Chem 4010
Nov 2003
theology

RHEOLOGY

THE STUDY OF FLOW AND DEFORMATION OF MATTER

RANGE OF MATERIAL BEHAVIOR

ELASTIC-*VISCO*ELASTIC-***VISCOUS***

SOLID LIKE - - - - - - LIQUID LIKE

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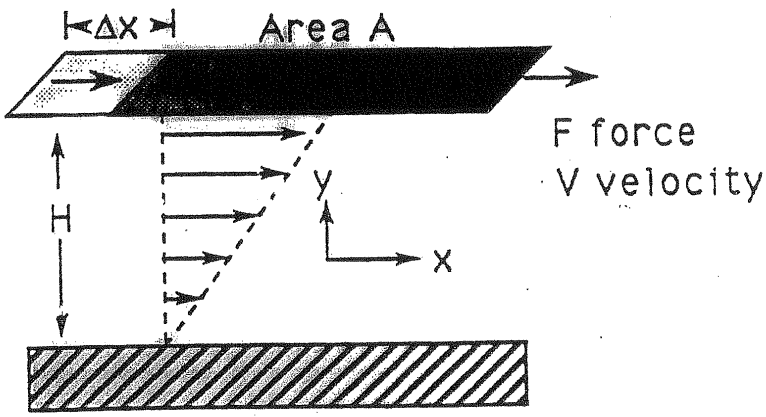
BASIC STRESS-STRAIN BEHAVIOR

DEFINITIONS:

STRESS: Force per unit area.
$t = F / A$

STRAIN: The magnitude of deformation relative to sample length (geometry).

SHEAR STRESS / STRAIN



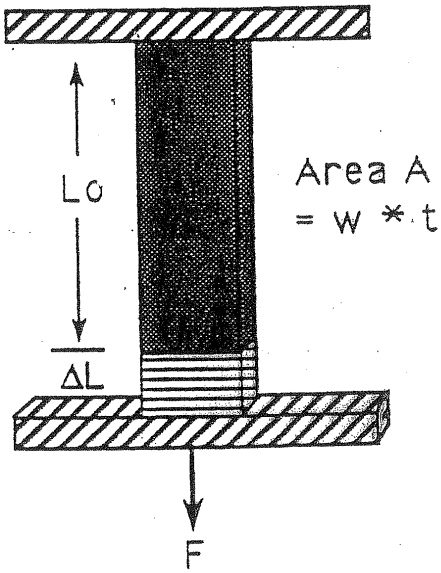
Stress: $\tau = F / A$

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

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

≡ shear rate

TENSILE STRESS - STRAIN



Stress: $\sigma = F / A$

Strain: $\varepsilon = \Delta L / Lo$

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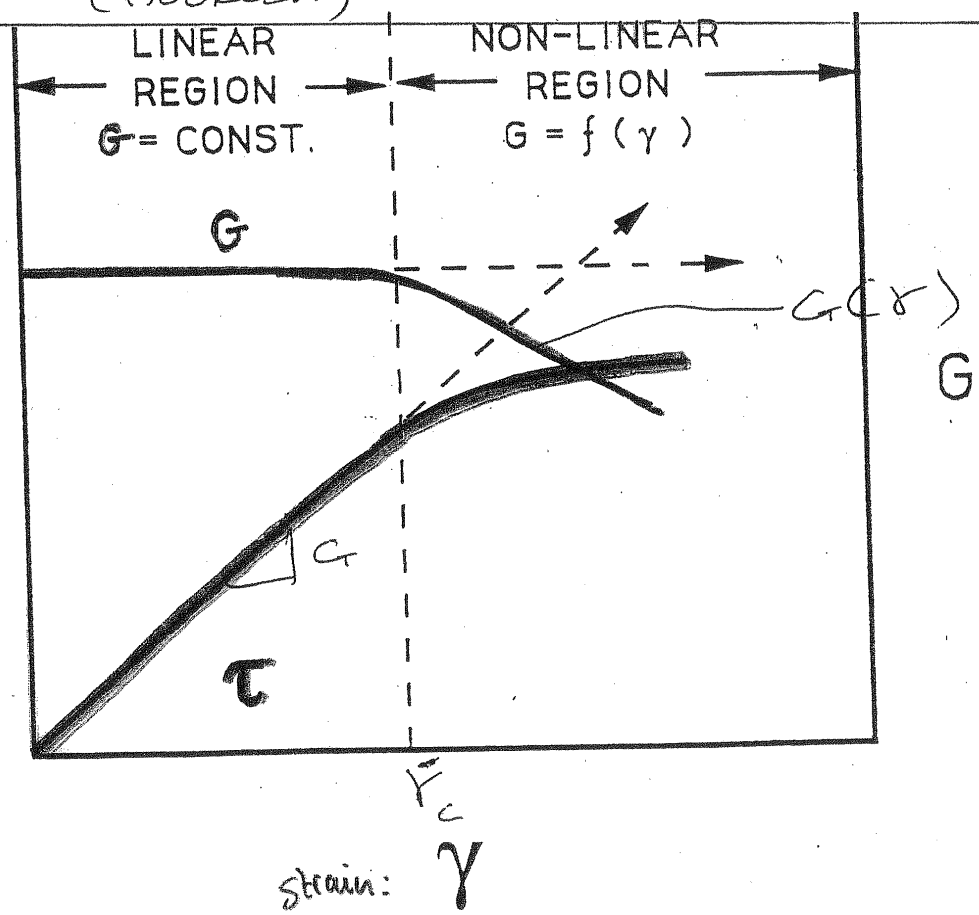
LINEAR AND NON-LINEAR STRESS-STRAIN BEHAVIOR OF SOLIDS

Hooke's law
$\tau = G\gamma$

(Hookean)

* Only measure in linear region

G: Modulus



stress: τ

strain: γ

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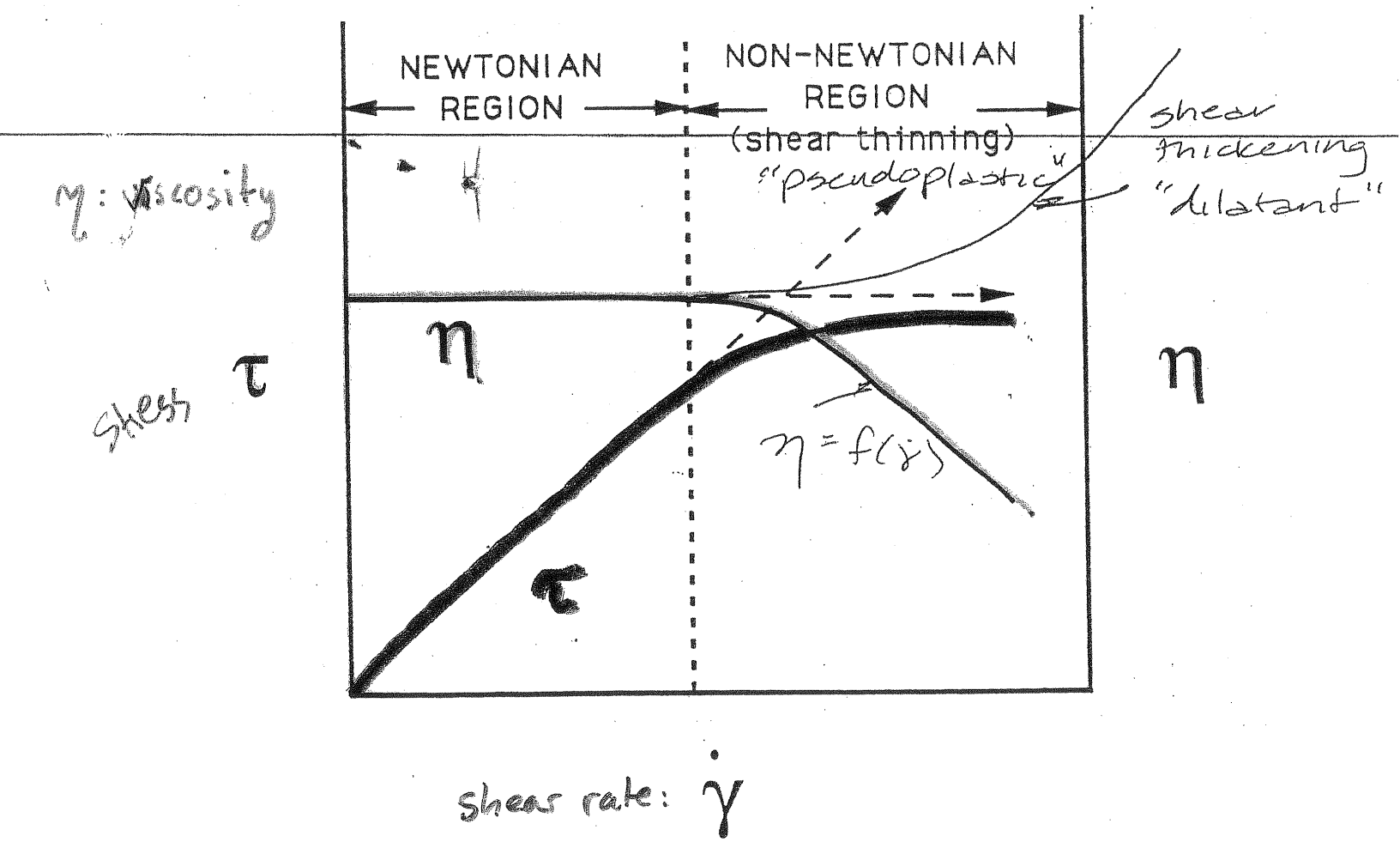
NEWTONIAN AND NON-NEWTONIAN BEHAVIOR OF FLUIDS

Newton's Law
stress $= \eta \dot{\gamma}$



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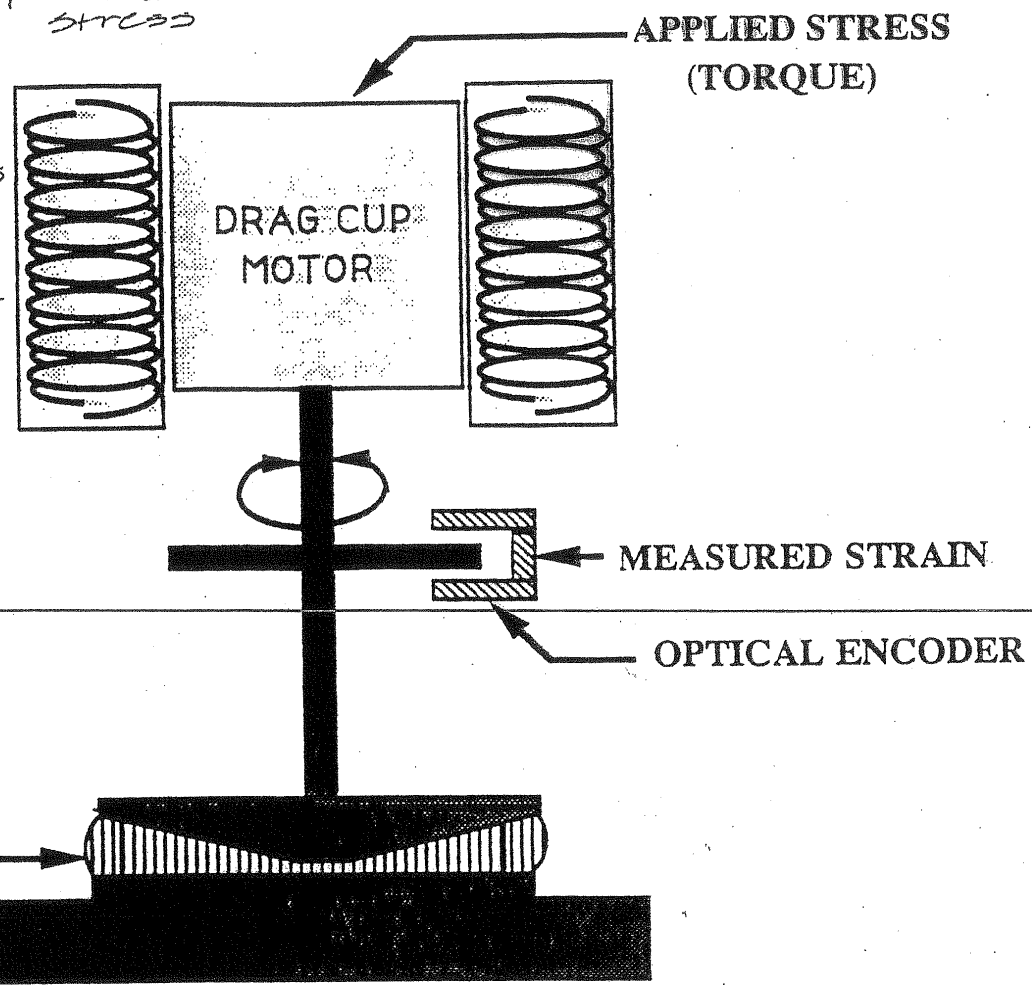
DYNAMIC MECHANICAL TESTING

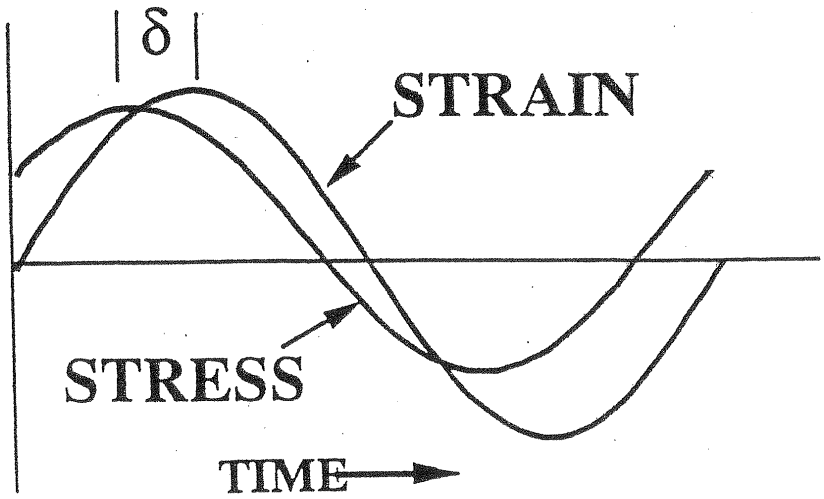
Strain input — Measure stress

ARES - Strain control

SR5000 - Stress control

Stress input — Measure strain





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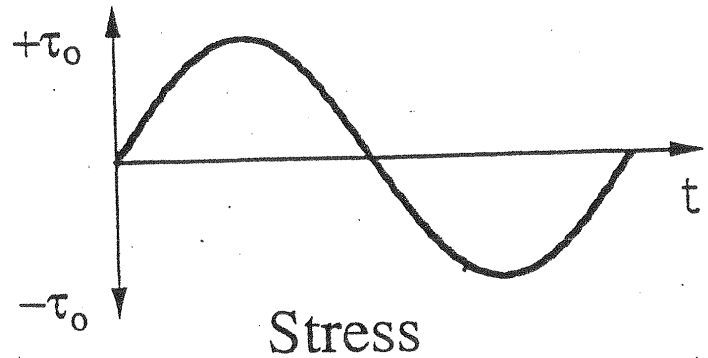
DYNAMIC MECHANICAL ANALYSIS

Sinusoidal stress applied to sample:



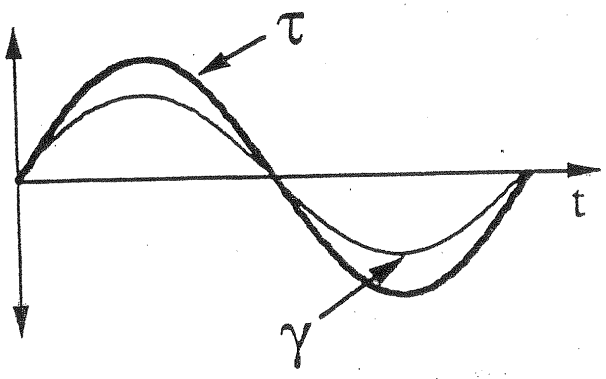
Stress

$$\tau(t) = \tau_o \sin(\omega t)$$

Amplitude

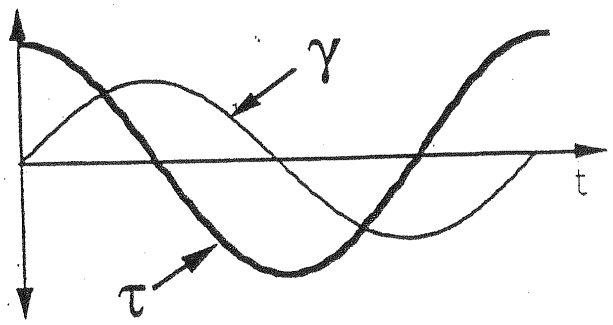
Material Response:

Elastic Response



$$\tau = G\ \gamma(t)$$
$$= G\ \gamma_o \sin(\omega t)$$

Viscous Response



$$\tau = \eta\ \dot{\gamma}(t)$$
$$= \eta\ \gamma_o \cos(\omega t)$$
$$= \eta\ \gamma_o \sin(\omega t + \pi/2)$$

* Stress and strain in phase for elastic material

* Stress leads strain by 90° ($\pi/2$ rad) for ideal fluid

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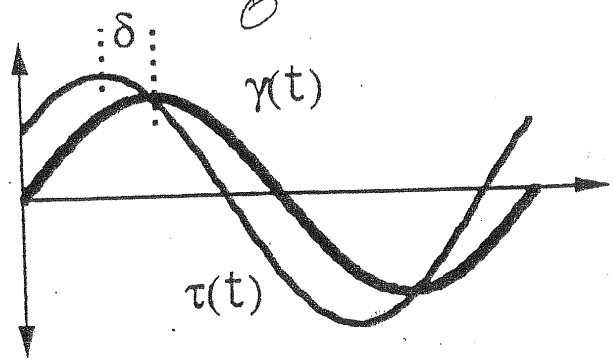
VISCOELASTIC MATERIAL

$0° < \delta < 90°$



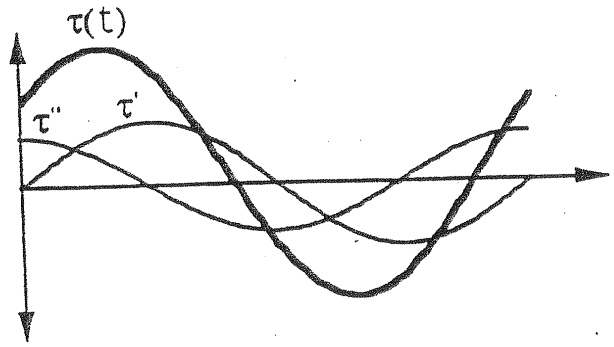
$\gamma(t) = \gamma_o \sin(\omega t)$ $\qquad$ $\tau = \tau_o \sin(\omega t + \delta)$

A little trig: $\tau = \tau_o[\sin(\omega t)\cos(\delta) + \cos(\omega t)\sin(\delta)]$

This can be broken-up into two stresses:

An elastic stress in phase with the strain $\qquad \tau' = \tau_o \cos\delta$

A viscous stress in phase with the strain rate $\qquad \tau'' = \tau_o \sin\delta$



This quantifies the degree of elastic and viscous behavior.

Note: these stresses are frequently expressed in the form of complex values: $\tau^* = \tau' + i\,\tau''$ (where $i = \sqrt{-1}$) as a mathematical convience.

$\Rightarrow G' + G''$

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DYNAMIC MECHANICAL TESTING

Frequently Used Variables

Complex Modulus: $G^* = \tau^* / \gamma = \sqrt{G'^2 + G''^2}$

Elastic Modulus: $G' = \tau' / \gamma = (\tau^* / \gamma) \cos \delta$

"Storage"

Viscous Modulus: $G'' = \tau'' / \gamma = (\tau^* / \gamma) \sin \delta$

"Loss"

Complex Viscosity: $\eta^* = G^* / \omega$

Loss Tangent: $\tan \delta = G'' / G'$

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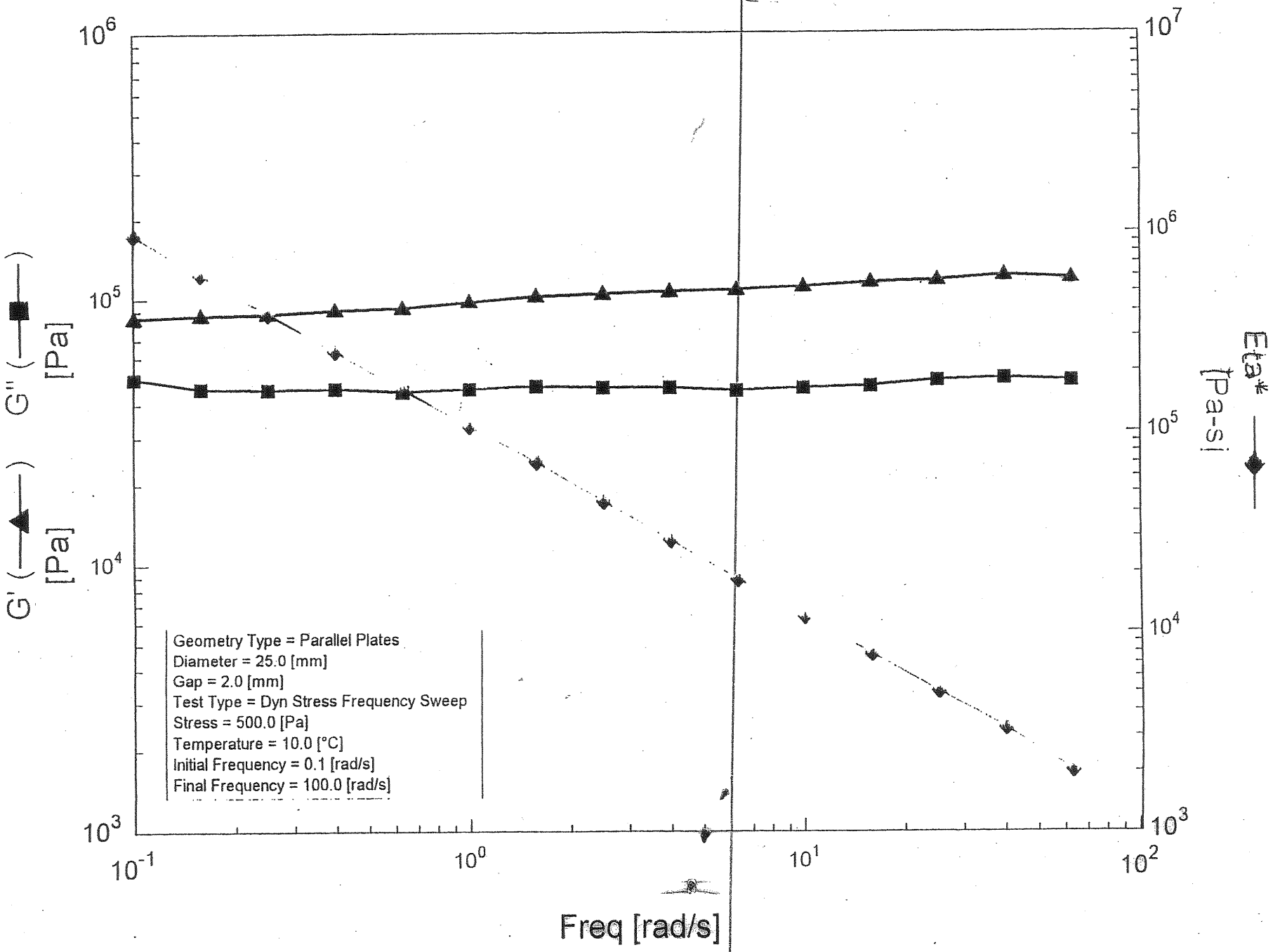
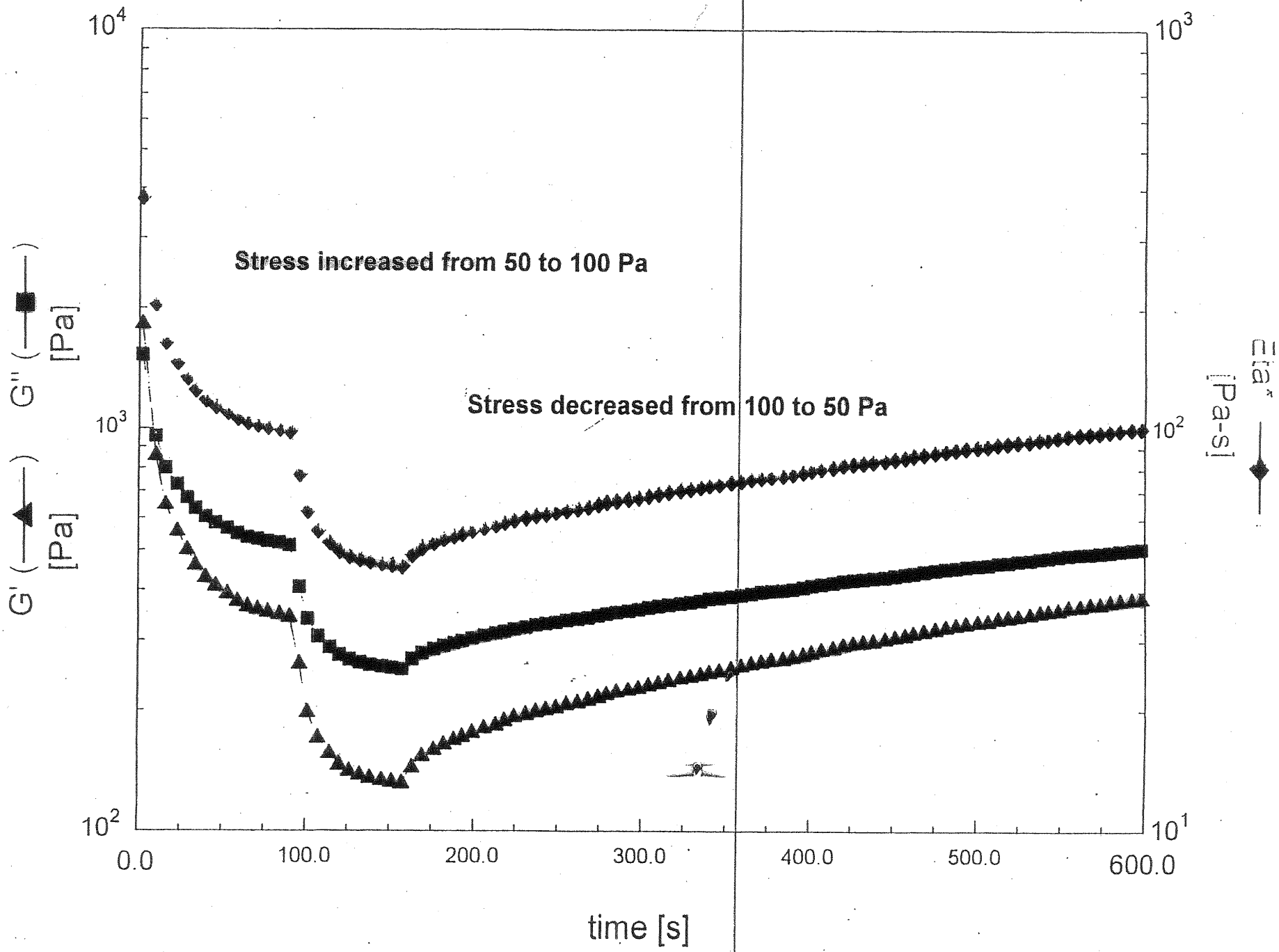
Dynamic Frequency Sweep for Creamy Peanut Butter



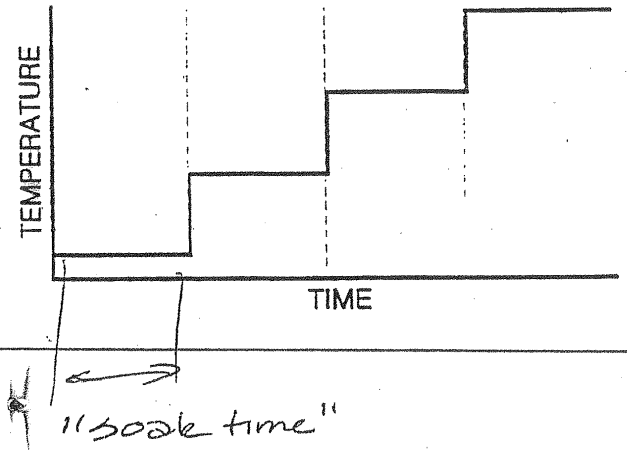
Dynamic Time Sweep of Aquafresh

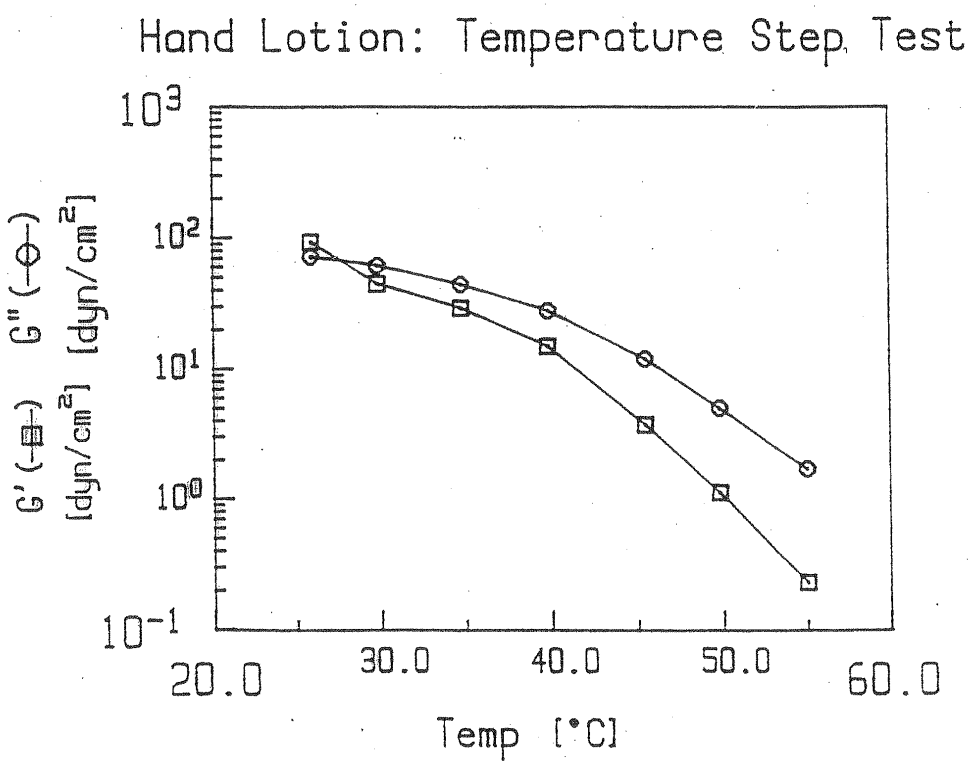
Structure Breakdown Study



TEMPERATURE STEP

Vary T stepwise





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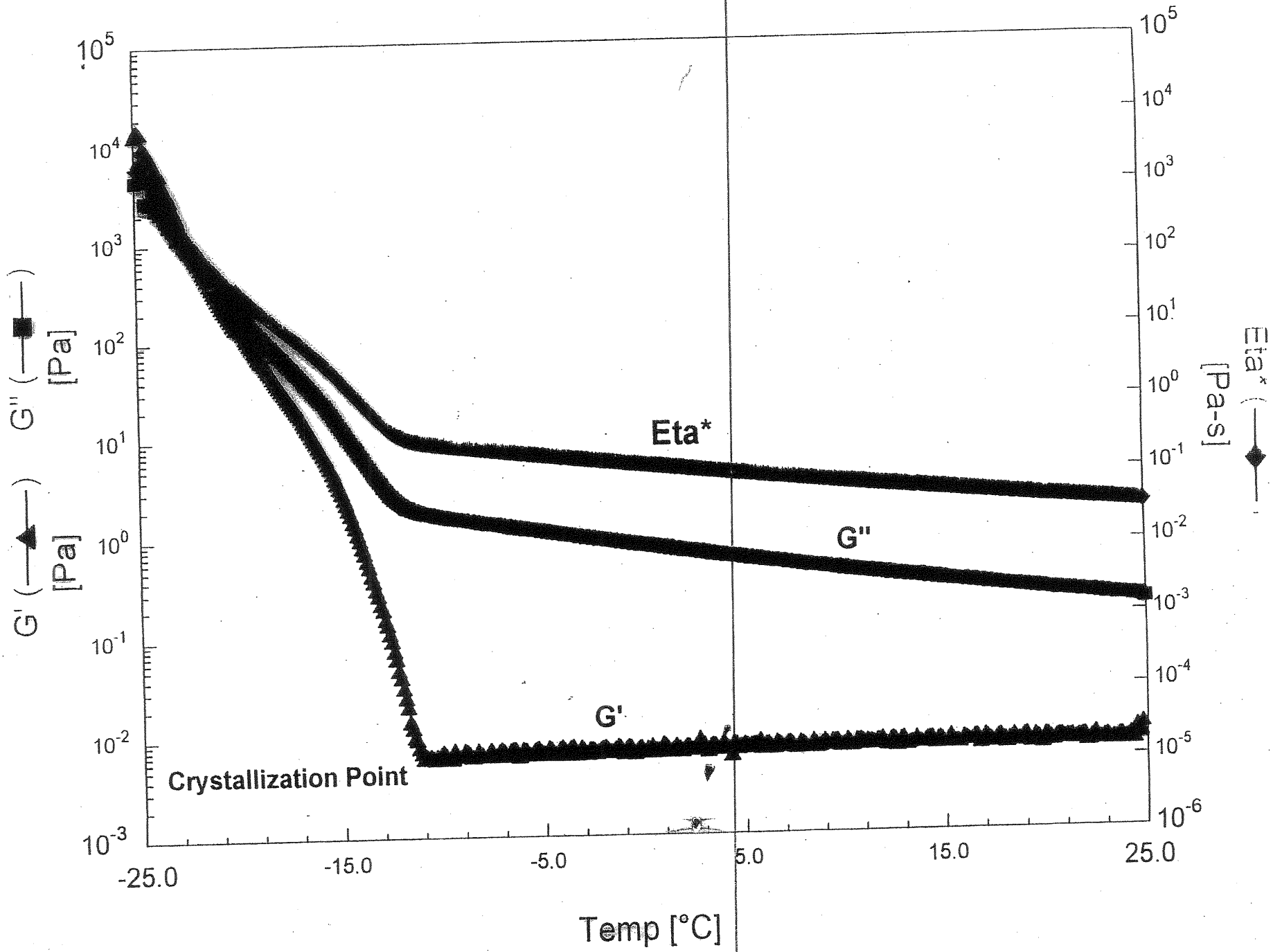
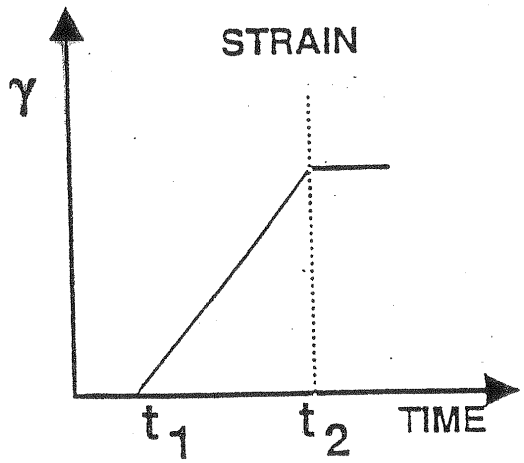
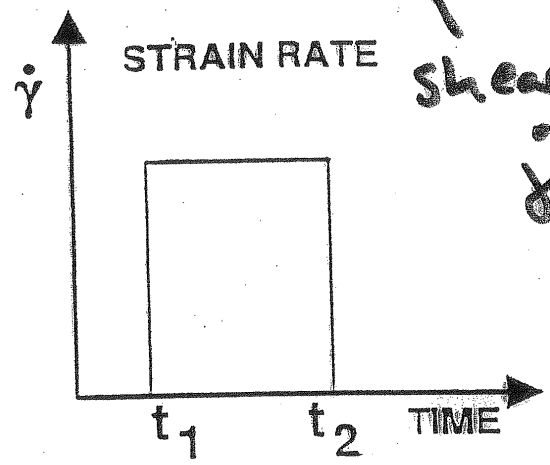
Dynamic Temperature Ramp of Oil

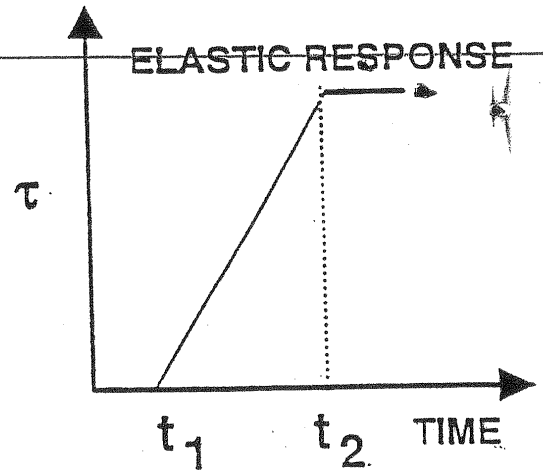


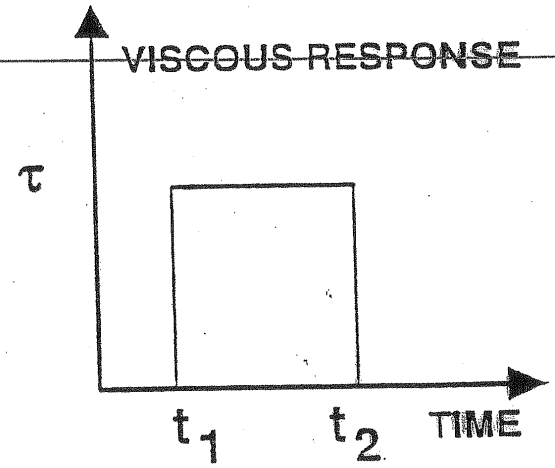
MATERIAL RESPONSE TO STEP CHANGE IN STRAIN RATE

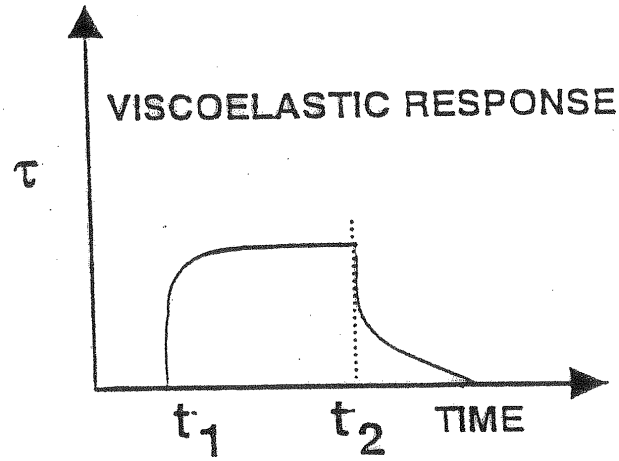
shear rate $\dot{\gamma}$











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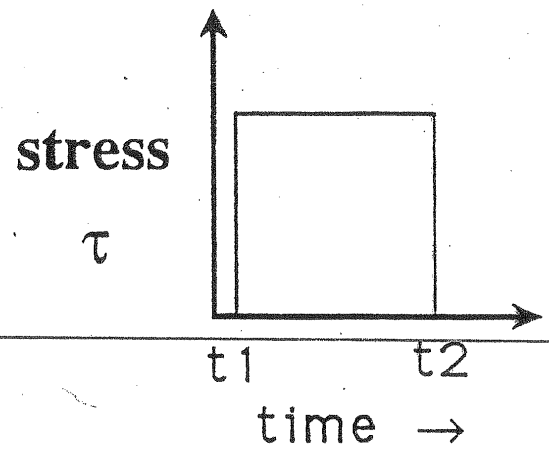
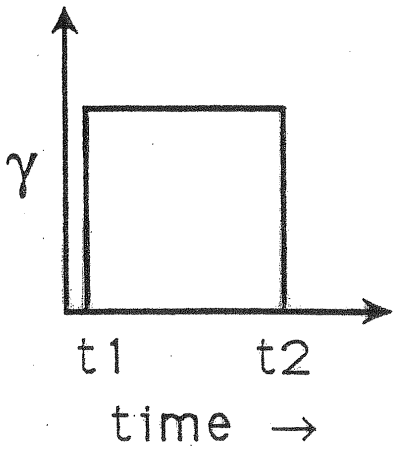
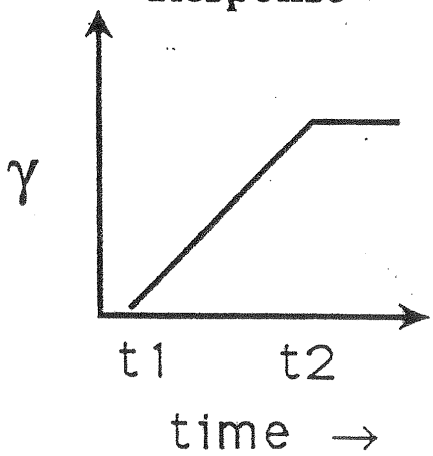
MATERIAL RESPONSE TO STEP CHANGE IN STRESS



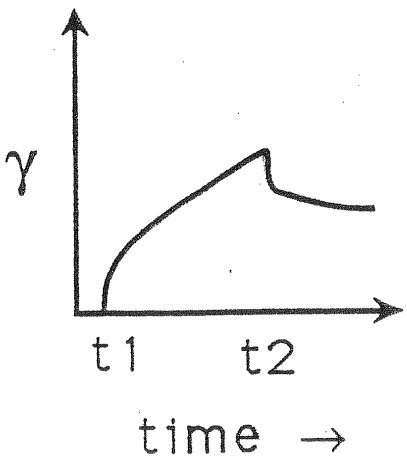
Elastic Response



Viscous Response



Viscoelastic Response



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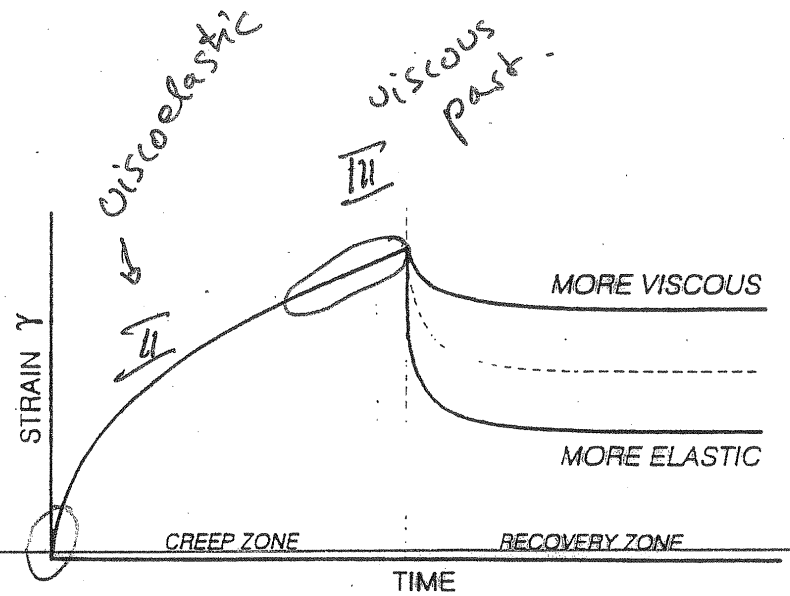
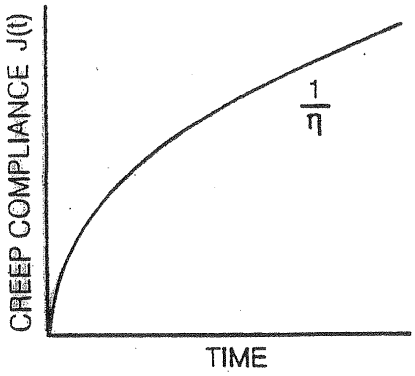
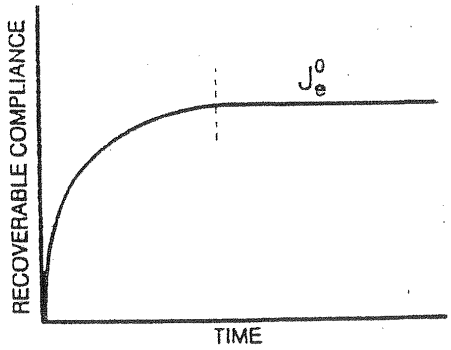
STEP STRESS (CREEP) TEST



elastic part

$$J(t) = \frac{\gamma(t)}{\sigma}$$





$$J(t) = \frac{\gamma_0}{\tau_0} + \underbrace{\frac{t\dot{\gamma}_\infty}{\tau_0}}_{=\frac{t}{\eta}}$$

— viscous flow

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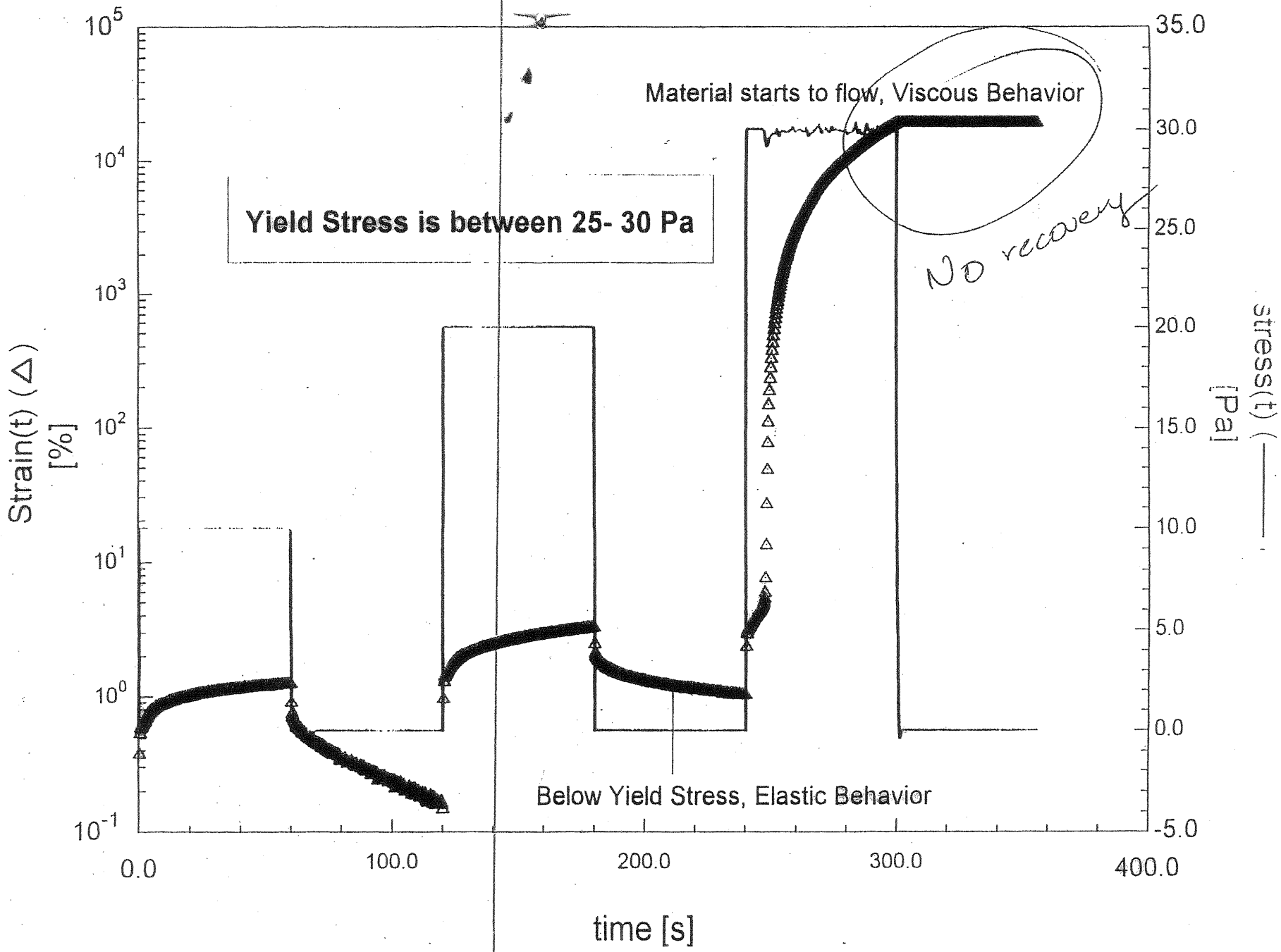
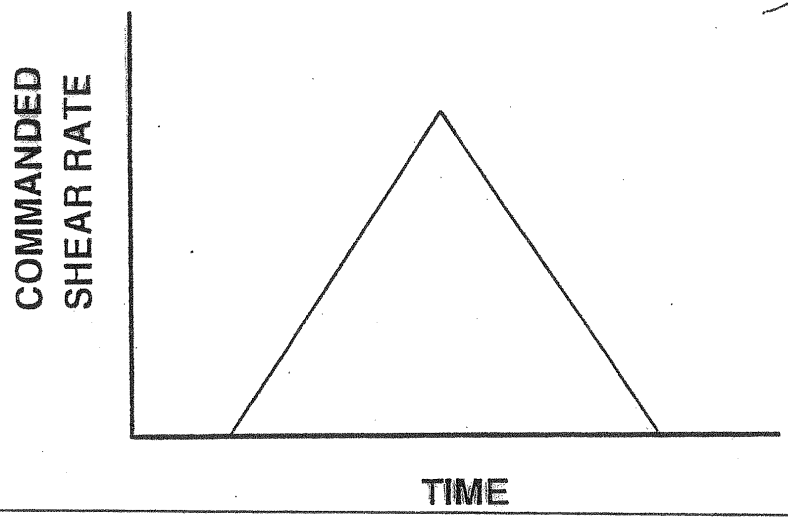
Creep and Recovery Test of Vaseline Cream



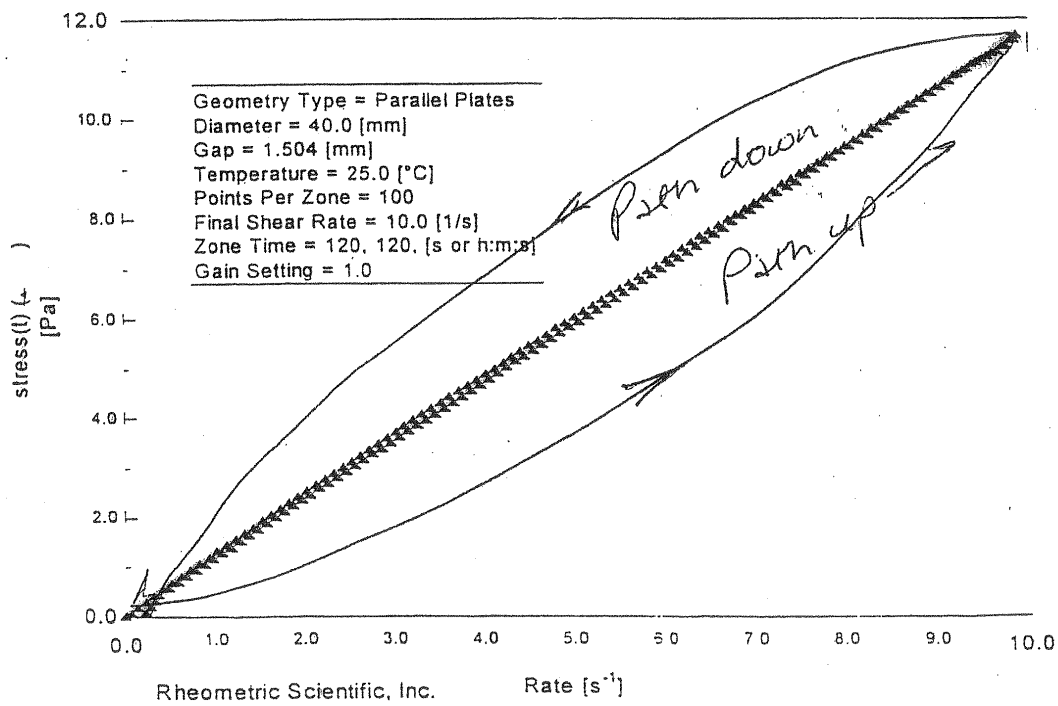
THIXOTROPIC LOOP

Time dep of material



Epoxy Resin, Shear Rate Ramp Test (Thixotropic Loop)

Newtonian



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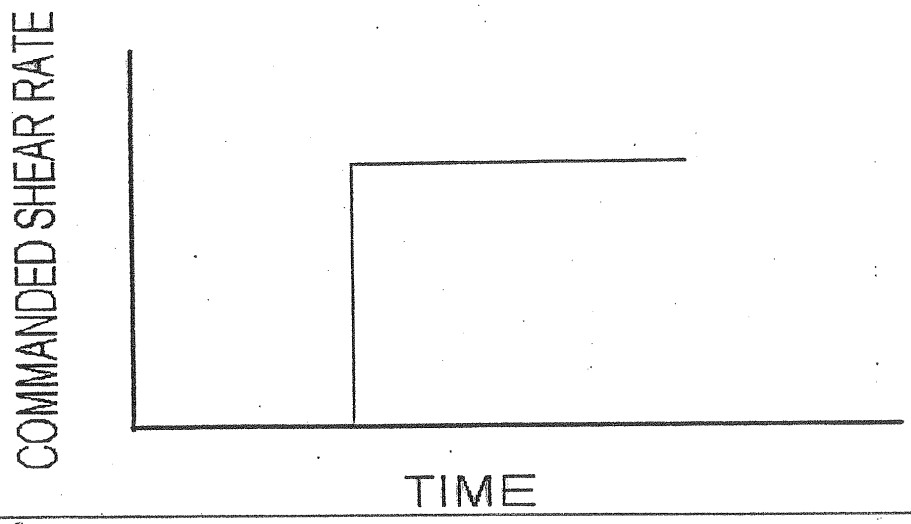
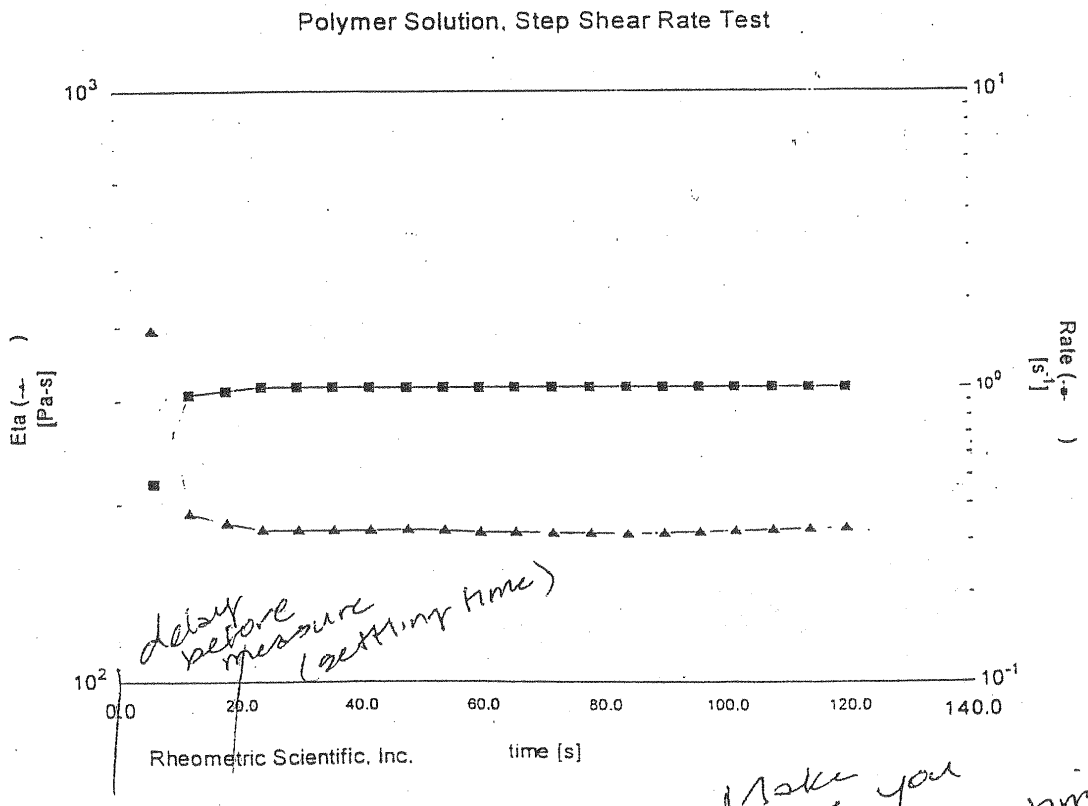
STEP RATE TEST





delay before measure (settling time)

Make sure you enter DELAY time

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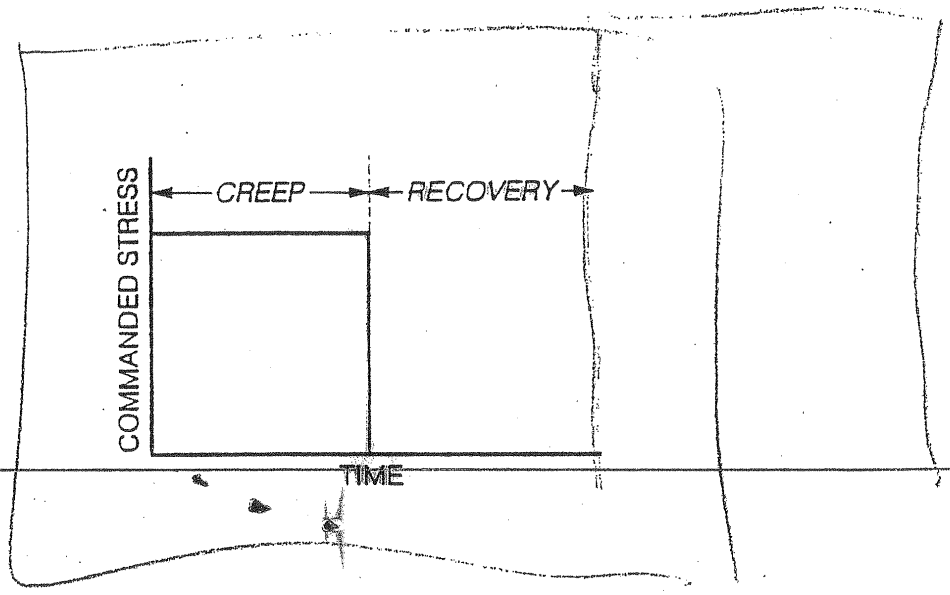
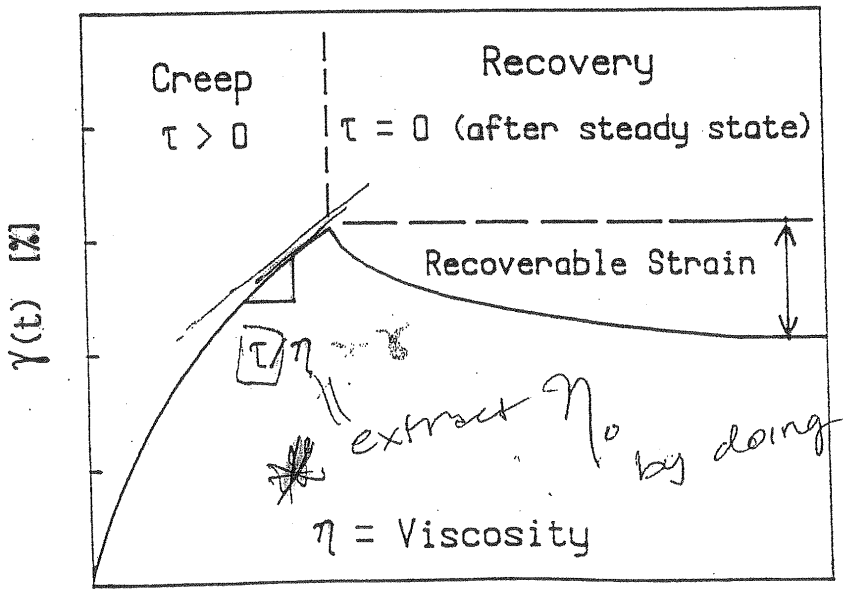
STEP STRESS (CREEP) TEST



Step Stress (Creep and Recovery) Test



$\eta(\dot{\gamma})$

extract η_0 by doing @ diff. τ to see where η converges to

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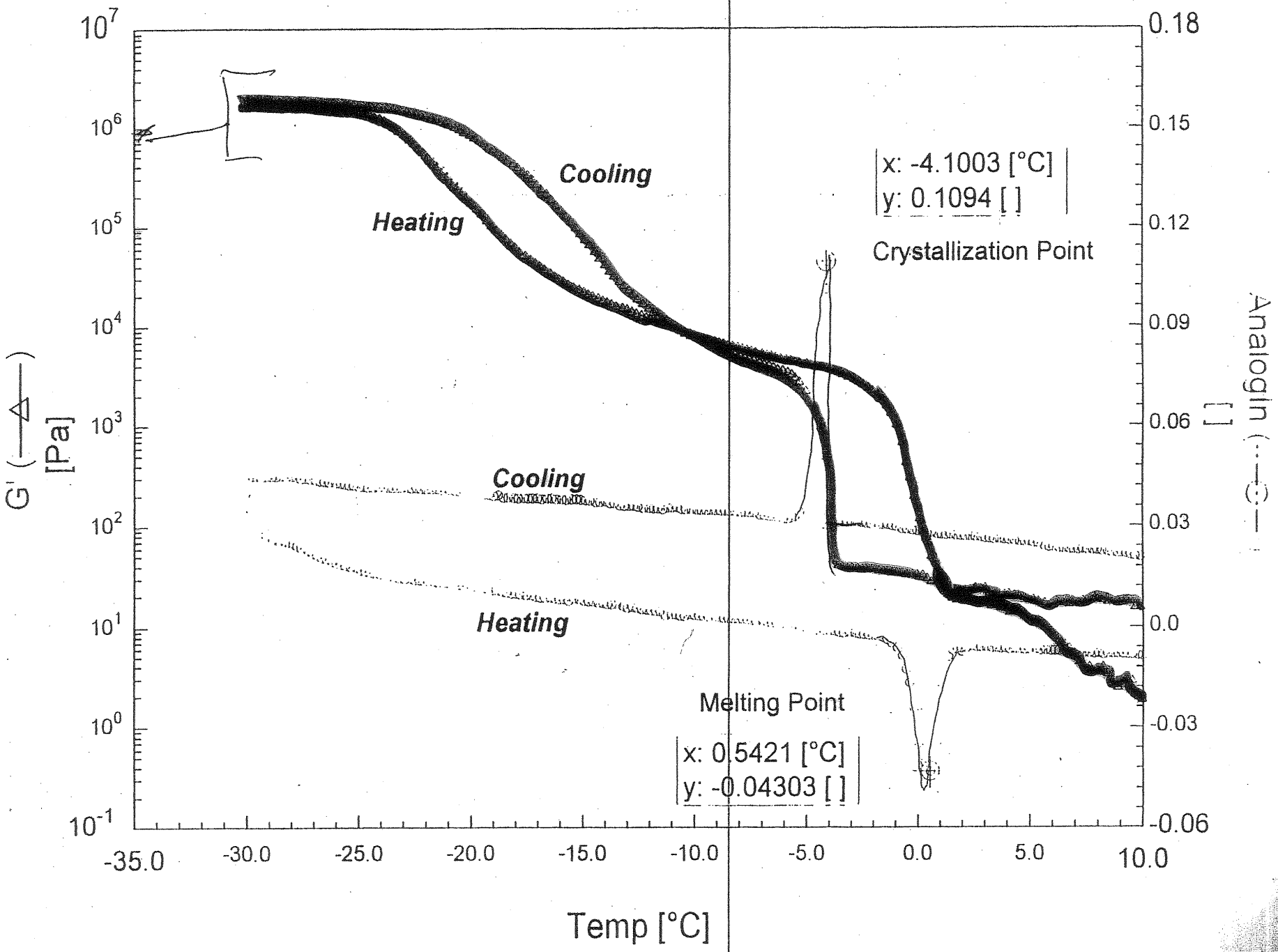
Dynamic Temperature Ramp of Ink Solution in DTR

Rheometer w/ DSC



Linear Viscoelasticity

(C.W. Macosko
Rheology (green book, chapter 3))

- time dependent response of polymeric materials = viscoelastic
- how to measure this? → stress relaxation

for polymers: stress relaxes in exponential fashion

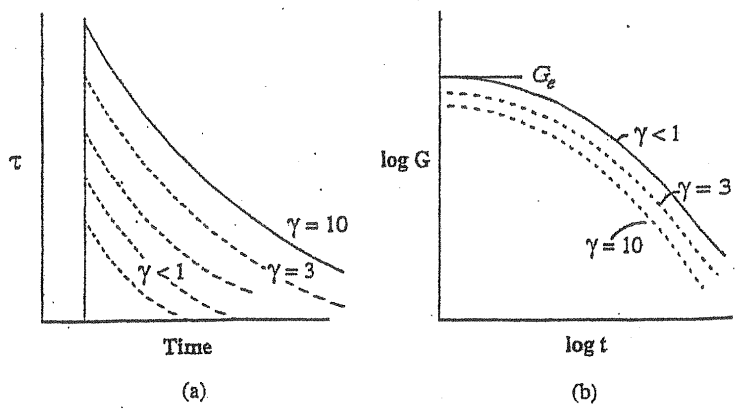


Figure 3.1.3.
Stress relaxation data for a polydimethylsiloxane sample. As in Figure 3.1.2a, shear strain is stepped nearly instantly to a constant value. (a) Shear stress jumps and then decays exponentially. (b) When a log of the time-dependent shear modulus, $G(t) = \tau(t)/\gamma$, is plotted versus log time, all the data at small strain fall on the same curve.

single relaxation or:
series of relaxations

General case

1 dimension

γ = strain

$\dot{\gamma}$ = shear rate

$$\boxed{d\tau = G\, d\gamma}$$

$$\boxed{d\tau = G \frac{d\gamma}{dt} dt = G \dot{\gamma} dt}$$

integrating

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

or

$$\boxed{\tau = \int_{0}^{\infty} G(s)\, \dot{\gamma}(t-s)\, ds}$$

$s = t - t'$

$G(t)$ can be measured directly

What form does the relaxation modulus function have?

$$\boxed{G(t) = G_0\, e^{-t/\lambda}}$$

λ = relaxation time

$\Downarrow$

we obtain the $\boxed{\text{single relaxation}}$ or Maxwell model

$$\boxed{\tau = \int_{-\infty}^{t} G_0\, e^{-(t-t')/\lambda} \cdot \dot{\gamma}(t')\, dt'}$$

?

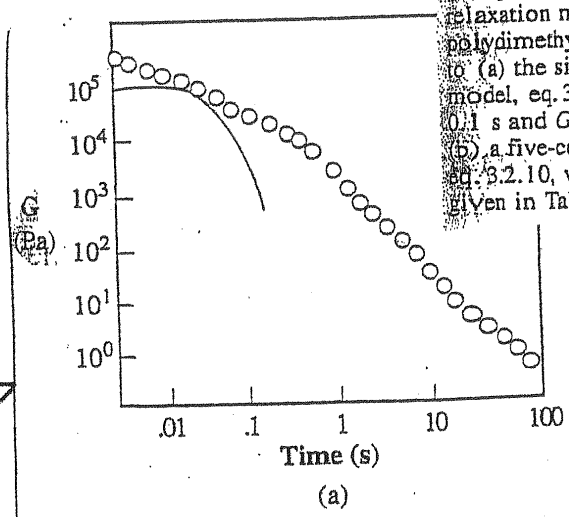


Figure 3.2.1. Comparison of experimental relaxation modulus data on a polydimethylsiloxane sample to (a) the single exponential model, eq. 3.2.8, with λ = 0.1 s and $G_0 = 10^5$ Pa and (b) a five-constant model, eq. 3.2.10, with the constants given in Table 3.2.1.

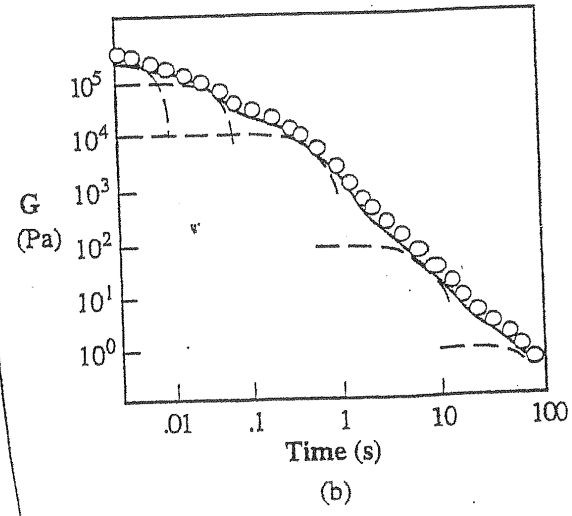
this model does not fit well!

Try $\boxed{\text{series of relaxation}}$ times λ_k

$$\boxed{G(t) = \sum_{k=1}^{N} G_k\, e^{-t/\lambda_k}}$$

$\Downarrow$

$$\boxed{\tau = \int_{-\infty}^{t} \sum_{k=1}^{N} G_k\, e^{-(t-t')/\lambda_k} \cdot \dot{\gamma}(t')\, dt'}$$



Small Strain Material Functions

- Stress relaxation
- creep (constant stress)
- oscillatory shear

Stress relaxation

- define relaxation modulus : stress relaxation after a step strain γ_0

$$\boxed{G(t) = \frac{\tau(t)}{\gamma_0}}$$

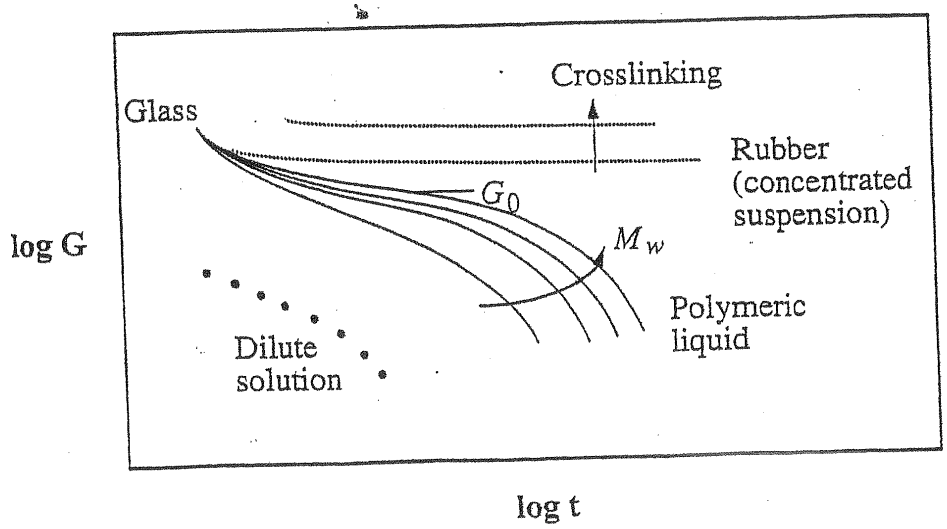
stress

modulus

strain (= deformation

- crosslinked rubber → short time relaxation followed by constant modulus.
- high Mw polymeric liquid → behave like rubber at short times, flow at long times.
- dilute solutions → complete relaxation in short time.

Figure 3.3.1.
Typical relaxation modulus data for several different materials.



Homework

What is the influence of Mw on relaxation behavior?

B $\boxed{\text{Creep}}$ (= constant stress experiment)

- good for the long time end of the relaxation spectra.

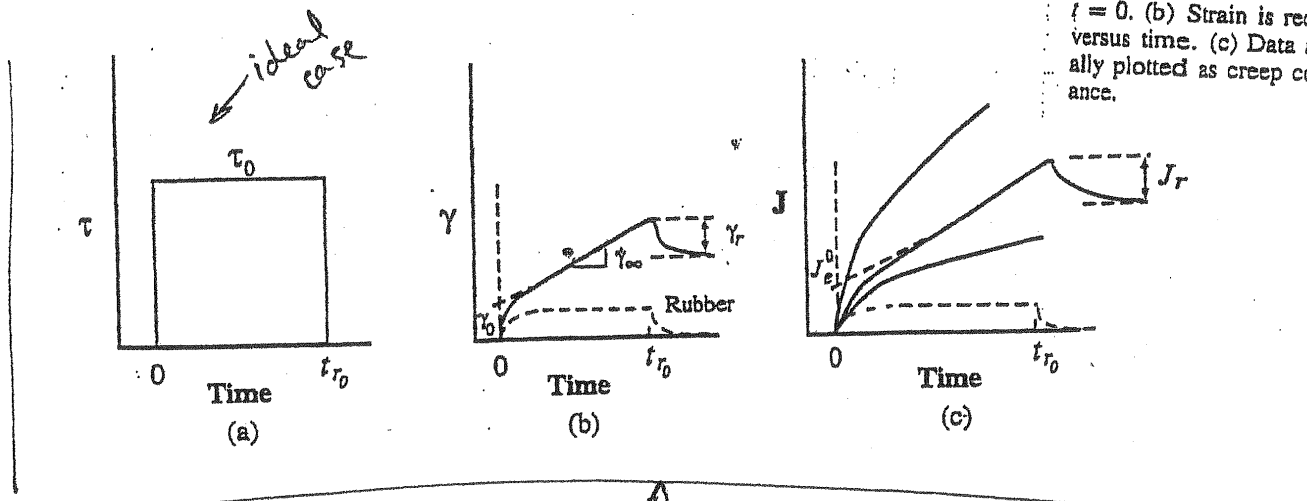


Figure 3.3.2. Creep experiment. (a) Stress is increased from 0 to τ_0 at $t = 0$. (b) Strain is recorded versus time. (c) Data are usually plotted as creep compliance.

imposed stress recorded strain

- Data are usually expressed in terms of $J(t)$ = compliance

$$\boxed{J(t) = \frac{\gamma(t)}{\tau_0}}$$

units $\frac{1}{Pa}$

- steady state creep compliance J_e^0 is defined by extrapolating the limiting slope to $t=0$

slope $= \frac{1}{\eta}$ (at low shear rate)

steady state: $\boxed{J(t) = \frac{\gamma_0}{\tau_0} + \frac{t\,\dot{\gamma}_\infty}{\tau_0}}$

$$\boxed{J(t) = J_e^0 + \frac{t}{\eta_0}}$$

c $\boxed{\text{Sinusoidal Oscillations}}$ (page 121 ff Macosko)

τ = stress
γ = strain
ω = frequency

$$\boxed{\gamma = \gamma_0 \cdot \sin \omega t}$$

$$\boxed{\tau = \tau_0 \sin(\omega t + \delta)}$$

How to analyze data? Fig 3.3.3.

⇒ decompose stress wave into 2 waves of the same frequency, one in phase with the strain wave ($\sin \omega t$) one 90° out of phase with the strain ($\cos \omega t$)

$$\boxed{\tau = \tau' + \tau'' = \underbrace{\tau_0' \sin \omega t}_{} + \underbrace{\tau_0'' \cos \omega t}_{}.}$$

$$\boxed{\tan \delta = \frac{\tau_0''}{\tau_0}}$$

see plot
trigonometry

⇓

2 dynamic moduli

$$\boxed{G' = \frac{\tau_0'}{\gamma_0}}$$ in phase elastic modulus.

$$\boxed{G'' = \frac{\tau_0''}{\gamma_0}}$$ out of phase loss modulus.

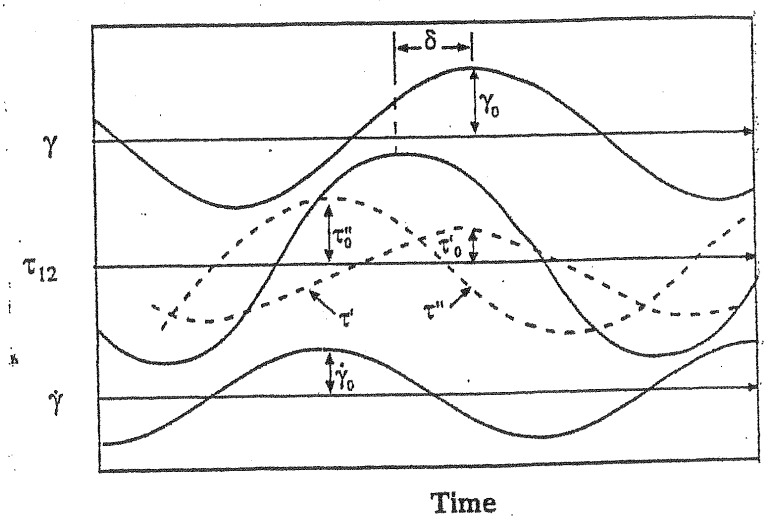


Figure 3.3.3. Sinusoidally oscillating shear strain produces a sinusoidal stress phase shifted by an amount δ. For analysis the stress wave is broken down into two waves, τ' in phase with γ and τ'' 90° out of phase. Note that τ'' is in phase with the rate of strain wave $\dot{\gamma} = d\gamma/dt$.

$$\boxed{G' = \frac{\tau_0'}{\gamma_0}} \qquad \boxed{G'' = \frac{\tau_0''}{\gamma_0}} \Rightarrow \boxed{\tan\delta = \frac{G''}{G'}}$$

$$\boxed{e^{i\theta} = \cos\theta + i\sin\theta} \qquad \boxed{i = \sqrt{-1}}$$ ← rules, complex numbers

γ = imaginary part of $(\gamma_0 e^{i\omega t})$

$\tau' = \mathrm{IM}$ of $(\tau_0 e^{i\omega t})$

$\tau'' = \mathrm{RE}$ of $(\tau_0 e^{i\omega t})$

$$\boxed{\tau_0 = |G^*|\gamma_0} \qquad \boxed{G^* = G' + iG''}$$

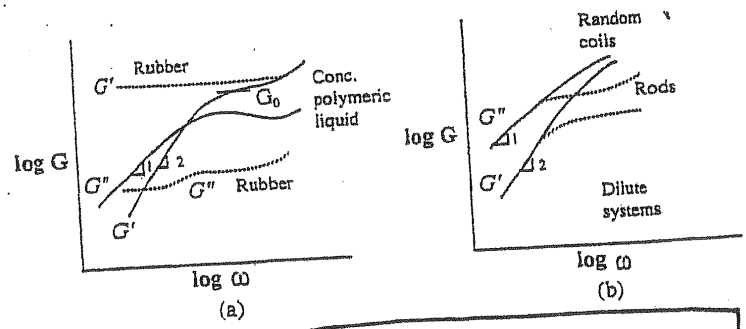
we had this equation before!

$$\Rightarrow \boxed{\tau = G'\gamma_0 \sin\omega t + G''\gamma_0 \cos\omega t}$$

stored elastic energy

G'' is a measure of the energy dissipated per cycle of deformation

Figure 3.3.5.
Typical behavior of the dynamic moduli for (a) rubber and concentrated polymeric liquids and (b) dilute solution of random coils and rodlike particles.



$G'(\omega)$ is in phase with γ
storage modulus

$G''(\omega)$ is in phase with $\dot{\gamma}$
loss modulus

$$\boxed{|G^*| = (G'^2 + G''^2)^{1/2} = \frac{\tau_0}{\gamma_0}}$$

Rheology of complex fluids

<u>complex fluids</u> : intermediate between solid and liquid, they maintain their shape for a time, then they flow
: solids at short times, liquids at long times
= viscoelastic

the characteristic time required to change from solid to liquid: fractions of a second → years

examples: with long relaxation time:
- glass-forming liquids
- polymer melts, solutions
- micellar solutions

other examples:
- gels
- electrorheological } suspensions
- magnetorheological
- liquid crystals
- block copolymers
- filled polymer systems.

Here: we will discuss rheological properties

⇒ <u>linear viscoelastic</u> behavior

A) — measured by frequency-dependent $\boxed{G' \; G''}$

reveal mechanical properties of the material at rest.

storage modulus

loss modulus

B) — <u>flow curve</u> = relationship between shear γ and shear rate $\dot{\gamma}$ → $\boxed{\eta(\dot{\gamma})}$

shows how material changes in response to continuous deformation.

shows if material can be processed, or shaped into a useful product

Examples of complex fluids:

Foods: the rheology, along with their flavor and texture determines their popularity

e.g. Mayonnaise contains oil, lemon juice, ... egg yolk
= emulsion
contains lecitin
= natural surfactan which stabilizes

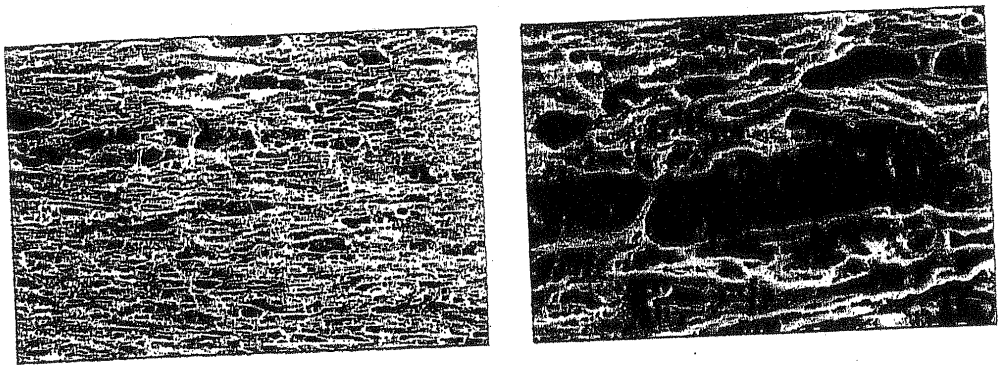


Figure 1.2 Low (**left**) and high (**right**) magnifications of scanning electron micrographs of mozzarella cheese samples. The protein fibers have an orientation roughly parallel to the stretch direction. (From Sharkasi and Kilara, MRS Bulletin, July 1994, p.47, reprinted with permission.)

Mayonnaise has a low yield stress, a stress below which it will not flow. The droplet size controls the yield stress

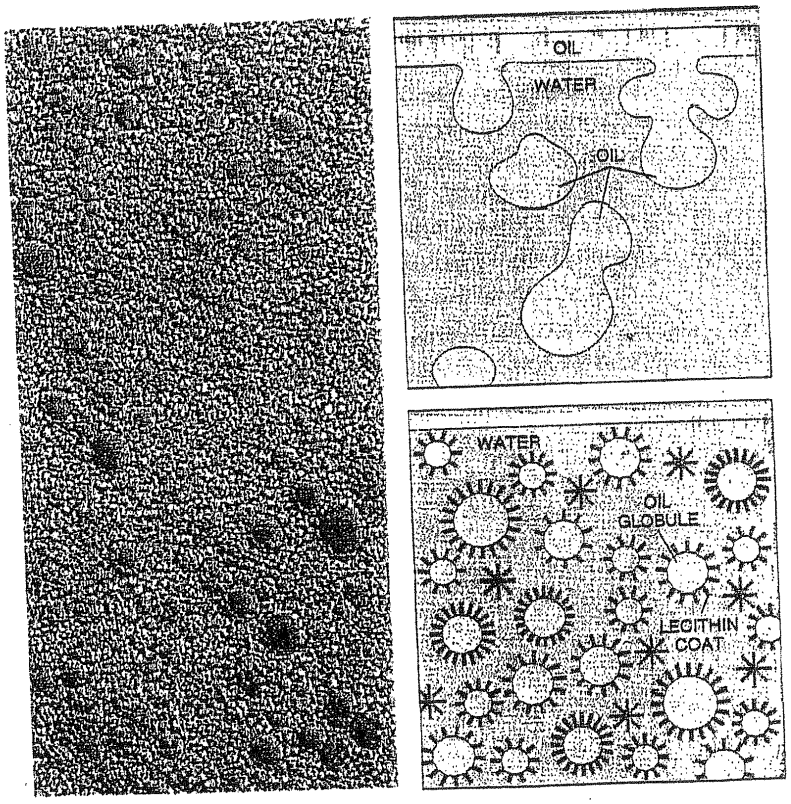


Figure 1-1 Mayonnaise (**left**, × 100) is a suspension of oil droplets in water. The tendency of oil and water to phase-separate (**top right**) is suppressed in mayonnaise by lecithin molecules from egg yoke that coat the oil droplets. Lecithin is a natural surfactant that can dissolve in either oil or water. (From Kurti and This-Benckhard 1994, with permission.)

ice cream = partially frozen emulsion, foamed with 40-50% by volume air

mustard = suspension or paste containing particles 30μm in diamet

cheese : protein fibre

solid state, it can be cold extruded — that is, forced to flow through a capillary under pressure (Beckett et al. 1994). This process transforms the chocolate from a brittle solid to a plastic, malleable one that can be reshaped at will. This plastic state lasts for several minutes, after which the chocolate reverts to its brittle form, possibly because of recrystallization of sugars that had been melted under the stresses of extrusion. Not only does solid chocolate become plasticized under flow, but molten chocolate can be solidified by electric fields (Browne 1996)! In the high-temperature molten state, chocolate is an emulsion, the droplets of which line up into columns under an electric field, producing a rigid structure. Fluids that are solidified by electric fields are called *electrorheological fluids*; their structure and properties are described in Chapter 8. For more on food rheology, see Dickenson (1991).

page 7...

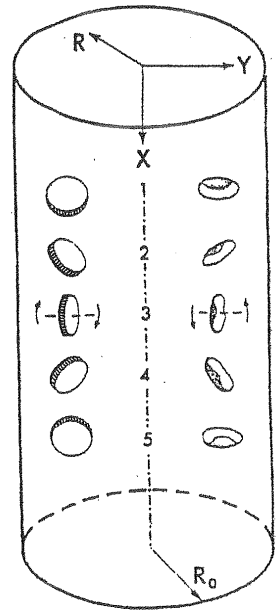


Figure 1.3 The "tumbling" motion of a red blood cell (**right**) as it is sheared in a Poiseuille flow down a tube at shear rates < 20 sec^{-1} is similar to that of a rigid disk (**left**). The tumbling rate is slowest in location 3. (From Goldsmith 1986, reprinted with permission from Academic Press.)

Biofluids

Blood = Suspension containing 40% by volume. blood cells. (= disks ; 10 μm. ϕ) in plasma = viscoelastic

brief mention
see Larson
diff. η

viscoelastic properties of blood determine pumping load on the heart
↖ rheology

At low shear rates, red blood cells often stack up like poker chips
At high shear rates → flow behavior like fluid droplets

Mucin contained in stomach lining and lungs
↖ rheological properties = contributor to asthma

Synovial fluid → lubricates joints.

Spittle, and other disgusting fluids see references Larson ff.

- Spiders synthesize complex fluids = tough dragline silk fibers
- silkworms make fibers, synthesizing liquid crystalline precursor solutions

personal care products
- shampoo
- deodorant
- toothpaste

lectronic and optical Materials
olymers

Rheological measurements tell how "hard" or "soft" materials are

Flow geometries:

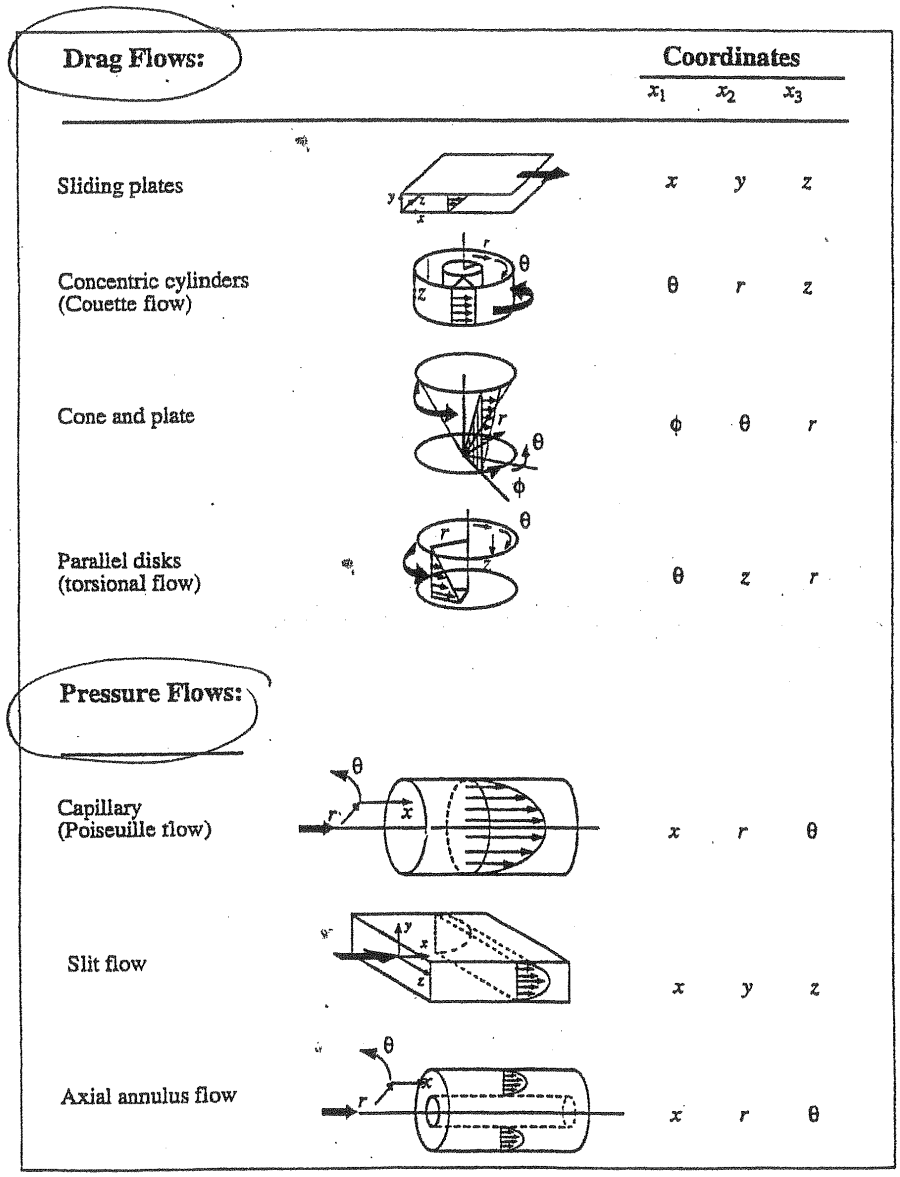


Figure 1.5 Geometries for producing shearing flows. (Adapted from Macosko, *Rheology Principles, Measurements, and Applications*, Copyright © 1994. Reprinted by permission from John Wiley & Sons.)

Couette device: good for liquids that are too runny to be held between cone-and-plate or plate-plate fixtures

A) Steady shear viscosity η

sliding plates: $\boxed{\dot{\gamma} = \frac{V}{h}}$

$\dot{\gamma}$ = shear rate
V = velocity of moving plate
h = gap between two plates.

cone and plate: $\boxed{\dot{\gamma} = \frac{\Omega}{\tan \alpha}}$

Ω = steady angular rotation speed
α = cone angle

shear stress σ = force that a flowing liquid feels on a surface per unit area in direction of flow.

shear viscosity η $\boxed{\eta = \frac{\sigma}{\dot{\gamma}}}$

The ratio of the steady shear stress σ to the shear rate $\dot{\gamma}$ is the steady-state shear viscosity $\eta(\dot{\gamma})$
$\dot{\gamma}$ = imposed

B) transient shear viscosity

often, the stress reaches a steady value only after a transient period of steady shearing starting from a state of rest.

→ transient start-up viscosity $\boxed{\eta^+(\dot{\gamma}, t) = \frac{\sigma(\dot{\gamma}, t)}{\dot{\gamma}}}$

Measurement of $\eta^+(\dot{\gamma}, t)$ give information about rates of structural rearrangement

creep test (constant stress exp). → time dependant rheological info
↳ especially useful for measuring the yield stress σ_{yield}

Storage and loss modulus

the experiment in cone & plate geometry: impose small-amplitude oscillatory shearing

$$\boxed{\Omega(t) = \Omega_0 \cos(\omega t)}$$

Ω: steady angular rotation speed

ω: frequency of oscillation (radians per second)

Shear rate $\dot{\gamma}$ is a sinusoidal function of time t:

ear rate:
$$\boxed{\dot{\gamma}(t) = \frac{\Omega(t)}{\tan\alpha} = \frac{\Omega_0 \cos(\omega t)}{\tan\alpha}}$$

Shear strain γ = time integral of the shear rate:

γ = deformation.

rain:
$$\boxed{\gamma = \left(\frac{\Omega_0}{\omega}\right) \frac{\sin(\omega t)}{\tan\alpha}}$$

$\left(\frac{\Omega_0}{\omega}\right)$ = amplitude of the angular deflection of the cone

$$\gamma_0 = \left(\frac{\Omega_0}{\omega}\right) \cdot \frac{1}{\tan\alpha}$$ = strain amplitude

Small-amplitude oscillatory shear:

for small strain amplitude $\gamma_0 \ll 1$

→ fluid structure is not much disturbed by deformation

→ relaxations or spontaneous rearrangements can be measured.

for small deformations: $\underbrace{\sigma(t)}_{\text{stress}} \sim \underbrace{\gamma_0}_{\text{strain}}$ ← sinusoidally varying in time

$$\Rightarrow \boxed{\sigma(t) = \gamma_0 \left[G'(\omega) \sin(\omega t) + G''(\omega) \cos(\omega t) \right]}$$

Storage modulus

in phase with the strain

G' represents storage of elastic energy

loss modulus

in phase with the rate of strain

G'' represents viscous dissipation of energy

$$\boxed{\frac{G''}{G'} = \delta}$$ — loss tangent

$\delta \gg 1$ for liquid like materials

$\delta \ll 1$ for solid like materials

⇒ complex modulus G^*. $\boxed{G^* \equiv G' + i\,G''}$ $i = \sqrt{-1}$

magnitude of G^*: $\boxed{|G^*| \equiv (G'^2 + G''^2)^{1/2}}$

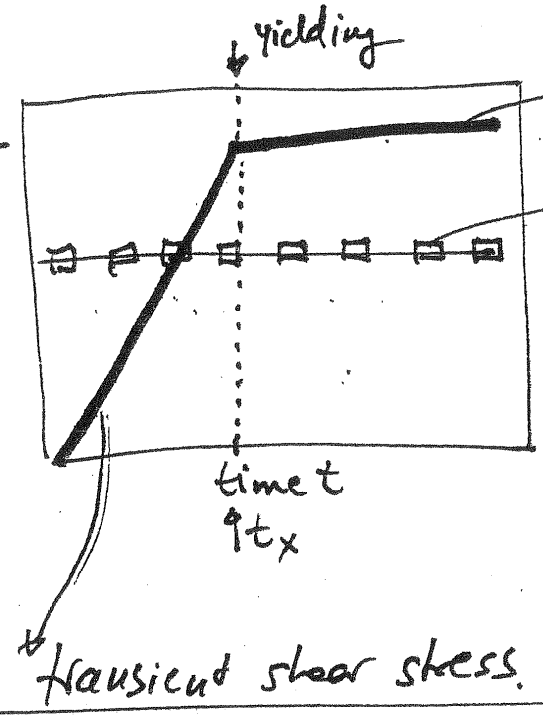
= amplitude of the stress waveform, divided by the strain amplitude

⇒ complex viscosity η^* $\boxed{\eta^* \equiv \eta' - i\eta'' \equiv \frac{G^*(\omega)}{i\omega}}$

$$\boxed{|\eta^*| = \frac{|G^*(\omega)|}{\omega}}$$

the regime of small amplitude straining in which the stress follows: $\sigma(t) = \gamma_0 \left[G'(\omega)\sin(\omega t) + G''(\omega)\cos(\omega t)\right]$ is called the <u>linear viscoelastic regime</u>

Types of Rheological Response



stress
↓
after t_x : steady state value of $\sigma(t)$
before t_x : "start up" stress $\sigma = \dot{\gamma}\eta^+(\dot{\gamma}, t)$

The liquid like fluid reaches the steady state instantaneously

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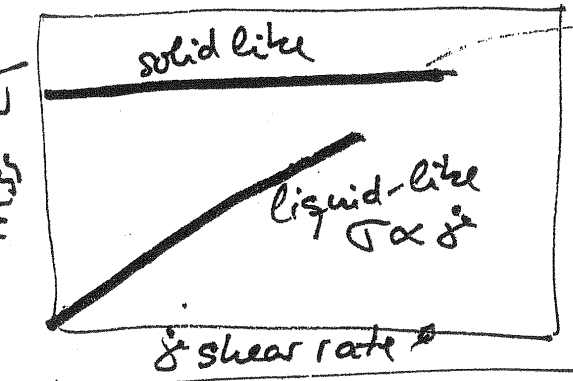
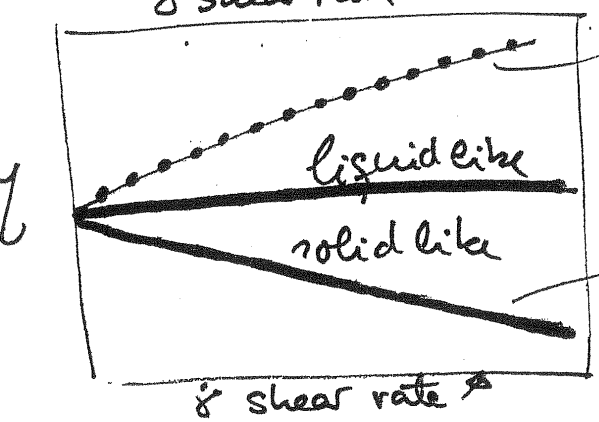
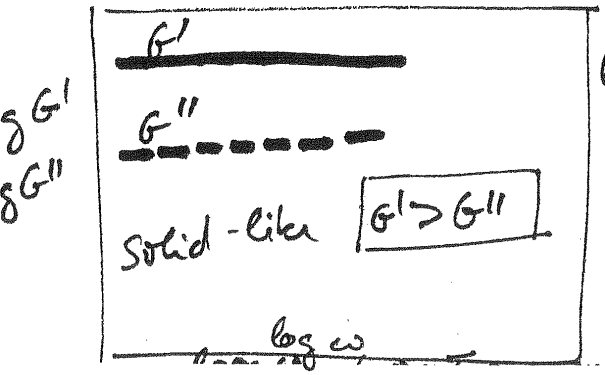
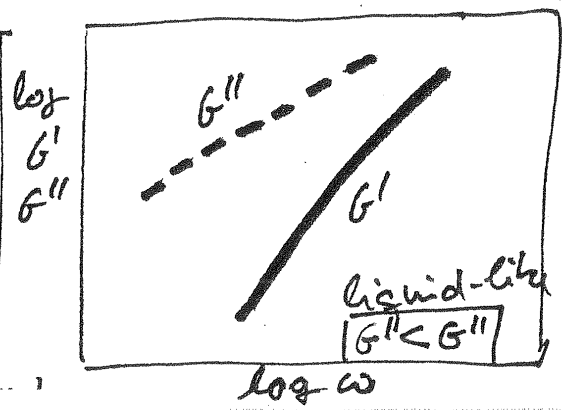


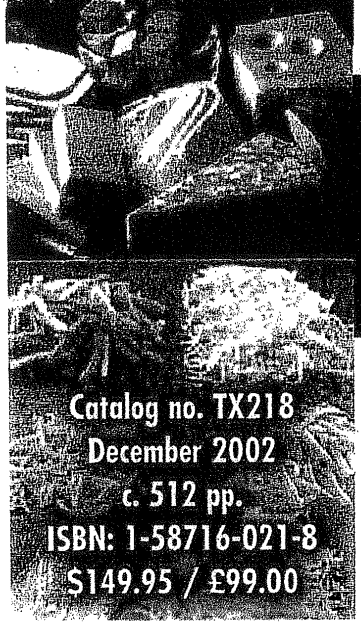
σ is independent of $\dot{\gamma}$
and $\eta \downarrow$ with $\dot{\gamma} \uparrow$ ($\eta(\dot{\gamma}) \propto \dot{\gamma}^{-1}$)
= shear thinning



Find examples!







NEW! **Essential information and state-of-the-art measurement techniques**

Cheese Rheology and Texture

Sundaram Gunasekaran, Ph.D.
Biological Systems Engineering, University of Wisconsin, Madison, USA

M. Mehmet Ak, Ph.D.
Department of Food Engineering, Istanbul Technical University, Turkey

Cheese Rheology and Texture is the first reference to bring together the essential information on the rheological and textural properties of cheese and state-of-the-art measurement techniques.

This comprehensive resource begins with an overview of cheesemaking technology and detailed descriptions of fundamental rheological test methods. Then it presents uniaxial testing and fracture mechanics, the theory and applications of linear viscoelastic methods (dynamic testing), and the nonlinear viscoelasticity of cheeses. The book focuses on mechanics in its examination of cheese texture, while it emphasizes measurement methods in its discussion of cheese meltability and stretchability. Finally it addresses the effects of various factors, such as the properties of milk, cheesemaking procedures, and post-manufacturing processes, on the functional properties of cheese.

Summarizing the vast literature available on the subject, **Cheese Rheology and Texture** helps those in the dairy industry and in academia choose the proper technique to measure properties that directly relate to food applications and ensure that cheese in their formulations will function as intended.

CONTENTS

Cheesemaking — An Overview
Fundamental Rheological Methods
Uniaxial Testing of Cheese
Fracture Properties of Cheese
Linear Viscoelasticity of Cheese
Nonlinear Viscoelasticity of Cheese
Cheese Texture
Measuring Cheese Melt and Flow Properties
Measuring Cheese Stretchability
Factors Affecting Functional Properties of Cheese

see reverse for other titles of interest and ordering information

FEATURES

- Includes data on texture and rheology for specific cheeses
- Presents techniques for measuring different rheological, textural, and functional properties
- Discusses major developments in the field of rheometry
- Relates new techniques to fundamental principles of rheology
- Contains detailed descriptions of several methods for studying food rheology in general and cheese in particular
- Serves as a tool for choosing the proper technique for a specific application

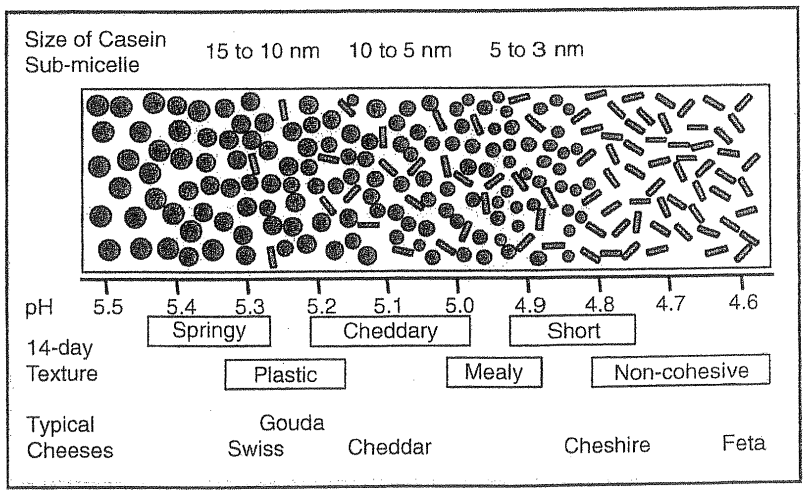


Figure 7.2 Effect of pH on cheese texture (after Lawrence *et al.*, 1991)

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