UNESCO/IUPAC Postgraduate Course in Polymer Science

Lecture:

Deformation and fracture of polymeric materials

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Macroscopic mechanical behaviour

- **Deformation**

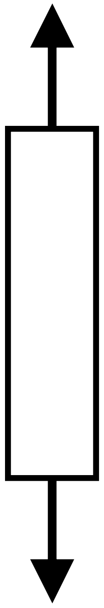
  = change in the shape and/or volume of a material under the action of applied force

- **Fracture (ultimate mechanical behaviour)**

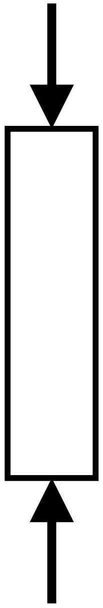
  = local separation of a material into 2 or more pieces under the action of applied force

Deformation

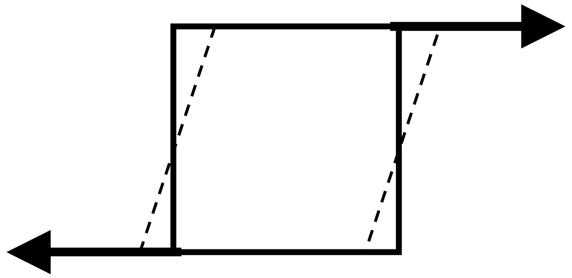
Whenewer a **force** is exerted on a solid material, the material will **deform** in response to the force.



- Tensile force



- Compressive force



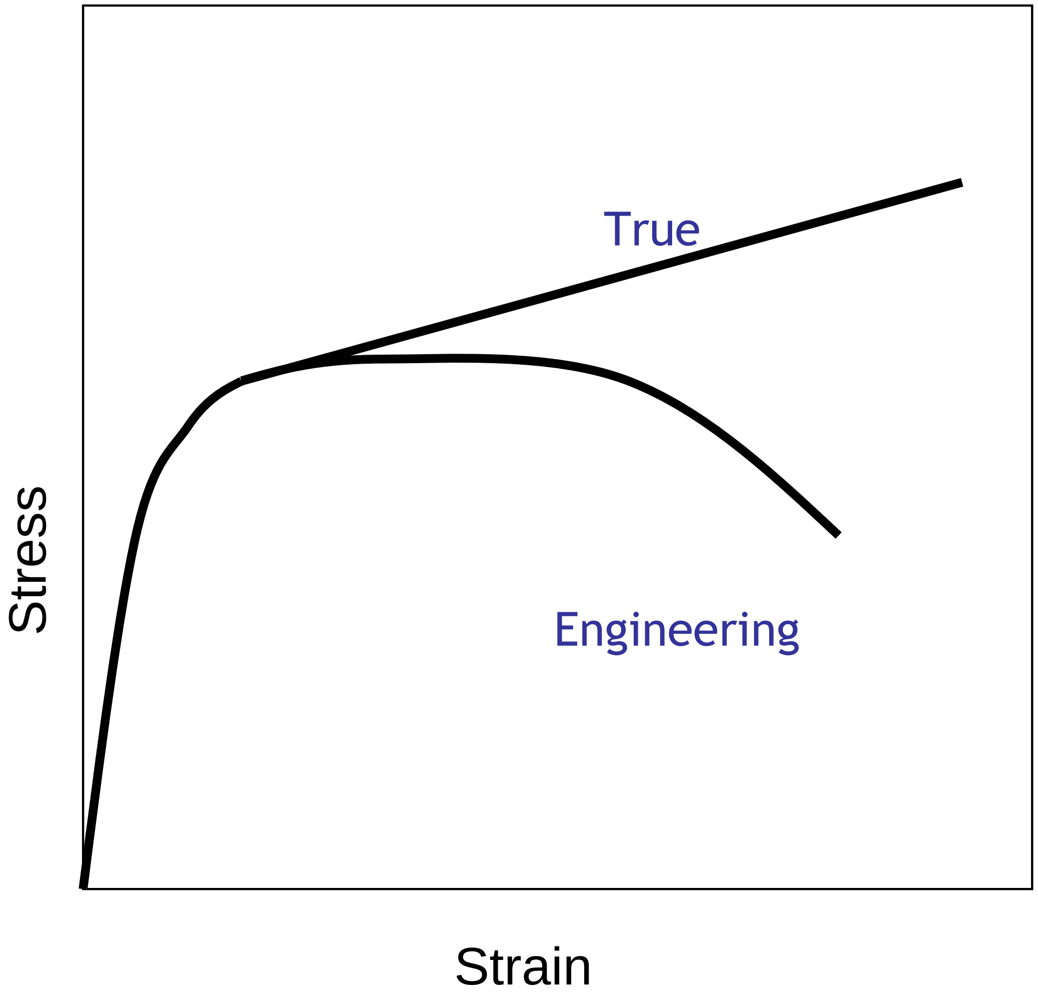
- Shear force

Deformation - stress and strain

- Engineering

$$\sigma[MPa]=\frac{F[N]}{A_0[mm^2]}$$

$$\varepsilon[-]=\frac{l-l_0}{l_0}$$

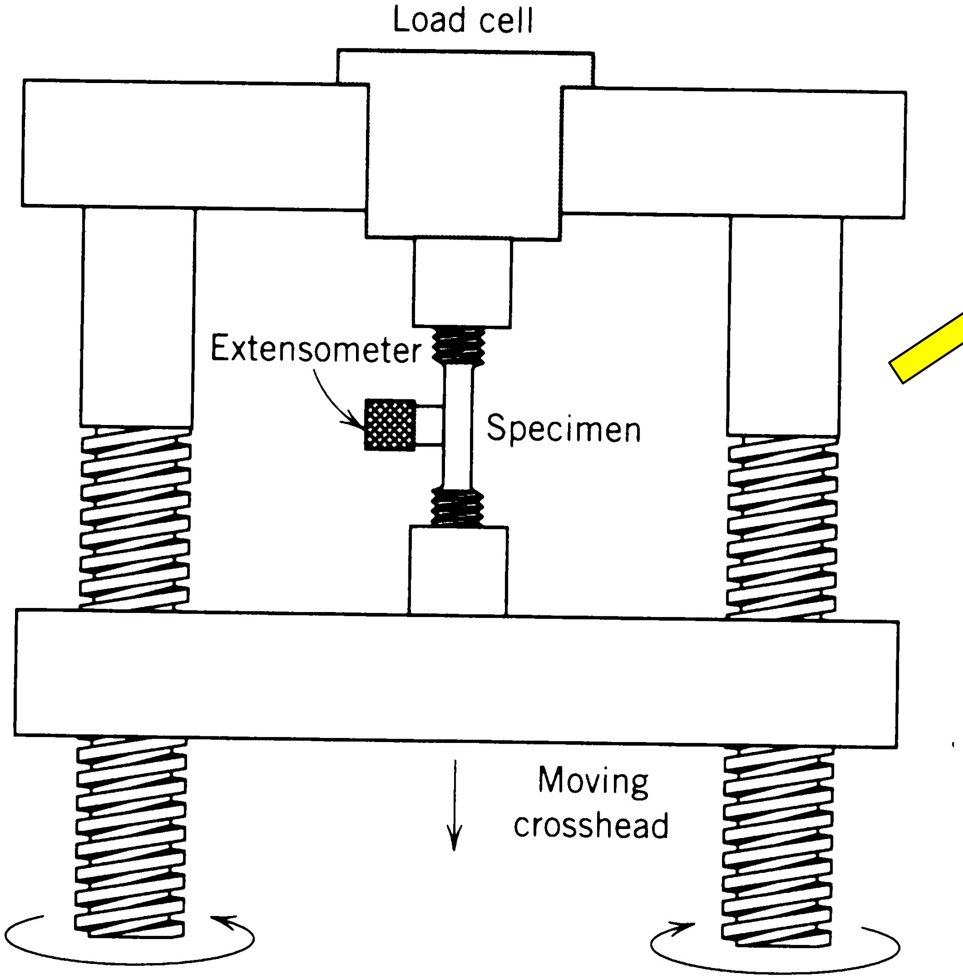


- True

$$\sigma_T[MPa]=\frac{F[N]}{A_i[mm^2]}$$

$$\varepsilon_T[-]=\ln\left(\frac{l_i}{l_0}\right)$$

Experimental supplement – tensile testing



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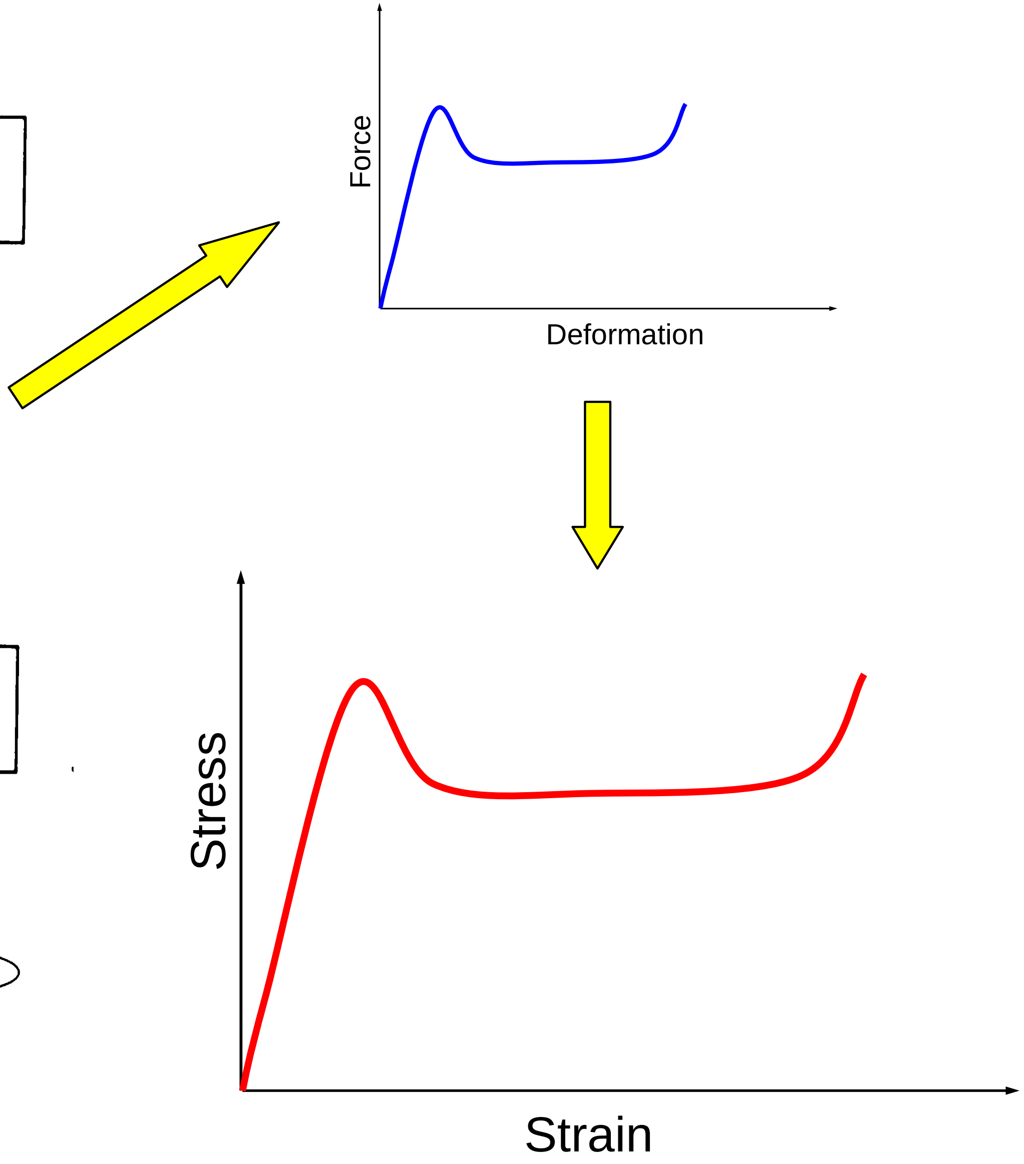
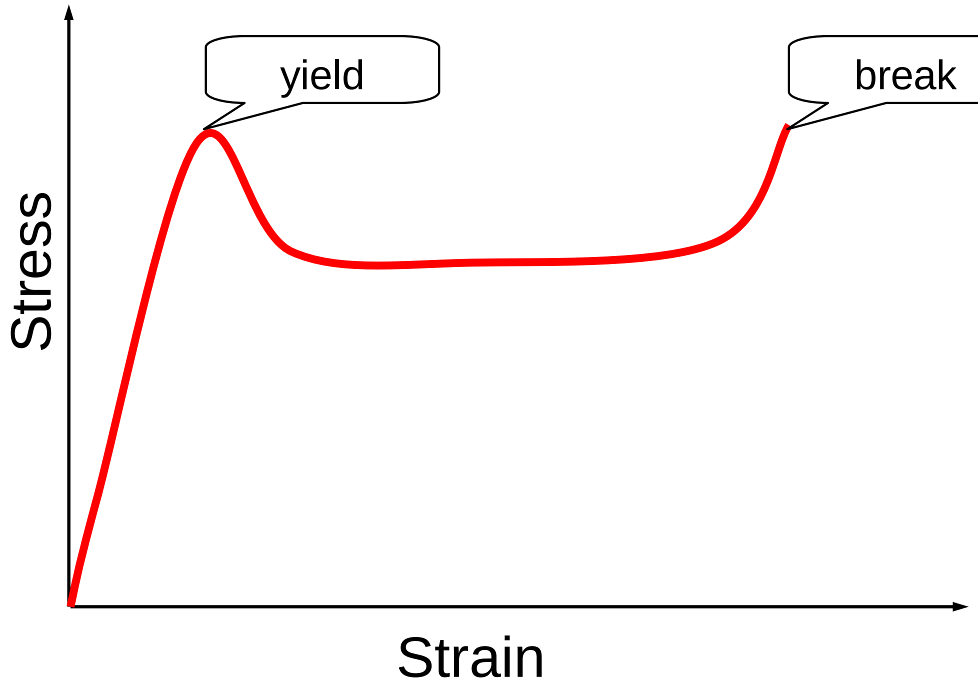


Experimental supplement – tensile testing



TENSION STRENGTH σ_M **-** the maximum tensile stress sustained by the specimen during a test (TS at yield, TS at break)

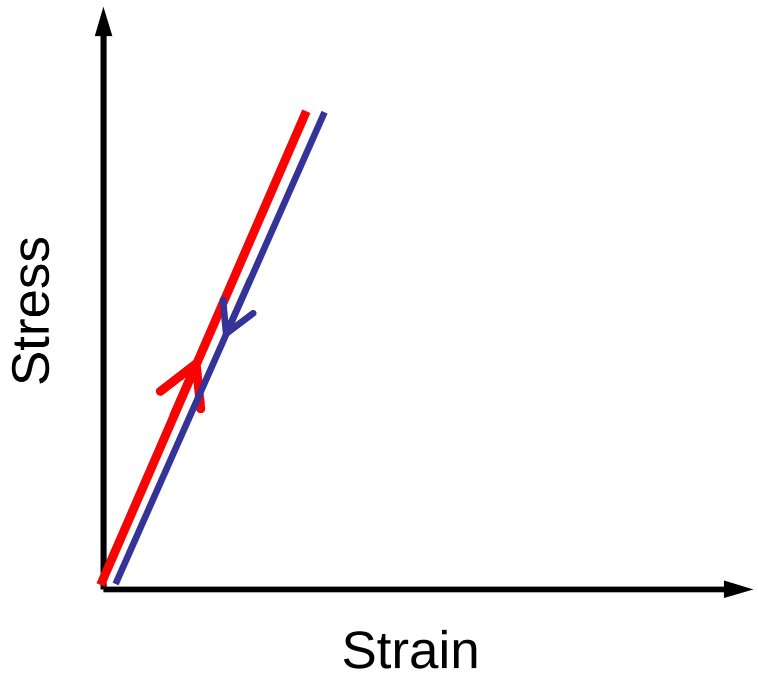
YIELD STRESS σ_y, YIELD STRAIN ε_y - (*YIELD POINT – the first point on the stress-strain curve at which an increase in strain occurs without an increase in stress)*

STRESS AT BREAK σ_b, STRAIN AT BREAK ε_b

MODULUS OF ELASTICITY (YOUNG MODULUS) E – stiffness, ≈ slope of the stress-strain curve in the elastic region

Elasticity (linear)

- At low strains for all materials



Hooke's law

$$E = \frac{\sigma}{\varepsilon}\left[MPa\right]$$

$$G = \frac{\tau}{\gamma}\left[MPa\right]$$

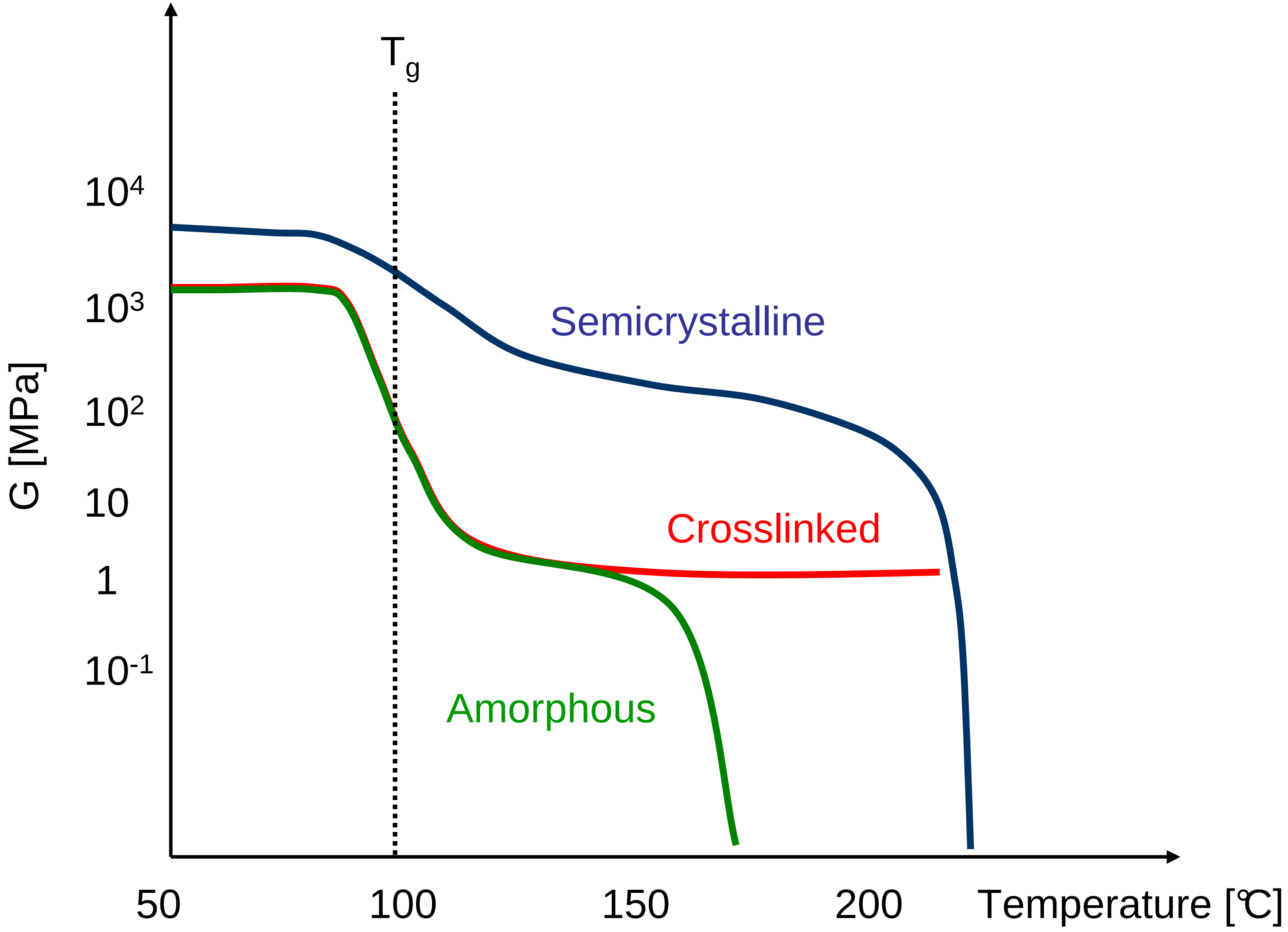
$$E = 2G(1+\nu)$$

Straightening of molecular chains

Deformation of bonds between chains

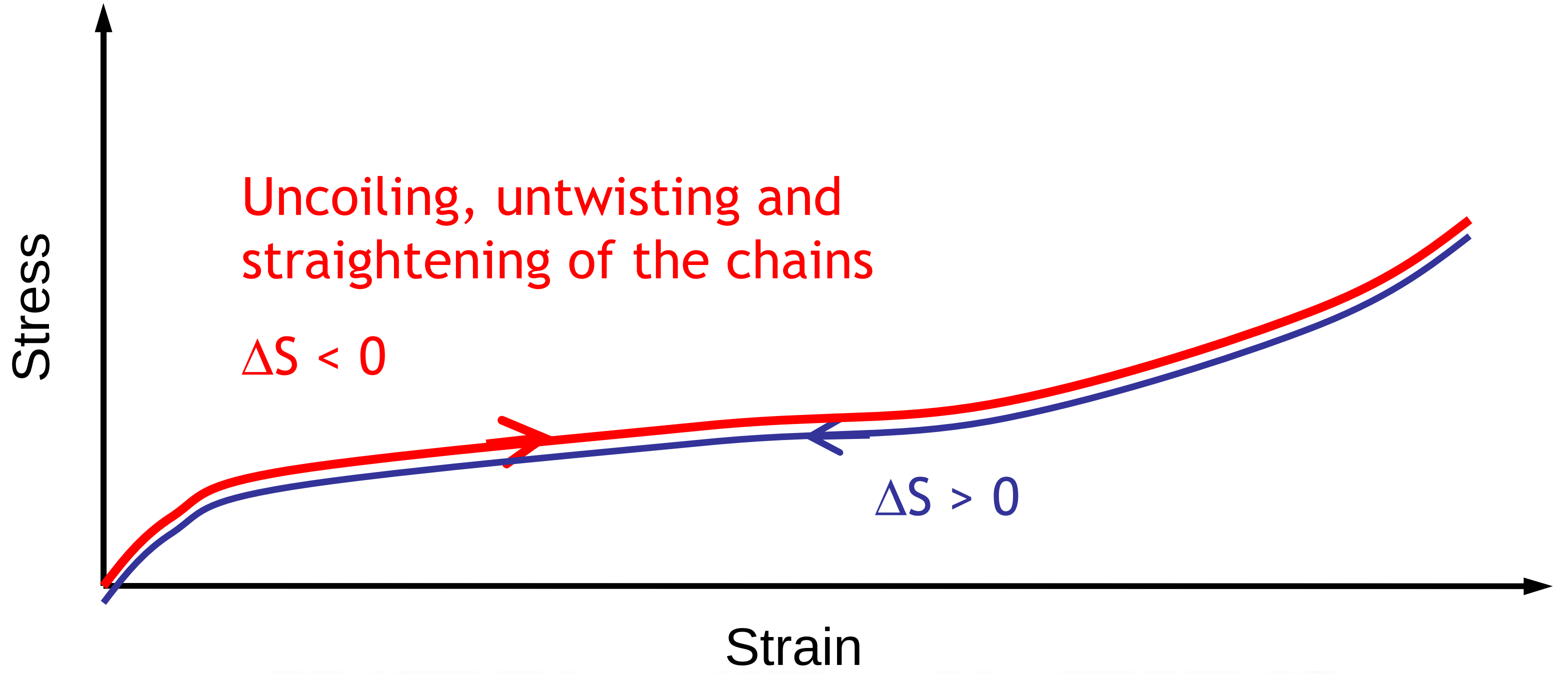
Temperature dependence of modulus

Ex. PS



Elasticity (non-linear)

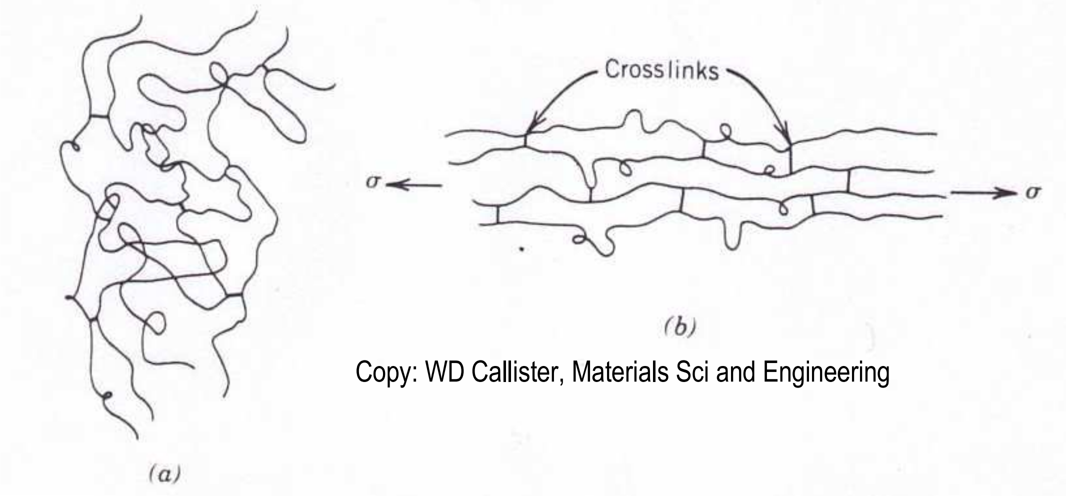
- At low stresses (but large deformations) for elastomers *(rubber elasticity)*



Uncoiling, untwisting and straightening of the chains

$\Delta S < 0$

$\Delta S > 0$



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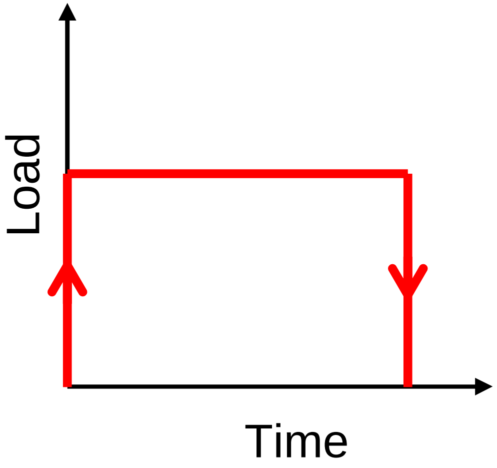
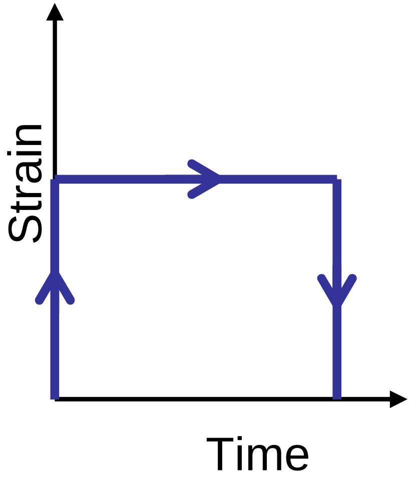
Viscoelasticity

- Load application

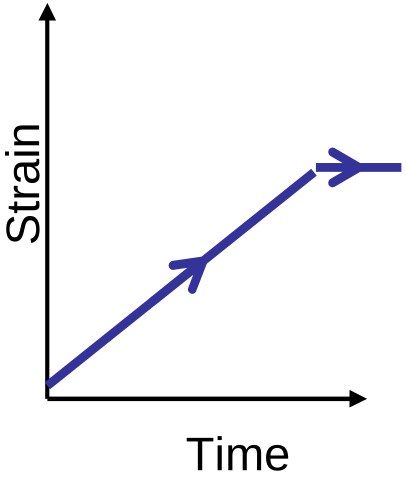


- Mechanical response (Deformation)

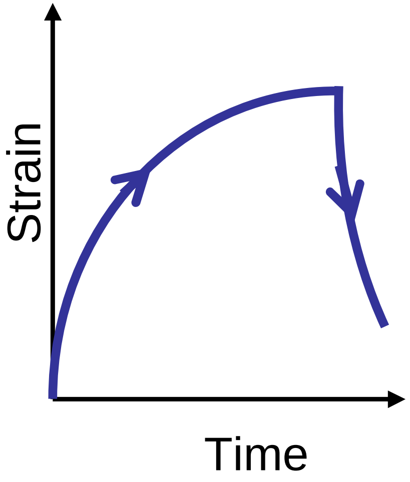
- Solids - Elastic behaviour



- Liquids – Viscous flow



- Polymers – Viscoelastic behaviour



Viscoelasticity (linear)

Creep - deformation of a material over time due to the application of a constant load

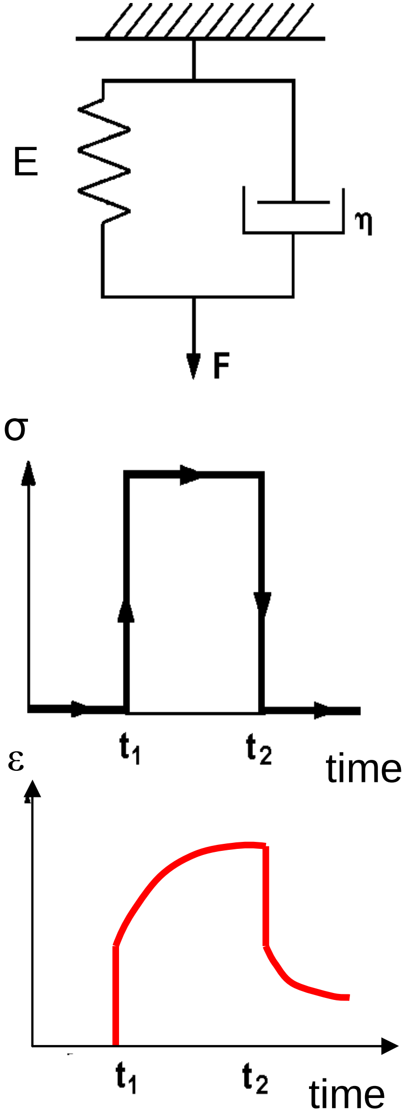
$$J(t) = \frac{\varepsilon(t)}{\sigma_0} \qquad E_c(t) = \frac{\sigma_0}{\varepsilon(t)}$$

Relaxation – stress relaxation over time in a material deformed at a constant strain

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

Viscoelasticity - Kelvin (Voight) model

Creep



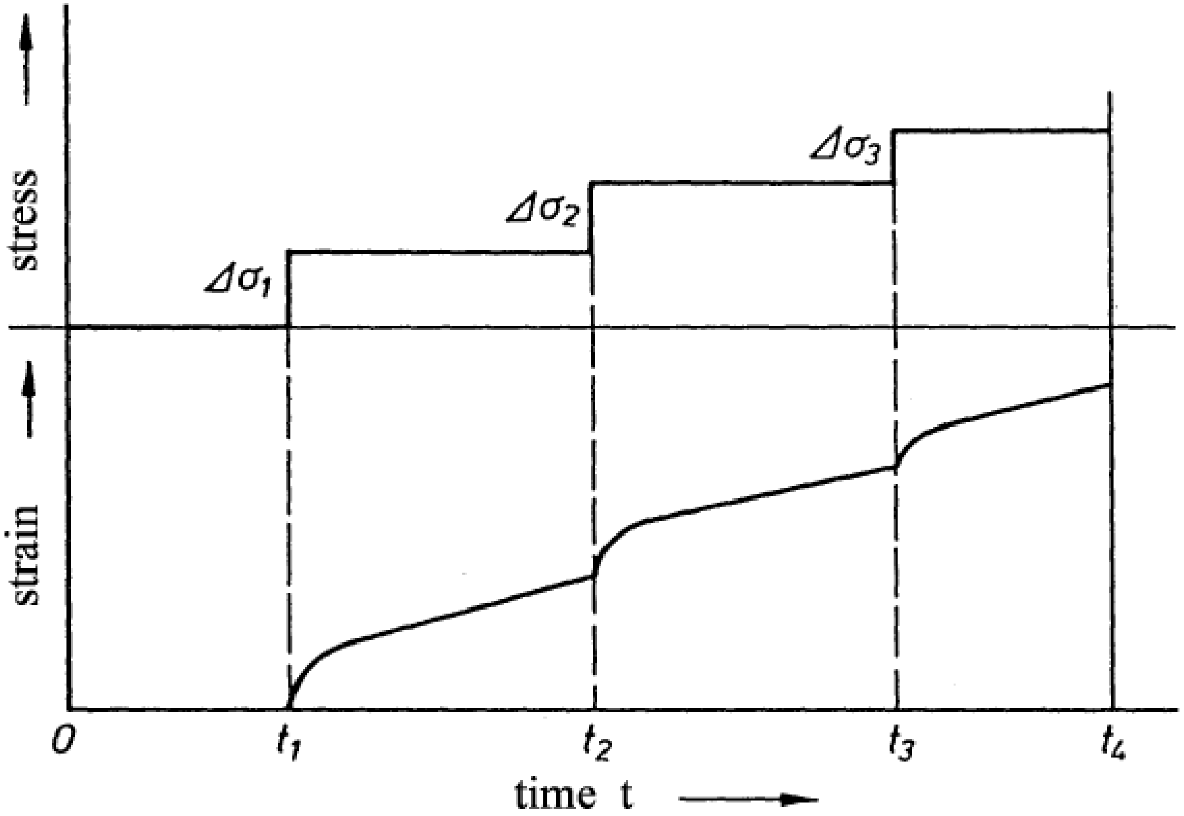
$$\varepsilon(t)=\frac{\sigma}{E}\left[1-\exp\left(-\frac{E\cdot t}{\eta}\right)\right]$$

Viscoelasticity – Boltzmann superposition principle

Creep is a function of the entire past loading of the material

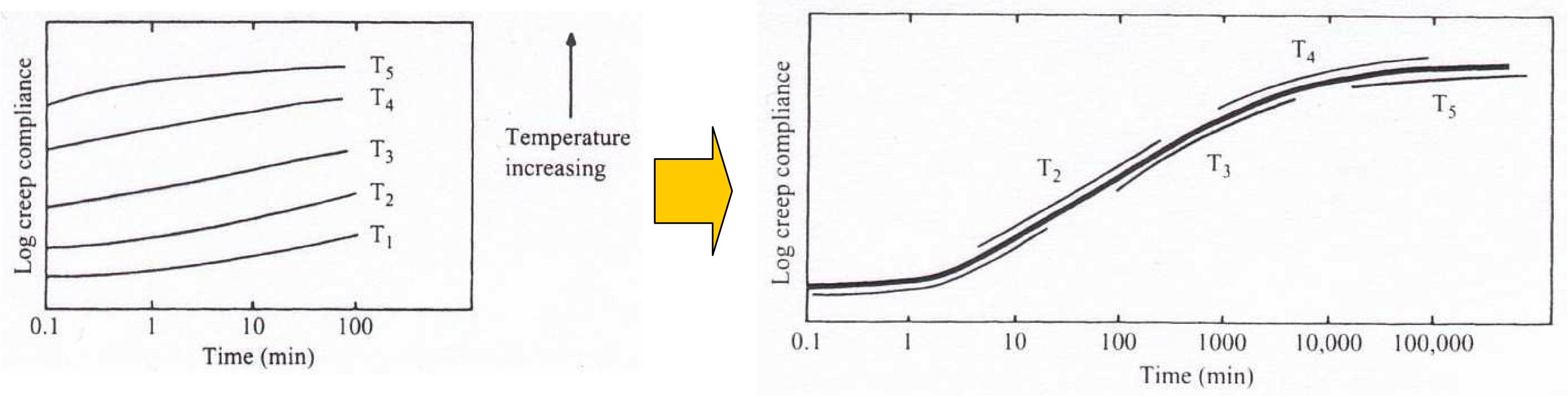
Each loading step makes an independent contribution to the final deformation – the total deformation can be obtained by addition of all the contributions

$$\varepsilon(t)=\varepsilon_1(t)+\varepsilon_2(t)+\ldots=\Delta\sigma_1 J(t-t_1)+\Delta\sigma_2 J(t-t_2)+\ldots$$
$$=\sum\Delta\sigma_i J(t-t_i)$$



Viscoelasticity - Time/Temperature superposition

Viscoelastic behaviour at one temperature can be related to that at another temperature by a change in the time-scale

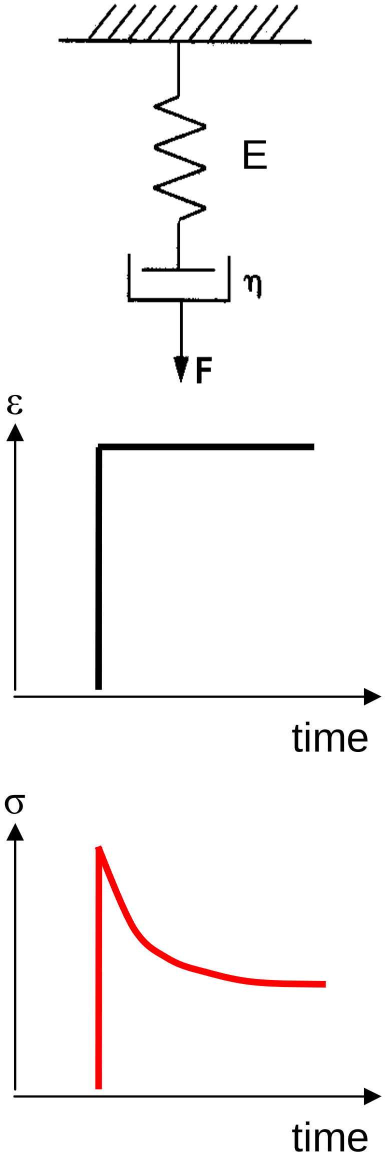


Copy: IM Ward, Mech. Props of Solid Polymers

Shift factor a_T : WLF (Williams, Landel, Ferry) Eq., Arhennius Eq.

Viscoelasticity - Maxwell model

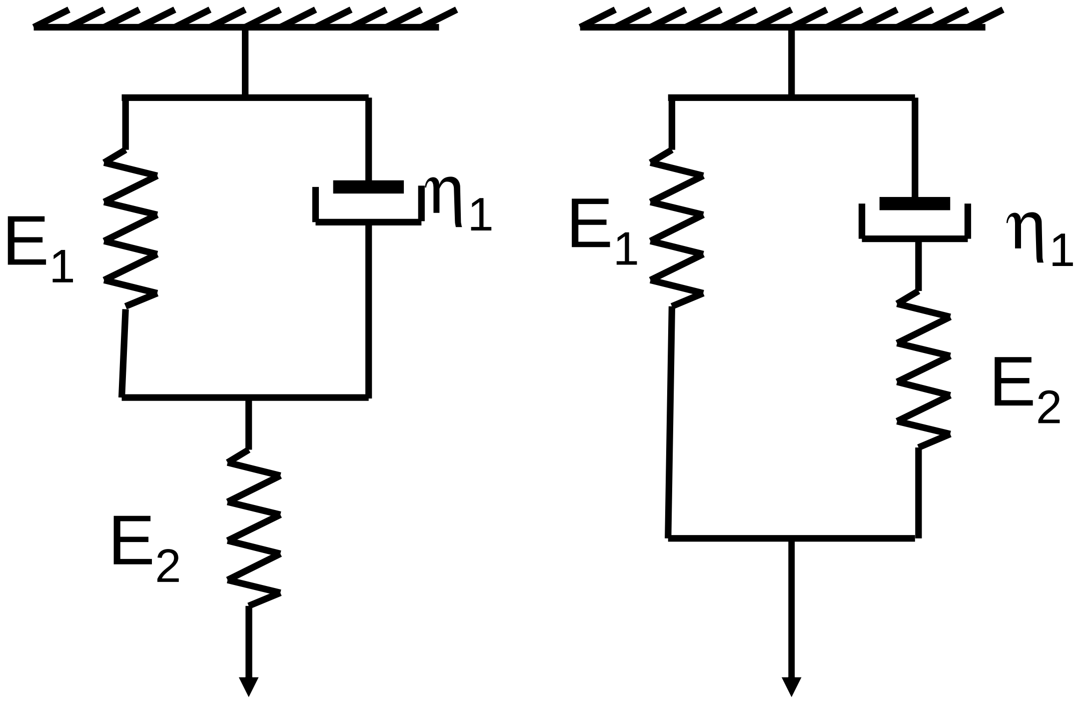
Relaxation



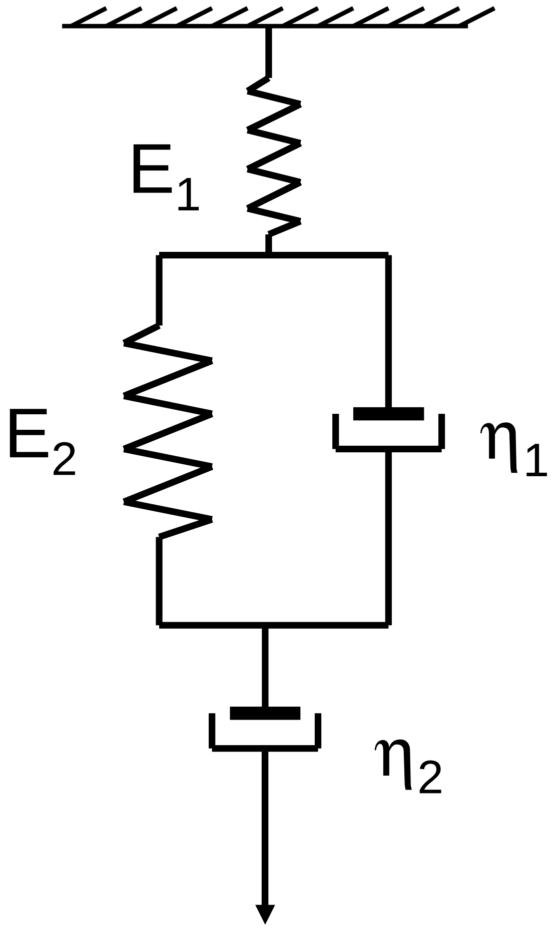
$$\sigma(t) = \sigma_0 \exp\left(-\frac{E.t}{\eta}\right)$$

Viscoelasticity - Multi-element models

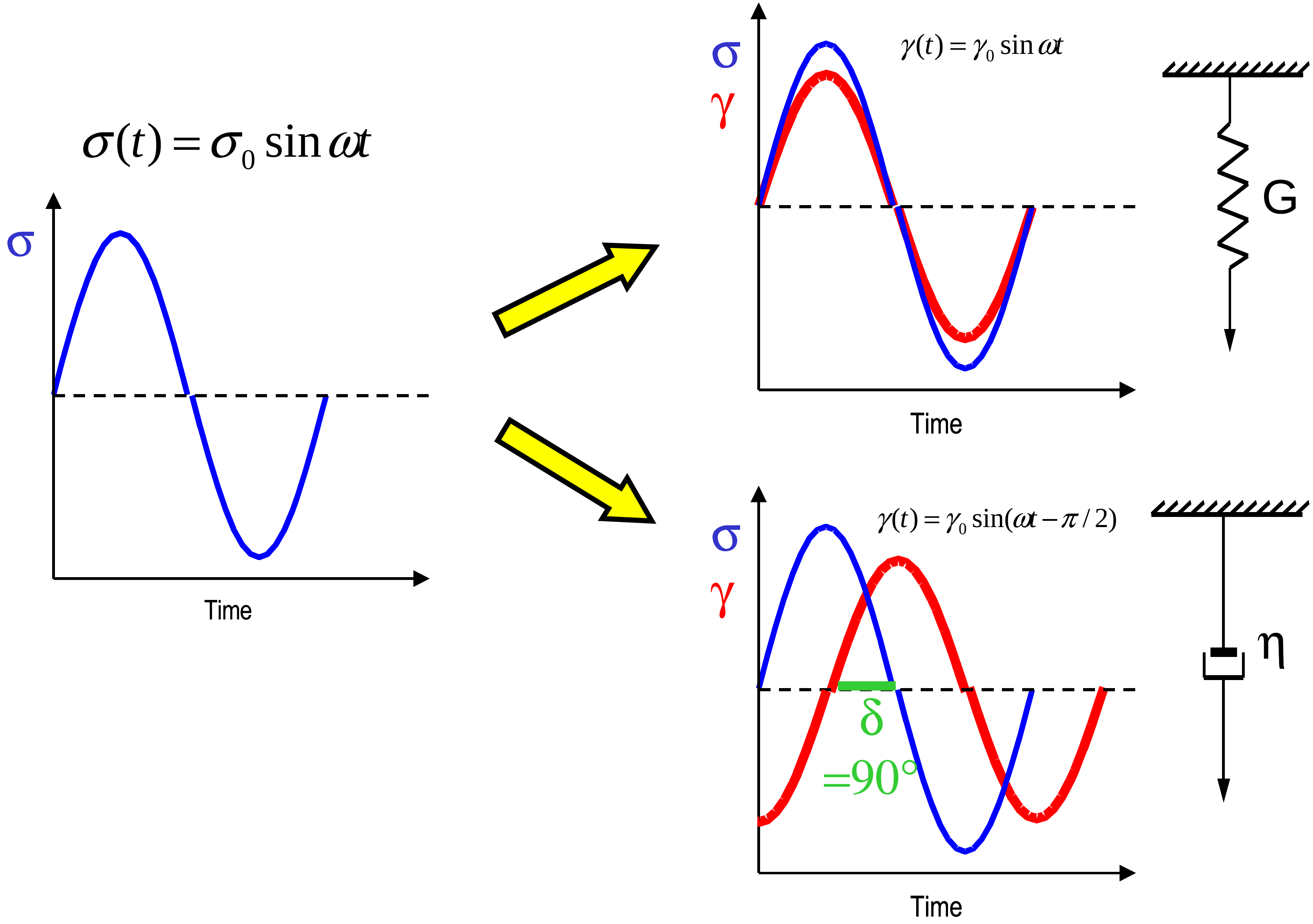
Zener



Tucket



Viscoelasticity - dynamic mechanical measurements



$$\sigma(t) = \sigma_0 \sin \omega t$$

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

$$\gamma(t) = \gamma_0 \sin(\omega t - \pi / 2)$$

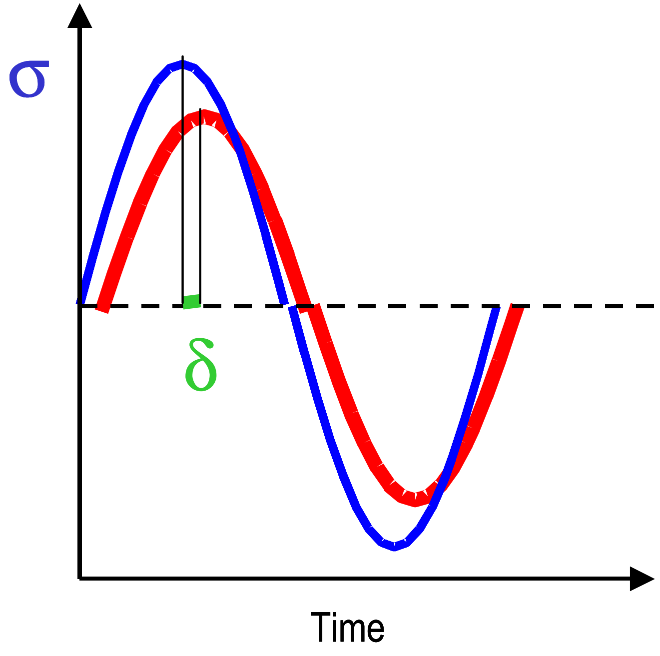
Viscoelasticity - dynamic mechanical measurements

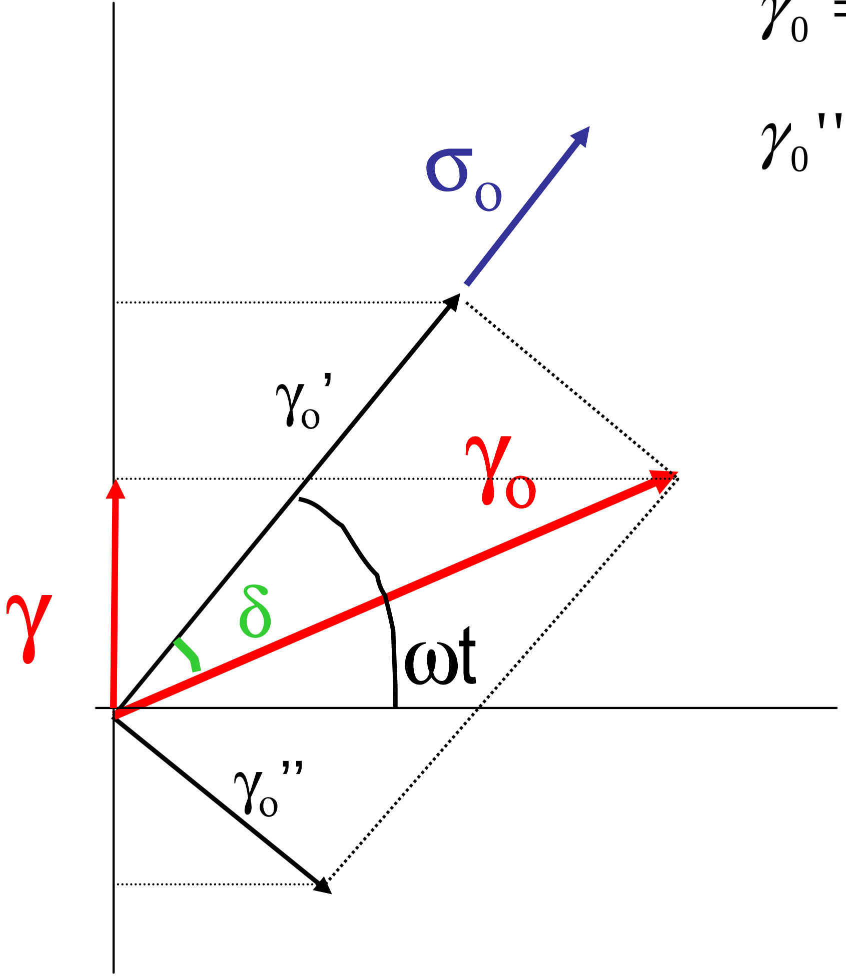
$$\sigma(t) = \sigma_0 \sin \omega t$$

$$\gamma(t) = \gamma_0 \sin(\omega t - \delta) = \gamma_0 ' \sin \omega t - \gamma_0 '' \cos \omega t$$

$$\gamma_0 ' = \gamma_0 \sin \delta$$

$$\gamma_0 '' = \gamma_0 \cos \delta$$

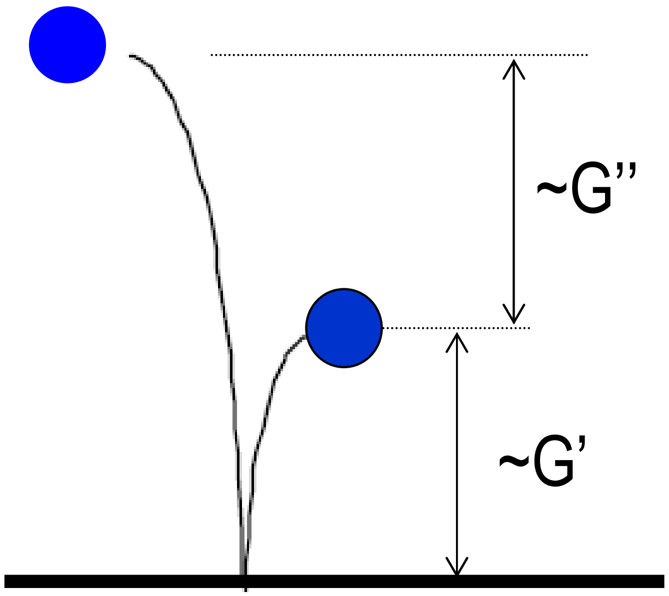




Viscoelasticity - dynamic mechanical measurements

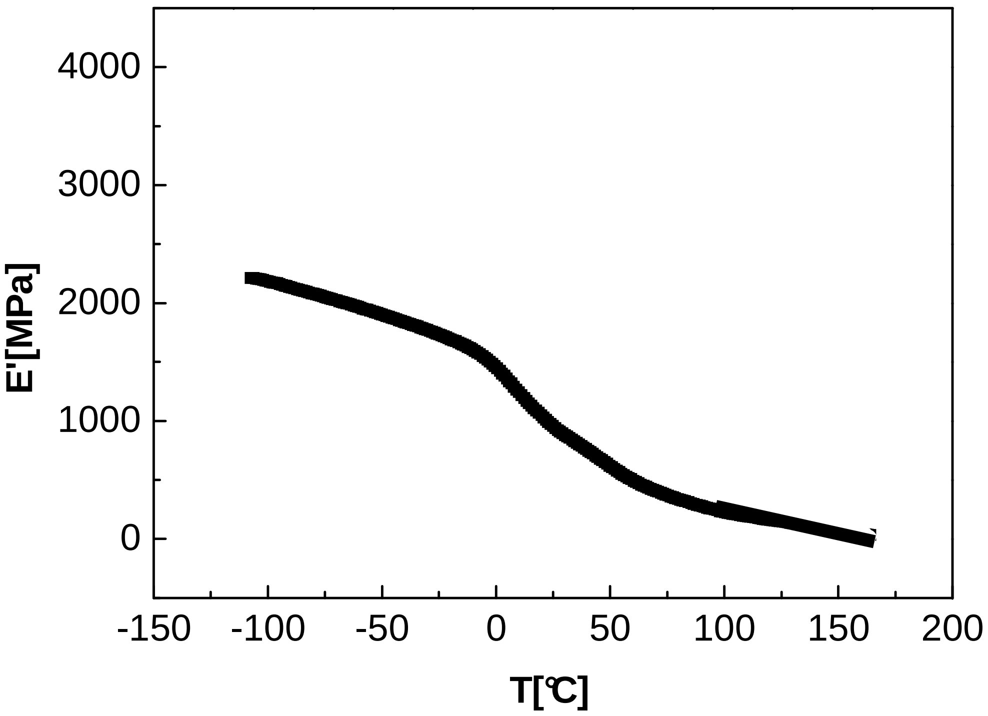
Complex modulus $$G^* = G' + iG''$$

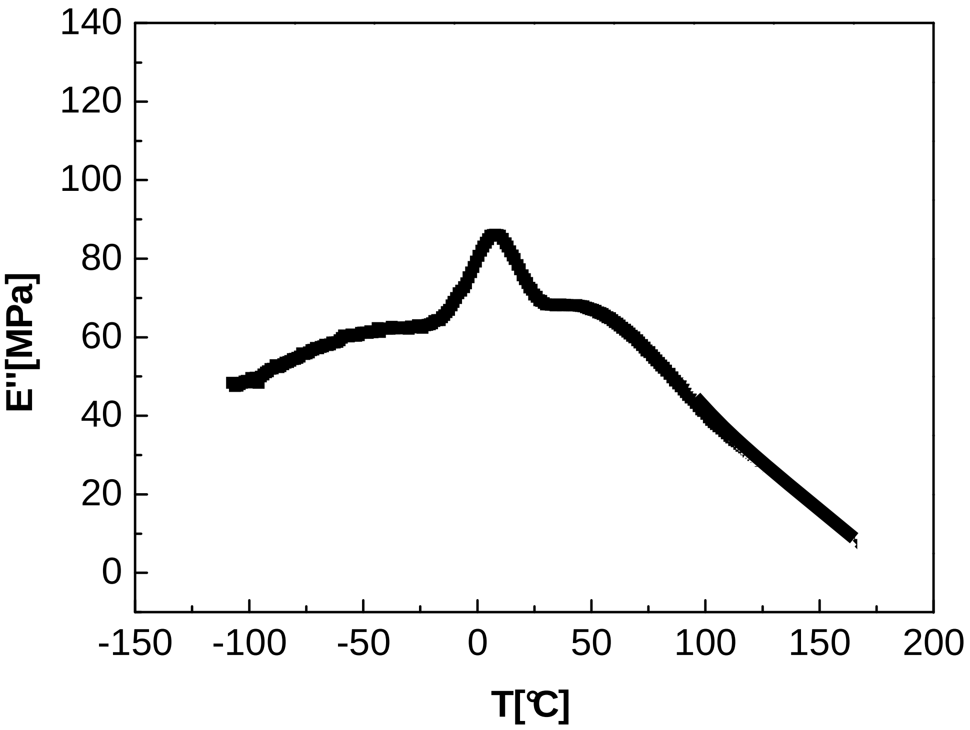
Loss factor $$\tan\delta = \frac{G''}{G'}$$



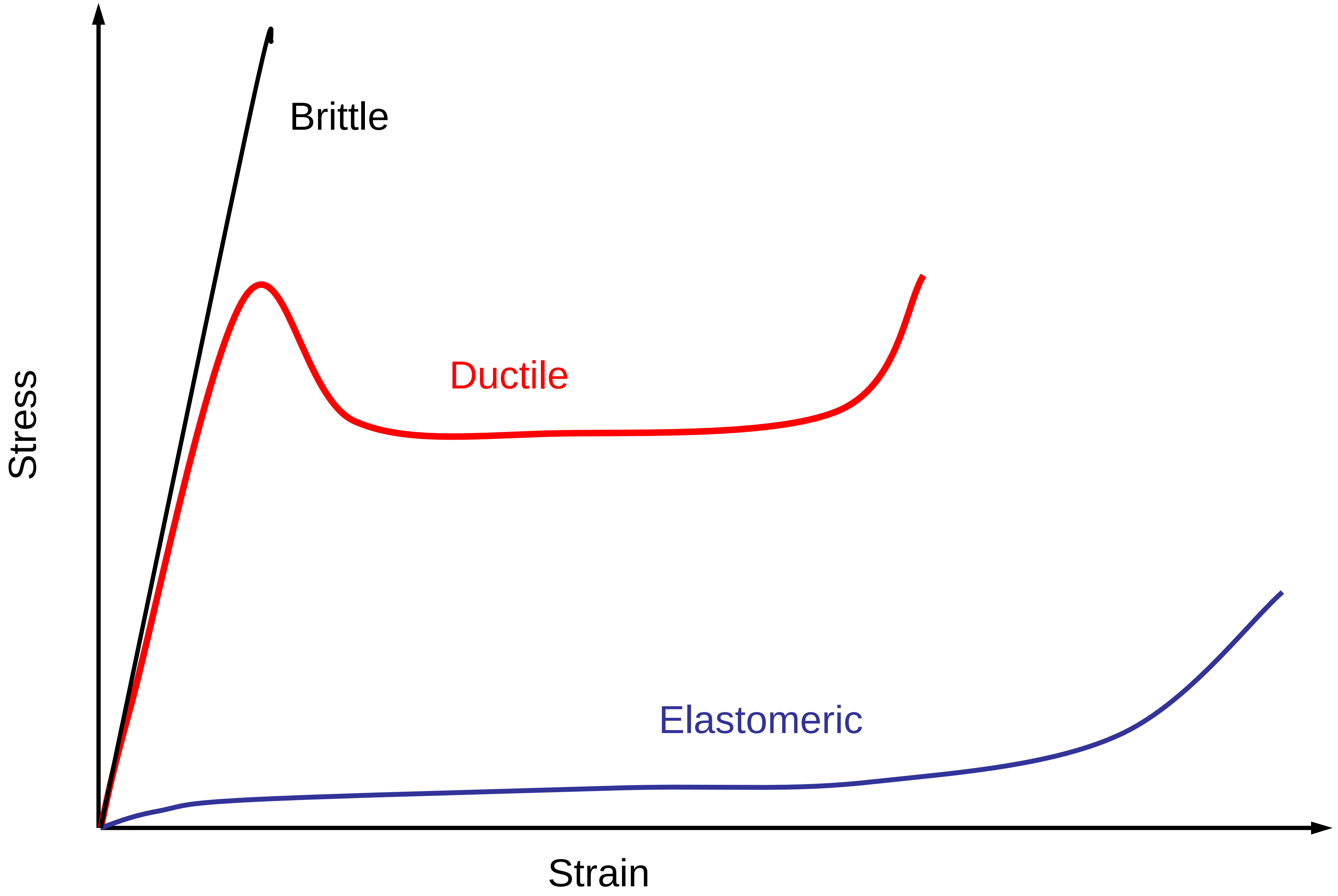
Viscoelasticity – dynamic mechanical measurements

Ex. PP





High strain behaviour and failure



Plasticity - high strain behaviour

- Viscoelasticity – changes in macromolecules’ conformations
- Plasticity – large, permatent morphological changes (chain orientation, lamelar → fibrillar morphology)

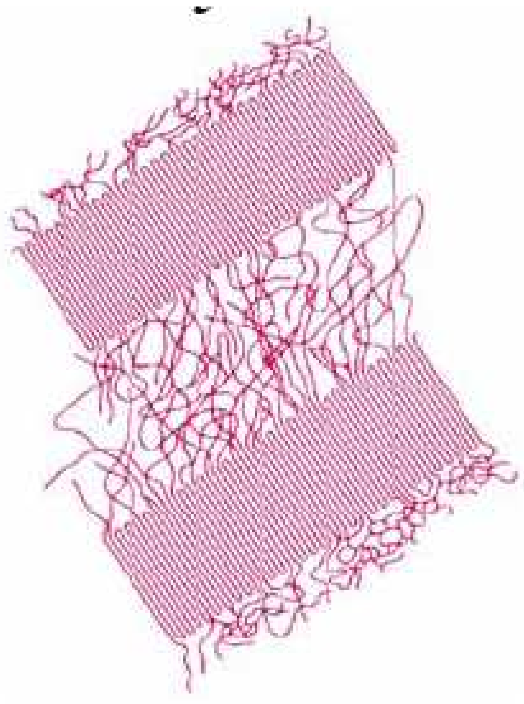
AMORPHOUS POLYMERS

- above T_g
- Chain stretching, rotating, disentagling, sliding

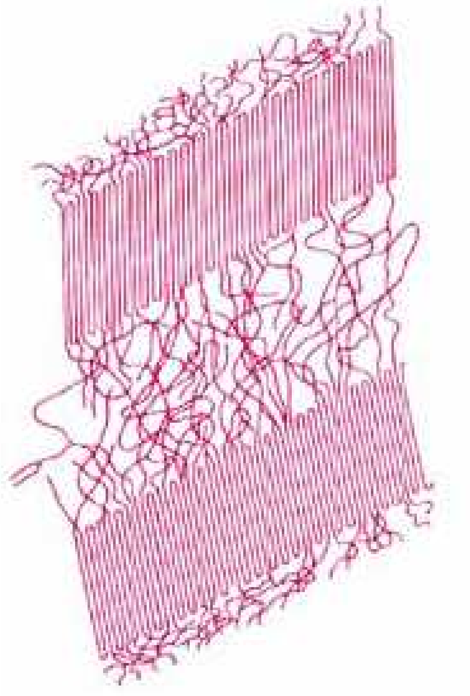
Plasticity - high strain behaviour

SEMICRYSTALLINE POLYMERS

1. Two adjacent chain-folded lamellae and interlamellar amorphous material before deformation



2. Elongation of amorphous tie chains during the first stage of deformation



3. Tilting of lamellar chain folds during the second stage

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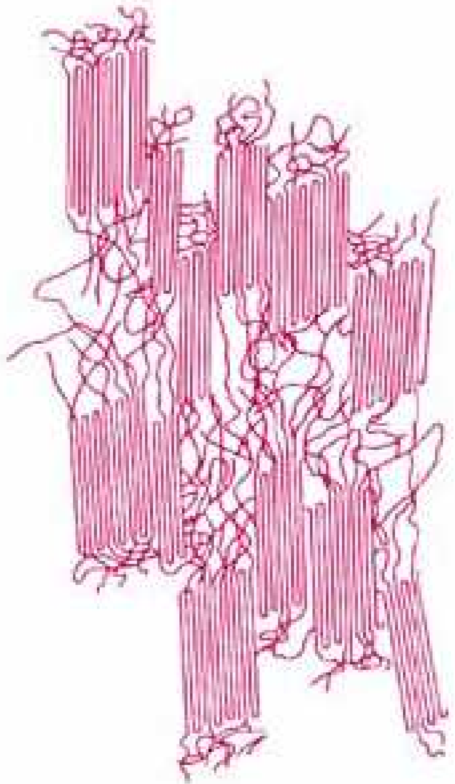
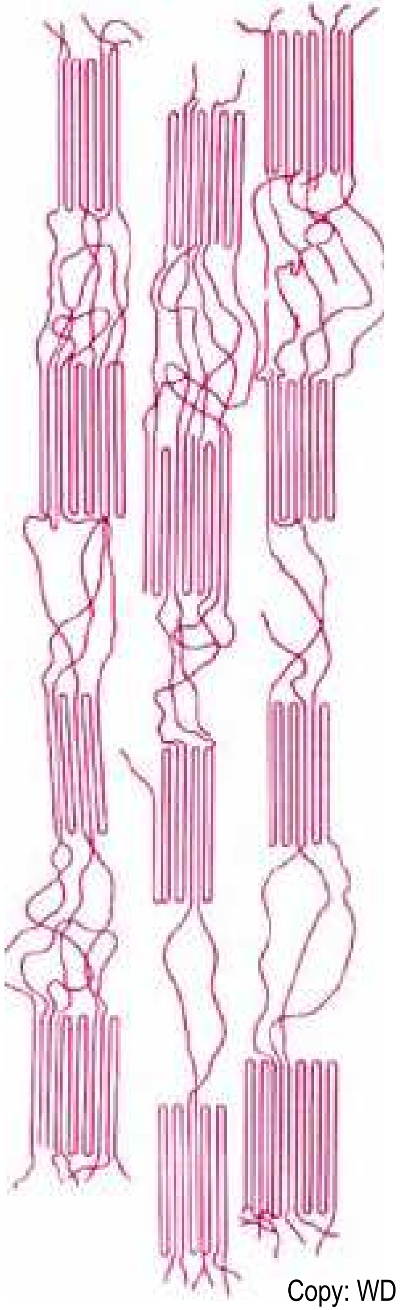
Plasticity - high strain behaviour

SEMICRYSTALLINE POLYMERS



4. Separation of crystalline block segments during the third stage



5. Orientation of block segments and tie chains with tensile axis in final deformation stage

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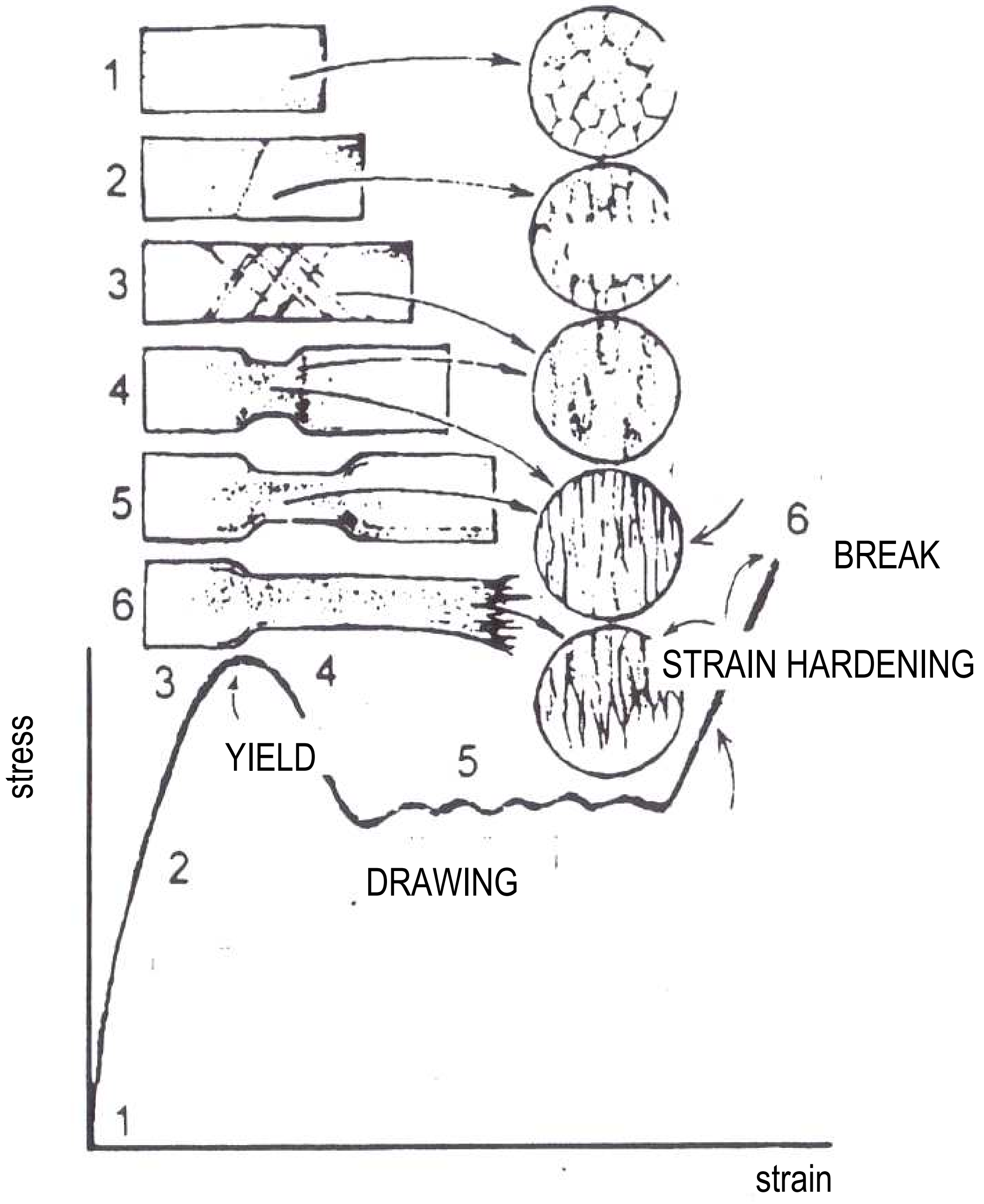
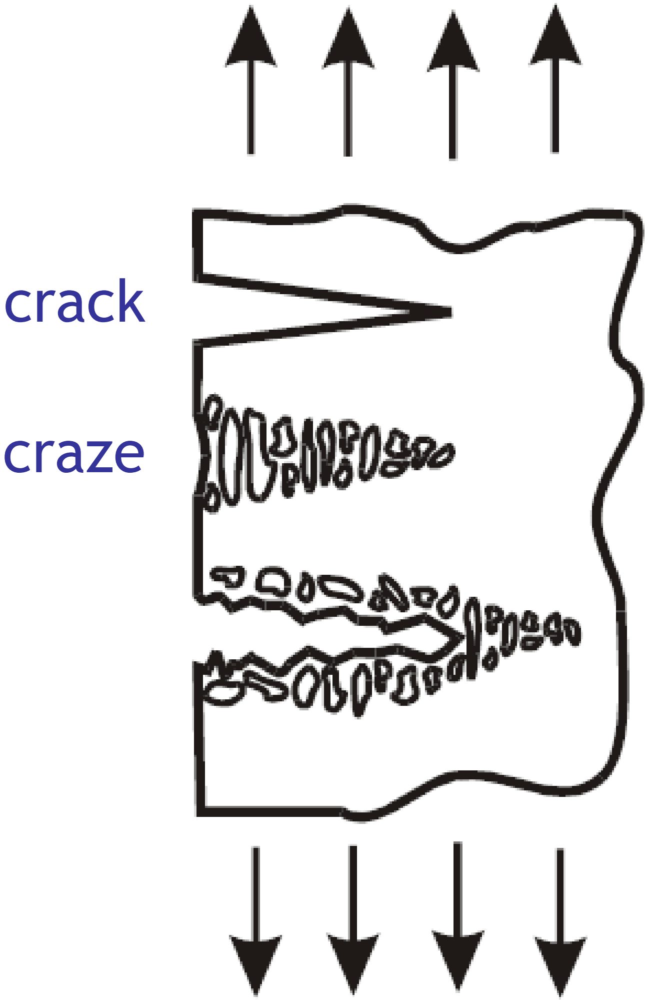
Necking – bulk plasticity



Courtesy of M.Raab

Crazing - localized plasticity

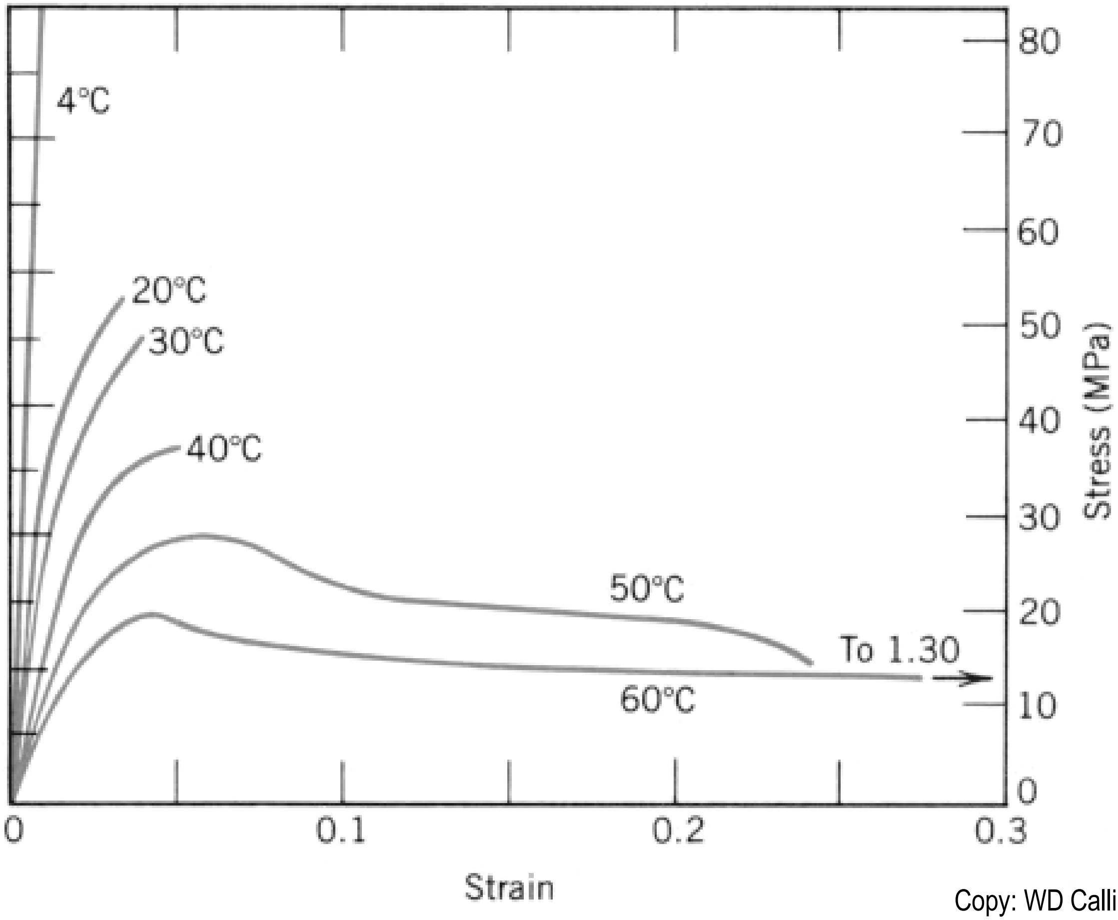


Mechanical behaviour - effects of time and temperature

Mechanical characteristics are highly sesitive to:

- strain rate
- environment /thermal & chemical/

Ex. PMMA



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Increasing temperature causes the same effect as decreasing strain rate

Fracture

TOUGHNESS – the ability of material to withstand the energy of a sudden impact

MODES OF FAILURE

BRITTLE FRACTURE

linear relationship between load and deformation

Ex. Ordinary window glass

highly localized crazing

DUCTILE FRACTURE

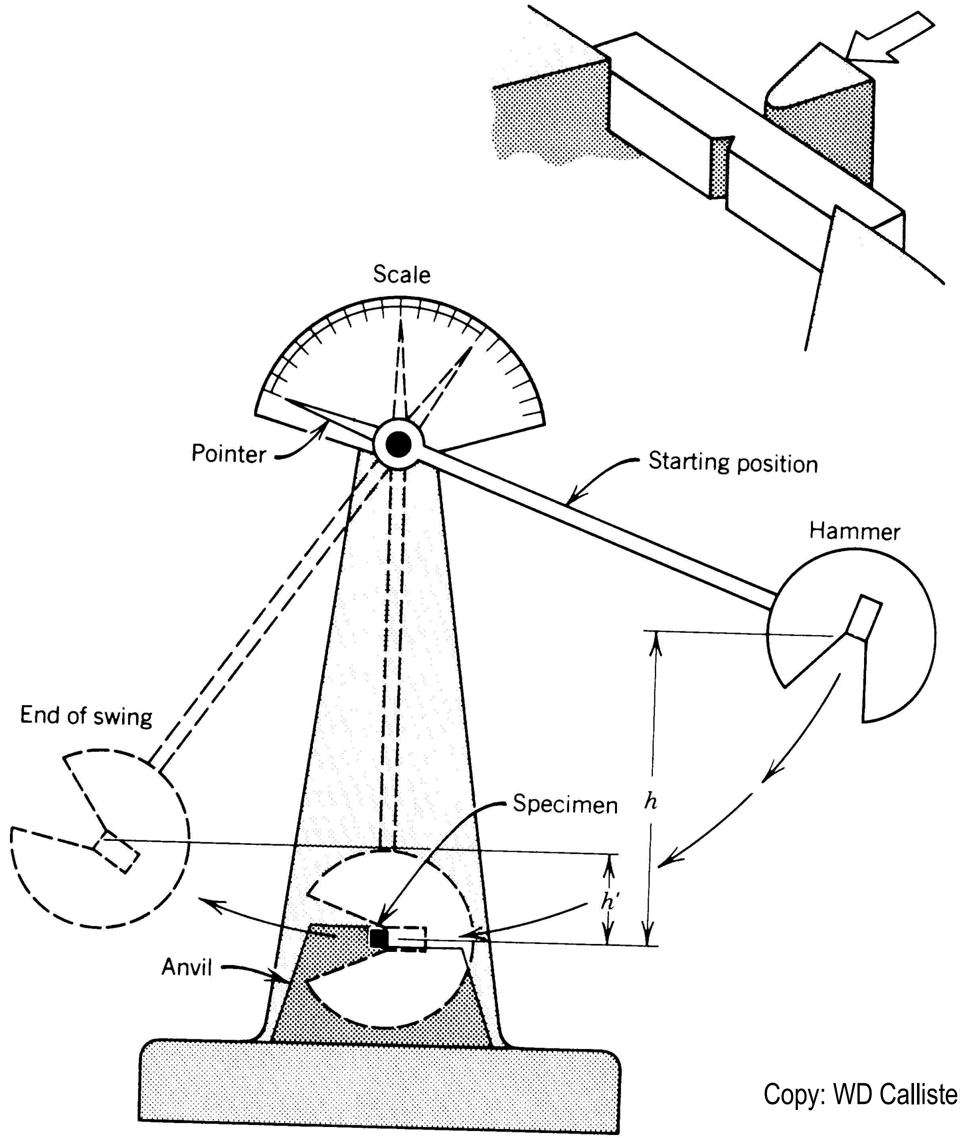
requires sufficient mobility of polymer chain segments

multiple crazing and/or shear yielding (plastic flow without crazing)

! *High impact strength does not necessarily imply ductile fracture, nor does brittle fracture necessarily imply low impact strength!*

Ex. Glass-reinforced polyester resin: extremely high impact strength, brittle failure

Experimental supplement – Charpy impact testing



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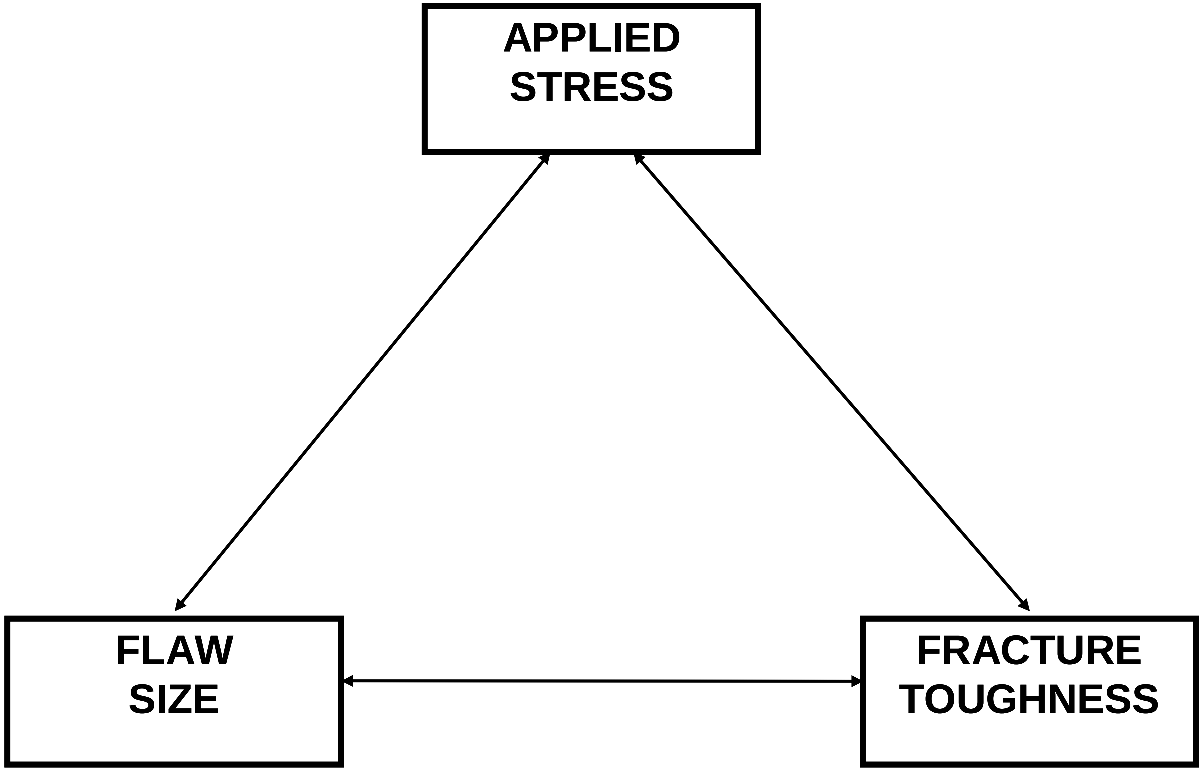
unnotched impact strength a_u = impact energy/cross section [J.m^{-2}]
notched impact strength a_n = impact energy/ligament area [J.m^{-2}]

Experimental supplement – Fracture mechanics



APPLIED STRESS

FLAW SIZE

FRACTURE TOUGHNESS

The fracture mechanics triangle, which identifies the three critical variables

Experimental supplement – Fracture mechanics

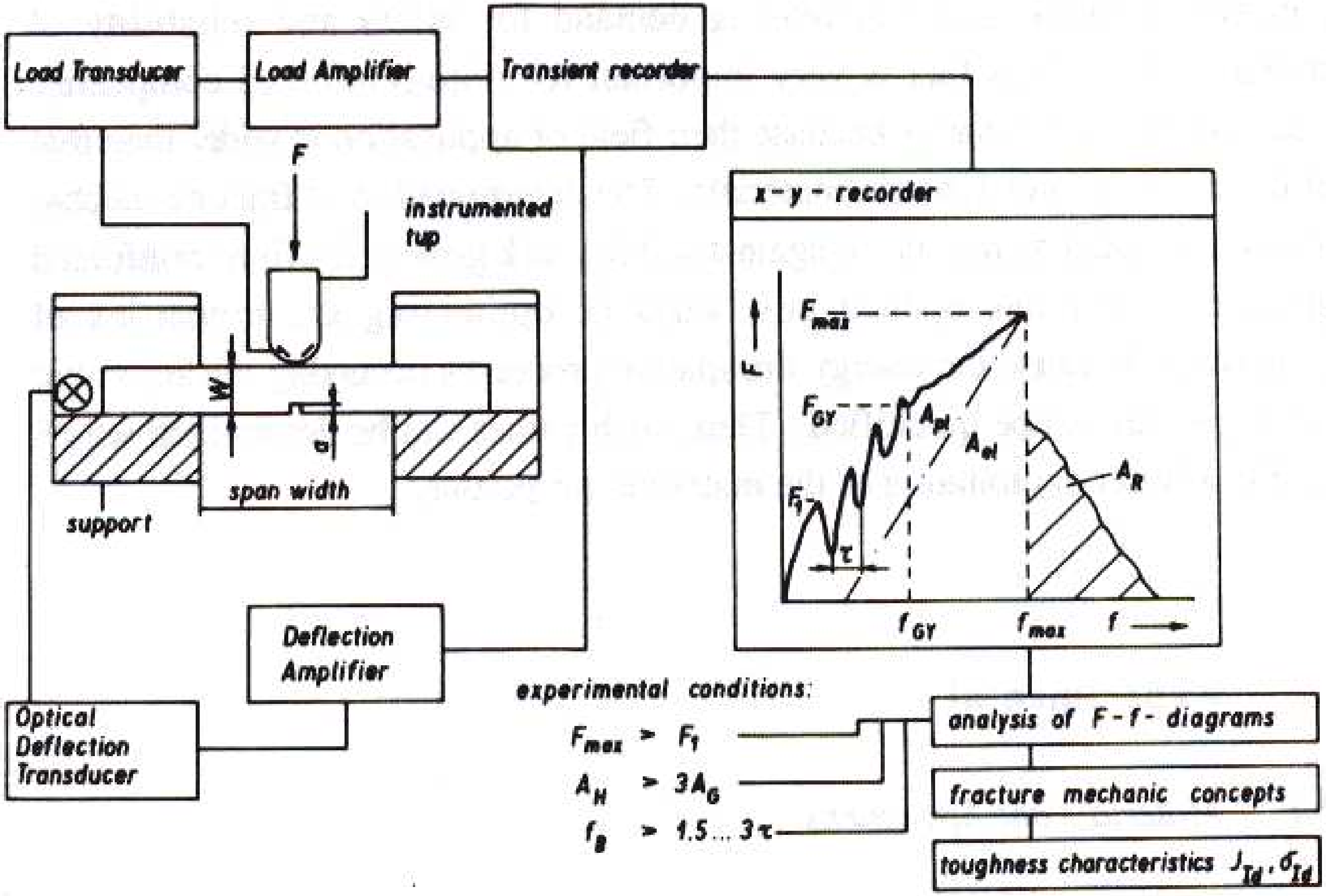
Toughness as a resistance against unstable crack growth

- LEFM (K_{IC}, G_c)
  - Stress intensity factor $K = Y\sigma\sqrt{2\pi a}$ [MPa.m$^{-1/2}$]
- EPFM (J_{IC}, COD)
  - J-integral $J = -\frac{1}{B}.\frac{dU}{da}$ [N.mm^{-1}]

Toughness as a resistance against stable crack growth

- R curves $J = f(\Delta a)$

Experimental supplement – Fracture mechanics



Courtesy of W. Grellmann

Effect of structure on mechanical behaviour

•Effect of monomer or bonding between chains

The type of monomer influences the bonding between chains and the ability of the chains to rotate and slide past one another

Ex. PE easy rotation and sliding, no strong polar bonds between chains → low strength, low stiffness

Larger atoms or groups (Cl, CH3, benzene group) → more difficult rotation and deformation of the chain → higher strength and stiffness

•Effect of monomers on bonding within chains

Oxygen, Nitrogen, Sulphur and benzene rings → more difficult rotation and sliding of the chains → higher strength and stiffness

•Degree of polymerization

Increase in chain length → more tangled chains → improved strength

•*Branching*

Branching reduces the density, strength and stiffness

•Tacticity

Very important: atactic PP – isotactic PP

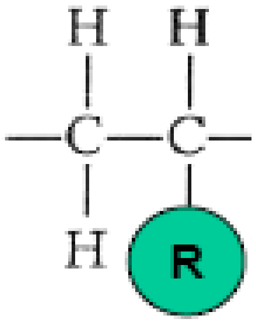
•Crosslinking

Thermosets: highly crosslinked polymer chains that form a 3D network structure → the chains cannot rotate andor slide → good strength, stiffness and poor ductility

•Crystallinity

Increasing crystallinity → higher density, strength and stiffness

Effect of structure on mechanical behaviour



H – PE (T_g: –120 °C; T_m: 130 °C, σ_y: 20 MPa)

CH_3 – PP (T_g: –20 °C; T_m: 170 °C, σ_y: 35 MPa)

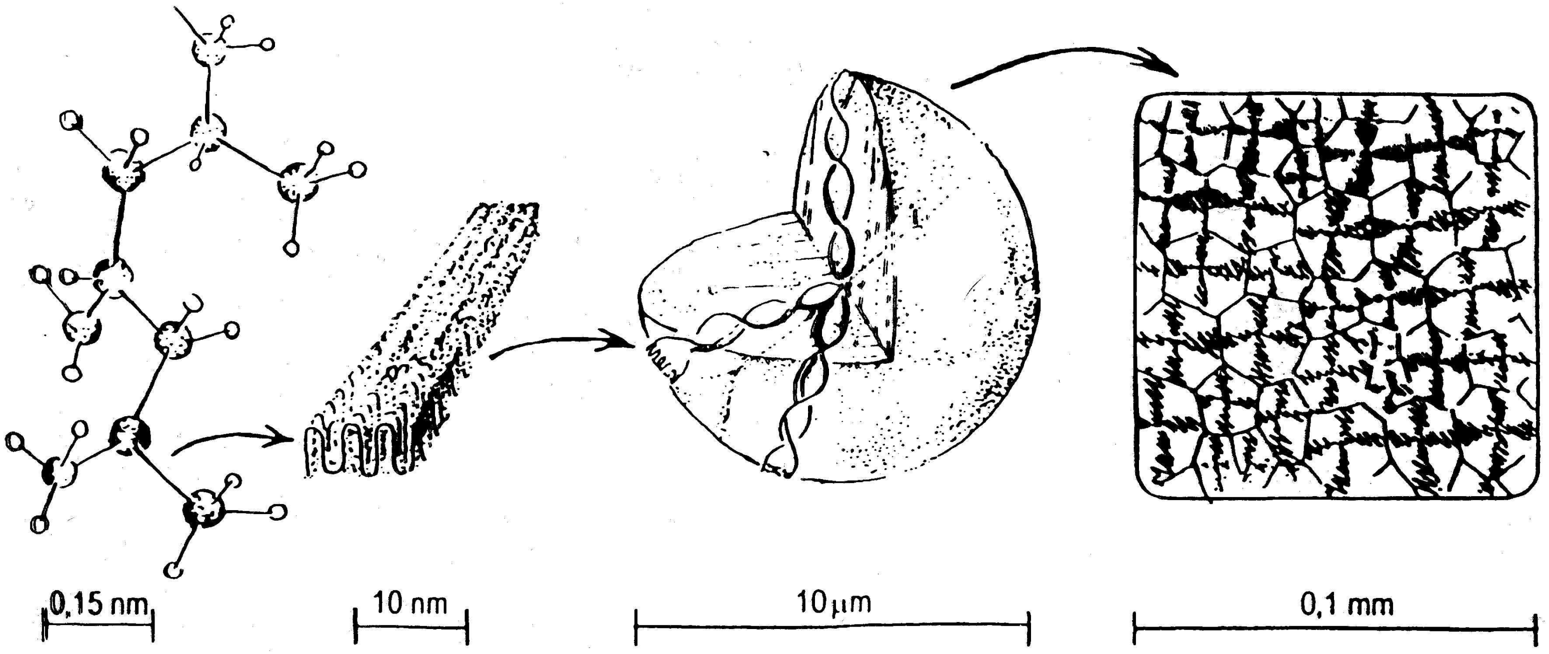
Cl – PVC (T_g: 75 °C; σ_y: 45 MPa)

Benzene ring – PS (T_g: 100 °C; σ_M: 50 MPa)

Effect of structure on mechanical behaviour

Reflects all levels of structural hierarchy!

Ex. Isotactic PP



Courtesy of M.Raab

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