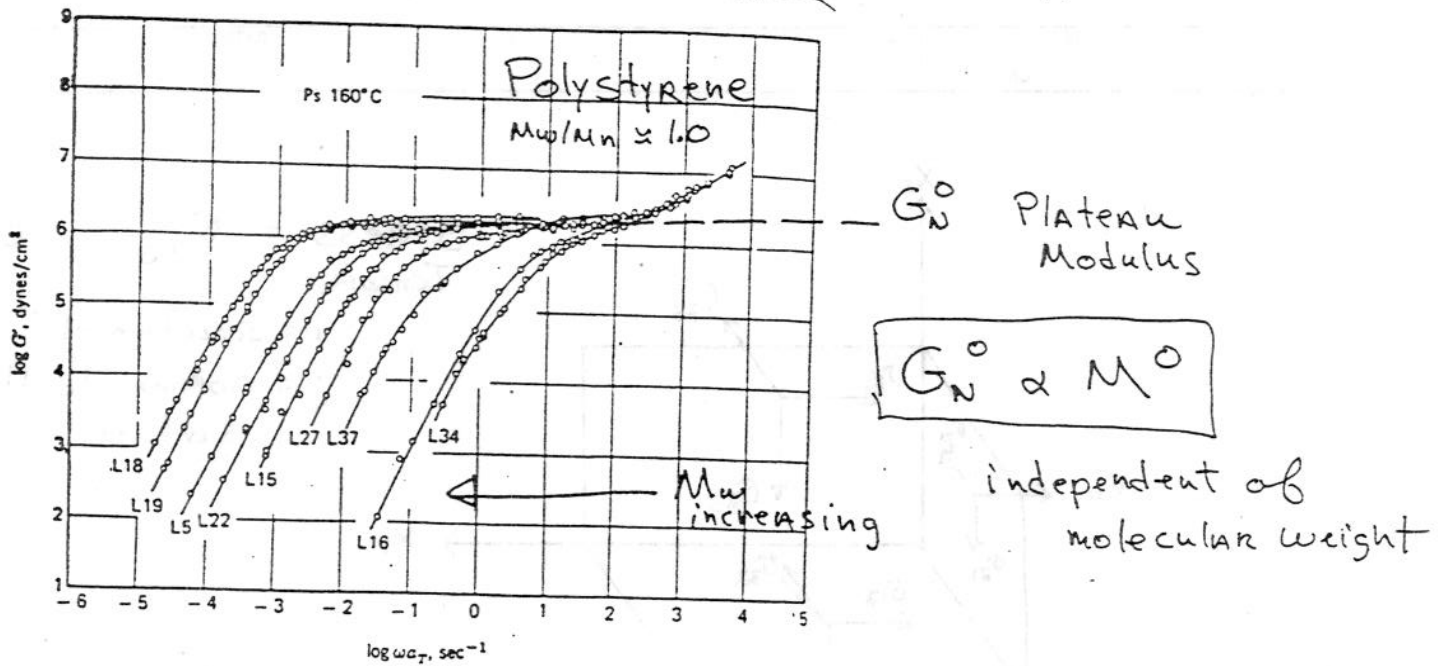


Fig. 4-4 Storage modulus G' , as a function of frequency reduced to 160°C for polystyrenes of narrow molecular-weight distribution. Molecular weight decreases from left to right from 580,000 to 47,000 (from Onogi et al.,¹³ reprinted with permission from Macromolecules © 1970 American Chemical Society).

Estimation of M_e from Dynamic Properties

M_e = Mol. Wgt. between entanglements

$$G_N^0 \approx \rho RT / M_e$$

- ① From G' data \rightarrow plateau region at high ω (see Above)
- ② From G'' data \rightarrow integrate over ω $G_N^0 = \frac{2}{\pi} \int_{-\infty}^{\infty} G'' d \ln \omega$

Estimation of entanglement (or crosslink) density:

$$G_N^0 = \nu RT$$

ν = entanglement density or crosslink density

Stress in a Continuum

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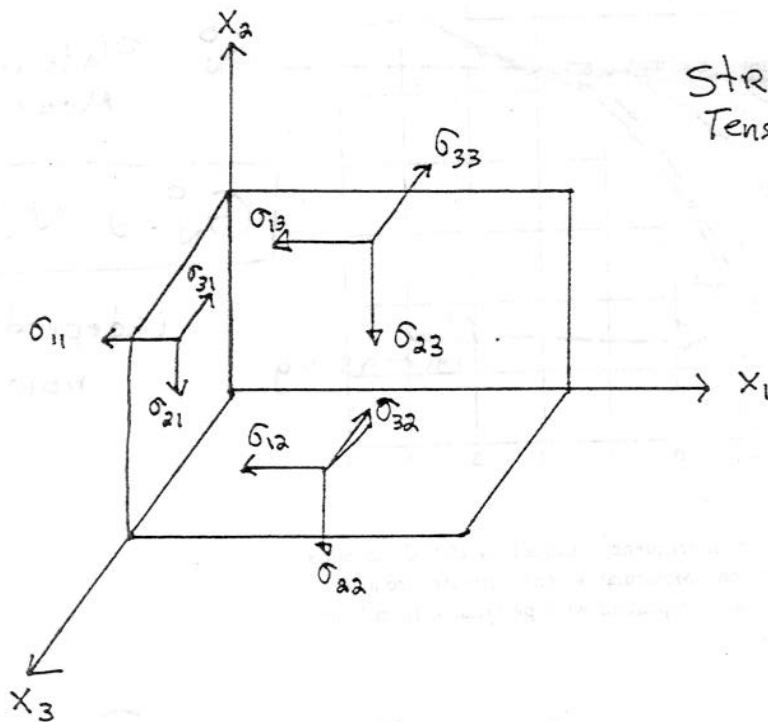
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OF



$$\text{Stress} = \sigma_{ij} = \underline{\underline{\sigma}}$$

Tensor

i = direction of flow
 j = normal to flow surface

$$\text{Stress tensor} = \underline{\underline{\sigma}} = \begin{pmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{pmatrix}$$

$$\text{shear stress} : \sigma_{12} = \sigma_{21}$$

$$\text{Normal stresses} : \sigma_{11}, \sigma_{22}, \sigma_{33}$$

$$1^{\text{st}} \text{ Normal Stress Difference} : \sigma_{11} - \sigma_{22}$$

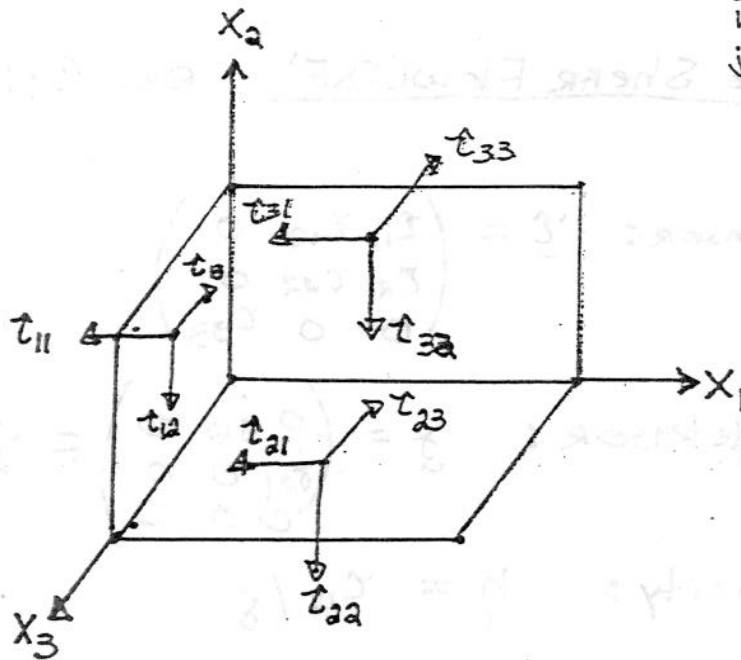
$$2^{\text{nd}} \text{ Normal Stress Difference} : \sigma_{22} - \sigma_{33}$$

Stress in a Continuum

(see Rosen, Ch. 17)

Stress tensor $(\tau_{ij}) = \underline{\underline{\tau}}$

i = normal to the surface
 j = direction of stress



$$\text{Stress tensor} = \underline{\underline{\tau}} = \begin{pmatrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{pmatrix}$$

(nine components)

shear stress: τ_{ij}

normal stress: τ_{ii}

Viscometric Flows of incompressible fluids.

shear stress: $\tau_{21} = \tau_{12}$ (no vorticity)

$$\tau_{13} = \tau_{31} = \tau_{32} = \tau_{23} = 0$$

Normal stress: two independent differences

$$N_1 = \tau_{11} - \tau_{22} \quad \text{1st Normal Stress Difference}$$

$$N_2 = \tau_{22} - \tau_{33} \quad \text{2nd Normal Stress Difference}$$

* Note: N_1 responsible for "rod climbing", die swell, etc.

22-141 50 SHEETS
 22-142 100 SHEETS
 22-144 200 SHEETS



Simple Flows

Viscometric Flows: well-characterized flow fields used to measure material properties

Simple Shear Flow (SSF) ex. CIP, COAXIAL CYLIN (Couette)

Stress tensor:
$$\underline{\underline{\tau}} = \begin{pmatrix} \tau_{11} & \tau_{12} & 0 \\ \tau_{21} & \tau_{22} & 0 \\ 0 & 0 & \tau_{33} \end{pmatrix}$$

Shear rate tensor:
$$\underline{\underline{\dot{\gamma}}} = \begin{pmatrix} 0 & \dot{\gamma} & 0 \\ \dot{\gamma} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \dot{\gamma} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

Viscosity: $\eta = \tau_{12} / \dot{\gamma}$

1st Normal Stress Difference: $N_1 = \tau_{11} - \tau_{22}$

* 1st Normal Stress Coefficient: $\psi_1 = (\tau_{11} - \tau_{22}) / \dot{\gamma}$

2nd Normal Stress Difference: $N_2 = \tau_{22} - \tau_{33}$

* 2nd Normal Stress Coefficient: $\psi_2 = (\tau_{22} - \tau_{33}) / \dot{\gamma}^2$

* $\dot{\gamma}^2$ because normal stresses are even functions of shear rate.

$\dot{\gamma}$ Shear stresses are odd functions of shear rate.

Example:

CIP flow: τ_{12} sign depends on direction of shearing

N_1, N_2 do not change sign with shear dir

Example: Weissenberg Effect ("Rod Climbing")

- normal stresses inwardly directed whether rod rotated CW or CCW.

SUBJECT

Viscometers and Simple Flows

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Viscometric Flows :

- well-characterized flow fields used to measure material properties.

Simple Shear Flow

(Cone and Plate)

$$\dot{\gamma} = \frac{W_0}{d} = \text{constant for small } d (< 1^\circ)$$

$$\eta = \sigma_{12} / \dot{\gamma}$$

$$N_1 = \sigma_{11} - \sigma_{22}$$

1st Normal Stress Difference

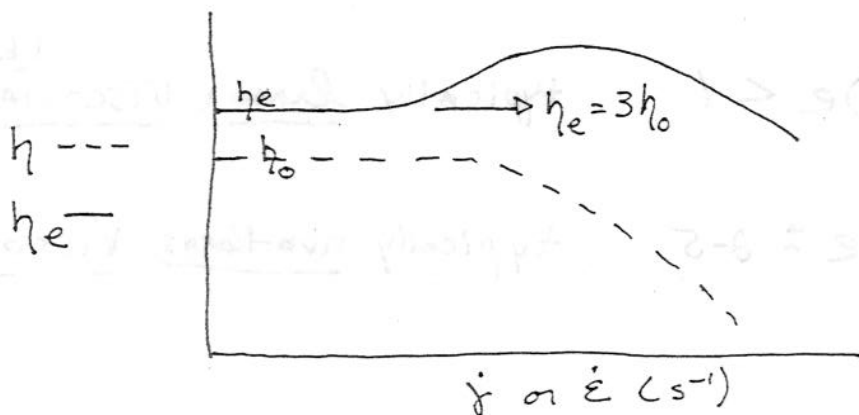
$$N_2 = \sigma_{22} - \sigma_{33}$$

2nd Normal Stress Difference

Simple Elongational Flow

$$\dot{\epsilon} = \text{extension rate} = \frac{1}{x_1} \frac{dx_1}{dt} \quad (x_1 = \text{stretch direction})$$

$$\eta_e = \frac{\sigma_{11} - \sigma_{22}}{\dot{\epsilon}} \quad (\Rightarrow \text{extensional viscosity})$$



Low Density PE
 $T = 150^\circ\text{C}$

Dimensionless #'s to Describe Viscoelasticity

Deborah #: $De = \frac{\lambda}{t_0}$

- unsteady flows

t_0 = time-scale of the deformation
(experiment)

λ = polymer relaxation time

Weissenberg #: $We = \lambda \dot{\gamma}$

- steady flows

$t_0 = 1/\dot{\gamma}$ \Rightarrow shearing time scale

De (or We) $\rightarrow \infty$

solid-like response (elastic)

De (or We) $\rightarrow 0$

liquid-like response (viscous)

$0 \leq De \leq \infty$ Viscoelastic

$De < 1$ typically linear viscoelastic (LVE)

$De \approx 2-5$ typically non-linear viscoelastic

Constitutive Equations

Definition: A CONSTITUTIVE Equation describes the relationship between the APPLIED STIMULUS (i.e., stress or shear (strain)) and the RESULTING RESPONSE which is CHARACTERISTIC of the FLUID. (i.e., CONSTITUTION of the FLUID).

Constitutive Equations

I. Linear (Newtonian)

Newton's LAW of Viscosity
 • independent of applied stress and rate of deformation

$$\sigma = \eta \dot{\gamma}$$


II Nonlinear (non-Newtonian)

- properties dependent on stress and/or rate of strain

a) shear rate dependent viscosity (i.e. Power-LAW Model)

b) Normal Stresses (Elastic phenomena - i.e. die swell)

c) Viscoelastic Behavior

- Stress Relaxation 
- Creep Recovery (recoil) (i.e., die swell)

linear VE behavior

- non-linear VE behavior → • stress overshoot
- disentanglement → entanglement density changes

General Categories of Constitutive Equations

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① linear : Generalized Newtonian Fluid (GNF)

$$\underline{\tau} = +\eta \dot{\gamma}$$

② non linear:

(A) Differential Models

- Generalized linear viscoelastic (LVE)

$$\underline{\tau} = \int_{-\infty}^t G(t-t') \dot{\gamma}(t') dt'$$

$G(t-t')$ = relaxation modulus (dependent on mechanical model chosen)

i.e. Maxwell element (spring G) and dashpot (μ)

$$\underline{\tau} + \lambda_0 \frac{d\underline{\tau}}{dt} = \eta_0 \dot{\gamma}$$

$$\lambda_0 = \eta_0 / G$$

$$\lambda_0 = 0 \quad (\text{Newtonian})$$

(B) Integral Models

$$\underline{\tau} = \int_{-\infty}^t M_1(t-t', I_{\dot{\gamma}'_0}, II_{\dot{\gamma}'_0}) \dot{\gamma}'_0 + M_2(t-t', I_{\dot{\gamma}'_0}, II_{\dot{\gamma}'_0}) \{\dot{\gamma}'_0 \cdot \dot{\gamma}'_0\} dt'$$

M_1, M_2 = material functions

$\dot{\gamma}'_0$ = strain tensor

• BKZ MODEL

BASIC STRESS-STRAIN BEHAVIOR

MATERIAL RESPONSE TO STRESS
CHANGE IN STRAIN

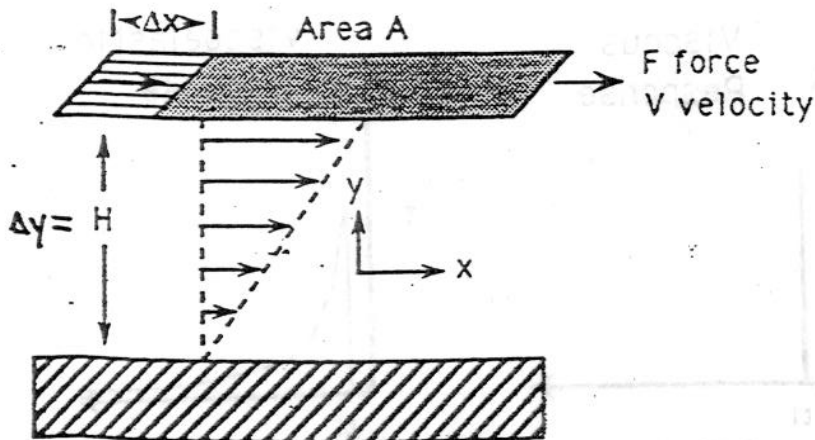
DEFINITIONS:

STRESS: Force per unit area.

$$\tau = F / A$$

STRAIN: The magnitude of deformation relative to sample length.

SHEAR STRESS / STRAIN

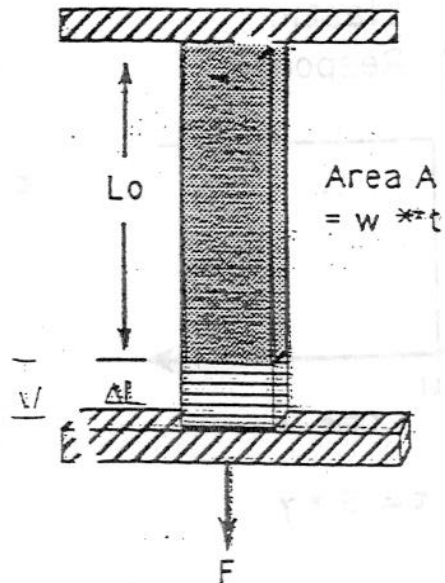


Stress: $\tau = F / A$

Strain: $\gamma = \Delta x / \Delta y = \Delta x / H$

Strain Rate: $\dot{\gamma} = V / H$

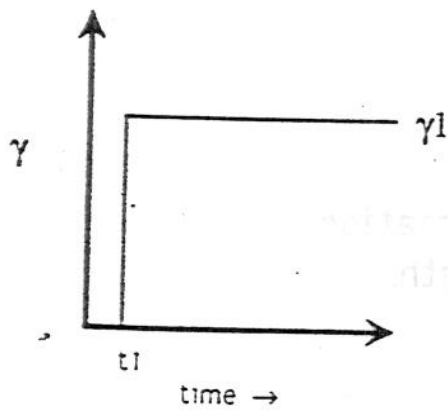
TENSILE STRESS - STRAIN



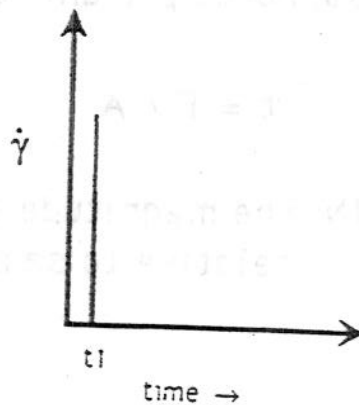
Stress: $\sigma = F / A$

Strain: $\epsilon = \Delta L / L_0$

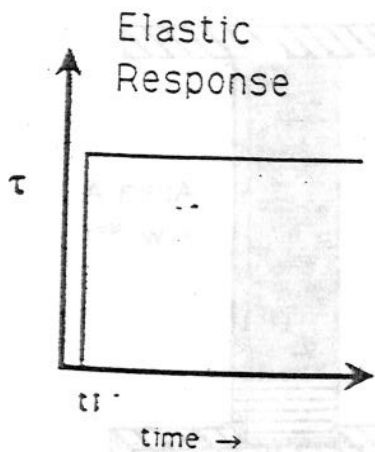
MATERIAL RESPONSE TO STEP CHANGE IN STRAIN



strain

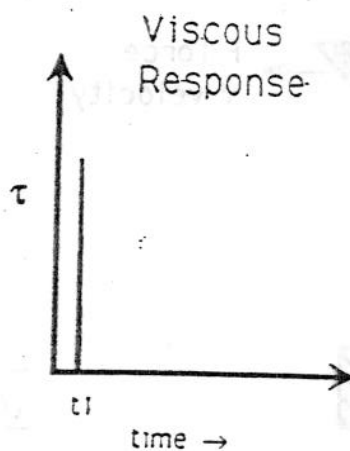


rate of strain
(shear rate)



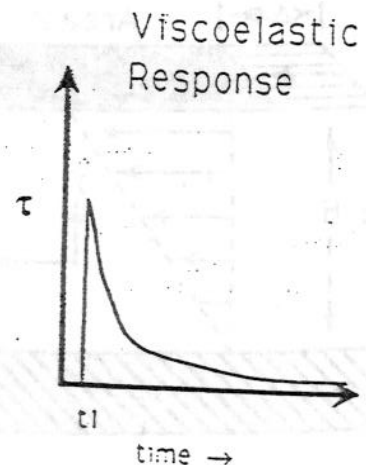
$$\tau = G * \gamma$$

$G = \text{Modulus}$



$$\tau = \eta * \dot{\gamma}$$

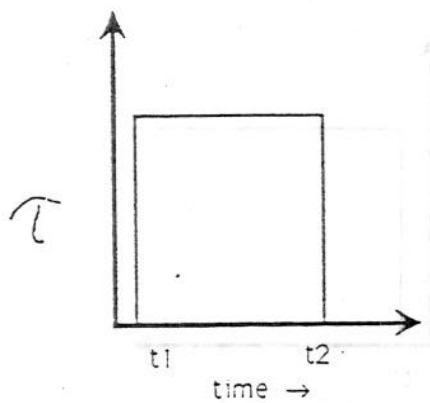
$\eta = \text{Viscosity}$



$$\tau = G(t) * \gamma$$

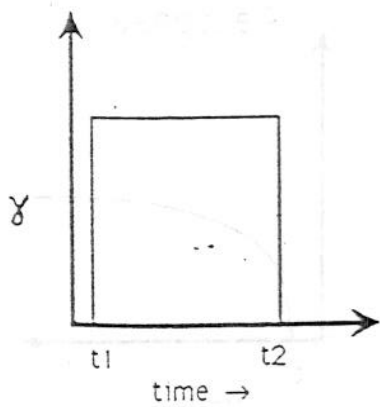
$G(t) = \text{Stress Relaxation Modulus}$

MATERIAL RESPONSE TO STEP CHANGE IN STRESS

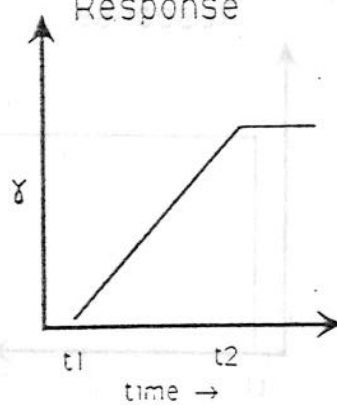


stress

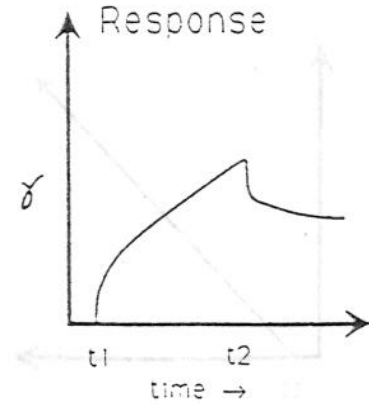
Elastic Response



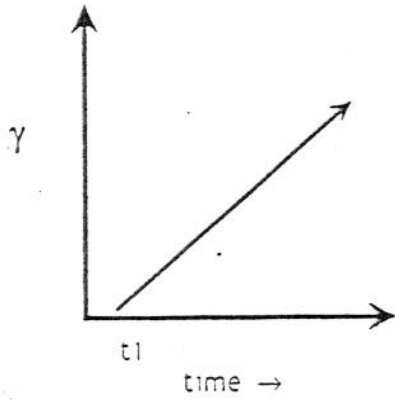
Viscous Response



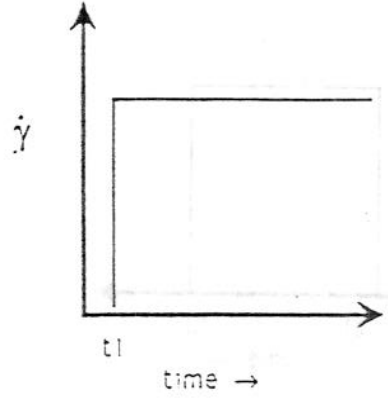
Viscoelastic Response



MATERIAL RESPONSE TO STEP CHANGE IN SHEAR RATE

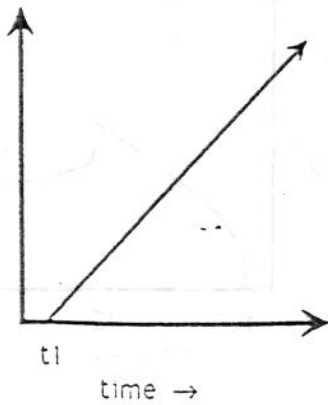


strain

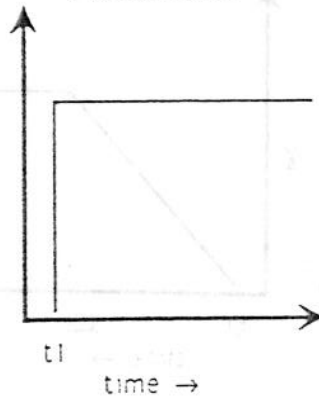


rate of strain
(shear rate)

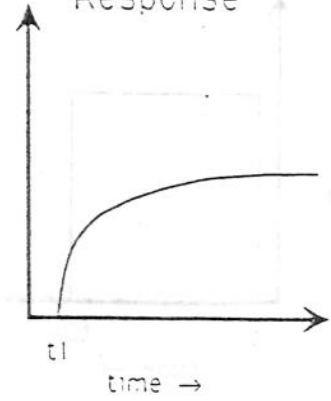
Elastic Response



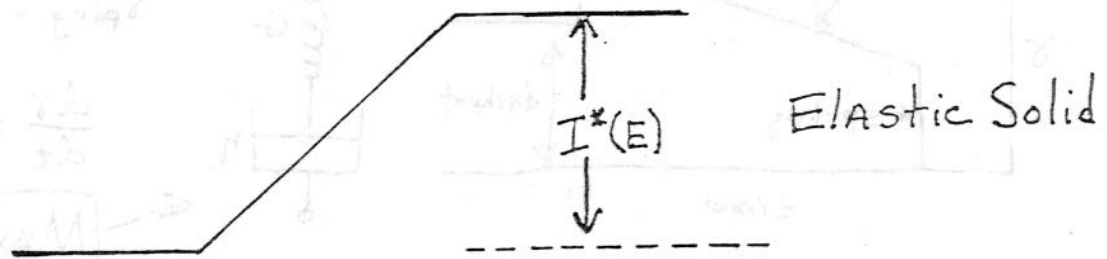
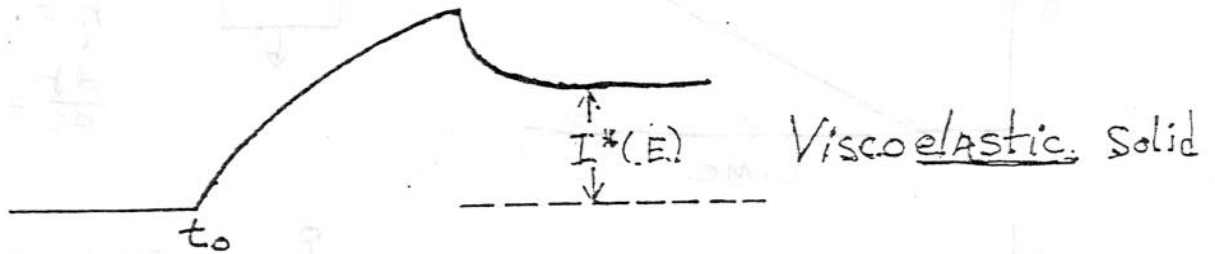
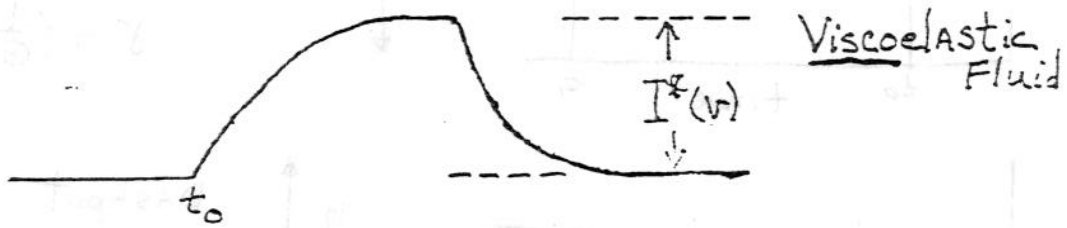
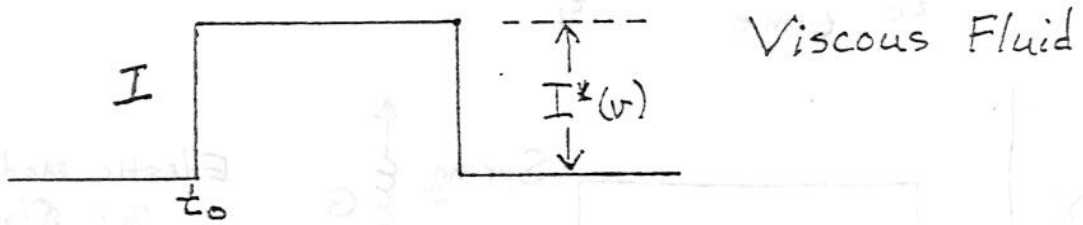
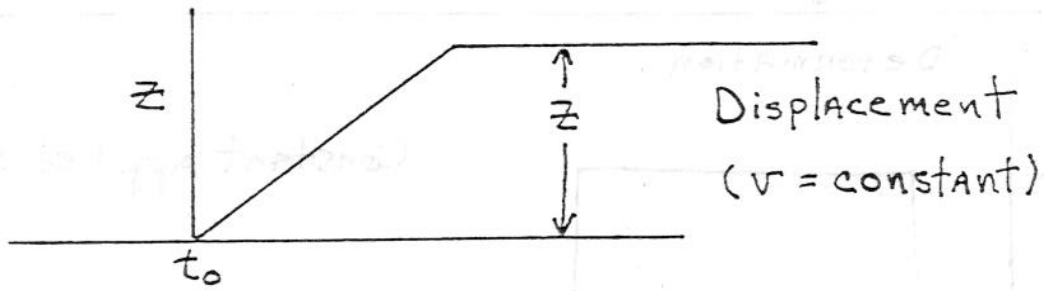
Viscous Response



Viscoelastic Response



Experimental Measurements

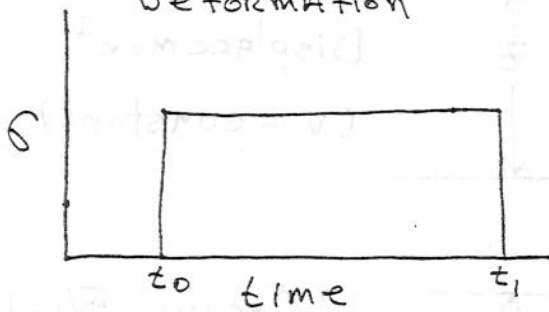


Note: $I^* \propto \text{stress}$

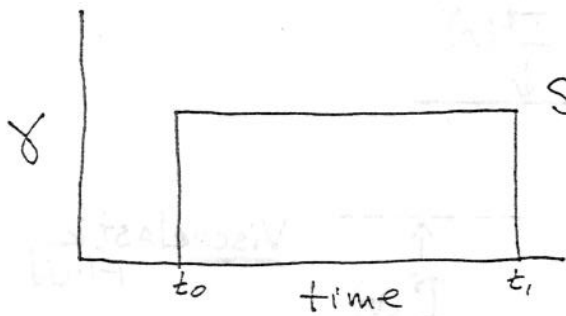
Mechanical Models

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Deformation



Constant Applied stress



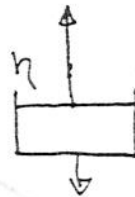
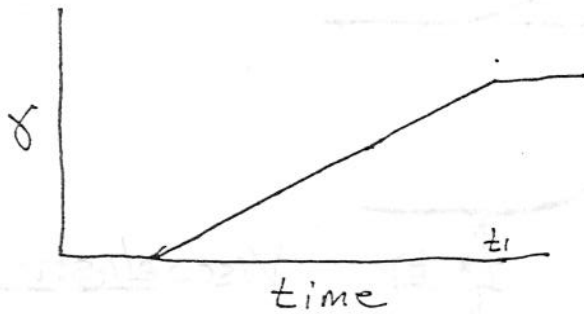
Spring



Elastic modulus

$$G = \sigma / \gamma$$

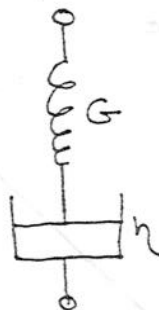
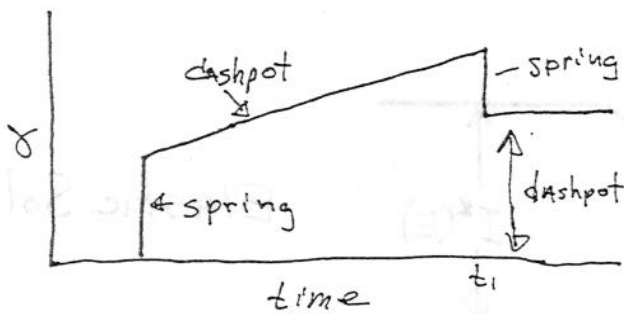
$$\gamma = \left(\frac{1}{G}\right) \sigma$$



Dashpot Viscosity

$$\eta = \sigma / \dot{\gamma}$$

$$\frac{d\gamma}{dt} = \left(\frac{1}{\eta}\right) \sigma$$

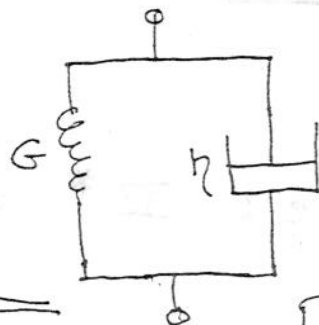
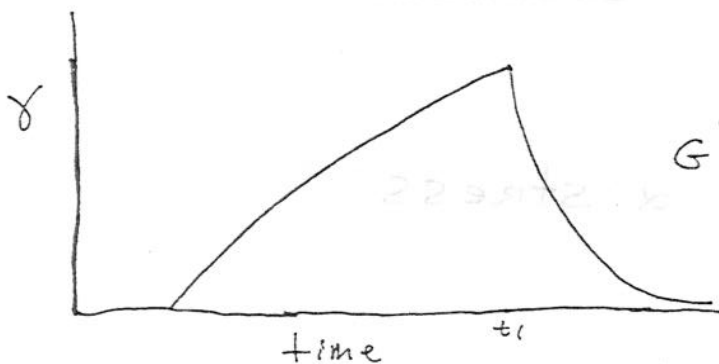


Dashpot - flows

Spring - recovers

$$\frac{d\gamma}{dt} = \frac{1}{\eta} \sigma + \frac{1}{G} \frac{d\sigma}{dt}$$

Maxwell Element



Viscoelastic

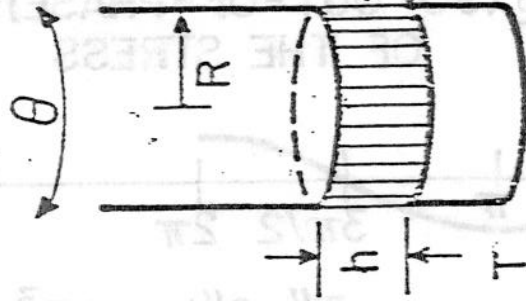
$$\eta \frac{d\gamma}{dt} + G \gamma = \sigma$$

Voigt Element

RHEOLOGY: THE STUDY OF THE DEFORMATION OF MATTER IN RESPONSE TO AN IMPOSED STRESS

TESTING OF POLYMERIC LIQUIDS

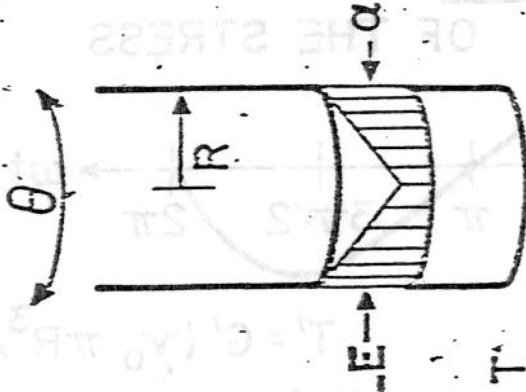
PARALLEL PLATE



$$\text{STRAIN } \gamma = \frac{R\theta}{h}$$

$$\text{STRESS } \sigma = \frac{2T}{\pi R^3}$$

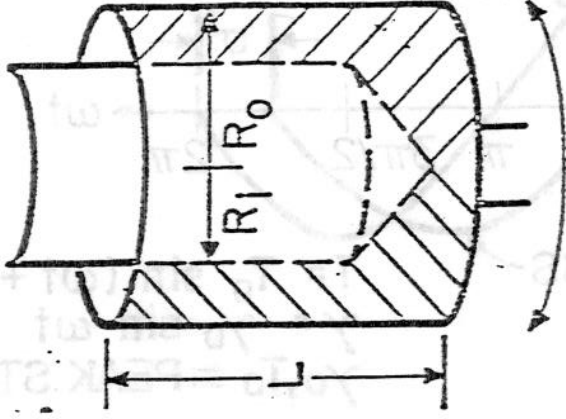
CONE AND PLATE



$$\gamma = \frac{\theta}{\alpha}$$

$$\sigma = \frac{3T}{2\pi R^3}$$

COUETTE

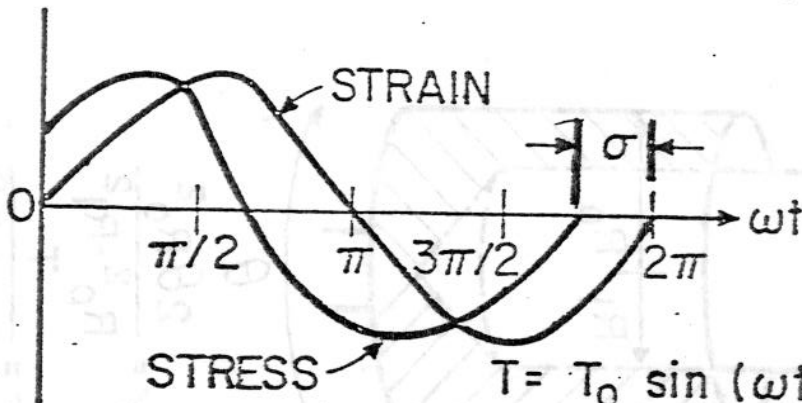


$$\gamma = \frac{2\theta R_0^2}{R_0^2 - R_1^2}$$

$$\sigma = \frac{T}{2\pi L R_0^2}$$

Steady Shear: replace θ with ω_0 to get $\dot{\gamma}$.
 $\dot{\gamma}$ is steady state strain rate

DYNAMIC MECHANICAL TESTING OF VISCOELASTIC LIQUIDS



Strain imposed
Stress (Torque) measured

$$T = T_0 \sin(\omega t + \sigma)$$

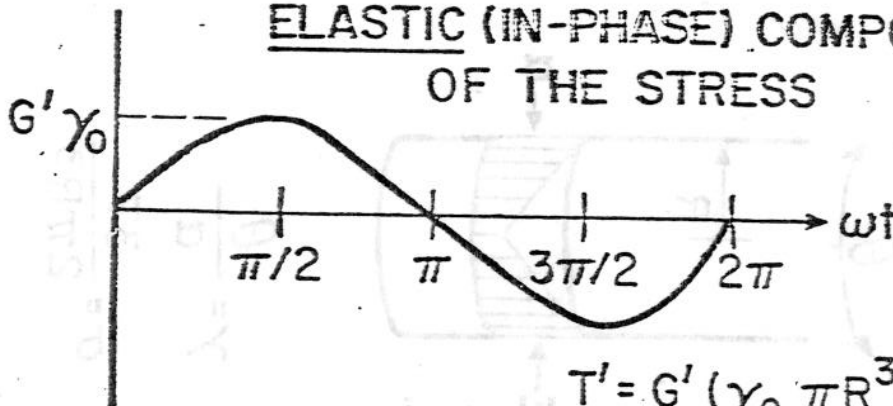
$$\gamma = \gamma_0 \sin \omega t$$

$\gamma_0, T_0 \equiv$ PEAK STRAIN, STRESS

$\sigma \equiv$ PHASE ANGLE

Newtonian $\sigma = 90^\circ$
Elastic $\sigma = 0^\circ$

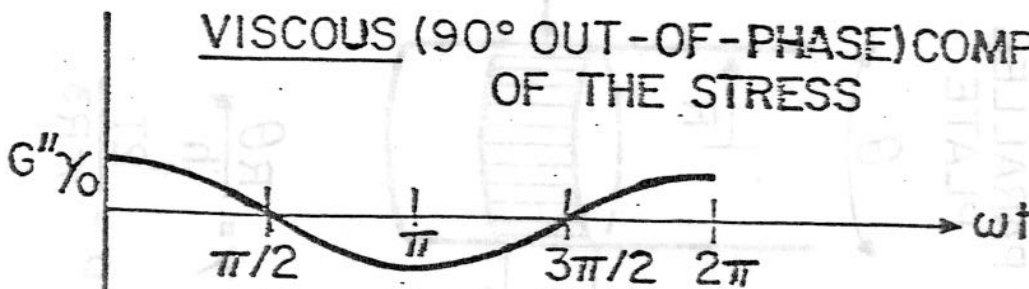
ELASTIC (IN-PHASE) COMPONENT OF THE STRESS



$$T' = G' (\gamma_0 \pi R^3 / 2) \sin \omega t$$

$G' \equiv$ DYNAMIC STORAGE MODULUS

VISCOUS (90° OUT-OF-PHASE) COMPONENT OF THE STRESS



$$T'' = G'' (\gamma_0 \pi R^3 / 2) \cos \omega t$$

$G'' \equiv$ DYNAMIC LOSS MODULUS

Rheological Functions

Dynamic Oscillatory Testing:

$$G^* = G' + i G'' \quad \text{Complex modulus}$$

$$G' = (\sigma/\gamma)_0 \cos \delta \quad \text{Elastic (storage) Modulus}$$

$$G'' = (\sigma/\gamma)_0 \sin \delta \quad \text{Viscous (loss) Modulus}$$

$$G''/G' = \tan \delta \quad \delta = \text{phase angle}$$

$$J^* = 1/G^* \quad \text{Complex Compliance}$$

$$\eta^* = \eta' - i \eta'' = (\eta'^2 + \eta''^2)^{1/2} \quad \text{Complex Viscosity}$$
$$= \frac{(G'^2 + G''^2)^{1/2}}{\omega}$$

$$\eta' = G''/\omega \quad \text{dynamic Viscosity}$$

Steady Shear Testing

$$\eta = \sigma_{12}/\dot{\gamma} \quad \text{steady shear viscosity}$$

$$\eta_0 = \lim_{\dot{\gamma} \rightarrow 0} \eta(\dot{\gamma}) \quad \text{zero-shear viscosity}$$

$$N_1 = \sigma_{11} - \sigma_{22} \quad 1^{\text{st}} \text{ Normal Stress Difference}$$

$$\Psi_1 = \frac{(\sigma_{11} - \sigma_{22})}{\dot{\gamma}^2} \quad 1^{\text{st}} \text{ Normal Stress coefficient}$$

$$\Psi_2 = \frac{(\sigma_{22} - \sigma_{33})}{\dot{\gamma}^2} \quad 2^{\text{nd}} \text{ Normal Stress Coefficient}$$

Constitutive Equation for Linear Viscoelasticity in Simple Shear

stress tensor: Simple Shear flow (SSF)

$$\sigma_{ij} = \begin{pmatrix} 0 & \sigma_{12} & 0 \\ \sigma_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

strain tensor:

$$\gamma_{ij} = \begin{pmatrix} 0 & \gamma_{12} & 0 \\ \gamma_{21} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad \gamma_{12} = \gamma_{21} = \frac{\partial u_1}{\partial x_2}$$

Stress and strain are time dependent and are connected by the constitutive equation for linear viscoelasticity (LVE), which for Simple Shear is based on the concept that the effects of sequential changes in strain are ADDITIVE.

$$\sigma_{21}(t) = \int_{-\infty}^t G(t-t') \dot{\gamma}_{21}(t') dt'$$

where $\dot{\gamma}_{21} = \partial \gamma_{21} / \partial t$ = shear rate

$G(t-t') \Rightarrow$ relaxation modulus

where integration is carried out over all past times (t') up to the current time, (t).

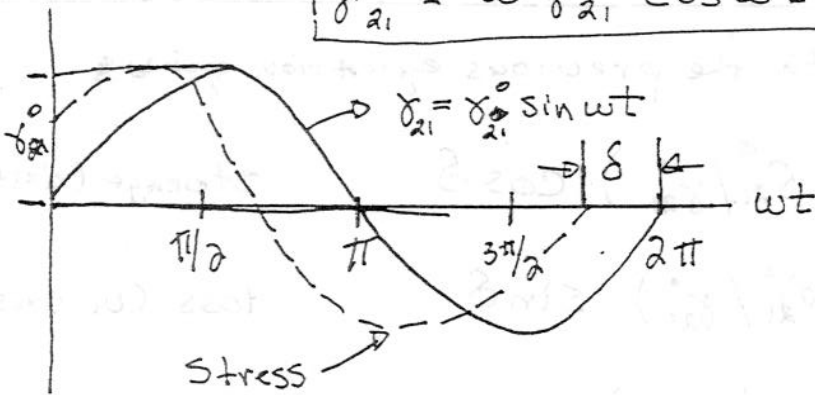
Dynamic Oscillatory Shear.

Strain (imposed):

$$\gamma_{21} = \gamma_{21}^0 \sin \omega t$$

γ_{21}^0 = peak strain ω = frequency.

$$\dot{\gamma}_{21} = \omega \gamma_{21}^0 \cos \omega t \Rightarrow \text{shear rate}$$



δ = phase angle

$\delta = 90^\circ$ (viscous)

$\delta = 0^\circ$ (Elastic)

Substituting into LVE Simple Shear Constitutive Eq.

with $(t-t') = s$

$$\sigma_{21}(t) = \int_0^\infty G(s) \omega \gamma_{21}^0 \cos[\omega(t-s)] ds$$

$$= \gamma_{21}^0 \left[\omega \int_0^\infty G(s) \sin \omega s ds \right] \sin \omega t + \gamma_{21}^0 \left[\omega \int_0^\infty G(s) \cos \omega s ds \right] \cos \omega t$$

\therefore $\sin \omega t$ term "in-phase" with γ_{21}

$\cos \omega t$ term "out-of-phase by 90° " with γ_{21}

- Stress (σ_{21}) \Rightarrow ① periodic in ω
② out-of-phase with γ_{21}

$$\sigma_{21} = \gamma_{21}^0 (G' \sin \omega t + G'' \cos \omega t)$$

defining G' = "in-phase" with γ_{21}

G'' = "out-of-phase" with γ_{21}

Dynamic Oscillatory Shear (continued)

An alternative form for the stress (σ_{21}) uses the Amplitude of the stress (σ_{21}^0) and the phase angle (δ)

$$\sigma_{21} = \sigma_{21}^0 (\sin \omega t + \delta) = \sigma_{21}^0 \cos \delta \sin \omega t + \sigma_{21}^0 \sin \delta \cos \omega t$$

Comparison with the previous equation gives:

$$G' = (\sigma_{21}^0 / \gamma_{21}^0) \cos \delta \quad \text{storage (elastic) modulus}$$

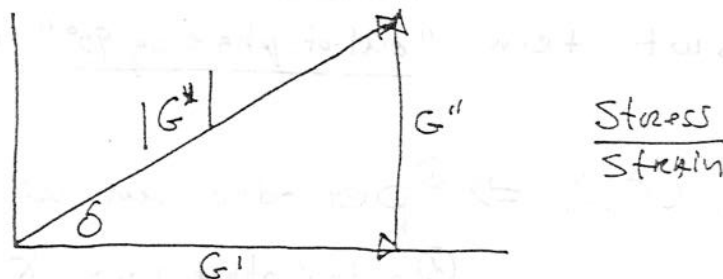
$$G'' = (\sigma_{21}^0 / \gamma_{21}^0) \sin \delta \quad \text{loss (viscous) modulus}$$

$$G''/G' = \tan \delta \quad \text{loss tangent}$$

It can be shown (with some work) that the sinusoidally varying stress can be expressed as a complex quantity: τ . The MODULUS is also complex, given by:

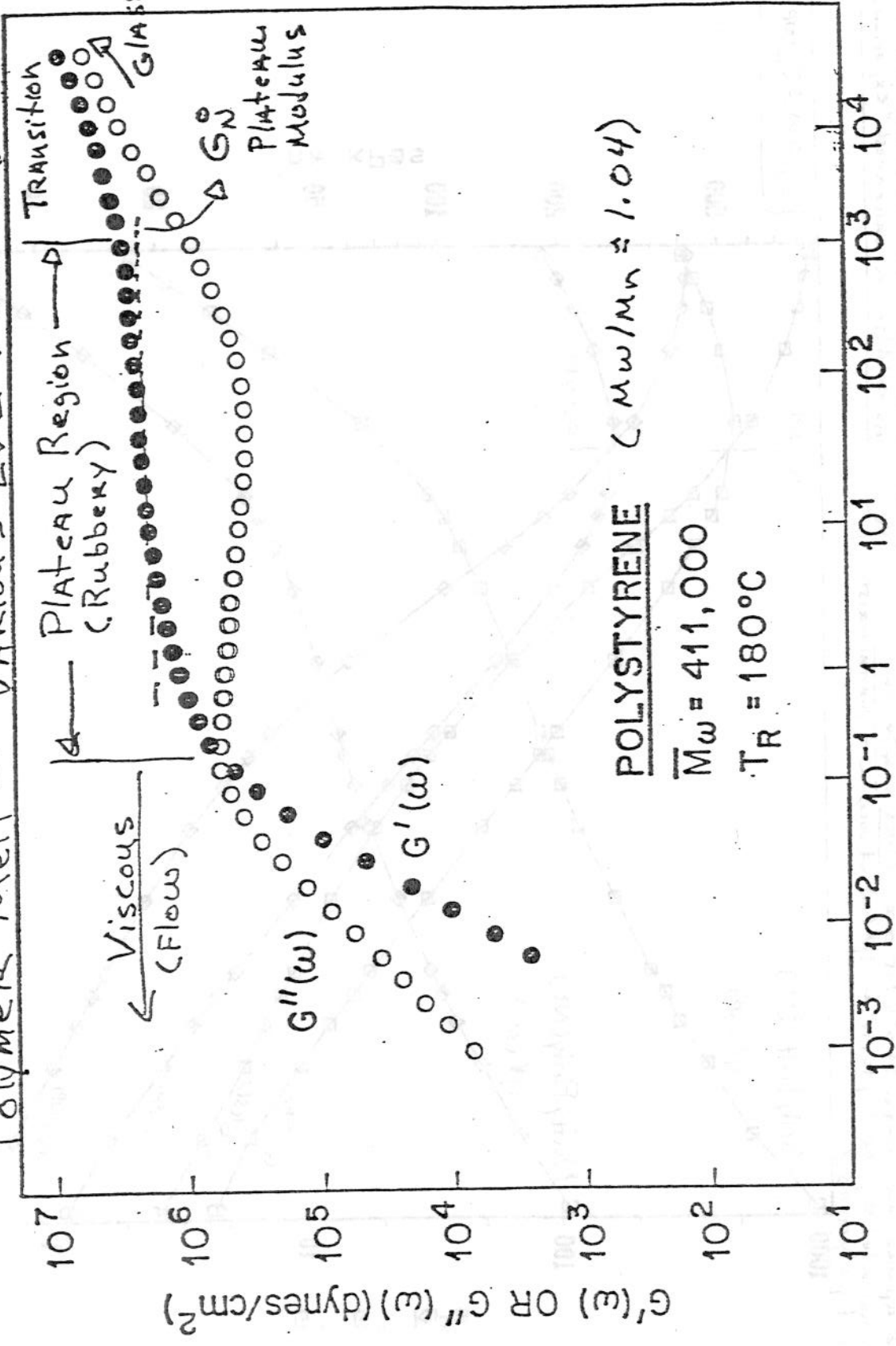
$$\sigma_{21}^* / \gamma_{21}^0 = G^* = G' + iG''$$

$$|G^*| = \sigma_{21}^0 / \gamma_{21}^0 = (G'^2 + G''^2)^{1/2}$$



$$G' = |G^*| \cos \delta$$
$$G'' = |G^*| \sin \delta$$

Polymer Melt - Various LVE Flow Regimes

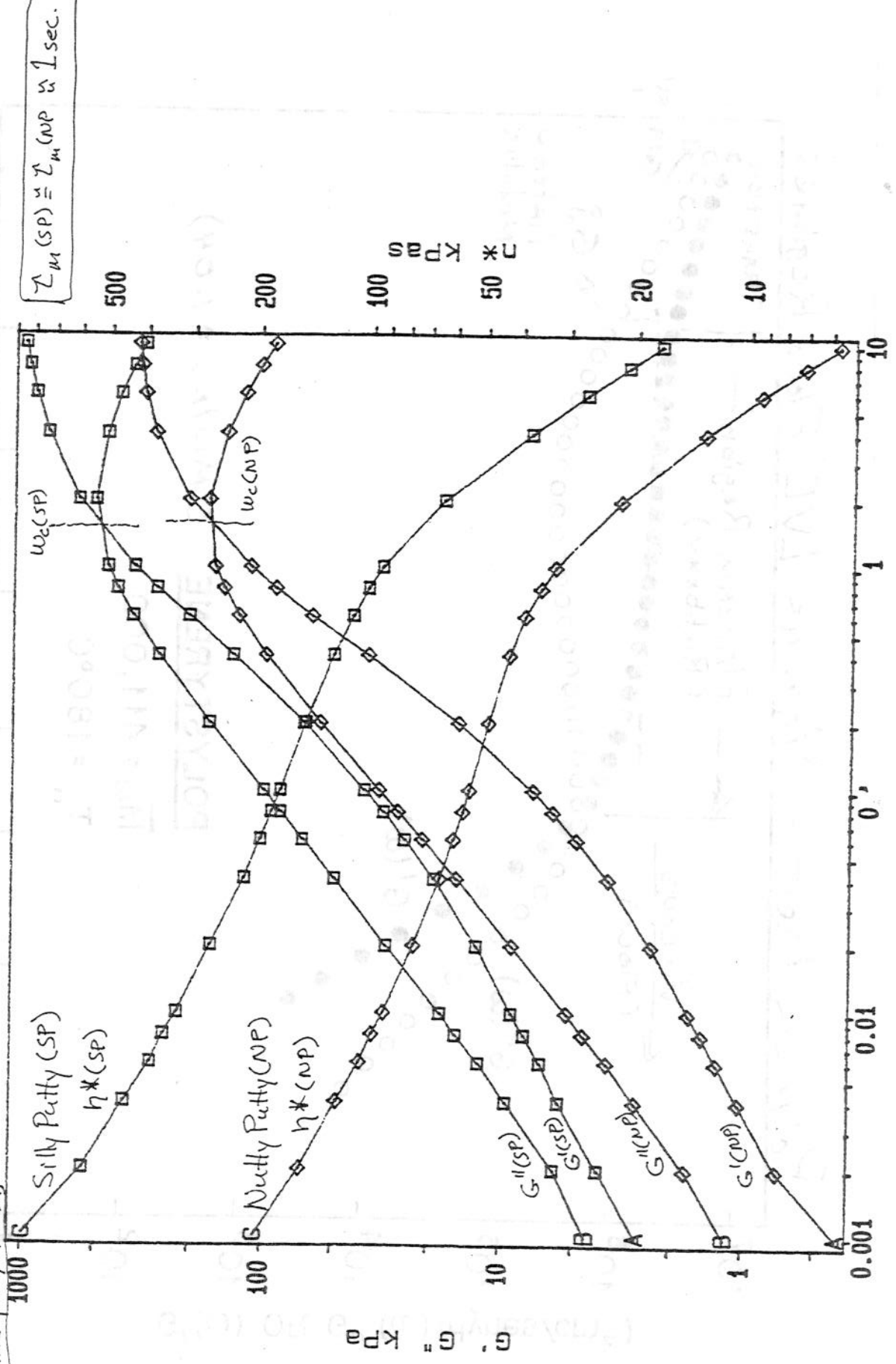


ω at (rad/sec)

- ① Label the curves A to G, G' , G'' , η^* and W_c .
- ② What is the maximum relaxation time for each polymer?
- ③ One curve is "Nutty Putty" and the other is "Silly Putty". Label the curves appropriately.
- ④ From looking at the $\eta^*(\omega)$ data, would you say that these two materials are "filled" polymers. Why or why not?

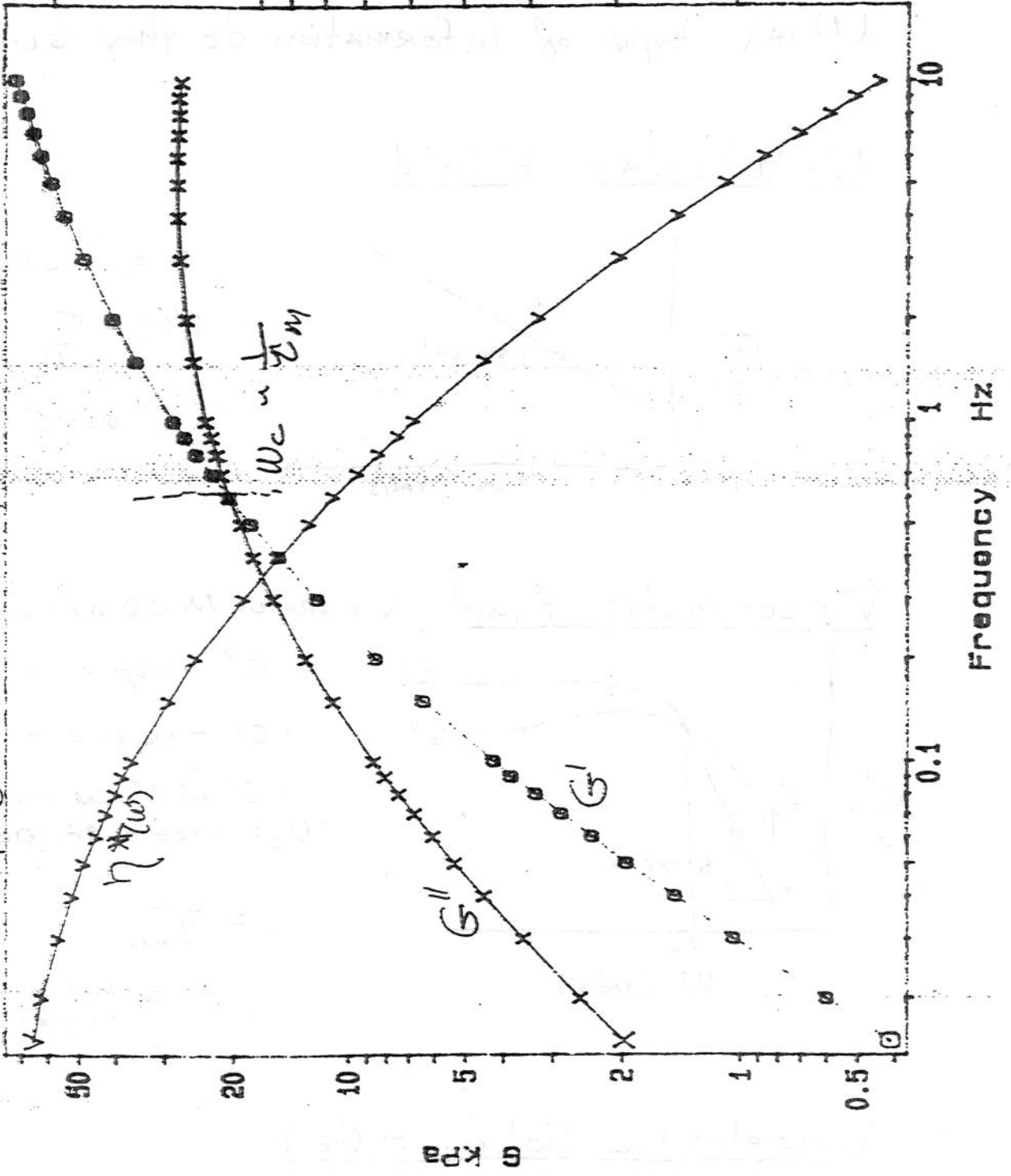
A. Do it would appear that both SP and NP are filled materials. This is indicated by the "upturn" in $\eta^*(\omega)$ at low ω - characteristic of filled polymers.

A. Silly Putty "stiffer" with less low shear flow As exhibited in "ball on desk" experiment.



$\tau_M(SP) \approx \tau_M(NP) \approx 1 \text{ sec}$

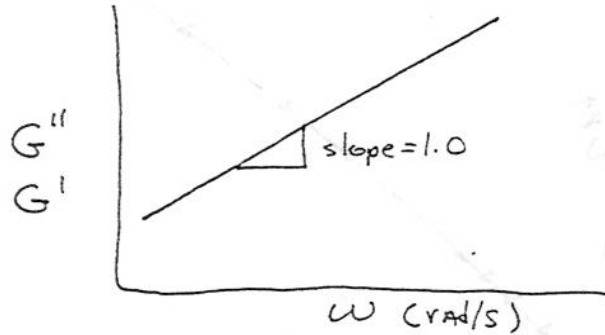
PDMS STANDARD



Dynamic Moduli - $G'(\omega)$ & $G''(\omega)$

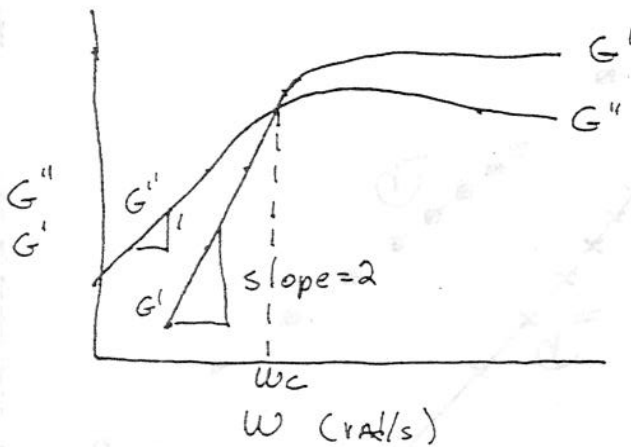
What type of information do they supply?

Newtonian Fluid.



$G' = 0$ (no elastic modulus)
 $\eta'(\omega) = \frac{G''}{\omega} = \text{constant}$
 (G'' vs ω has slope = 1.0)

Viscoelastic Fluid. (narrow MWD material)

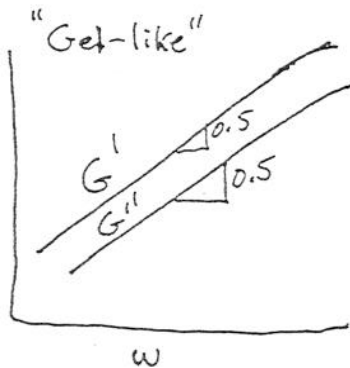


- G'' - slope = 1 in terminal region
 - G' - slope = 2 in terminal region
 - G' and G'' are functions of ω
- $\omega_c = \text{crossover point}$

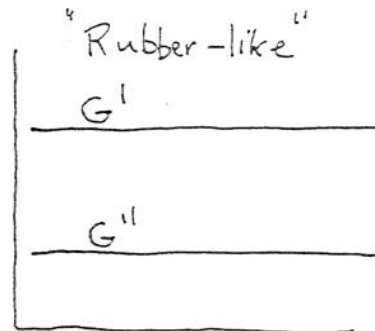
$$\omega_c \approx \frac{1}{\tau_{\text{max}}}$$

\rightarrow maximum polymer relaxation time

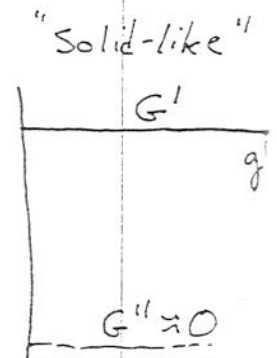
Viscoelastic Solid. (or Gel)



G' and $G'' \propto \omega^{0.5}$
 $G' > G''$ for all ω .



$G', G'' \neq f(\omega)$
 $G' > G''$



$G' \neq f(\omega)$
 G' increasing at high ω
 $G'' \approx 0$ ($\ll G'$)

Cox-Merz Rule

- correlation in the limit of low shear (frequency) between steady shear and dynamic data.

Viscosity

$$\eta(\dot{\gamma}) = \eta^*(\omega) = \eta'(\omega) \quad \lim_{\substack{\dot{\gamma} \rightarrow 0 \\ \omega \rightarrow 0}}$$

for isotropic melts it is also found that:

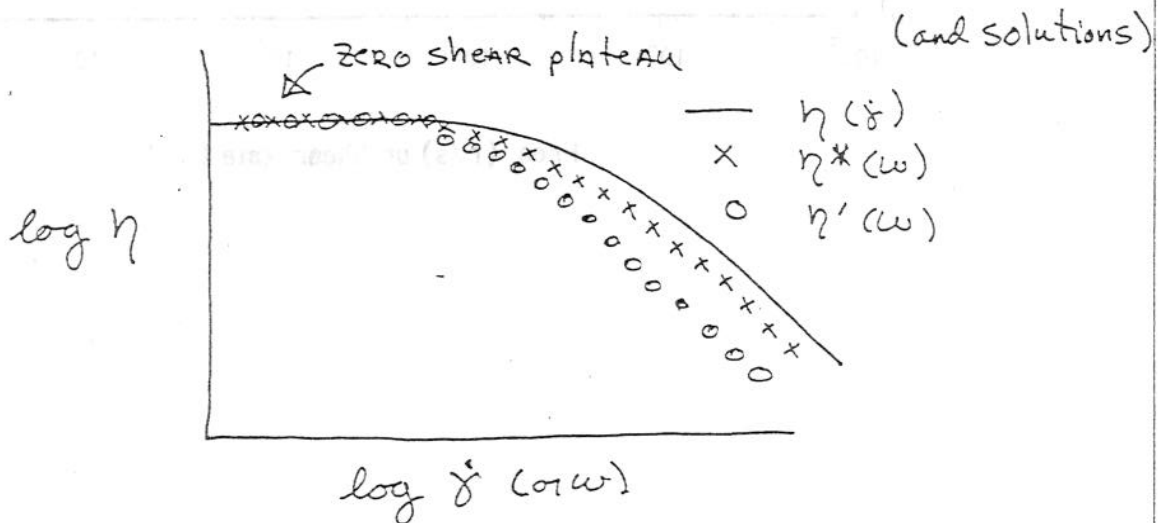
$$\eta(\dot{\gamma}) = \eta^*(\omega) \quad \text{at } \omega = \dot{\gamma}$$

(outside low shear region)

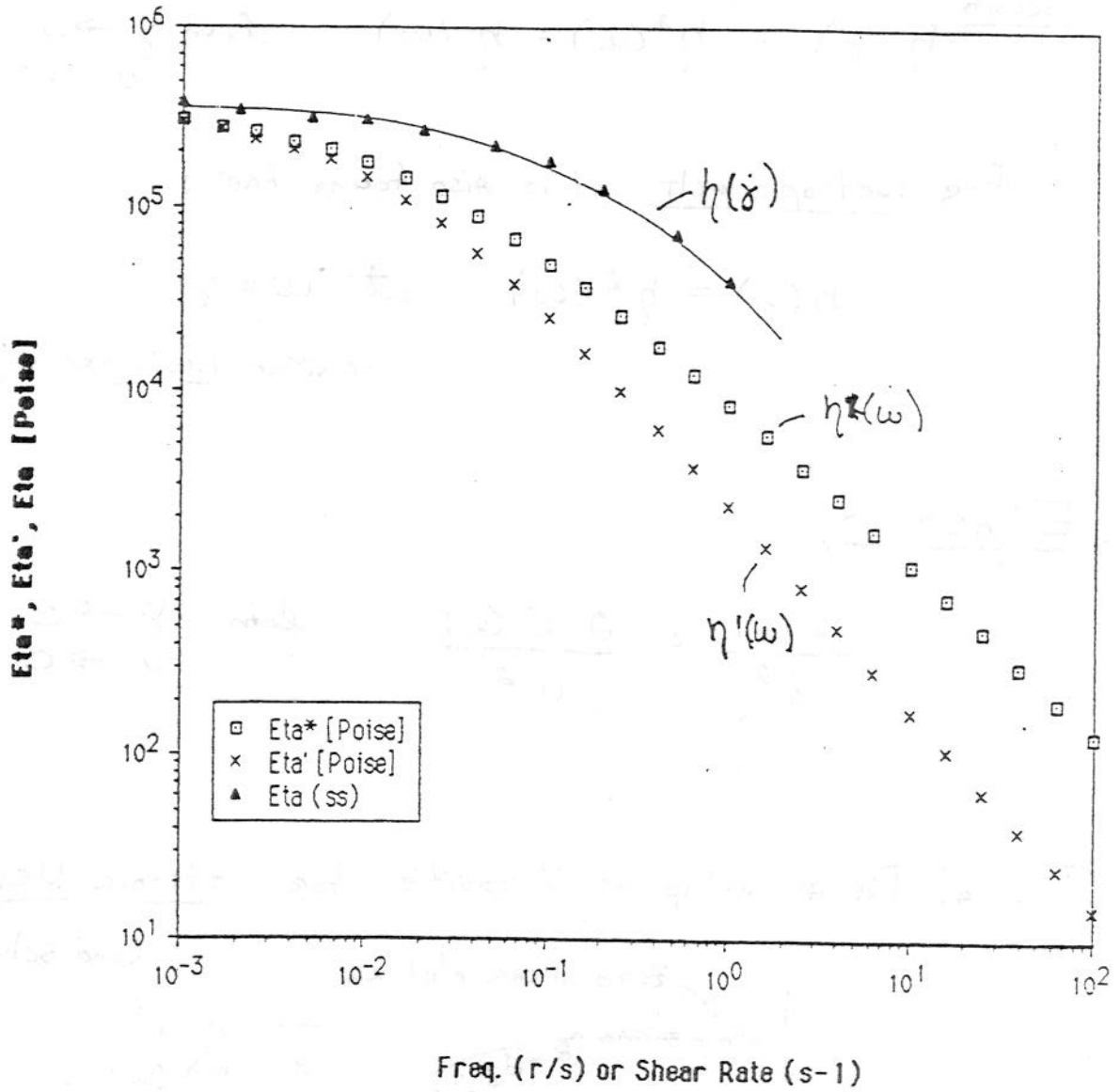
Elasticity

$$\frac{N_1(\dot{\gamma})}{\dot{\gamma}^2} \approx \frac{2 G'(\omega)}{\omega^2} \quad \lim_{\substack{\dot{\gamma} \rightarrow 0 \\ \omega \rightarrow 0}}$$

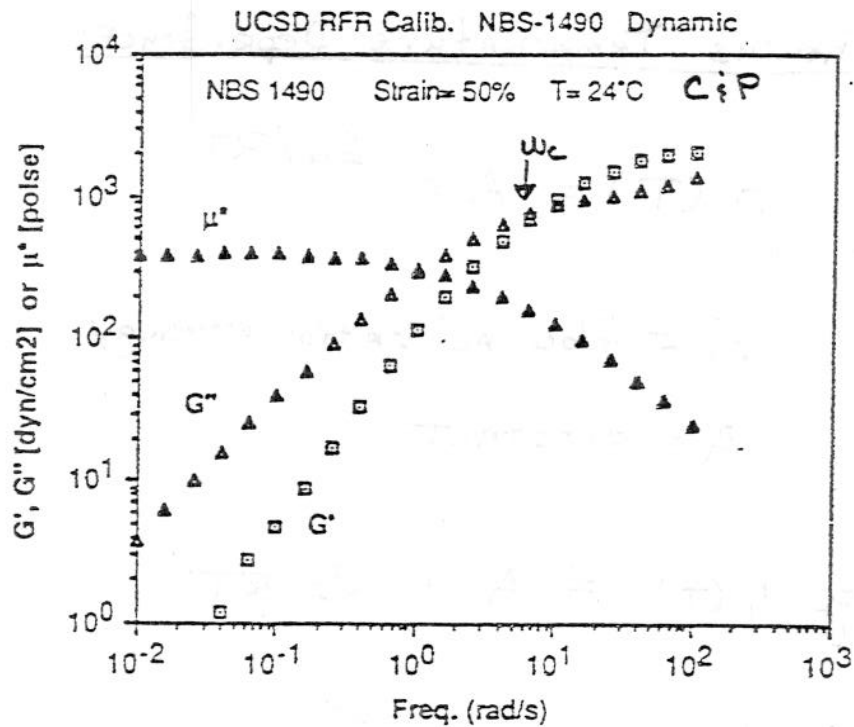
Typical Relationship of Viscosities for isotropic melts



Data from "PI L-11/Sq.25% \neq 1.Eta"



Dynamic and Steady Shear Testing of a Polymeric Liquid (NBS-1490 Viscoelastic Standard)

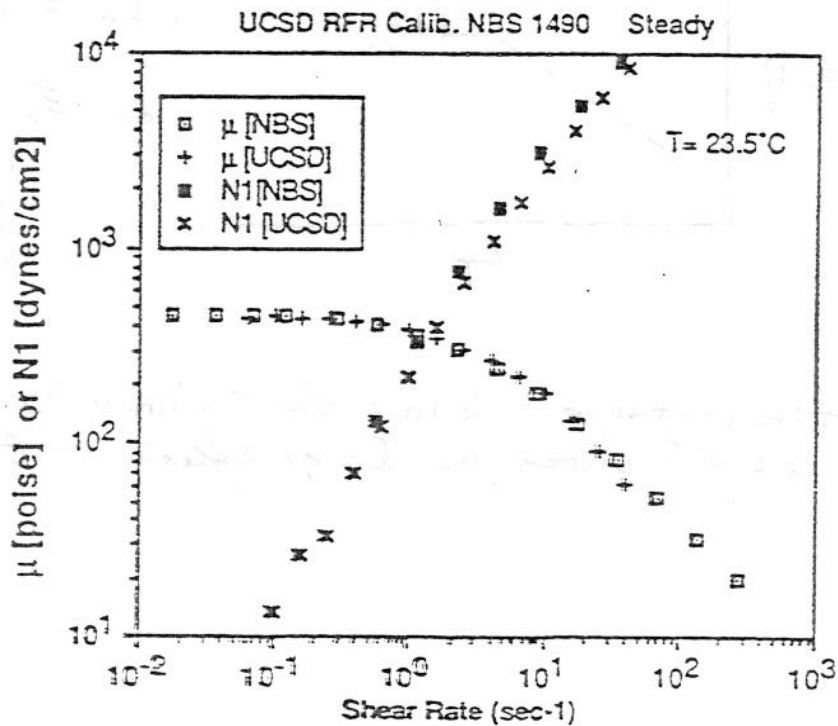


μ^* = Complex viscosity

G', G'' Moduli

G' storage (elastic)

G'' loss (viscous)



μ = steady shear viscosity

N_1 = Normal Force (elasticity)

Figure B-3 Calibration of RFR with a viscoelastic standard (NBS-1490).
Comparison of UCSD and NBS data in steady and dynamic shear.

SUBJECT

Temperature Behavior of Viscosity

JOB NO.

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DATE

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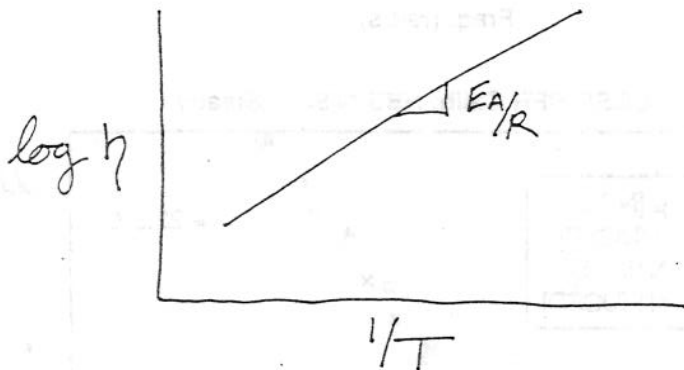
Arrhenius Temperature Dependence

$$\eta(T) = A e^{E_a/RT}$$

E_a = flow activation energy

A = constant

$$\log \eta(T) = A + E_a/RT$$



$E_a \neq f(\text{Mol. Wgt.})$

∴ E_a is related only to the local segmental character of the polymer

- for instance, long or short chain branching would have a large effect on E_a

SUBJECT

Time-Temperature Superposition

JOB NO.

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• Principle :

Materials with a temperature independent flow activation energy (EA) can be reduced to a single temperature using a temperature shift factor (usually designated a_T).

Thus, data at various T can be shifted to a reference temperature T_R using a_T .

$$\text{i.e. } \log \frac{\eta(T)}{\eta(T_R)} = \frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_R} \right) = \log a_T$$

Dynamic Mechanical Moduli.

$$G'(T, \omega) = b_T G'(T_R, \omega a_T)$$

$$G''(T, \omega) = b_T G''(T_R, \omega a_T)$$

$$b_T = \frac{\rho T}{\rho T_R} \quad , \quad \text{where } \rho = \text{melt density}$$

(Note: $b_T \approx 1.0$ in most cases)

a_T = frequency shift factor

SUBJECT

Time-Temperature Shift (Maxwell element)

JOB NO.

SHEET

FILE

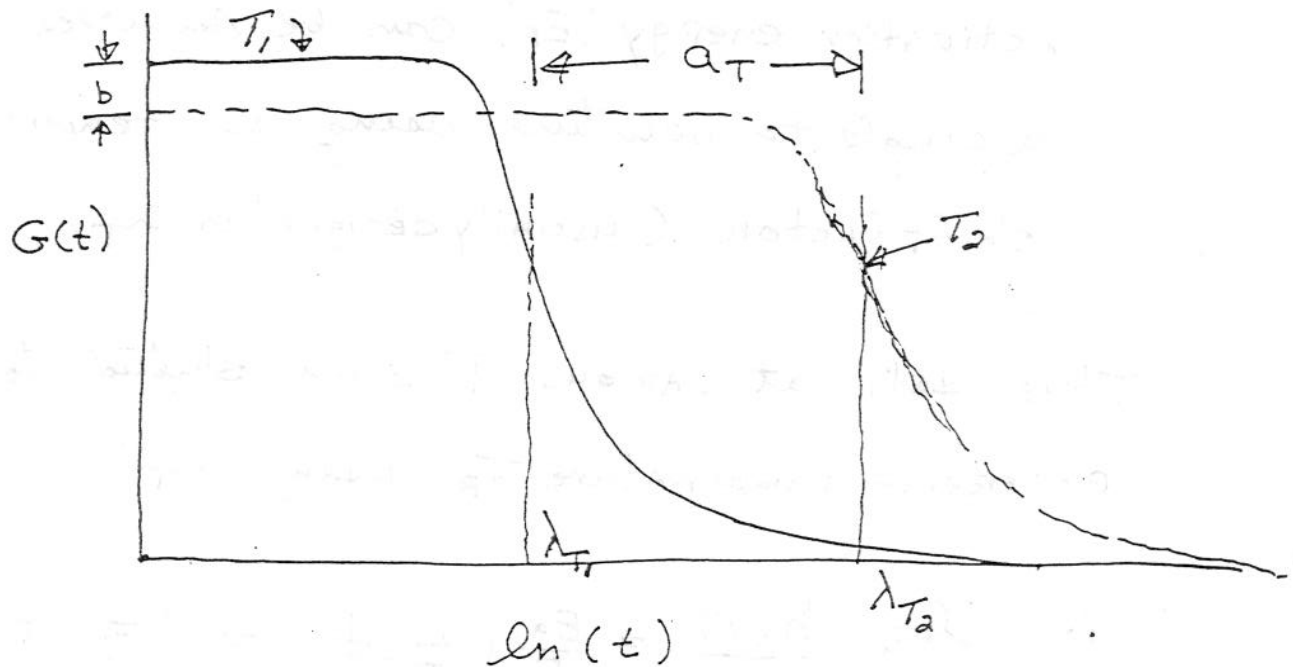
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Maxwell Element: single relaxation time (λ).

Stress Relaxation Experiment. $G(t) = G_0 e^{-t/\lambda}$



a_T = temperature shift factor

$$\log(a_T) = \log\left(\frac{\lambda_{T_2}}{\lambda_{T_1}}\right)$$

Time - Temperature Superposition

• $E(T_1, t) = E(T_2, t/a_T)$ where a_T = shift factor

• WLF Equation: $\log a_T = \frac{-C_1 (T - T_g)}{C_2 + T - T_g}$

where T_g = glass transition temperature
 C_1, C_2 = constants for a polymer system

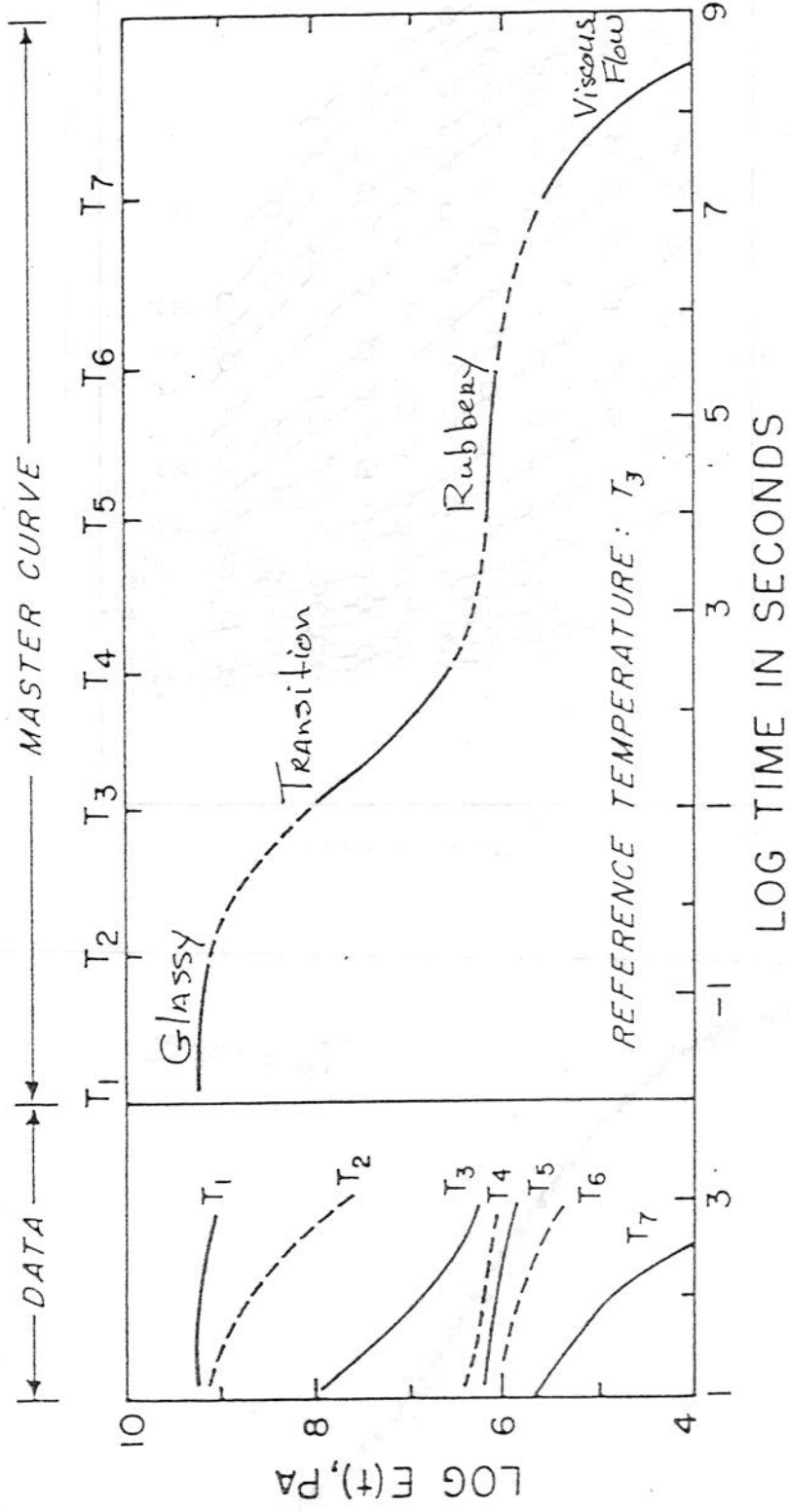
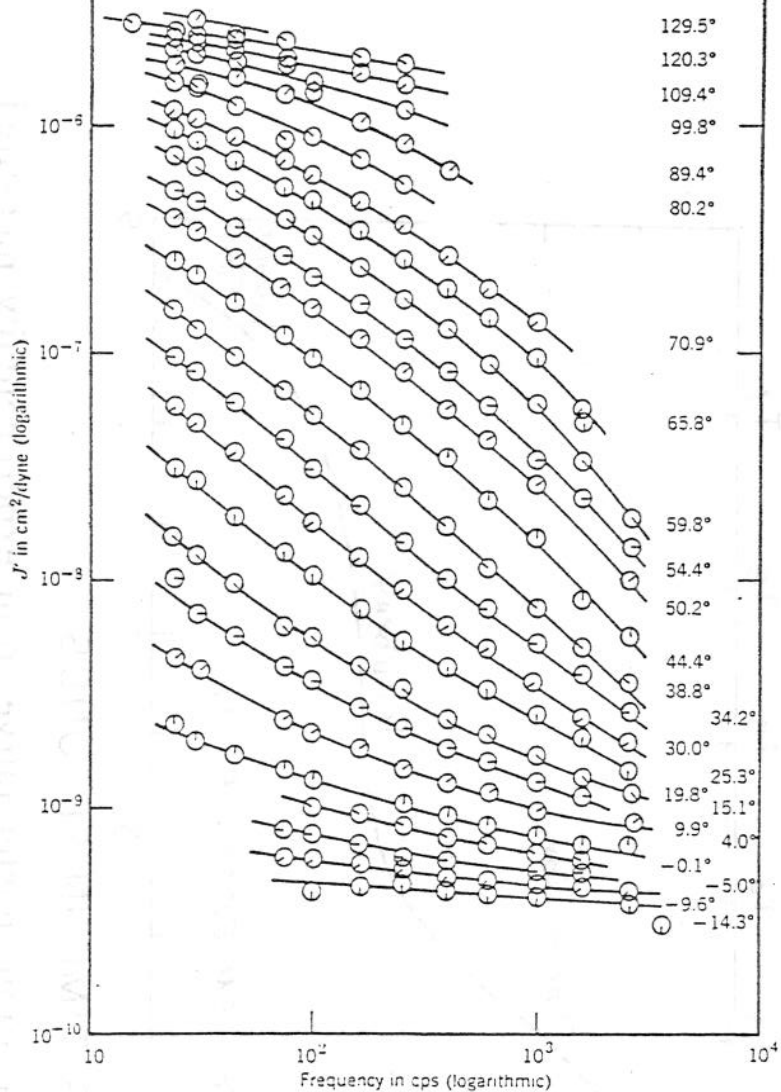


Figure 3-5. Preparation of a stress relaxation master curve from experimentally measured modulus-time curves at various temperatures.

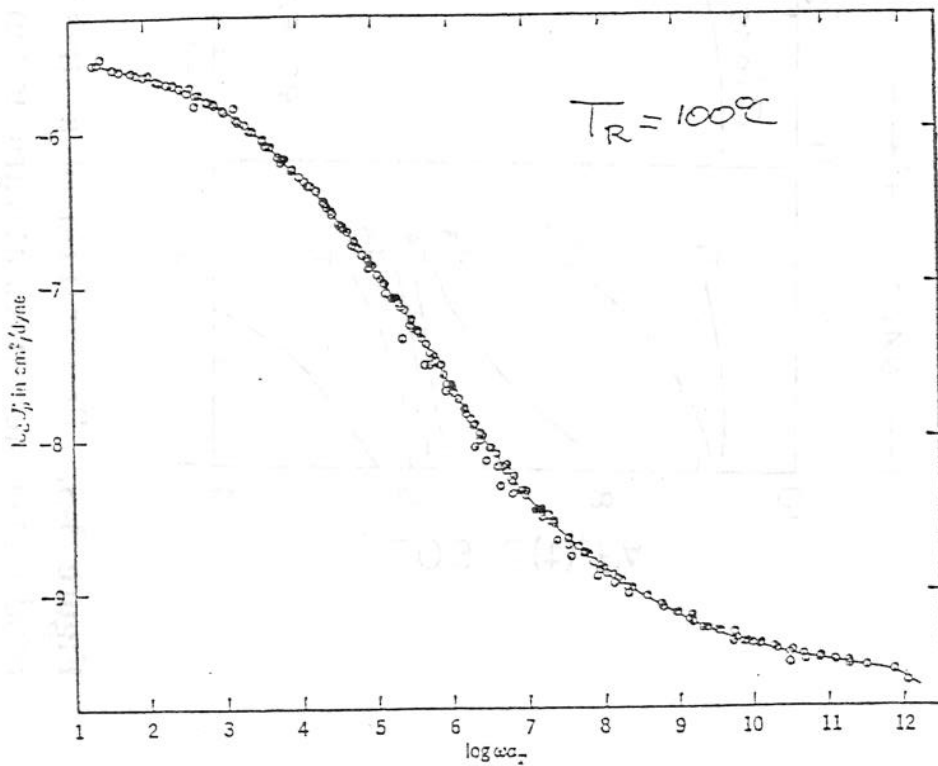
poly (n-octyl methacrylate)



Compliance vs. frequency

$$J' = 1/G' \text{ vs. } \omega$$

$$T = -14.3^\circ\text{C to } 129.5^\circ\text{C}$$



Master Curve
using
Time-Temperature
Superposition

Reprinted from

J. FERRY

"Viscoelastic Properties of Polymers"

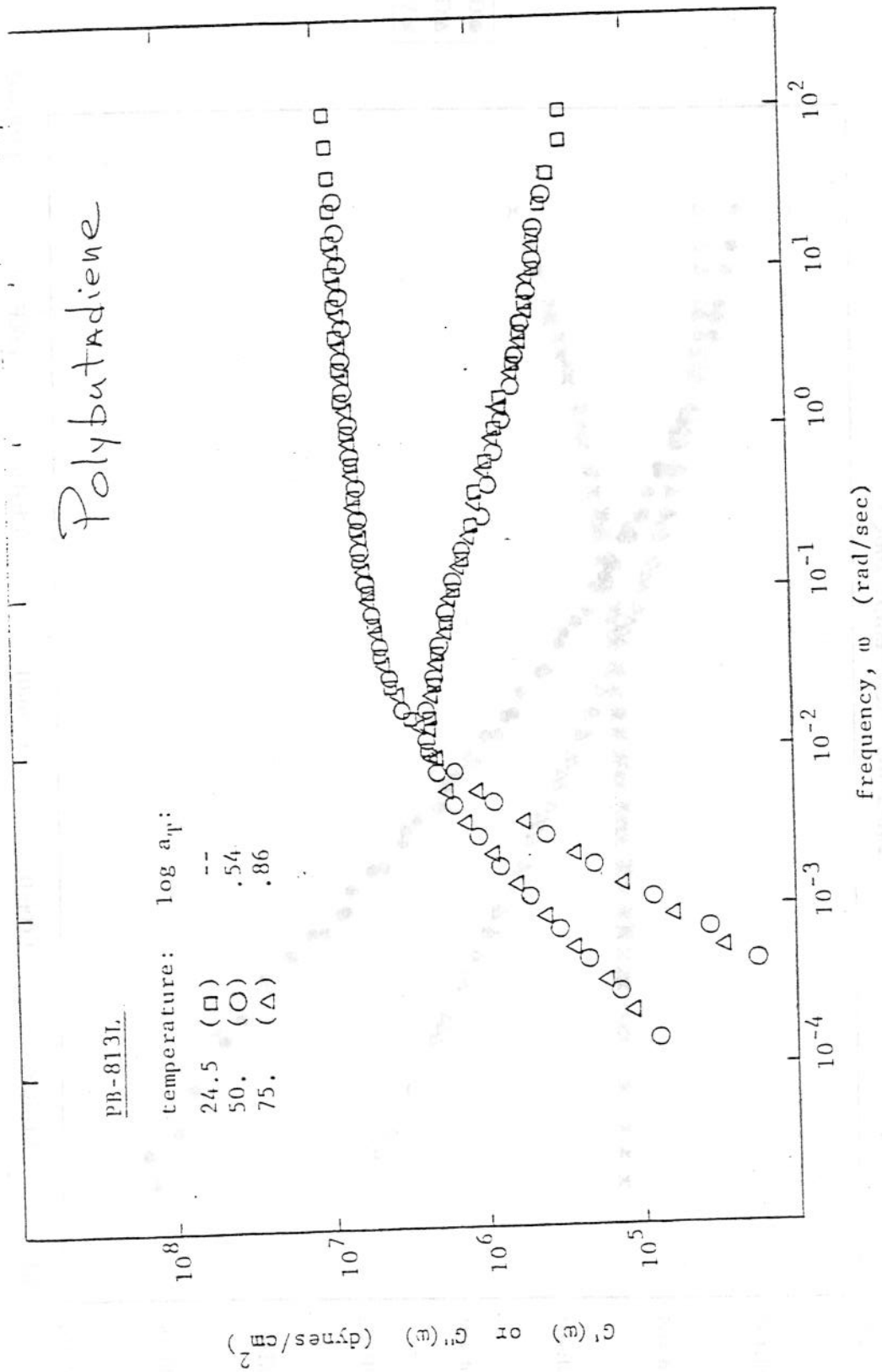
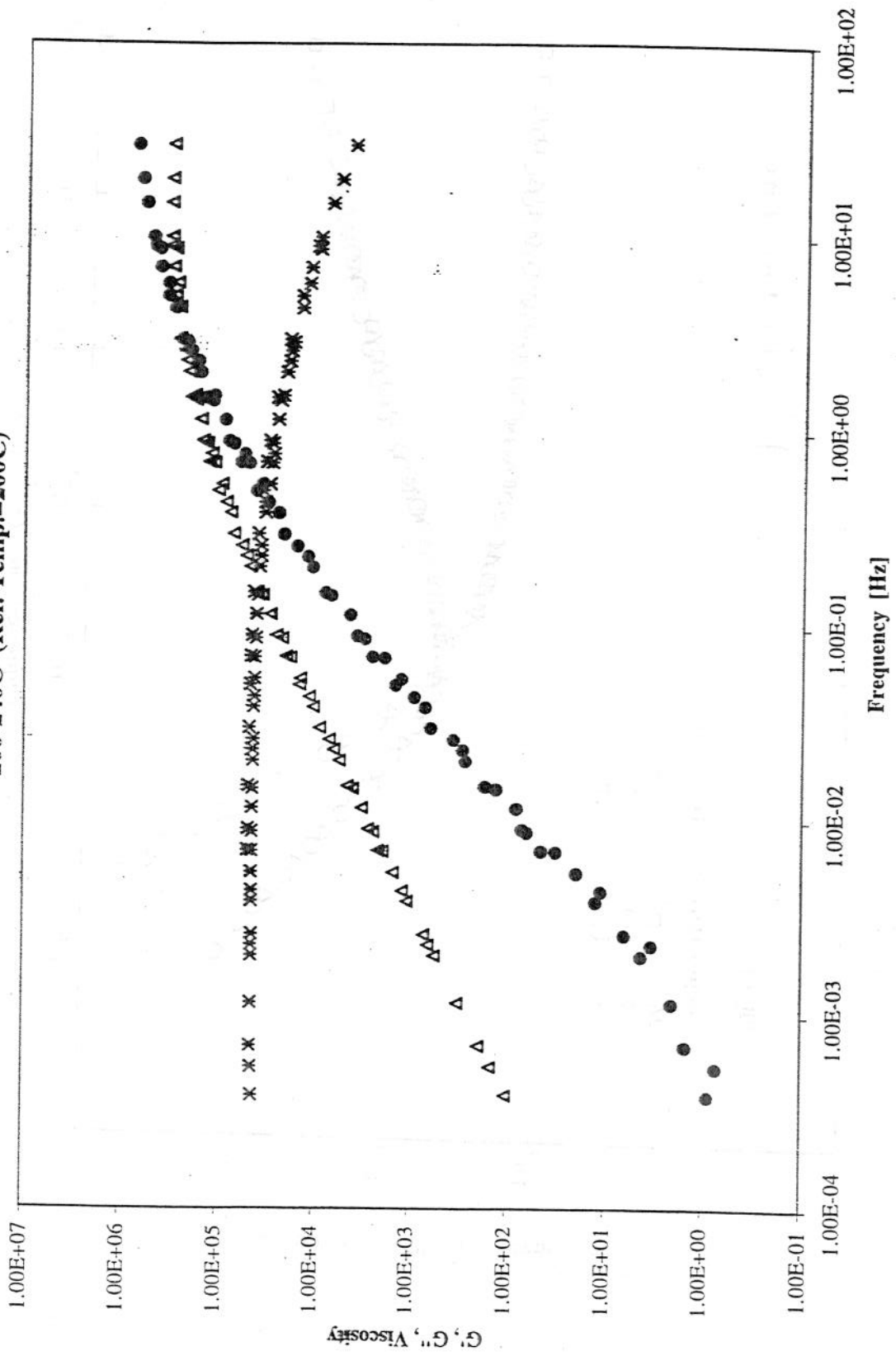


Figure 3.7. Frequency-temperature superposition of polybutadiene (PB-813I, $T_R = 24.5^\circ\text{C}$)

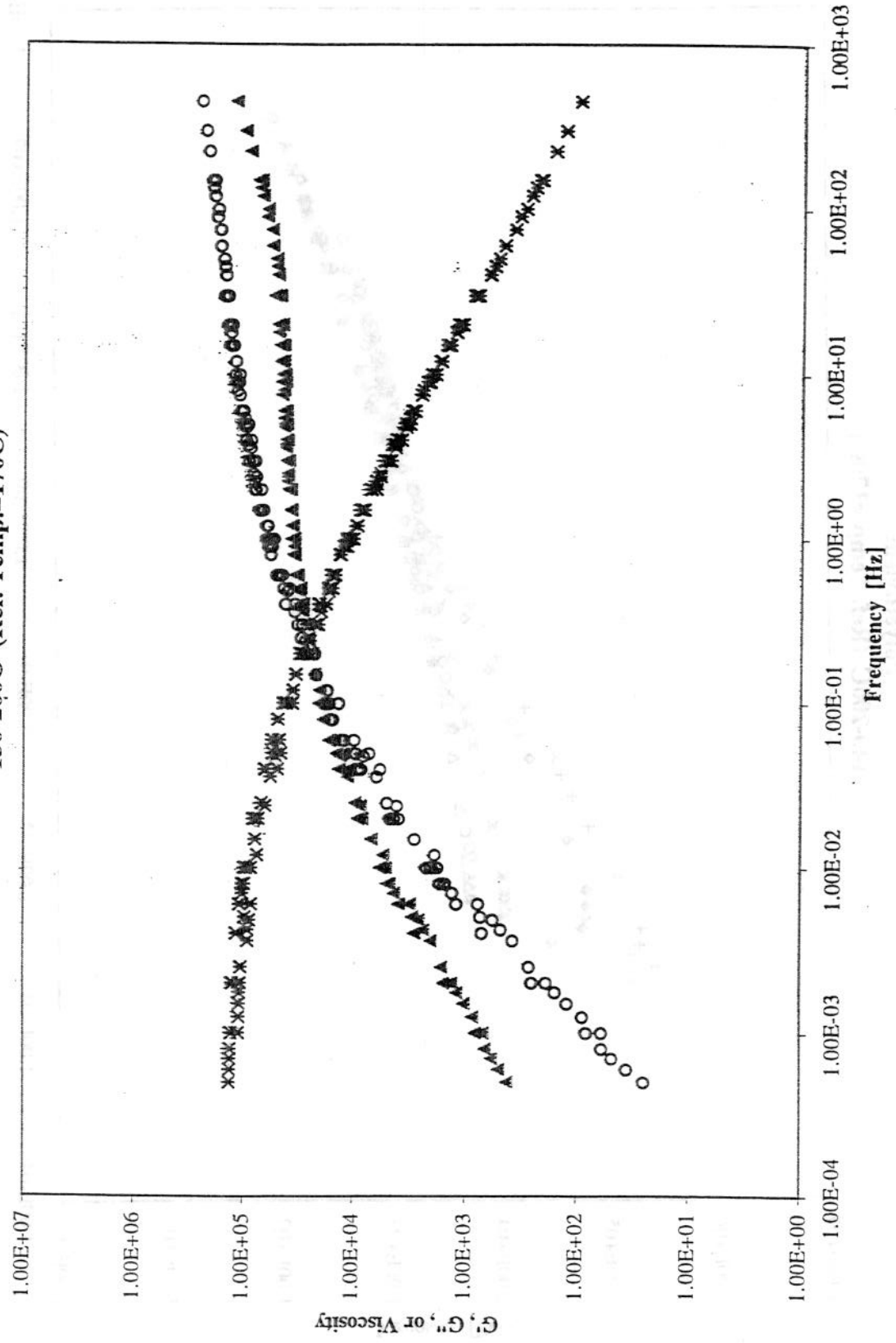
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M.S. Thesis

Time-Temperature-Superposition
 Polycarbonate-Bisphenol A
 200-240C (Ref. Temp.=200C)



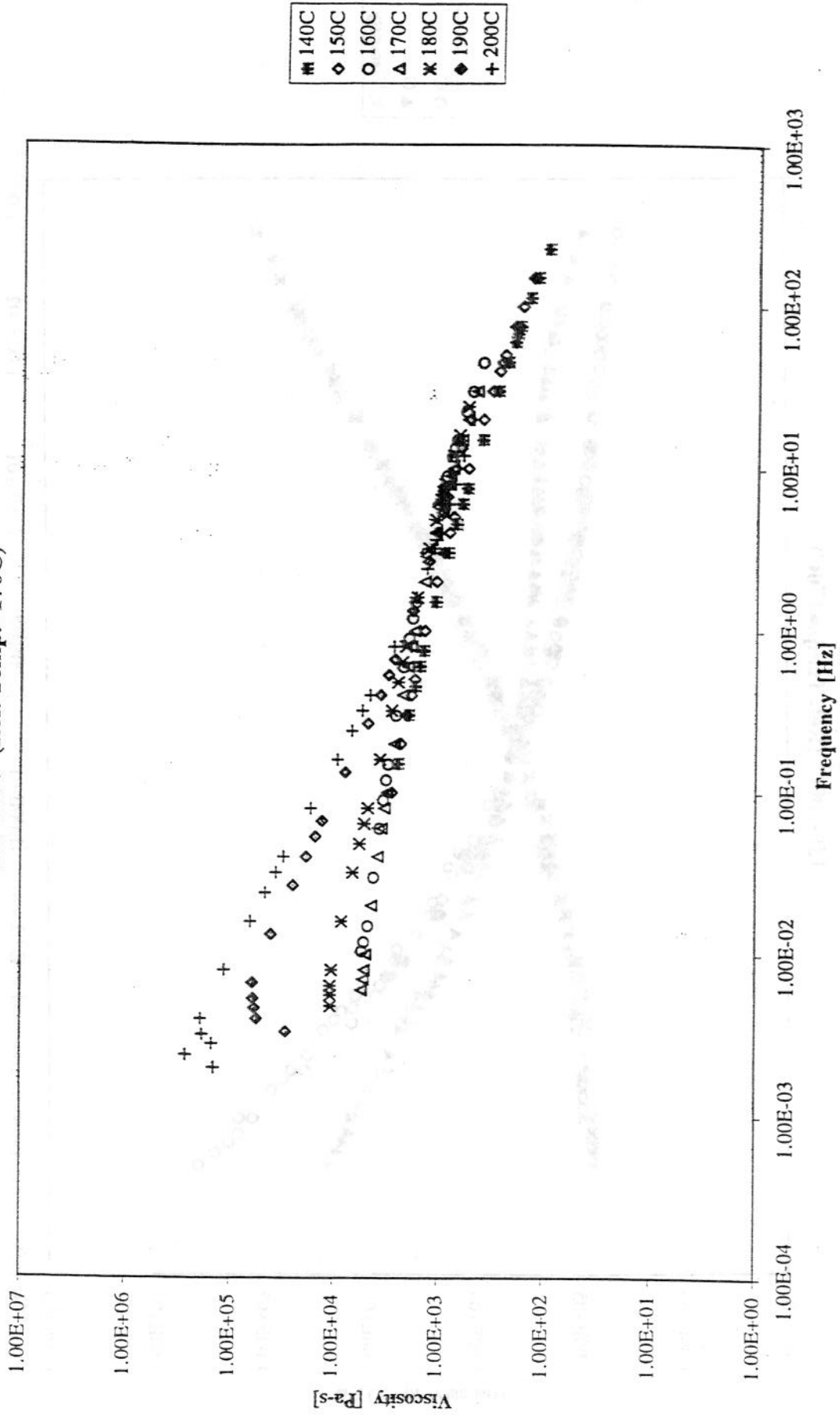
● G'
 △ G''
 * Viscosity

Time-Temperature-Superposition
 Polystyrene
 150-200C (Ref. Temp. = 170C)



○ G'
 ▲ G''
 * Viscosity

Time-Temperature-Superposition Viscosity
 Polyethylene
 140-200C (Ref. Temp.=170C)



Time-Temperature-Superposition G"
Polyethylene 140-200C
Reference Temp. = 170C

