# Viscoelastic Behaviour of Polymers

Objectives

▶ Discuss common forms of viscoelastic behaviour

▶ Discuss phenomena in terms of deformation of elastic solids with focus on linear viscoelasticity

▶ Discuss phenomenological mechanical models of viscoelasticity

▶ Experimental determination of parameters

Introduction

Polymers

▶ Word Polymer originates from Greek word polymeros, meaning many membered

▶ Often word Polymer is thought of composed of two words

 ▶ Poly meaning many

 ▶ mer meaning unit

▶ Thus Polymer means many units describing a polymer molecule
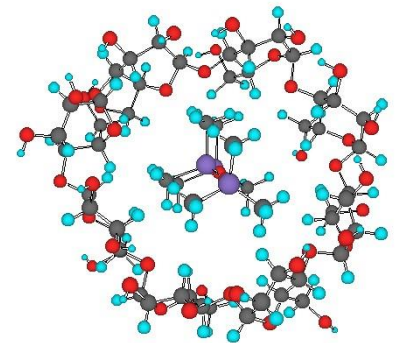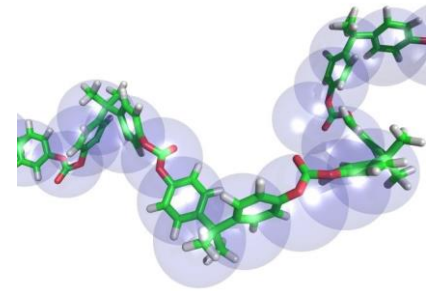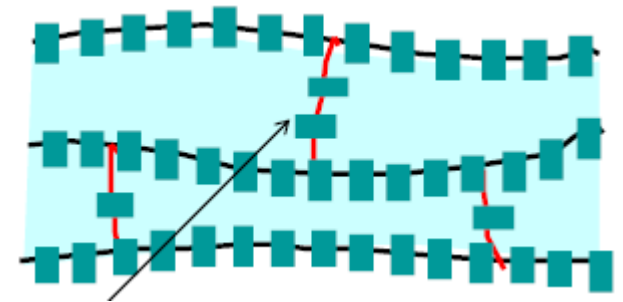
Polymers Classification

- Thermoplastics (linear)

  - Have only secondary bonds between chains

  - Can be melted and molded

  - Examples: Polyvinyl Chloride(PVC), Polystyrene (PS)
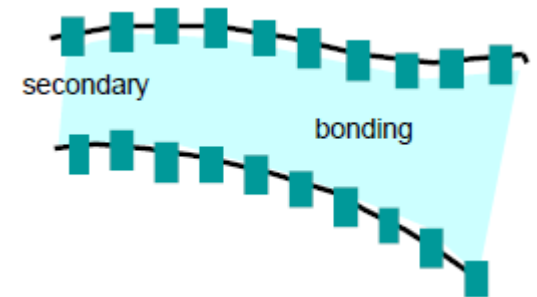
- Thermosets (crosslinked)

  - Have primary and secondary bonds between chains

  - Not possible to melt and mold

  - Examples: Epoxides, Polyesters

Polymers Definitions

- **Structure**
  - **Amorphous:** when polymer chains are arranged randomly in no particular order
  - **Crystalline:** when polymer chains are arranged in an orderly manner
- **Glass transition temperature**
  - Not same as melting. Melting happens in crystalline polymers
  - It's a transition that happens in amorphous polymers
  - A reversible transition from a hard and relatively brittle state into a soften or rubber like state
- **Cross-linking**
  - A bond that links one polymer chain to other. Once cross linking takes place, the material can no longer be shaped.
- **Curing**
  - Toughening or hardening of a polymer material by cross-linking of polymer chains

Stiffness of Polymers

▶ Much engineering design – particularly with polymers – is based on **stiffness**

▶ Designer aims to keep the elastic deflections below some critical limit

▶ Material property which is most important is **Young's modulus, E**

▶ Metals and ceramics have Young's moduli which, near room temperature, can be thought of as constant

▶ This is **not true for polymers**. Polymers have time and temperature dependent modulus

▶ The modulus E of a polymer can change by as much as a factor of 1000 when the temperature is changed

Glassy regime, with a large modulus, around 3 GPa

Glass-transition regime, in which the modulus drops steeply from 3 GPa to around 3 MPa
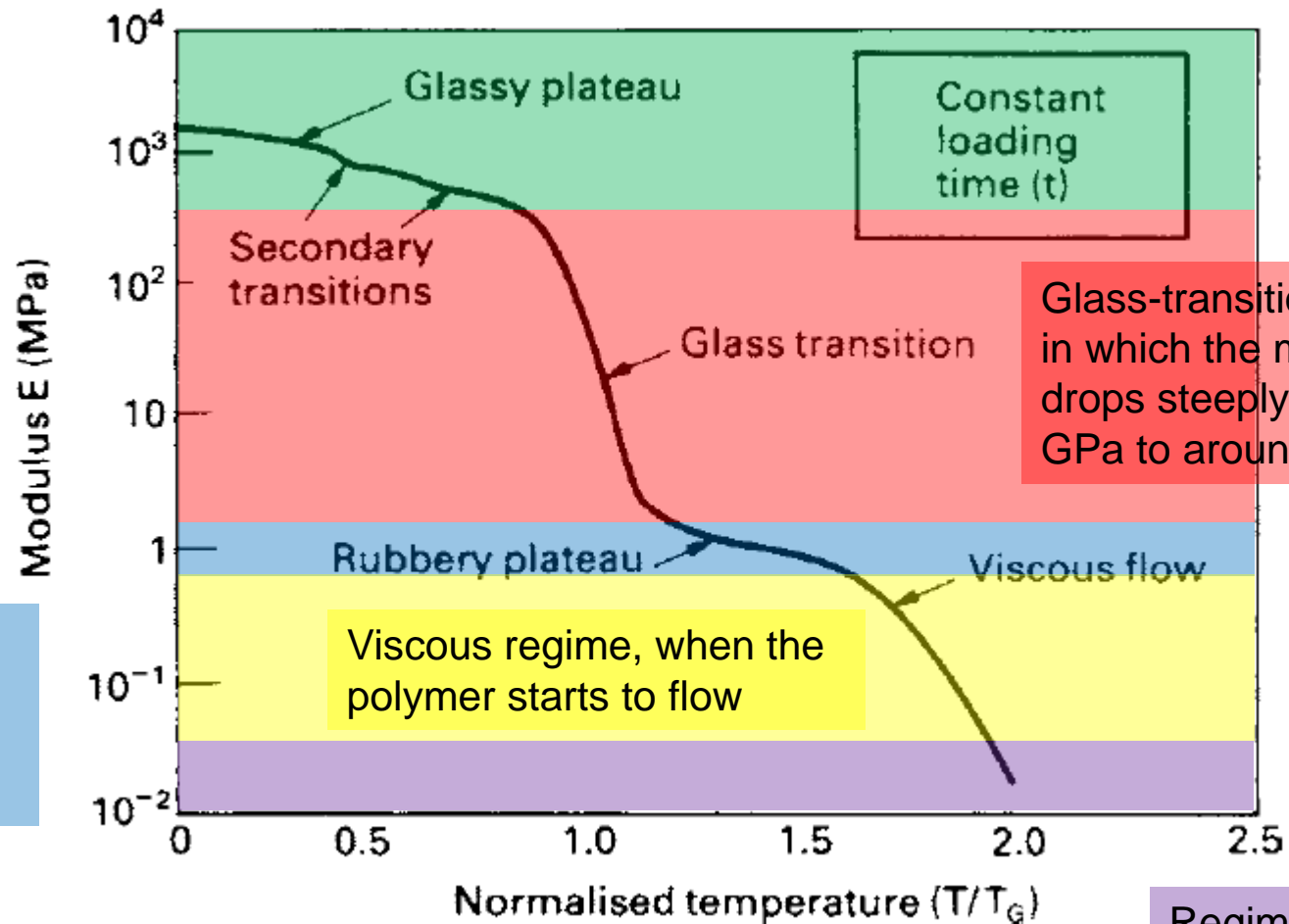
Rubbery regime, with a low modulus, around 3 MPa

Viscous regime, when the polymer starts to flow

Regime of decomposition in which chemical breakdown starts

**Five regimes of deformation in linear-amorphous polymers**

Viscoelasticity

- Two main types of ideal materials

- Elastic solid

  - Has a definite shape and deforms under external forces

  - Stores all energy that is obtained from external forces

  - Stored energy restores the original shape once the force is removed

- Viscous liquid

  - No definite shape

  - Flows irreversibly under the action of external forces

Viscoelasticity

▶ A polymer can exhibit all intermediate range of properties between an elastic solid and a viscous liquid

▶ Properties depends on temperature and experimental time scale

▶ Material response which combines both liquid and solid like features is termed **Viscoelasticity**

▶ Implies that the mechanical properties are a function of time due to intrinsic nature of the material and

▶ Material possess a memory (fading) of past events

Linear Viscoelastic Behaviour
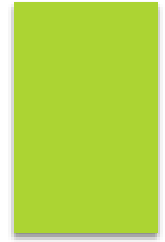
Linear Viscoelastic Behaviour

▶ Newton's law of viscosity defines viscosity η as

$$\sigma = \eta \frac{\partial V}{\partial y}$$
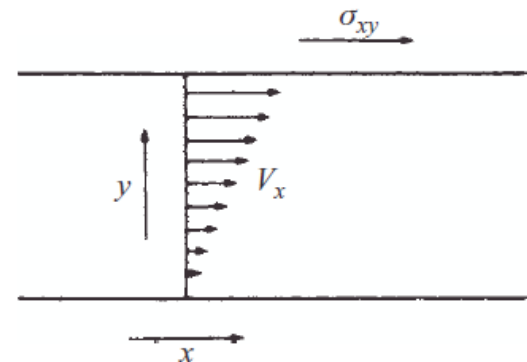Velocity gradient in liquid

V is velocity, y is direction of velocity gradient

▶ For velocity gradient in xy plane

$$\sigma_{xy} = \eta \left(\frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right)$$

▶ Since

$$V_x = \frac{\partial u}{\partial t} \quad and \quad V_y = \frac{\partial v}{\partial t} \quad where \; u \; and \; v \; are \; displacements \; in \; x \; and \; y \; direction$$

Linear Viscoelastic Behaviour

▶ Thus

$$\sigma_{xy} = \eta \left[\frac{\partial}{\partial y}\left(\frac{\partial u}{\partial t}\right) + \frac{\partial}{\partial x}\left(\frac{\partial v}{\partial t}\right) \right]$$

$$\sigma_{xy} = \eta \left[\frac{\partial}{\partial t}\left(\frac{\partial u}{\partial y} + \frac{\partial v}{\partial x}\right) \right]$$

$$\sigma_{xy} = \eta \frac{\partial e_{xy}}{\partial t}$$

▶ Thus **shear stress** is directly proportional to **rate of change of shear strain** with time

▶ In Hook's law, stress is linearly related to stain

▶ In Newton's law for viscosity, stress is linearly related to rate of change of strain or strain rate

Linear Viscoelastic Behaviour

▶ A simple constitutive relation for behaviour of a linear viscoelastic solid is obtained by combining the two laws

$$\sigma_{xy} = Ge_{xy} + \eta \frac{\partial e_{xy}}{\partial t}$$

▶ The equation represents the Kelvin or Voigt model for linear viscoelastic solid

▶ Hook's law is valid only for small strains

▶ Newton's law of viscosity is valid for small flow rates

▶ Most useful plastics show some non-linearity at strains around 1 percent

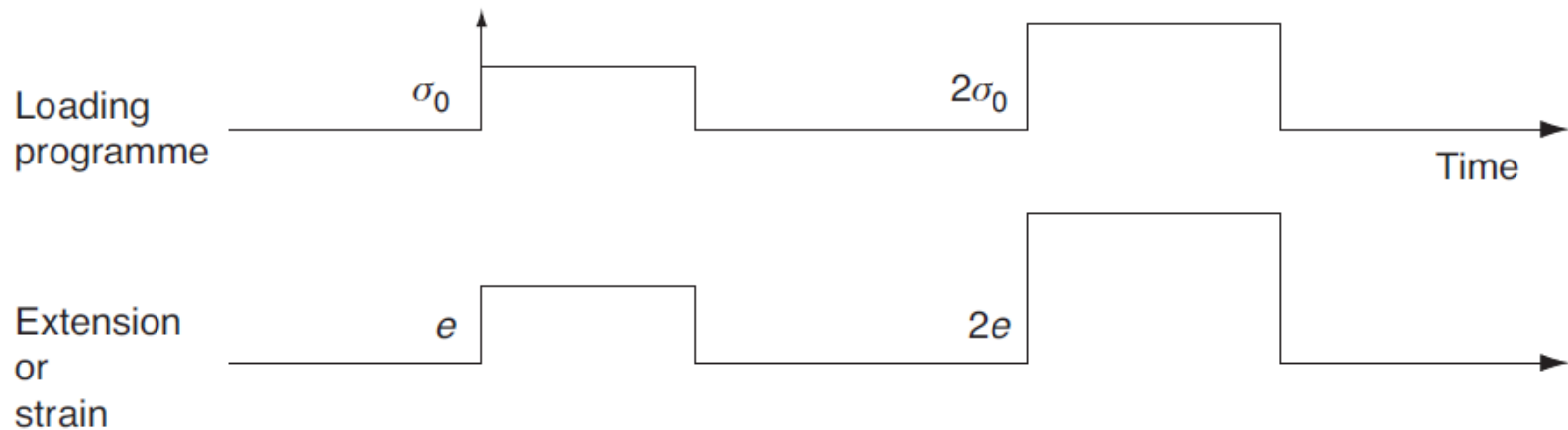# Linear Viscoelastic Behaviour

▶ Two main phenomena observed in materials as a result of viscoelastic deformation are

    ▶ Creep

    ▶ Stress Relaxation

Creep

- Tendency of a solid material to move slowly or deform under the influence of mechanical stresses

- Occurs as a result of long-term exposure to high levels of stress that are still below the yield strength of the material

- Not to be confused with metallic creep

- Creep in polymers at low strains (1 percent) is essentially recoverable after unloading

Creep

- Response of a linear elastic solid under two levels of stress

Loading programme	σ_0		$2\sigma_0$	Time
Extension or strain	e		$2e$	

- Strains follows the pattern of loading programme exactly
- Strain is in exact proportionality to the applied stress

Creep

▶ Response of a linear viscoelastic solid under two levels of stress
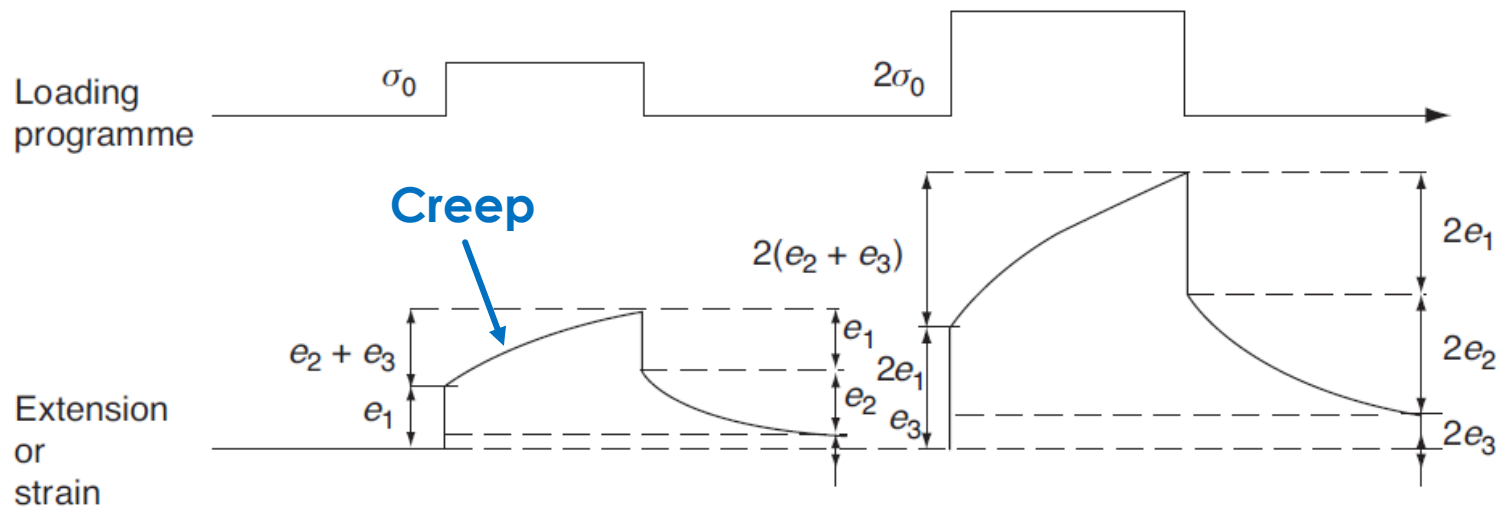
▶ Total strain e is sum of three parts

  ▶ e_1 immediate elastic deformation
  ▶ e_2 delayed elastic deformation
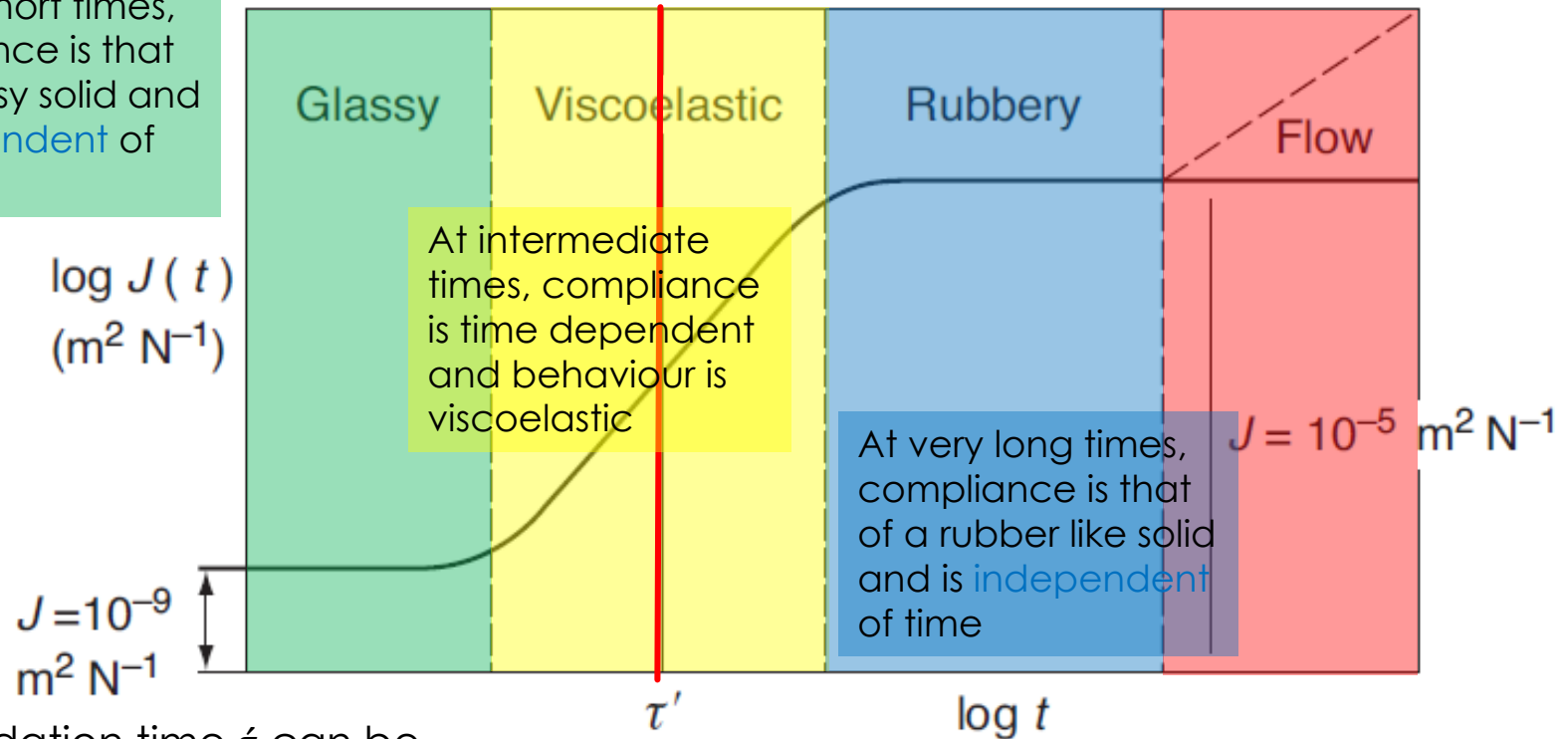 ▶ e_3 Newtonian flow

Creep

▶ Since the material shows linear behaviour, the magnitudes of e_1, e_2 and e_3 are exactly proportional to applied stress

▶ **Creep compliance $J(t)$**, which is function of time, is defined as

$$J(t) = \frac{e(t)}{\sigma} = J_1 + J_2 + J_3$$

▶ Linear amorphous polymers

 ▶ Significant J_3 creep above T_g where creep may continue till material fracture

 ▶ At lower temperatures, J_1 and J_2 dominates

▶ Cross linked and crystalline polymers do not show J_3 term

Log Creep Compliance vs Log Time

At very short times, compliance is that of a glassy solid and is independent of time


At intermediate times, compliance is time dependent and behaviour is viscoelastic

At very long times, compliance is that of a rubber like solid and is independent of time

$\log J(t)$
$(m^2\ N^{-1})$

$J = 10^{-9}$
$m^2\ N^{-1}$

Glassy | Viscoelastic | Rubbery | Flow

$J = 10^{-5}\ m^2\ N^{-1}$

τ' | $\log t$

Retardation time t can be defined in middle of viscoelastic region to characterise the time-scale for creep

t is very small at room temperature for rubbery materials

t is very large at room temperature for glassy materials

# Creep and Recovery

▶ At any selected time, the extent of recovery is directly proportional to the formerly applied stress

▶ Recovery behaviour is basically similar to the creep behavior if we neglect the quantity e_3 (Newtonian flow)

▶ Direct consequence of linear viscoelastic behaviour
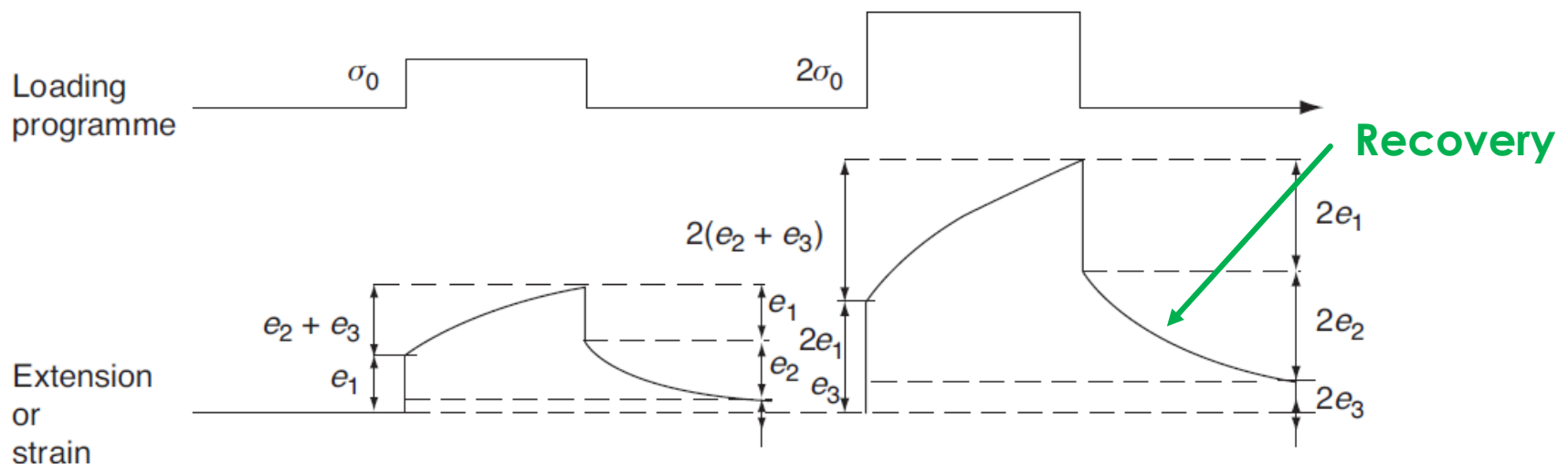
Stress Relaxation

▶ When instantaneous strain is applied to an ideal elastic solid, finite and constant stress will be recorded

▶ For a linear viscoelastic solid, the instantaneous stress will be proportional to applied strain and will decrease with time
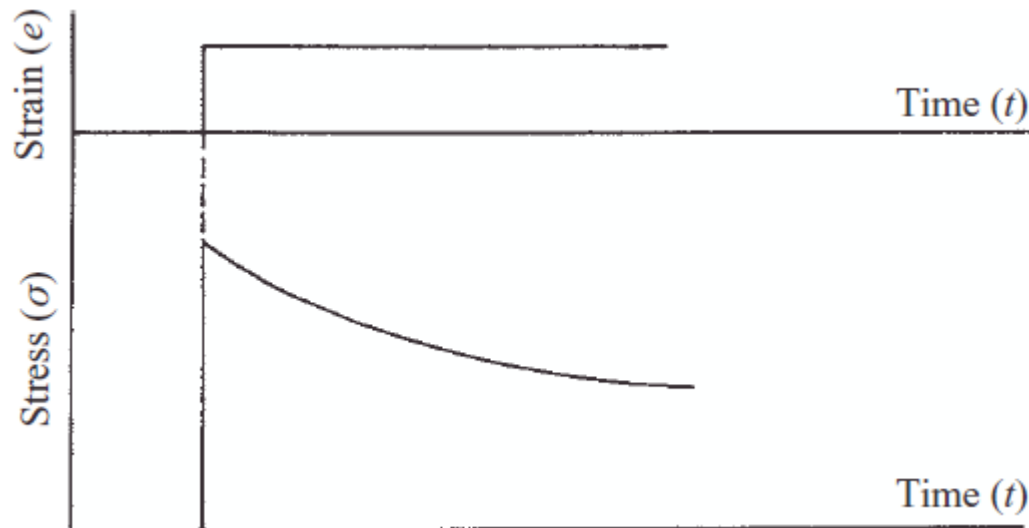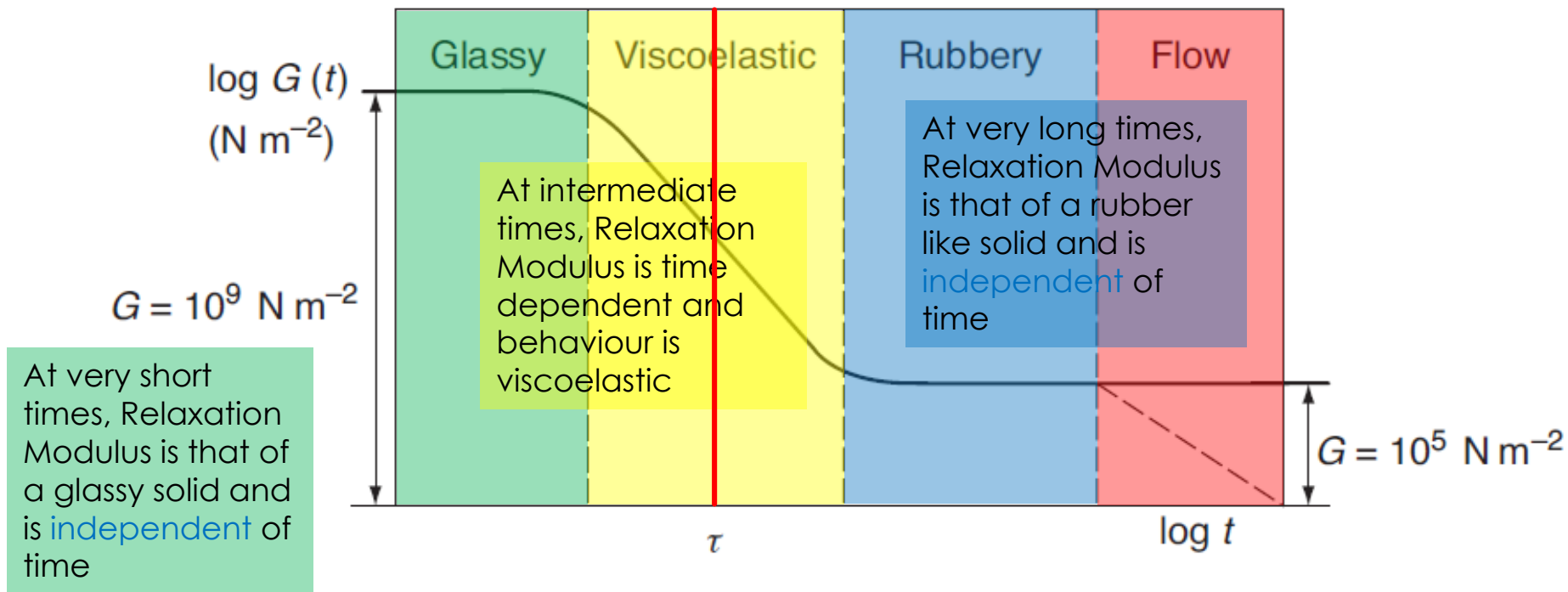
Stress Relaxation

▶ Stress **Relaxation Modulus** may be define as

$$G(t) = \frac{\sigma(t)}{e}$$

▶ For amorphous linear polymers at high temperatures, the stress may eventually decay to zero

▶ If there is no viscous flow, the stress decays to a finite value

▶ Gives an equilibrium or relaxed modulus G_r at finite time

Log Relaxation Modulus vs Log Time

Glassy | Viscoelastic | Rubbery | Flow

$\log G(t)$ $(N\,m^{-2})$

$G = 10^9\ N\,m^{-2}$

At very short times, Relaxation Modulus is that of a glassy solid and is independent of time

At intermediate times, Relaxation Modulus is time dependent and behaviour is viscoelastic

At very long times, Relaxation Modulus is that of a rubber like solid and is independent of time

$G = 10^5\ N\,m^{-2}$

τ

$\log t$

Relaxation time τ can be defined in middle of viscoelastic region

The relaxation time τ and retardation time $\acute{t}$ are of the same general magnitude, but identical only for simpler models

# Mathematical Modelling of Linear Viscoelasticity
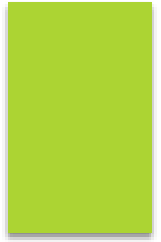
Mathematical Modelling

- ▶ *Phenomenological models:* have no direct relationship with chemical composition or molecular structure

- ▶ Enable response to a complicated loading pattern to be deduced from a single creep or stress-relaxation plot

- ▶ Models validity depend upon the assumptions of linear viscoelasticity

- ▶ *Assumption:* Total deformation can be considered as sum of independent elastic and viscous components

Mathematical Modelling

Boltzmann Superposition Principle

▶ Creep is a function of entire past loading history

▶ Each loading step makes an independent contribution to final deformation

▶ Total deformation is the sum of all deformation contributions

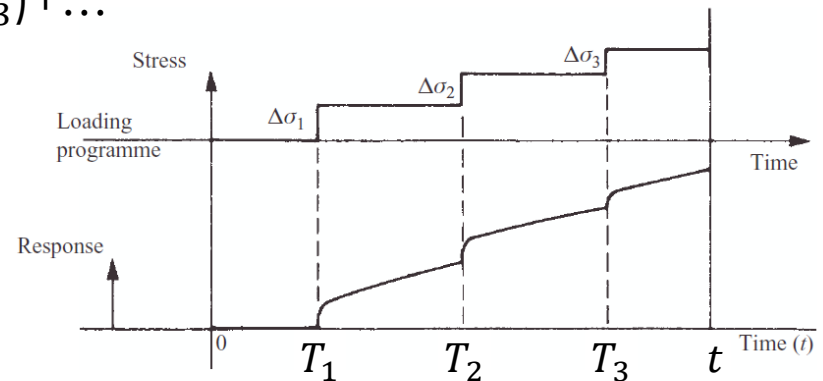Creep behaviour of a viscoelastic solid under multi-step loading
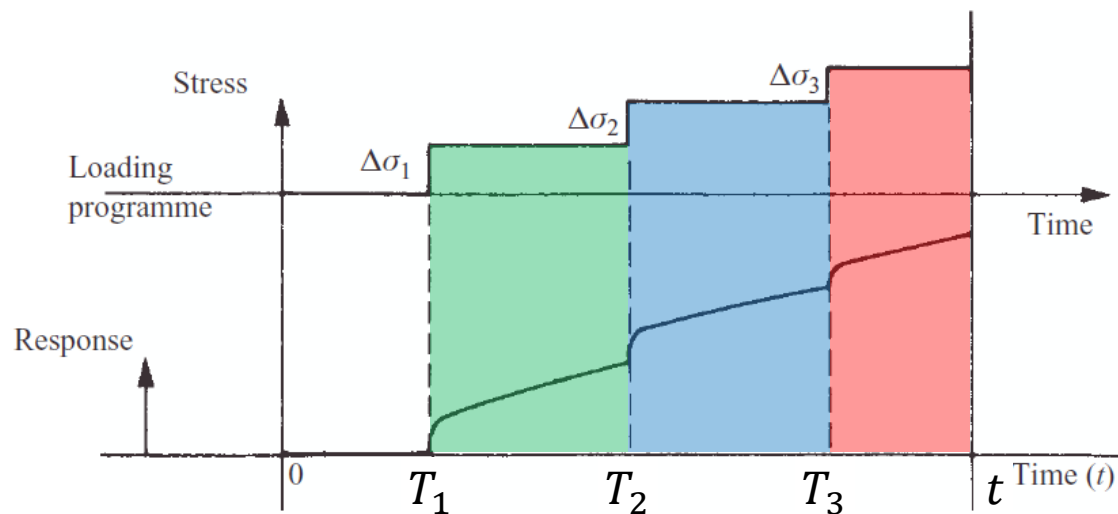
Mathematical Modelling

▶ Total creep at time t

$$e(t) = \Delta\sigma_1 J(t - T_1) + \Delta\sigma_2 J(t - T_2) + \Delta\sigma_3 J(t - T_3) + \ldots$$

Creep compliance

$$e(t) = \int_{-\infty}^{t} J(t - T)\, d\sigma(T)$$

▶ Above can be written by separating instantaneous elastic response in terms of the unrelaxed modulus G_u

$$e(t) = \frac{\sigma}{G_u} + \int_{-\infty}^{t} J(t - T)\frac{d\sigma(T)}{dT}\, dT$$

Concept Check Point

▶ Consider a strain loading programme with strain increments of Δe_1, Δe_2, Δe_3 added at times T_1, T_2, T_3 respectively

▶ Using the Boltzmann Superposition principle, write expression for total stress at time t

▶ Hint: use the analogy with the total strain equation

$$e(t) = \Delta\sigma_1 J(t - T_1) + \Delta\sigma_2 J(t - T_2) + \Delta\sigma_3 J(t - T_3) + \ldots$$

Answer

$$\sigma(t) = \Delta e_1 G(t - T_1) + \Delta e_2 G(t - T_2) + \Delta e_3 G(t - T_3)$$

General Equation of Linear Viscoelasticity

▶ The Boltzmann superposition principle is one starting point for a theory of linear viscoelastic behavior

▶ It is sometimes called the '*integral representation* of linear viscoelasticity' because it defines an integral equation

▶ An equally valid starting point is to relate the stress to the strain by a linear differential equation

▶ This leads to a differential representation of linear viscoelasticity

▶ In its most general form, the equation is expressed as

$$P\sigma = Qe.$$

where *P* and *Q* are linear differential operators with respect to time

General Equation of Linear Viscoelasticity

▶ Most generally the differential equation is

$$a_0\sigma + a_1\frac{d\sigma}{dt} + a_2\frac{d^2\sigma}{dt^2} + \cdots = b_0 e + b_1\frac{de}{dt} + b_2\frac{d^2 e}{dt^2} + \cdots$$

▶ Often adequate to represent the experimental data by including only one or two terms on each side of this equation

▶ This is equivalent to describing the viscoelastic behaviour by mechanical models constructed of mechanical components

Mechanical Models
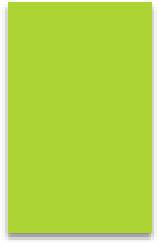
Mechanical Models

- Viscoelastic behaviour can be described by mechanical models constructed using elastic springs and viscous dashpots

- Elastic springs follow Hooke's law

$$\sigma = Ee$$

- Viscous dashpots follow Newton's law of viscosity

$$\sigma_{xy} = \eta \frac{\partial e_{xy}}{\partial t}$$

Kelvin or Voigt Model

▶ Consists a spring of modulus E_k and a dashpot of viscosity η_k

▶ Constant stress σ is applied at $t = 0$

▶ Stress is shared by both components

▶ Due to dashpot, instantaneous extension can not happen

▶ Deformation occurs at a varying rate

▶ After a time, depending on viscosity, spring reaches maximum extension
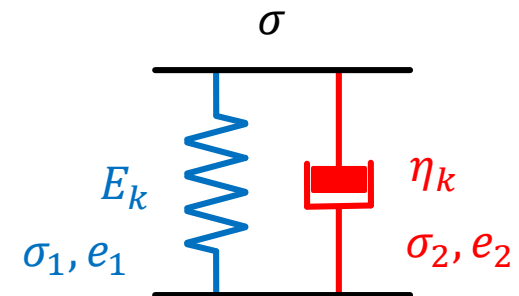
Kelvin or Voigt Model

▶ Recovery occurs as stress is removed

▶ No instantaneous retraction

▶ Thus stress for spring and dashpot

$$\sigma_1 = E_K e_1 \qquad \sigma_2 = \eta_K \frac{de_2}{dt}$$

▶ Total stress $\qquad \sigma = \sigma_1 + \sigma_2$

▶ Total strain $\qquad e = e_1 = e_2$

▶ Thus

$$\sigma = E_K e + \eta_K \frac{de}{dt}$$

Recovery

Strain

Time

Kelvin or Voigt Model

▶ Solving for $0 < t < t_1$, when the stress is σ

$$\frac{E_K}{\eta_K} \int\limits_0^t \mathrm{d}t = \int\limits_0^e \frac{\mathrm{d}e}{\sigma/E_K - 1}$$

▶ where $\frac{\eta_K}{E_K}$ has the dimensions of time, and represents the rate at which the deformation occurs: it is the retardation time t

▶ By Integration

$$\frac{t}{\tau'} = \ln\left(\frac{\sigma/E_K}{\sigma/E_K - e}\right)$$

Kelvin or Voigt Model

▶ An expression for strain can be obtained in the form

$$e = \frac{\sigma}{E_K}[1 - \exp\left(-\frac{t}{\acute{t}}\right)]$$

where $\acute{t}$ is the retardation time

▶ In terms of compliance

$$e = J\sigma[1 - \exp\left(-\frac{t}{\acute{t}}\right)]$$

▶ For t > t_1 after unloading, the solution becomes

$$e = e_{t_1}\exp\left(\frac{t_1 - t}{\tau'}\right), \text{ where } e_{t_1} = J\sigma\left[1 - \exp\left(-t_1/\tau'\right)\right]$$

Kelvin or Voigt Model

▶ The retardation time $\acute{t}$ is the time after loading for the strain to reach

$$\left(1 - \frac{1}{\exp(1)}\right)$$

of its equilibrium value; after stress removal the strain decays to (1/exp(0)) of its maximum value in time $\acute{t}$

Limitations

▶ Kelvin model is *unable* to describe stress relaxation: At constant strain dashpot can not relax

$$\frac{de}{dt} = 0 \ thus \qquad \sigma = E_K e + \eta_K \frac{de}{dt} = E_K e$$

Maxwell Model

▶ Consists of a spring and dashpot in series
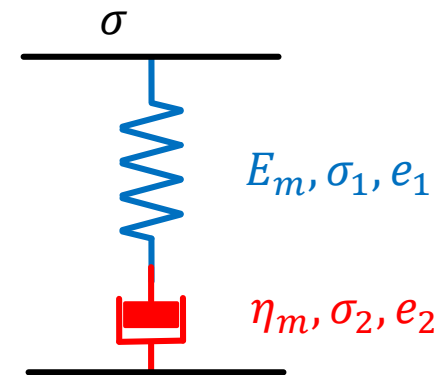
▶ Total stress $\qquad \sigma = \sigma_1 = \sigma_2$

▶ Total strain $\qquad e = e_1 + e_2$

▶ Stress can be written as $\quad \sigma_1 = E_m e_1 \Rightarrow \dfrac{d\sigma}{dt} = E_m \dfrac{de_1}{dt}$

▶ Thus, total strain rate $\qquad \dfrac{de}{dt} = \dfrac{1}{E_m}\dfrac{d\sigma}{dt} + \dfrac{\sigma}{\eta_m}$

▶ Considering stress relaxation

$$\frac{de}{dt} = 0 \; so \; 0 = \frac{1}{E_m}\frac{d\sigma}{dt} + \frac{\sigma}{\eta_m} \; thus \quad \frac{d\sigma}{\sigma} = -\frac{E_m}{\eta_m}dt$$

σ

E_m, σ_1, e_1

η_m, σ_2, e_2

Creep & recovery behaviour

Strain
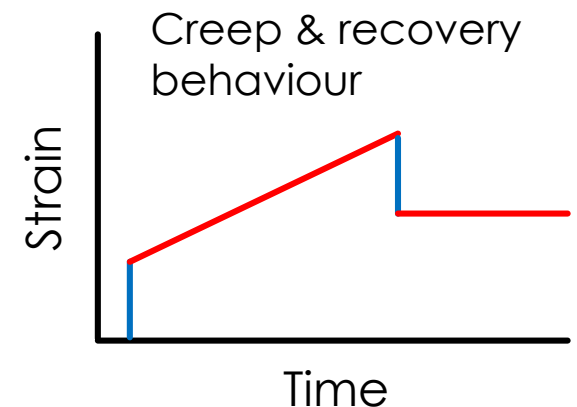
Time

Maxwell Model

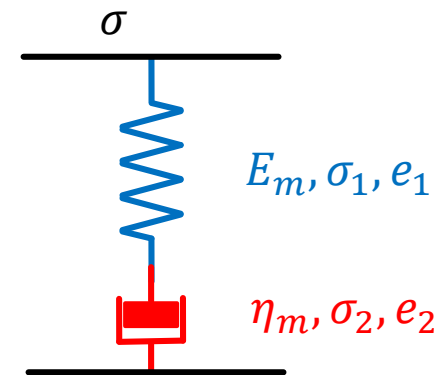▶ At time t=0, $\sigma = \sigma_0$ (initial stress). After integrating

$$\sigma = \sigma_0 \exp\left(\frac{-E_m}{\eta_m}\right) t$$

E_m, σ_1, e_1

η_m, σ_2, e_2

▶ This equation shows that the stress decays exponentially with a characteristic time constant $\frac{\eta_m}{E_m}$

$$\sigma = \sigma_0 \exp\left(-\frac{t}{\tau}\right)$$

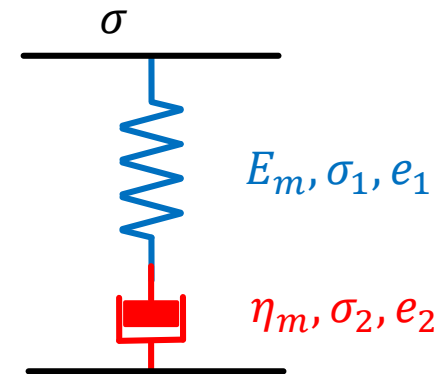where τ is the relaxation time

Maxwell Model

Limitations
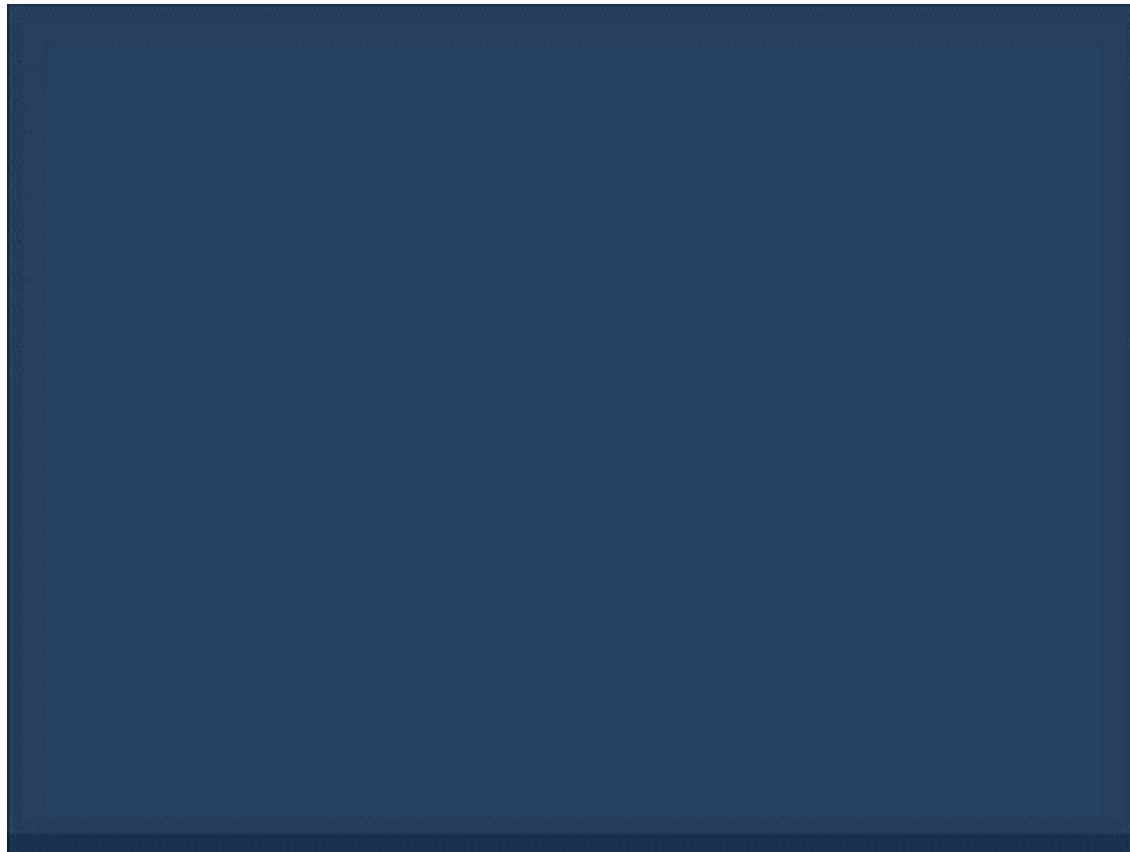
▶ Under constant stress (creep)

$$\frac{d\sigma}{dt} = 0 \ thus \qquad \frac{de}{dt} = \frac{\sigma}{\eta_m}$$

where Newtonian flow is observed which is generally not true for viscoelastic materials

▶ Stress relaxation behaviour cannot be usually represented by a single exponential decay term

σ

E_m, σ_1, e_1

η_m, σ_2, e_2

Maxwell Model

The Standard Linear Solid

▶ Consider the general linear differential equation

$$a_0\sigma + a_1\frac{d\sigma}{dt} + a_2\frac{d^2\sigma}{dt^2} + \cdots = b_0 e + b_1\frac{de}{dt} + b_2\frac{d^2 e}{dt^2} + \cdots$$

▶ To obtain even an approximate description of both stress relaxation and creep, at least the first two terms on each side of Equation must be retained

▶ The simplest equation will be of the form

$$a_0\sigma + a_1\frac{d\sigma}{dt} = b_0 e + b_1\frac{de}{dt}$$

The Standard Linear Solid

$$a_0\sigma + a_1\frac{d\sigma}{dt} = b_0 e + b_1\frac{de}{dt}$$

▶ This will be adequate to a first approximation for creep (when $d\sigma/dt$ = 0) and

▶ for stress relaxation (when de/dt = 0), giving an exponential response in both cases

The Standard Linear Solid

▶ Kelvin and Maxwell models can not define the general behaviour of viscoelastic solid completely

▶ A more real model is obtained by adding a second spring in parallel with a Maxwell unit
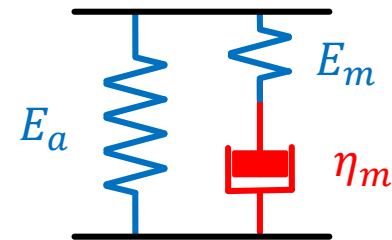
▶ In creep, both spring extend

$$\acute{t} = \eta_m \left[\frac{1}{E_a} + \frac{1}{E_m} \right]$$

▶ In stress relaxation, E_a is unaffected

$$\tau = \frac{\eta_m}{E_m}$$

▶ Stress strain relationship is given by

$$\sigma + \tau \frac{d\sigma}{dt} = E_a e + (E_a + E_m)\tau \frac{de}{dt}$$

The Standard Linear Solid

Limitations

▶ Standard linear solid model predicts an exponential response only

▶ To describe the observed viscoelastic behaviour quantitatively would require the inclusion of many terms in the linear differential equation

▶ These more complicated equations are equivalent to either a large number of Maxwell elements in parallel or a large number of Voigt elements in series

Concept Check Point

▶ How would this model predict the creep and relaxation response?
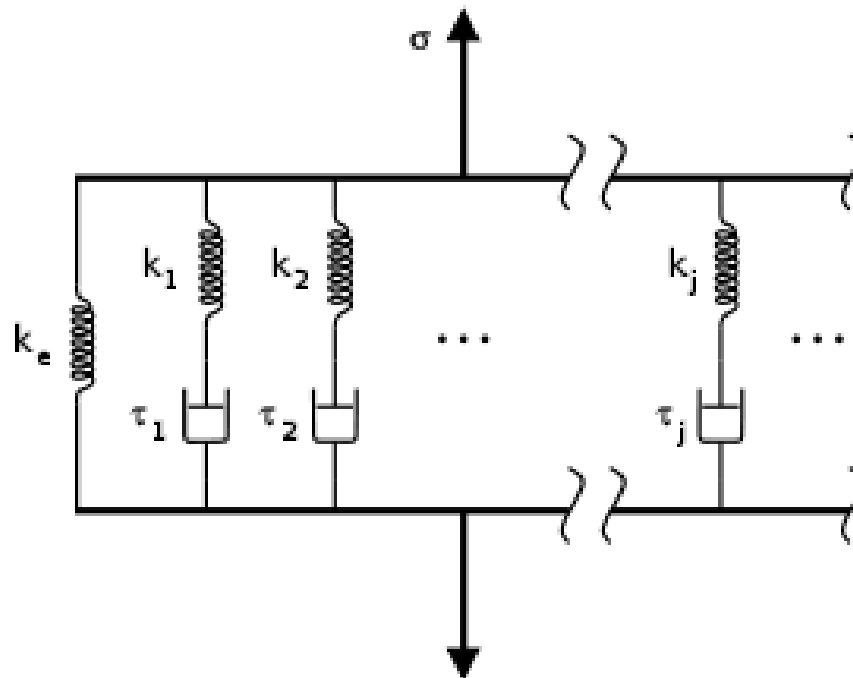
Dynamical Mechanical Measurements
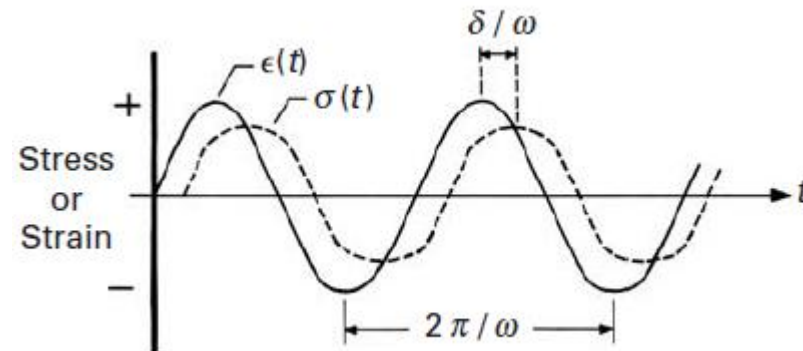
THE COMPLEX MODULUS

AND

COMPLEX COMPLIANCE

Complex Modulus and Complex Compliance

▶ To characterise the viscoelastic behaviour, material is sinusoidally deformed and resulting stress is recorded

▶ For linear viscoelastic behaviour, stress and strain will vary sinusoidally

▶ For an ideal elastic material, stress and strain are in phase i.e. phase shift $\delta = 0$

▶ For an ideal viscous material, stress and strain are 90° out of phase $\delta = 90$

▶ Strain lags behind stress

$$Strain \quad e = e_0 \sin \omega t$$

$$Stress \quad \sigma = \sigma_0 \sin(\omega t + \delta)$$

where ω is frequency and δ is phase lag

Complex Modulus and Complex Compliance

▶ So stress can be written as

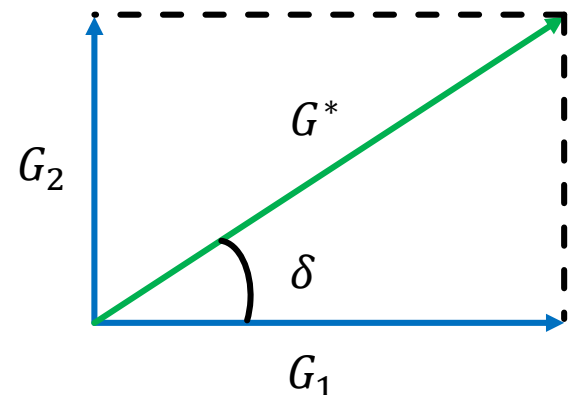$$\sigma = \sigma_0 \cos\delta \sin\omega t + \sigma_0 \sin\delta \cos\omega t$$

▶ For viscoelastic material, stress has two components

  ▶ First of magnitude $\sigma_0 \cos\delta$ in phase with strain

  ▶ Second of magnitude $\sigma_0 \sin\delta$ which is 90° out of phase with strain

▶ Stress-strain relation can be defined by

  ▶ G_1 in phase with strain

  ▶ G_2 90° out of phase with strain

$$G_1 = \frac{\sigma_0}{e_0}\cos\delta \qquad G_2 = \frac{\sigma_0}{e_0}\sin\delta$$

Phasor diagram

Complex Modulus and Complex Compliance

▶ A phasor diagram indicate that G_1 and G_2 define a complex modulus G^*

▶ If

$$e = e_0 \exp(i\omega t) \qquad and \qquad \sigma = \sigma_0 \exp[i(\omega t + \delta)]$$

▶ Thus

$$G^* = \frac{\sigma}{e} = \frac{\sigma_0}{e_0}\exp(i\delta) = \frac{\sigma_0}{e_0}(\cos\delta + i\sin\delta) = G_1 + iG_2$$

▶ G_1, in phase with strain, is called ***storage modulus***

   ▶ Defines the energy stored in specimen due to applied strain

▶ G_2, which is $\pi/2$ out of phase with strain, is called ***loss modulus***

   ▶ Defines the dissipation of energy

Complex Modulus and Complex Compliance

▶ Calculating the **energy dissipated per cycle, ΔE**

$$\Delta E = \oint \sigma \, de = \int_0^{2\pi/\omega} \sigma \frac{de}{dt} dt$$

▶ Subtituting for σ and e $\quad \Delta E = \omega e_0^2 \int_0^{2\pi/\omega} (G_1 \sin \omega t \cos \omega t + G_2 \cos^2 \omega t) dt$

▶ Solving the integral we get $\quad \Delta E = \pi G_2 e_0^2$

▶ If integral for ΔE is evaluated over a quarter cycle rather than over the complete period, the first term

$$\omega e_0^2 \int_0^{2\pi/\omega} G_1 \sin \omega t \cos \omega t \, dt$$

gives the **maximum stored elastic energy, E** $\quad E = \frac{1}{2} G_1 e_0^2$

Complex Modulus and Complex Compliance

▶ The ratio of loss modulus to storage modulus can be written as

$$\frac{G_2}{G_1} = \tan \delta = \frac{\Delta E}{2\pi E}$$

Where ΔE is energy dissipated per cycle and E is maximum stored elastic energy

▶ The ratio $\frac{\Delta E}{E}$ is called specific loss

$$\frac{\Delta E}{E} = 2\pi \tan \delta$$

▶ Typical values of G_1, G_2 and $\tan \delta$ for a polymer are 10^9 Pa, 10^7 Pa and 0.01

▶ In such cases, $|G^*|$ is approximately equal to G_1

▶ Similarly, complex compliance can be developed

$$J^* = J_1 + iJ_2 \qquad \text{Where} \qquad G^* = {^1}\!/_{J^*}$$

Response of a Sample to Sinusoidal Shear Strain

- G_1 is stress measured at maximum strain divided by applied strain amplitude γ_o

- G_2 is stress measured at zero strain divided by applied strain amplitude γ_o

- Strain is zero but stress in general won't be zero

- Rate of strain is maximum when strain passes through zero

$$G_1 = \frac{\sigma_0}{e_0}\cos\delta \qquad G_2 = \frac{\sigma_0}{e_0}\sin\delta$$
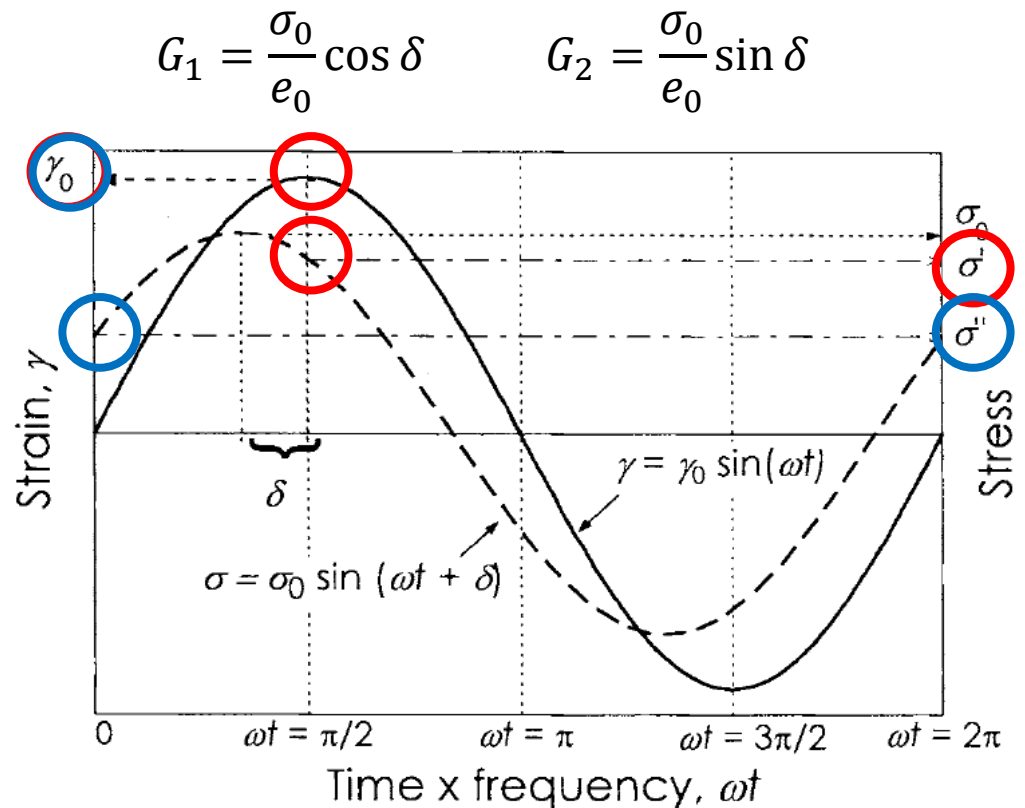
Response of a Sample to Sinusoidal Shear Strain

- Stress at zero strain is result of sample responding to strain rate as would a purely viscous material (free flow, no strain produced)

- As strain reaches its peak, strain rate approaches to zero

- Sample at this point must only be responding to strain as would an elastic material
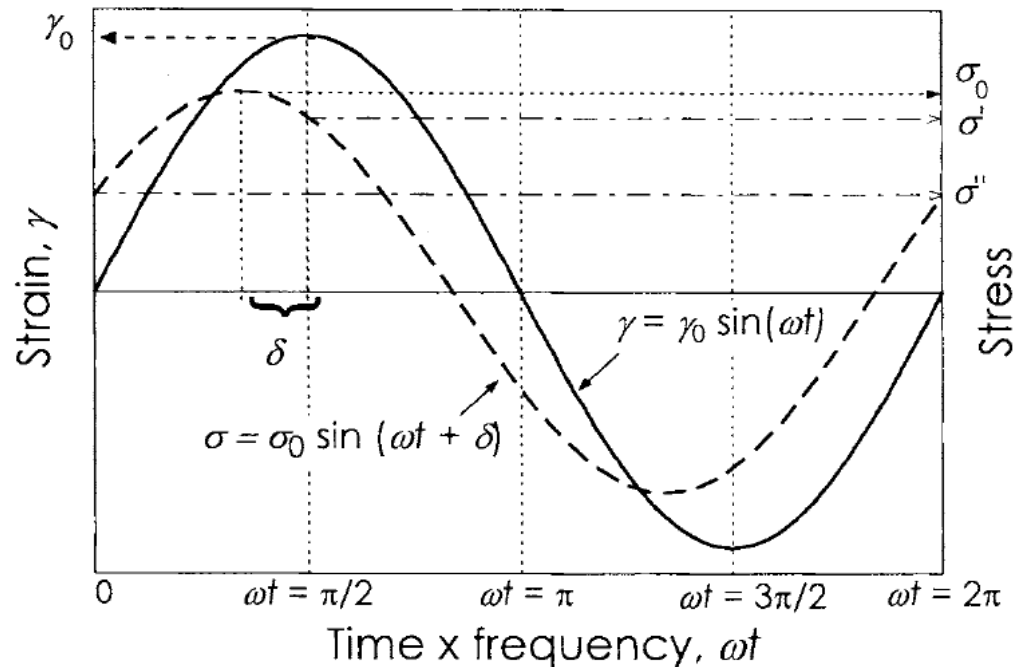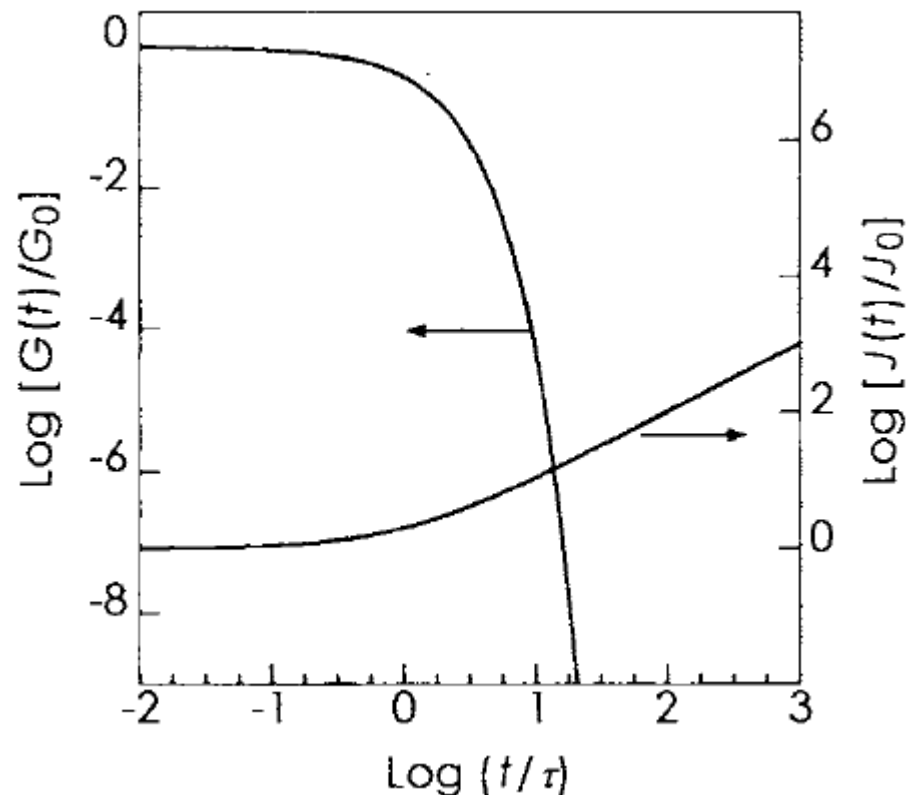
Creep Compliance & Stress Relaxation Modulus

- As a consequence of Boltzmann superposition principle, a relationship between creep compliance and stress relaxation modulus exits

- In time independent functions, compliance and modulus are simply reciprocal to each other

- This no longer holds in time dependent case

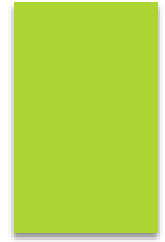- The general solution is given by

$$t = \int_0^t G(s)J(t-s)ds$$

Calculated using Laplace transformation

Creep Compliance & Stress Relaxation Modulus

- Relationship between creep compliance and stress relaxation modulus

- Shapes of the two curves are markedly different

- The two would be mirror images if reciprocally related

Example Problems

Problem 1

▶ Stress relaxation modulus of a certain polymer can be described by
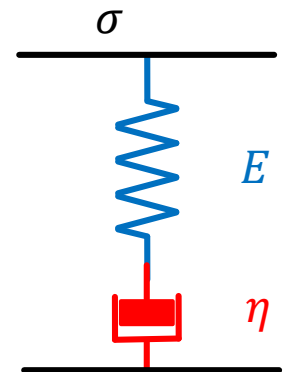
$$G(t) = G_0 e^{-t/\tau}$$

And has the values 2.0 GPa and 1.0 GPa at t=0 and 10^4 sec respectively. Calculate the form of the creep compliance and so evaluate the strain 1000 sec after the rapid application of a stress of 100 MPa.

SOLUTION

▶ The stress relaxation term is the form of Maxwell element and

$$G(t) = E e^{-t/\tau} \qquad \tau = {}^{\eta}/_{E}$$

Problem 1

▶ At t=0 $\qquad G(t) = Ee^{-t/\tau} = E = 2.0\ GPa \qquad$ (given)

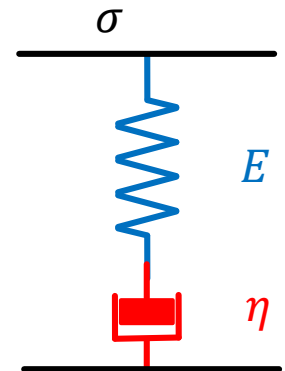▶ At t=10⁴ $\qquad G(t) = Ee^{-t/\tau} = 2e^{-10^4/\tau} = 1.0\ GPa \qquad$ (given)

$$e^{10^4/\tau} = 2 \Rightarrow \frac{10^4}{\tau} = ln_e(2) = 0.693$$

$$\tau = \frac{10^4}{0.693} = \frac{\eta}{E} \Rightarrow \eta = \frac{2 \times 10^4}{0.693}\ GPa\ s$$

▶ Total strain $\qquad \varepsilon = \varepsilon_E + \varepsilon_v$

▶ For viscous element $\qquad \varepsilon_v = \dfrac{\sigma t}{\eta}$

▶ Total strain $\qquad \varepsilon(t) = \dfrac{\sigma}{E} + \dfrac{\sigma t}{\eta} = \sigma\left(\dfrac{1}{E} + \dfrac{t}{\eta}\right)$
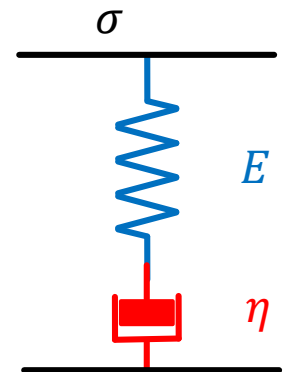
Problem 1
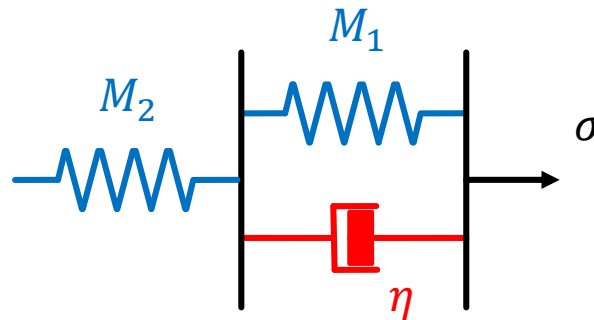
▶ Putting $J_0 = 1/E$

$$J(t) = J_0 + \frac{t}{\eta}$$

$$\varepsilon(1000) = 0.1 \left(\frac{1}{2} + \frac{10^3 \times 0.693}{2 \times 10^4} \right) = 0.1(0.5 + 0.0347)$$

$$\varepsilon(1000) = 5.35 \; percent$$

Problem 2

▶ The creep deformation of a linear viscoelastic solid under constant stress can be represented by the model shown, in which spring is in series with a Kelvin unit

Here, M_1 and M_2 represent Young's moduli, η the viscosity and σ the total constant stress. Show that the total strain is dependent on the relaxation time, $\tau_1 = \eta/M_1$ and is given by

$$\varepsilon = \frac{\sigma}{M_2} + \frac{\sigma}{M_1}[1 - \exp\left(-\frac{t}{\tau_1}\right)]$$

Problem 2

Immediately after applying stress, the strain is 0.002; after 1000 sec the strain is 0.004; after a very long time the strain tends to 0.006. What is the retardation time τ_1?

Note: It is not necessary to know the stress or the values of M_1, M_2 and η

SOLUTION

▶ When load is applied, spring 2 extends by σ/M_2 and remains stretched

▶ Time dependency is due entirely to the Kelvin unit, where

▶ In Kelvin unit, total strain $e = e_E = e_V$

▶ In Kelvin unit, Total stress $\sigma = \sigma_E + \sigma_V$

Problem 2

▶ Thus

$$\sigma_E = M_1\varepsilon \qquad \sigma_V = \eta\frac{d\varepsilon}{dt}$$

$$\sigma = M_1\varepsilon + \eta\frac{d\varepsilon}{dt} \Rightarrow \frac{\sigma}{M_1} = \varepsilon + \frac{\eta}{M_1}\frac{d\varepsilon}{dt}$$

▶ Rearranging

$$\int_0^\varepsilon \frac{d\varepsilon}{(\frac{\sigma}{M_1} - \varepsilon)} = \frac{M_1}{\eta}\int_0^t dt \quad \Rightarrow -ln\left[\frac{\sigma}{M_1} - \varepsilon\right]_0^\varepsilon = \frac{M_1}{\eta}t \quad \Rightarrow ln\left(1 - \frac{\varepsilon}{\sigma/M_1}\right) = -\frac{M_1}{\eta}t$$

▶ where η/M_1 is the relaxation time τ_1

$$1 - \frac{\varepsilon}{\sigma/M_1} = \exp(-t/\tau_1) \Rightarrow \varepsilon = \frac{\sigma}{M_1}[1 - \exp(-t/\tau_1)]$$

Problem 2

▶ Total strain is obtained by adding instantaneous deformation of Spring 2

$$\varepsilon = \frac{\sigma}{M_2} + \frac{\sigma}{M_1}[1 - \exp(-t/\tau_1)]$$

▶ At time t=0 $\qquad \varepsilon = \frac{\sigma}{M_2} = 0.002 \qquad (given)$

▶ As t tends to infinity $\qquad 0.006 = 0.002 + \frac{\sigma}{M_1} \Rightarrow \frac{\sigma}{M_1} = 0.004$

▶ At time t=1000 sec $\qquad 0.004 = 0.002 + 0.004[1 - \exp(-t/\tau_1)]$

$1 - \exp(-t/\tau_1) = 0.5 \qquad \Rightarrow \exp(-t/\tau_1) = 0.5 \qquad \Rightarrow \exp(t/\tau_1) = 2$

$$t/\tau_1 = ln_e 2 = 0.693 \qquad \Rightarrow \tau_1 = \frac{1000}{0.693} = 1440 \; sec$$

Problem 3

▶ A strip of linear viscoelastic polymer 200 mm long, 10 mm wide and 1 mm thick and with an extensional Young's modulus of 2 GPa, is mounted in a dynamic testing apparatus. The specimen is initially extended by 1 mm, and then subjected to a sinusoidally varying strain with an amplitude of $\pm$ 1 mm.

▶ At 20°C and 5 Hz the phase lag between stress and strain is 0.1 rad. Calculate the maximum stress developed, the elastic energy stored during the positive quarter cycle and the work dissipated per cycle

▶ Another specimen of the same polymer is tested in a simple torsion pendulum at 20°C. The period of vibration is 2 sec and the logarithmic decrement is 0.2. What would you expect the phase lag in a dynamic tester to be at 20°C and 0.5 Hz?

Problem 3

SOLUTION

▶ The maximum stress occurs at 1 percent extension

$$\sigma = 2 \times 10^9 \times 0.01 = 20 \; MPa$$

▶ Thus amplitude of vibrating stress $\quad \sigma_0 = \pm 10 \; MPa$

▶ and amplitude of vibrating strain $\quad \varepsilon_0 = \dfrac{1}{200} = 0.005$

▶ Maximum stored elastic energy $\quad E = \dfrac{1}{2} A L \sigma_0 \varepsilon_0 \cos \delta = 0.005$

$$Aera = A = 10^{-5} \; m^2 \qquad\qquad Length = L = 0.2 \quad m$$

Problem 3

▶ Phase lag $\quad\quad\quad \tan \delta = 0.1 \approx \sin \delta$

$$\cos \delta = (1 - 0.01)^{1/2} \approx 0.995$$

$$E = \frac{1}{2} \times 10^{-5} \times 0.2 \times 10^7 \times 5 \times 10^{-3} \times 0.995 \approx 5 \times 10^{-2} \; J$$

▶ Energy dissipated per cycle

$$\Delta E = \pi A L \sigma_0 \varepsilon_0 \sin \delta$$

$$\Delta E = \pi \times 10^{-5} \times 0.2 \times 10^7 \times 5 \times 10^{-1} \approx 3.1 \times 10^{-2} \; J$$

▶ At 0.5 Hz, logarithmic decrement = 0.2

$$0.2 = \pi \tan \delta_{0.5} \implies \tan \delta_{0.5} = \frac{0.2}{\pi} = 0.064 \quad\quad \text{(Phase lag)}$$

Measurement of Viscoelasticity

Measurement of Viscoelastic Behaviour

▶ Five main classes of experiments

    ▶ Transient measurements: creep and stress relaxation

    ▶ Low frequency vibrations: free oscillations methods

    ▶ High frequency vibrations: resonance methods

   ▶ Forced vibration non-resonance methods

    ▶ Wave propagation methods
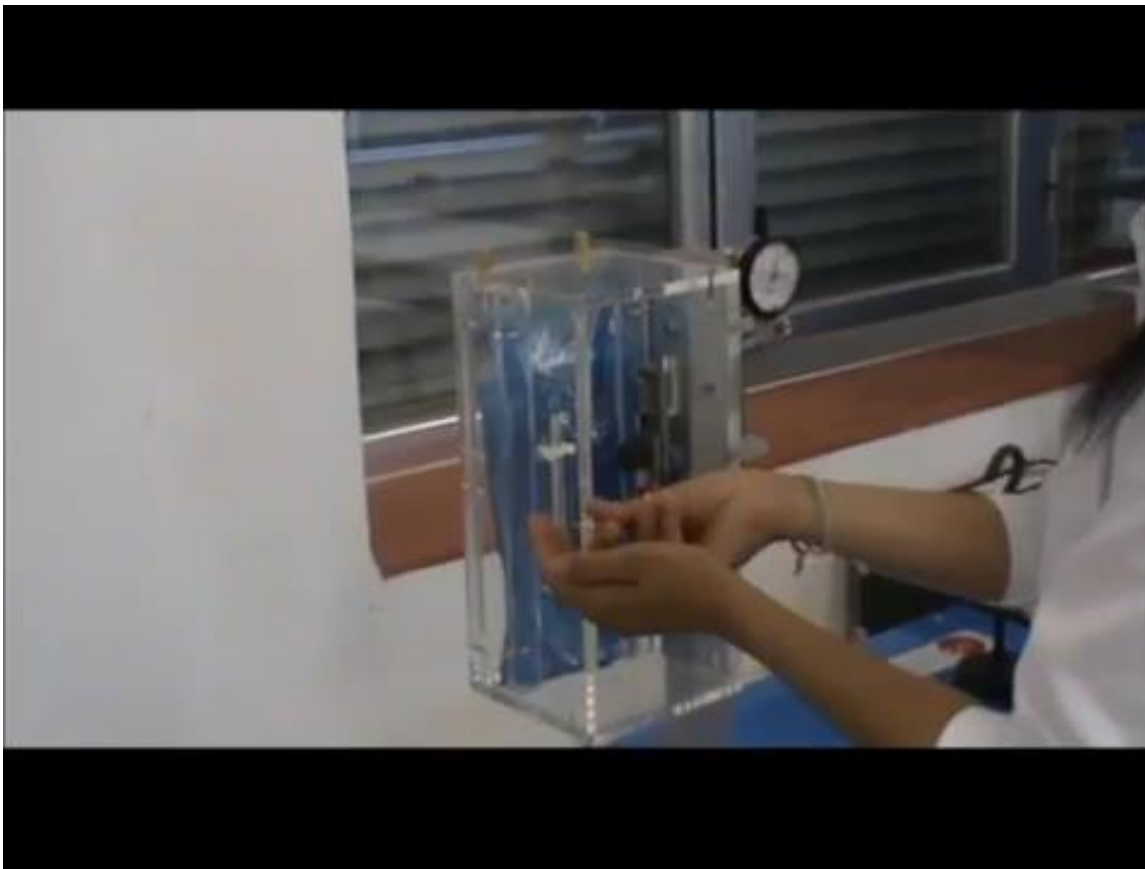
Measurement of Viscoelasticity

▶ Creep Experiment

  ▶ Sample is subjected to constant shear stress and its shear strain is measured as a function of time

  ▶ Shear compliance is given by

$$J(t) = \frac{\gamma(t)}{\sigma_0}$$

  ▶ Thermal equilibrium should be attained before starting the experiment

  ▶ Commercial instruments use low inertia, low friction, constant torque motor instead of weights
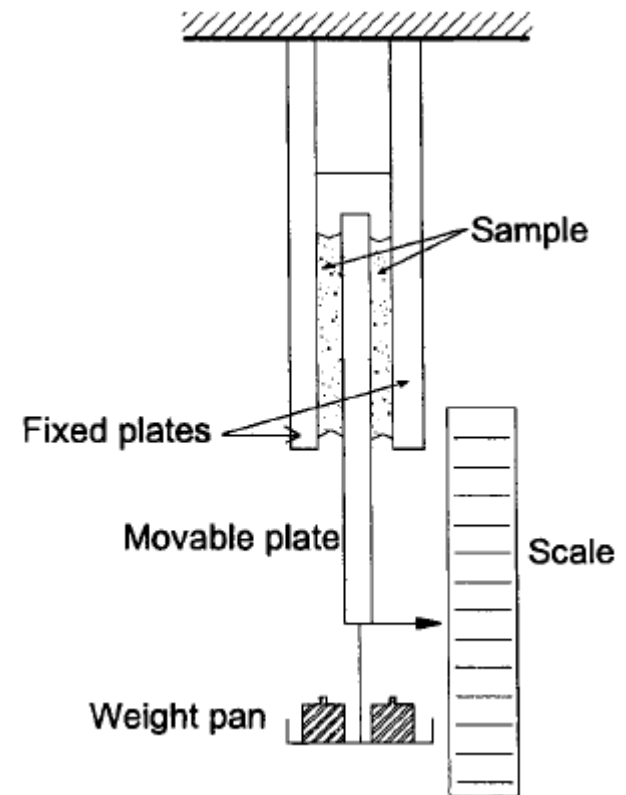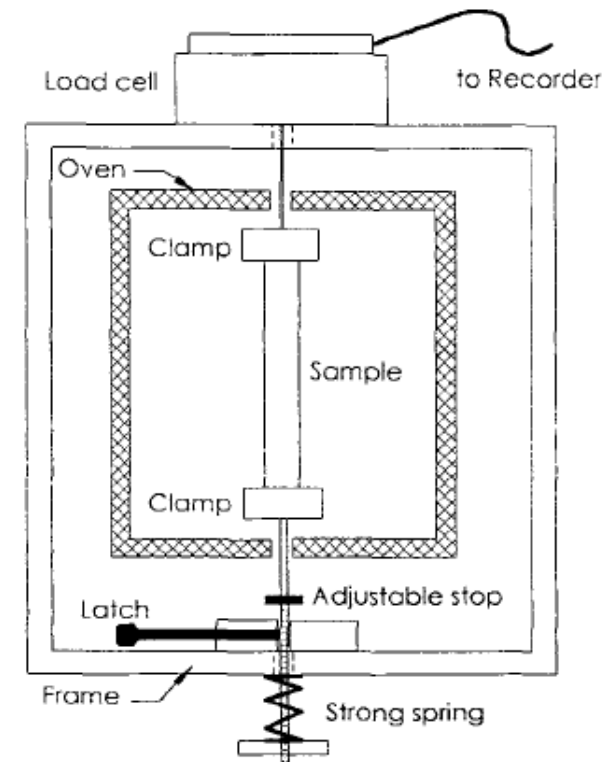
Creep Measurement

Measurement of Viscoelasticity

▶ **Stress Relaxation Test**

  ▶ Strain is kept constant and stress is measured as a function of time
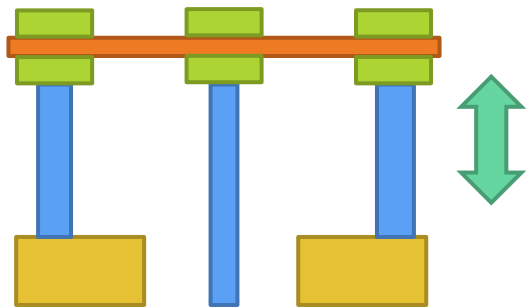
  ▶ Relaxation modulus is given by

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}$$

  ▶ Sample is heated to desired temperature and thermal equilibrium is achieved

  ▶ Latch is released and spring stretches the sample until the stop is reached

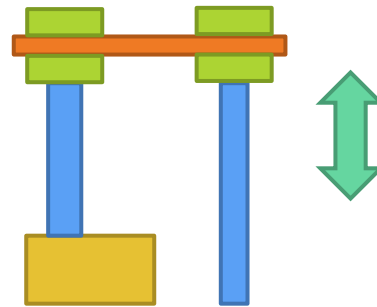▶ Relationships between stiffness and compliance are not valid

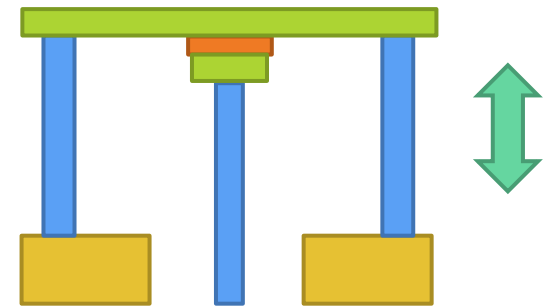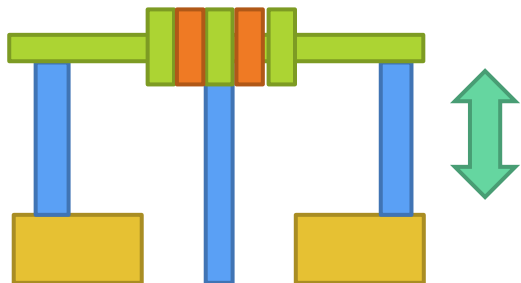$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \neq \frac{\sigma_0}{\varepsilon(t)}$$

Load cell — to Recorder
Oven
Clamp
Sample
Clamp
Latch — Adjustable stop
Frame — Strong spring

DMA Testing Modes

Dual Cantilever

Single Cantilever

Compression

Shear

Tension

Sample

Clamp / Support
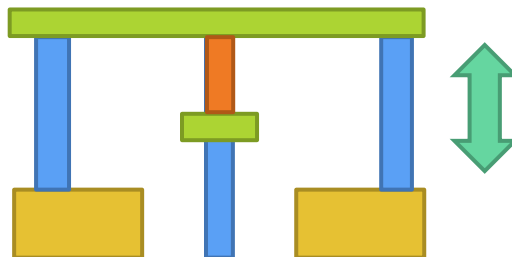
DMA Test Equipment

References

- An Introduction to The Mechanical Properties of Solid Polymers, 2nd Ed, I. M. Ward, J. Sweeney, John Wiley & Sons, 2004

  - (Ch 4, Ch 5, Ch 6)

- Mechanical Behaviour of Materials, 2nd Ed, Marc Meyers and Krishan Chawla, Cambridge University Press, 2009

  - (Ch 2.12)