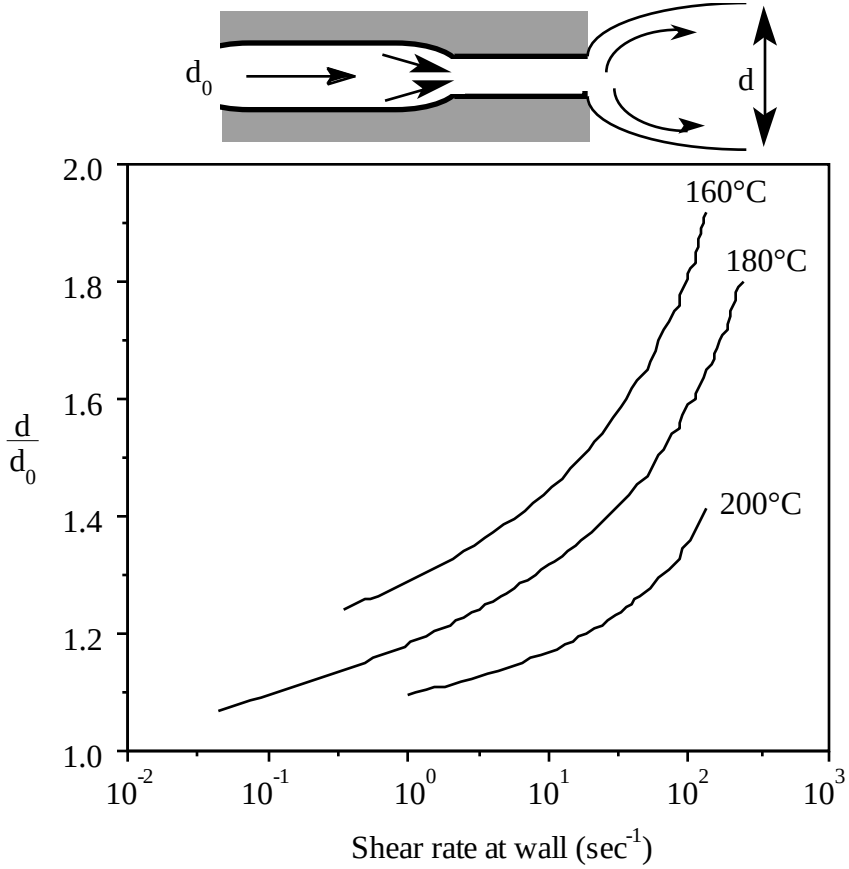
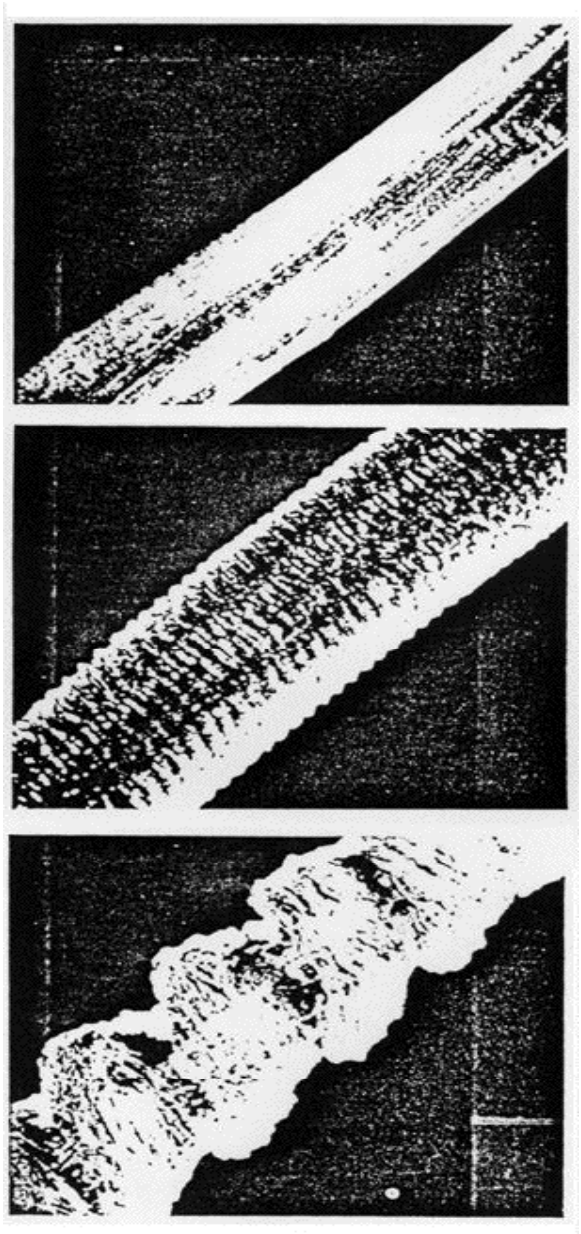
ENTANGLEMENTS AND THE ELASTIC PROPERTIES OF POLYMER MELTS

Depending upon the rate at which chains disentangle relative to the rate at which they stretch out, there is an elastic component to the behaviour of polmer melts. There are various consequences as a result of this.



JET SWELLING

MELT FRACTURE



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VISCOELASTICITY

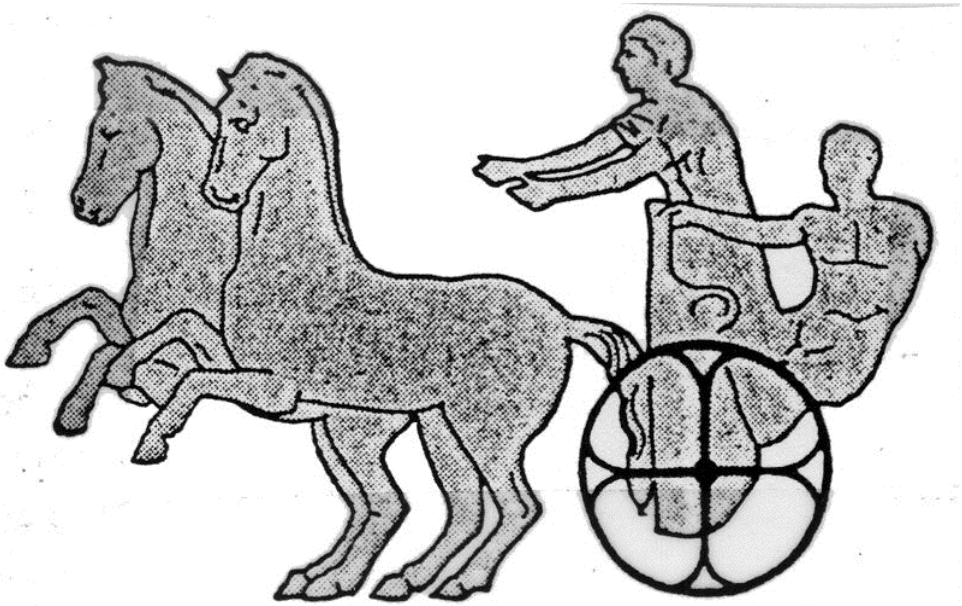
If we stretch a crystalline solid, The energy is stored in the Chemical bonds

If we apply a shear stress to A fluid, energy is dissipated In flow

Ideally elastic behaviour

Ideally viscous behaviour

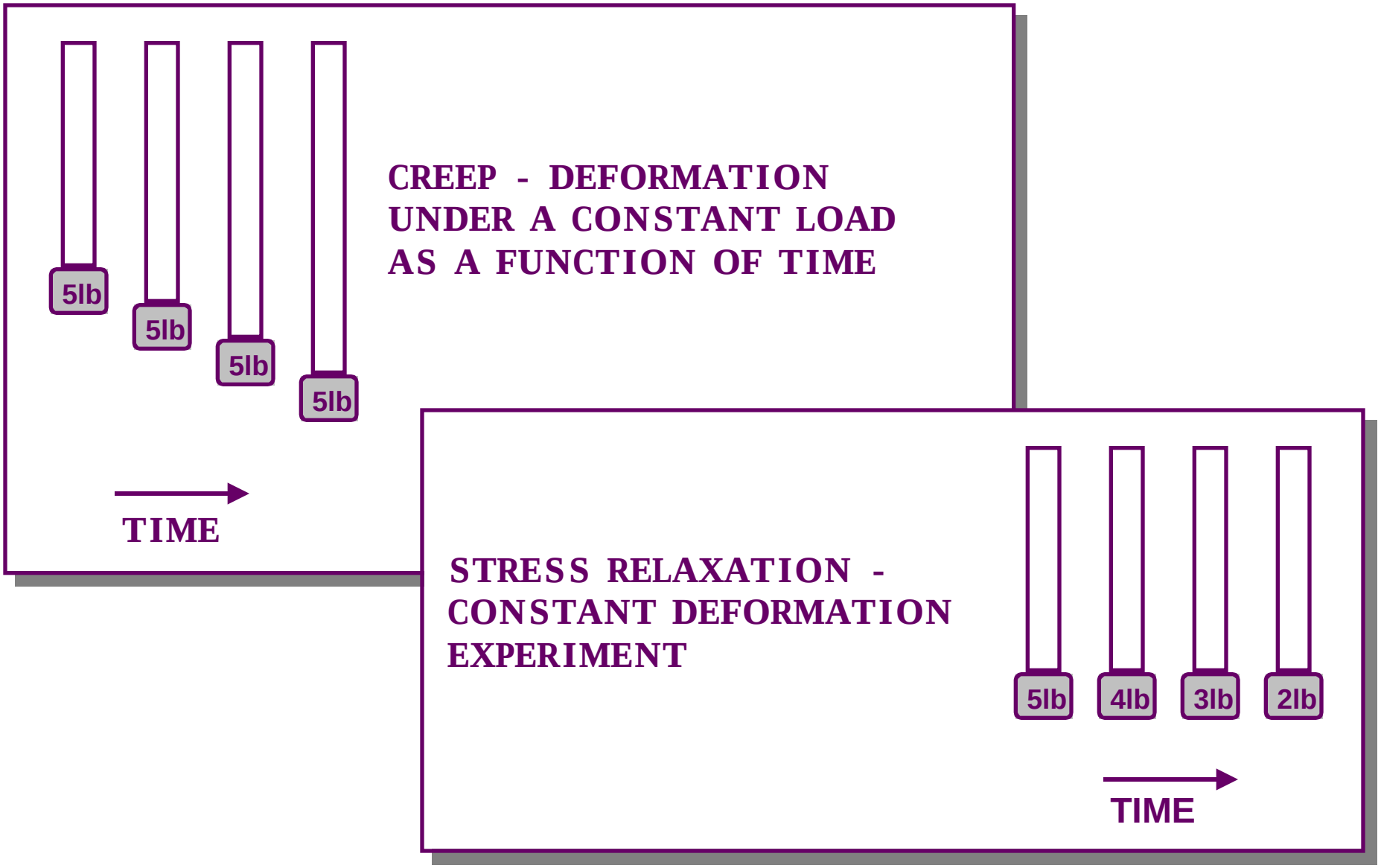
VISCOELASTICITY



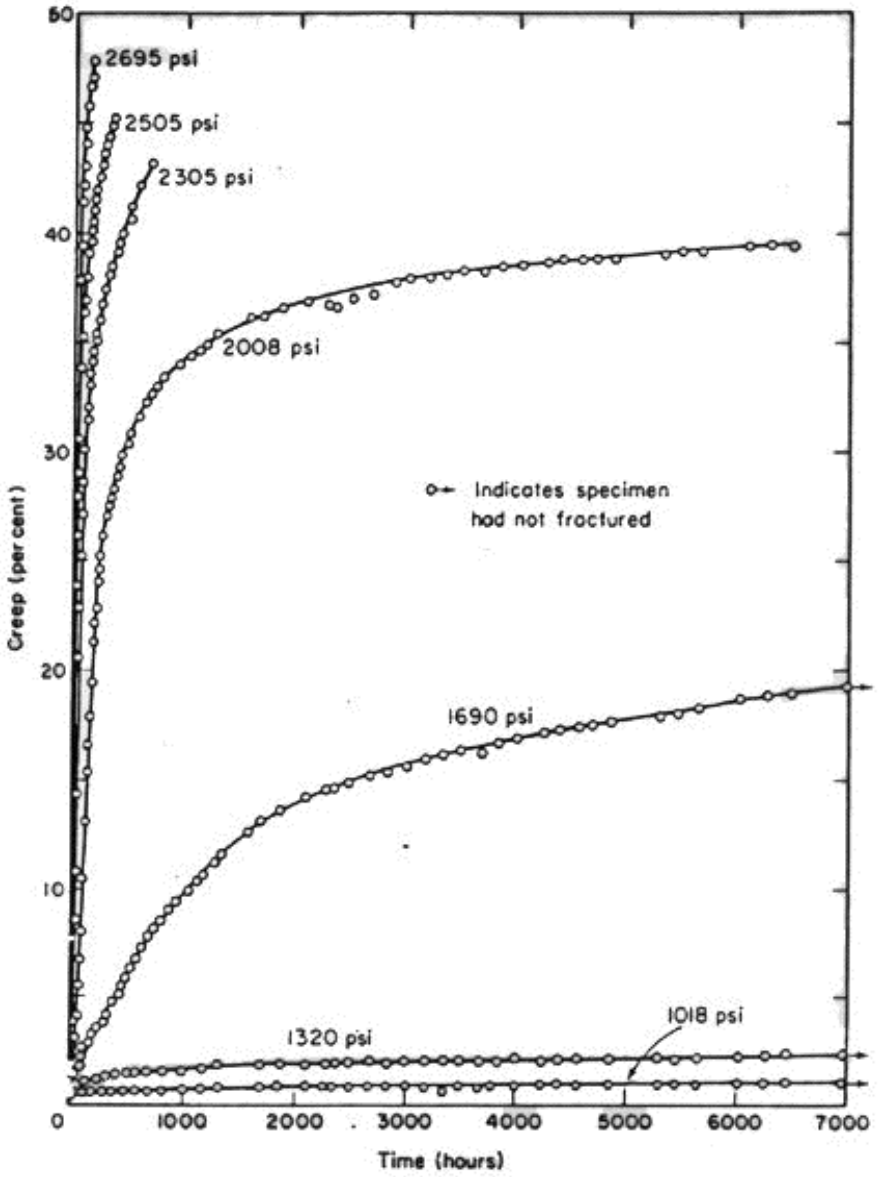
HOMER KNEW THAT THE FIRST THING TO DO ON GETTING YOUR CHARIOT OUT IN THE MORNING WAS TO PUT THE WHEELS BACK ON.
(TELEMACHUS, IN *THE ODYSSEY*, WOULD TIP HIS CHARIOT AGAINST A WALL)

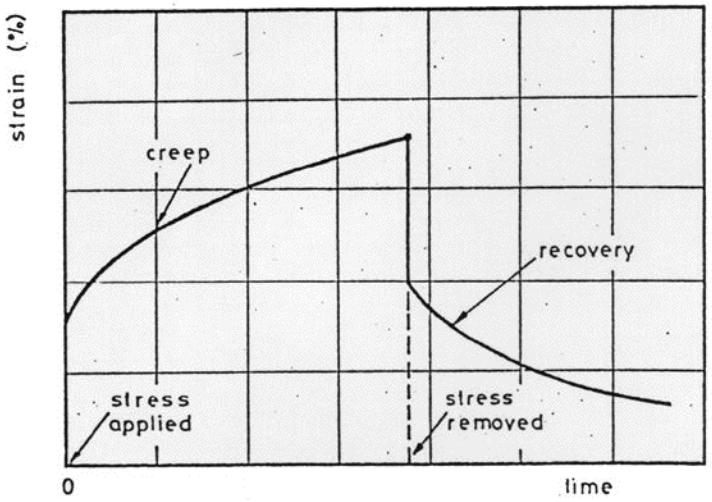
ROBIN HOOD KNEW NEVER TO LEAVE HIS BOW STRUNG

CREEP AND STRESS RELAXATION



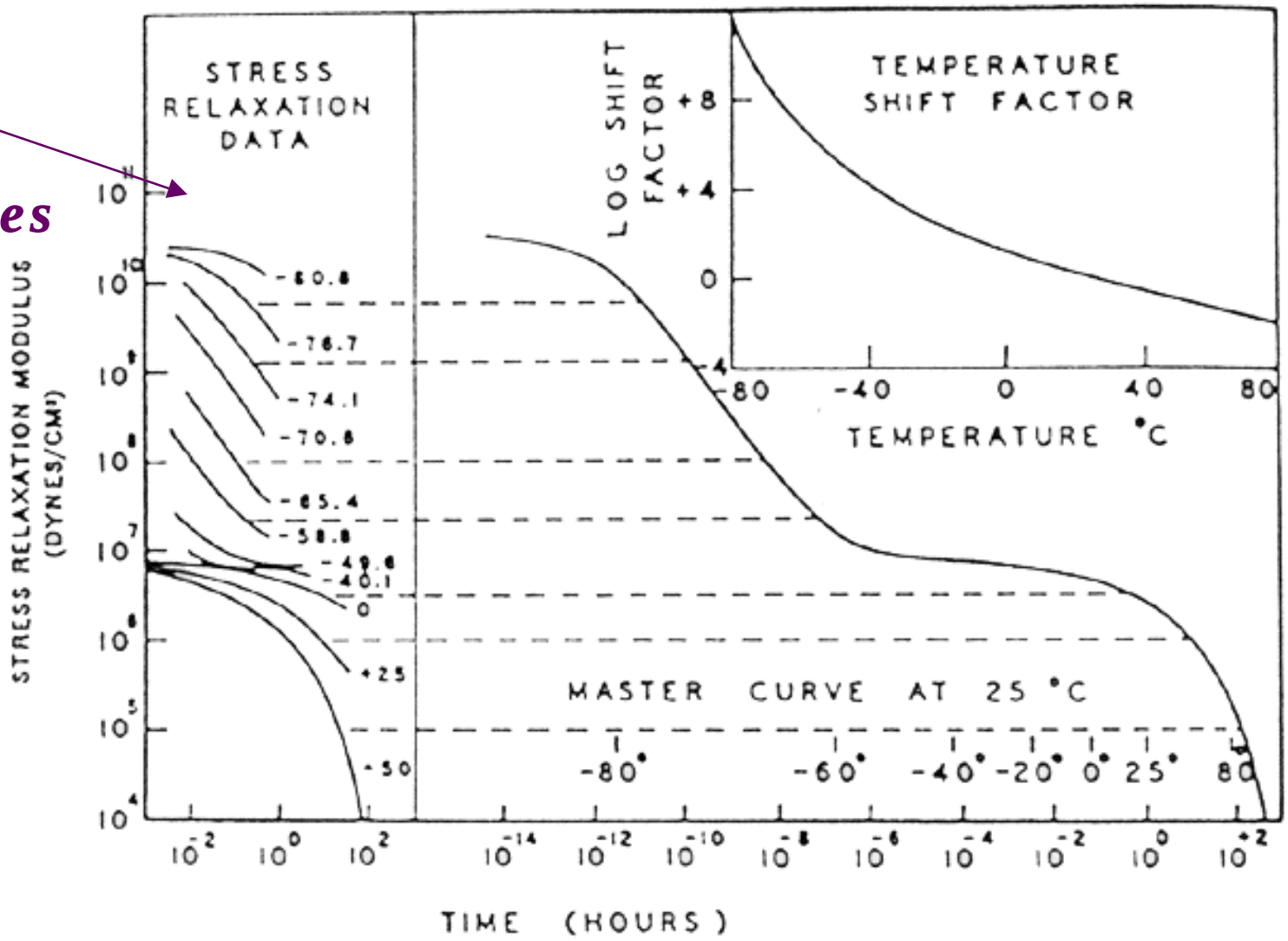
CREEP AND RECOVERY



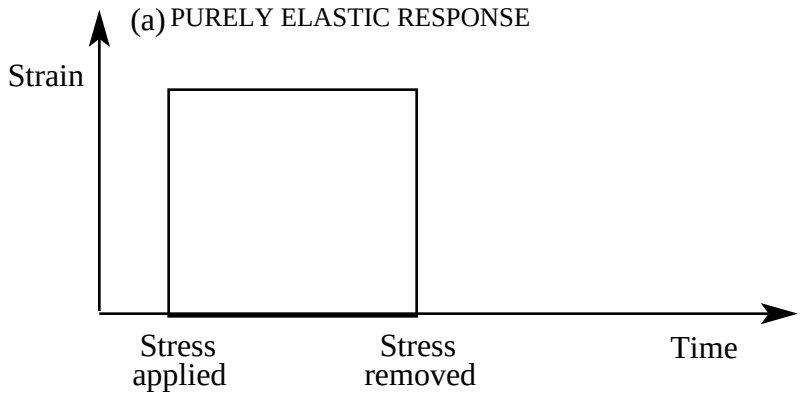


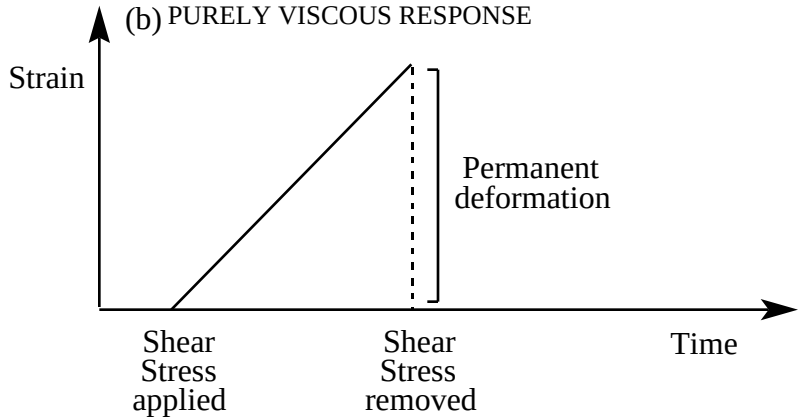
STRESS RELAXATION

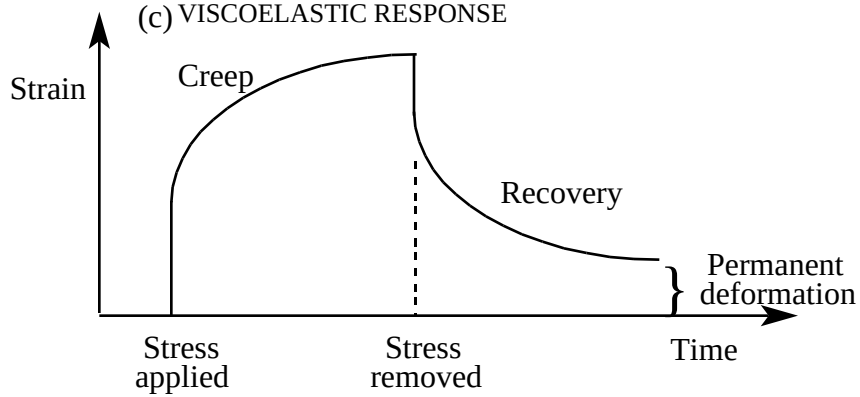
Data;
More on
Master curves
Later !



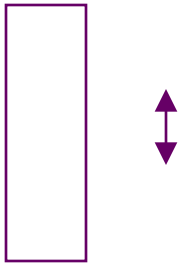
STRAIN vs. TIME PLOTS







DYNAMIC MECHANICAL ANALYSIS



Apply an oscillating tensile
Or shear stress.
Assume we get an oscillating
Strain of the form

$$\gamma = \gamma_0 \sin 2\pi f t = \gamma_0 \sin \omega t$$

Using Hooke's law

$$\tau(t) = G\gamma_0 \sin \omega t$$

ie. FOR A PERFECT ELASTIC SOLID STRESS AND STRAIN ARE EXACTLY IN PHASE

FLUIDS

$$\tau(t) = \eta\dot{\gamma}(t)$$

$$= \eta \frac{d}{dt}\{\gamma_0 \sin \omega t\}$$

$$\tau(t) = \eta\gamma_0 \omega \cos \omega t$$

ie 90^0 out - of - phase

Viscoelastic solid - in-between !

ie a phase angle between $^0_0$ and $^0_{90}$

VISCOELASTIC MATERIALS

Define a phase angle δ *such that*

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

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

Then obtain

$$\tau(t) = (\tau_0 \cos \delta) \sin \omega t + (\tau_0 \sin \delta) \cos \omega t$$

Hence

$$\tau(t) = \gamma_0 [G'(\omega) \sin \omega t + G''(\omega) \cos \omega t]$$

Where

STORAGE MODULUS

$$G'(\omega) = \frac{\tau_0}{\gamma_0} \{\cos \delta\}$$

LOSS MODULUS

$$G''(\omega) = \frac{\tau_0}{\gamma_0} \{\sin \delta\}$$

and

$$\tan \delta = \frac{G''(\omega)}{G'(\omega)}$$

VISCOELASTIC MATERIALS - DMA

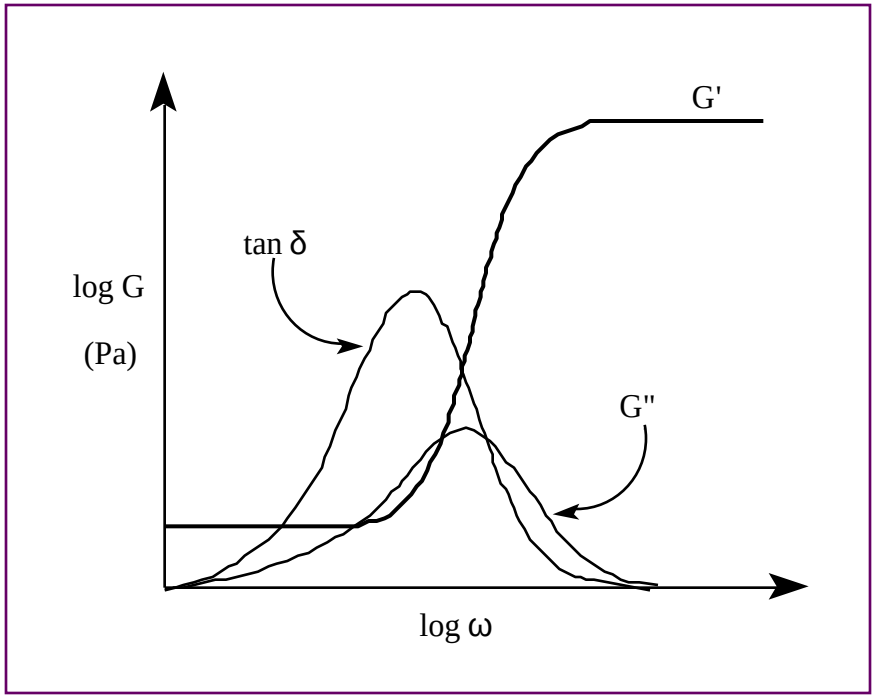
STORAGE MODULUS

$$G'(\omega) = \frac{\tau_0}{\gamma_0}\{\cos\delta\}$$

LOSS MODULUS

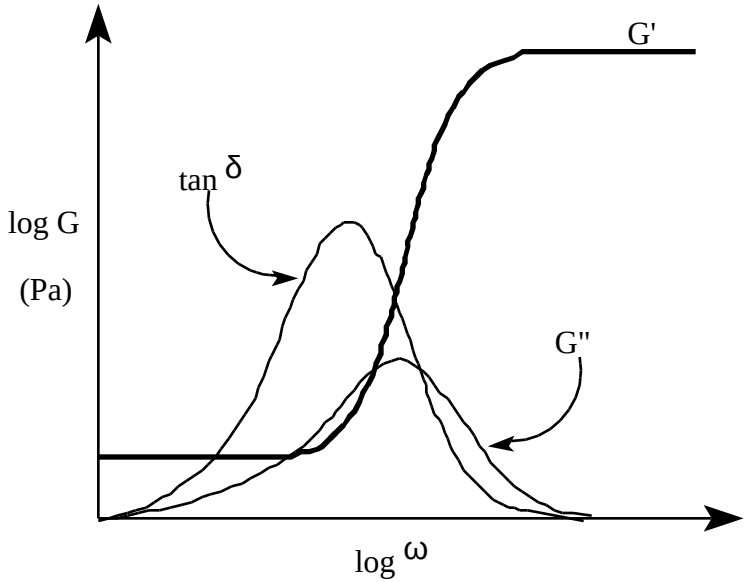
$$G''(\omega) = \frac{\tau_0}{\gamma_0}\{\sin\delta\}$$

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)}$$

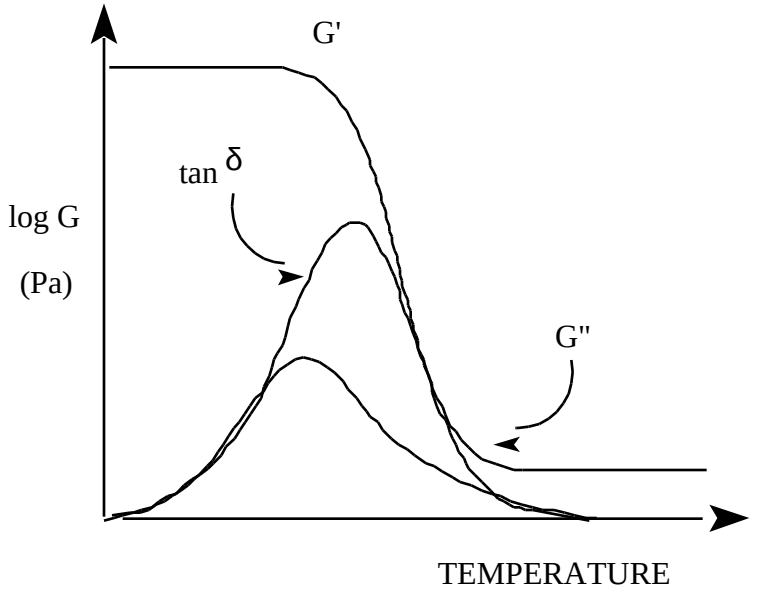


TIME TEMPERATURE EQUIVALENCE

MEASURE AT CONSTANT T



MEASURE AT CONSTANTω



SUMMARY - DMA

- *In Dynamic Mechanical Analysis experiments two moduli Are measured, storage (G'(ω)) and loss (G''(ω)).*

- *We defined a factor* $\tan\delta = \frac{G''(\omega)}{G'(\omega)}$

- *This shows a maximumwhen the storage modulus changes From a value charecteristic of rubbers to one charecteristic Of the glassy state*

- *There is apparently a TIME - TEMPERATURE EQUIVALENCE The results appear simlar if we vary ω at constant T or if We vary T at constant ω*

AMORPHOUS POLYMERS - RANGE OF VISCOELASTIV BEHAVIOUR