Properties of Materials

Theme: Polymers and Composites

Lecture 1: Structures of Polymers

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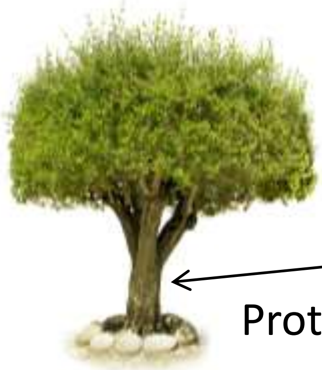
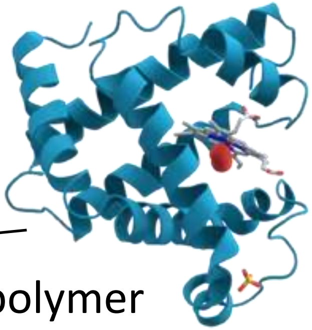
Lecture Contents

- Lecture 1
  - Introduction
  - Basic structure of polymers
- Lecture 2
  - Deformation
  - Chain alignment and viscoelasticity
- Lecture 3
  - Composites
  - Modulus and strength

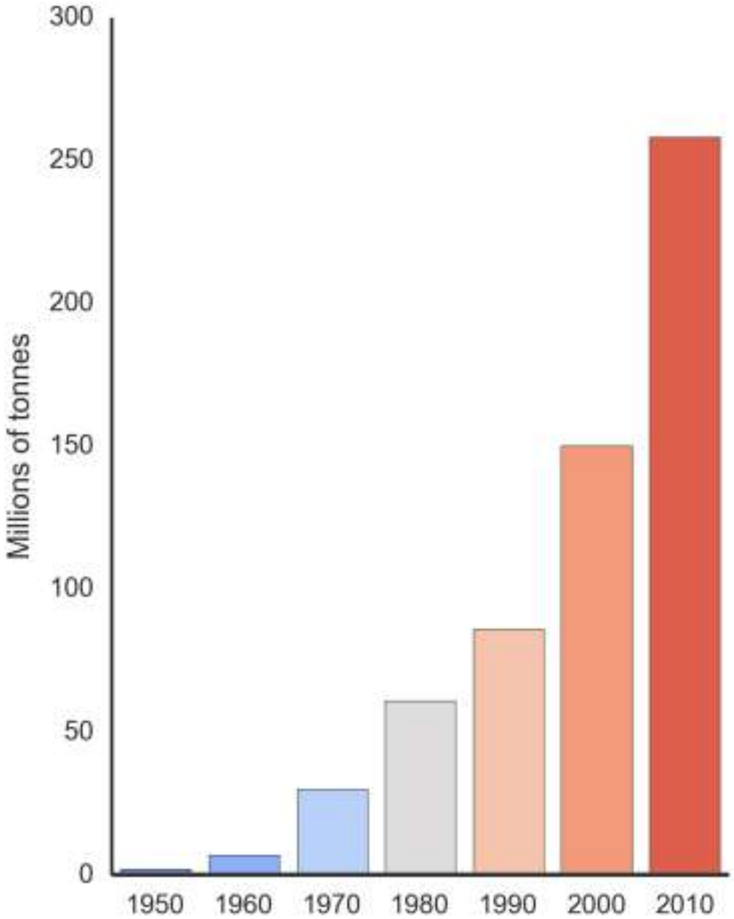
Introduction

Generally, engineers say *polymers* but we mean *plastics*





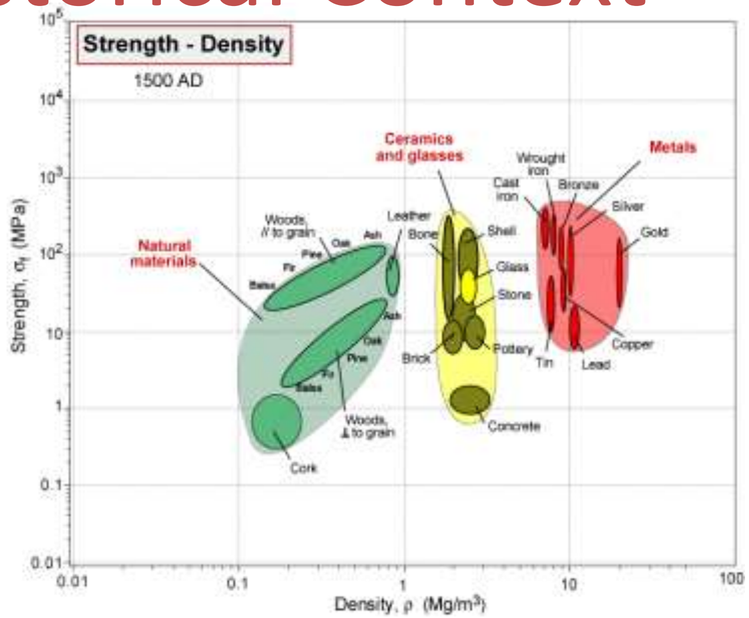
Protein = polymer

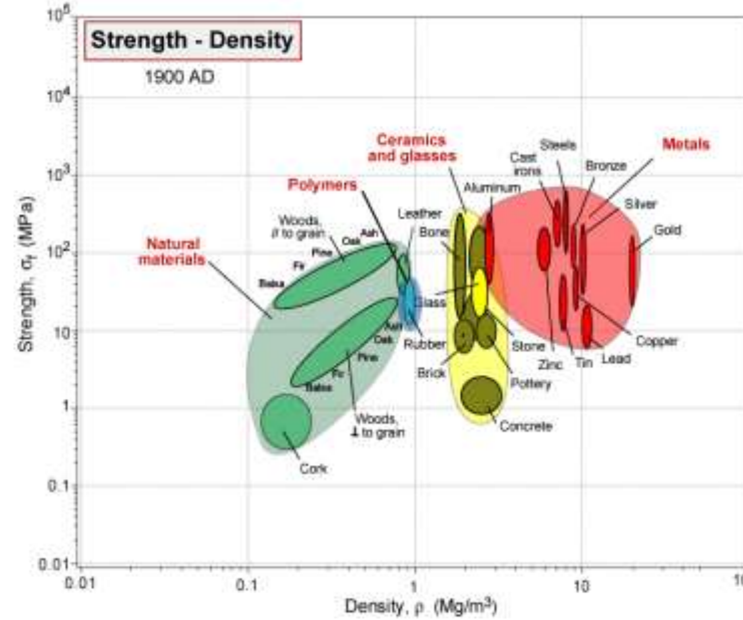


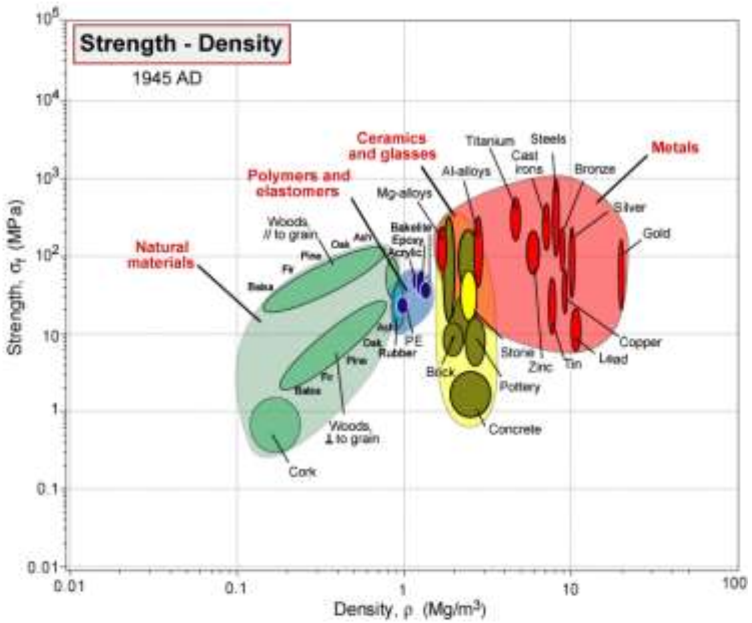
Car
Average 10-20% plastic

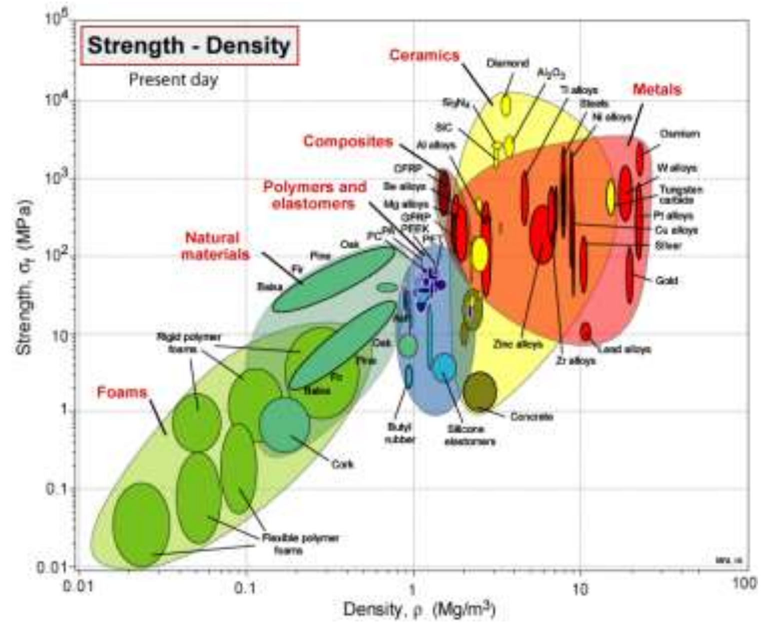
Buildings
ETFE (Ethylene tetrafluoroethylene)

Historical Context



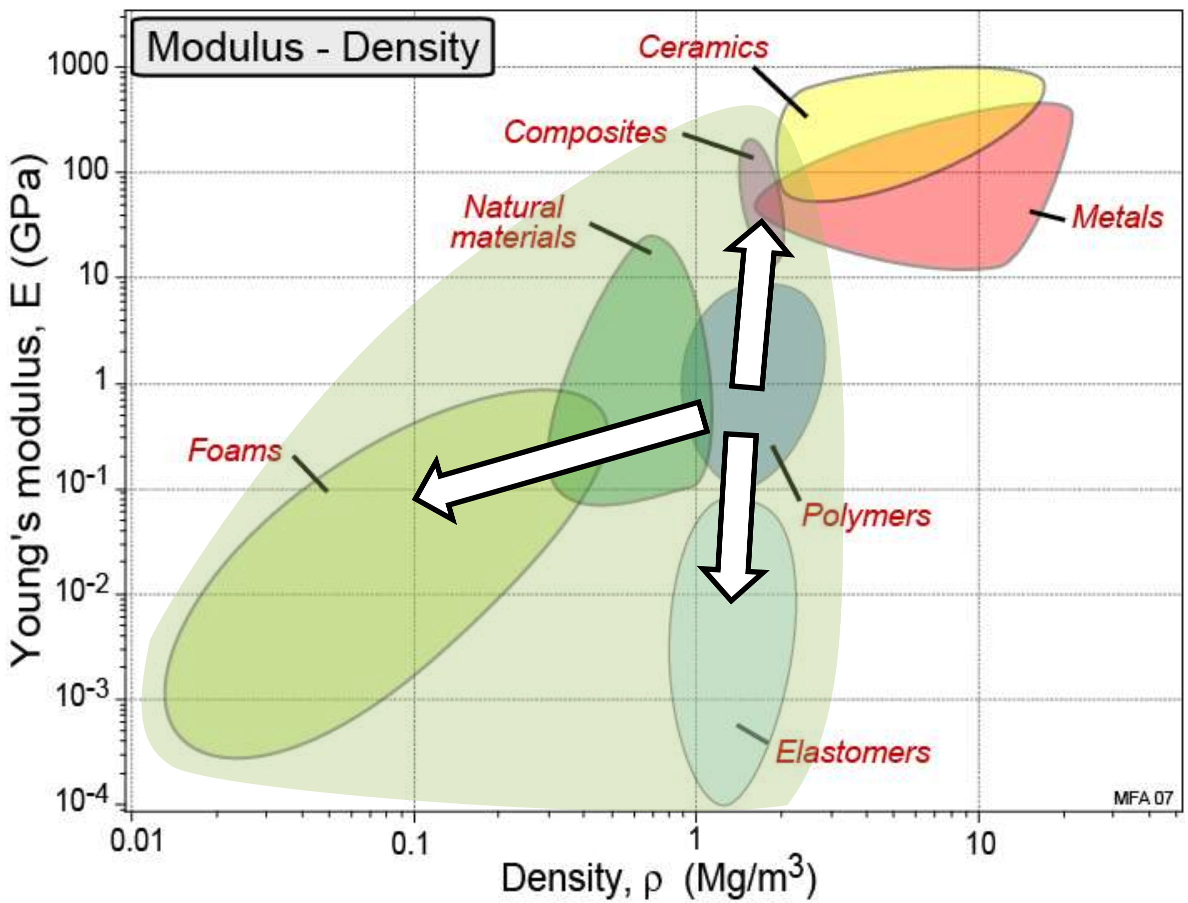






Properties Context

Polymers open up huge areas of property space

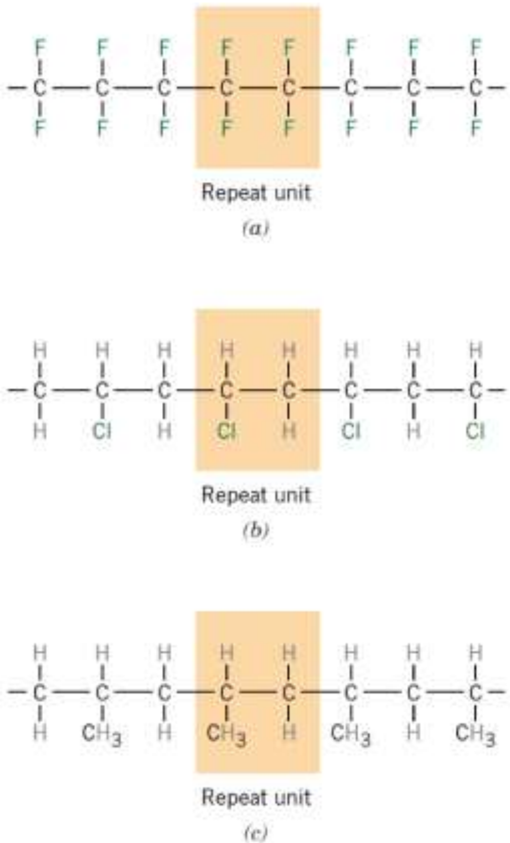


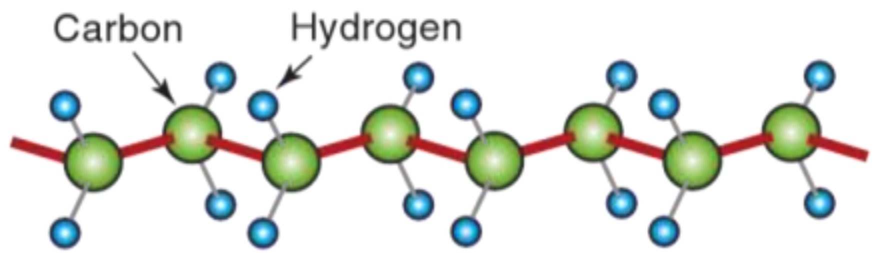
Polymers show more capacity to customise properties than any other material class

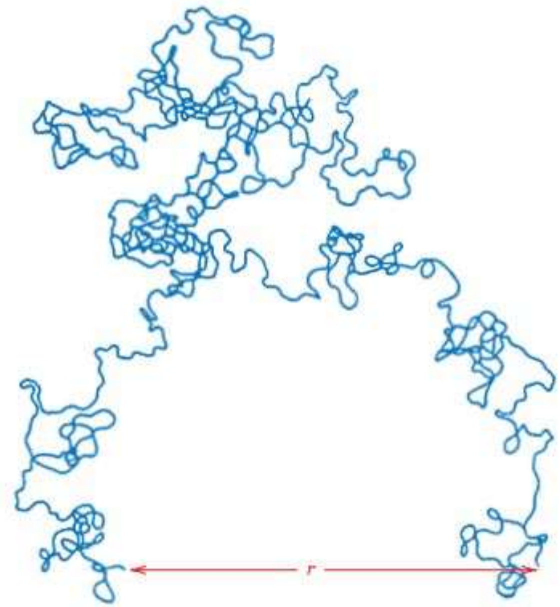
Why use rubber?

- Low density
- Low modulus
  - Conformable
  - High resilience
- Cheap to produce
- Easy to form into complex shapes
- High friction coefficient
- Easy to colour (and robust colour)

Structure


Repeat unit
(a)
Repeat unit
(b)
Repeat unit
(c)


Carbon
Hydrogen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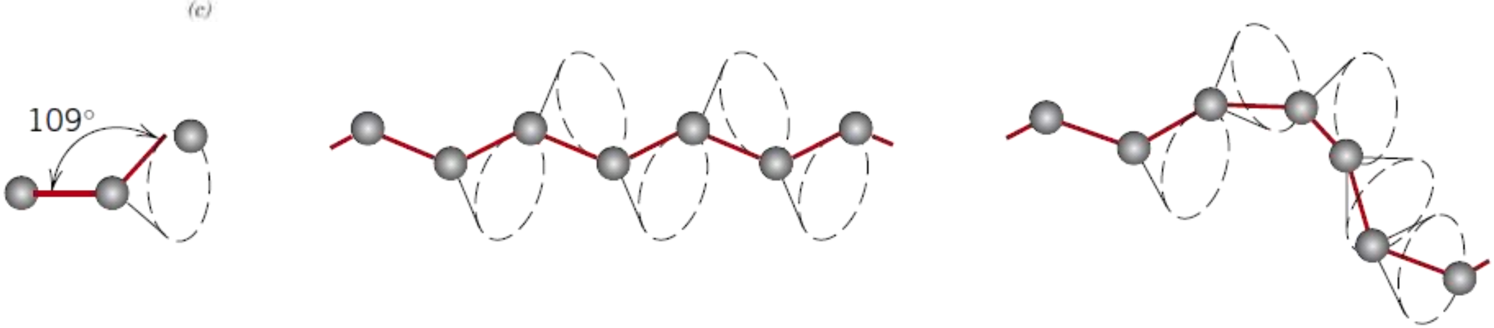
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Customising polymers

Polymer

Longer chains
Bigger, heavier more entangled chains

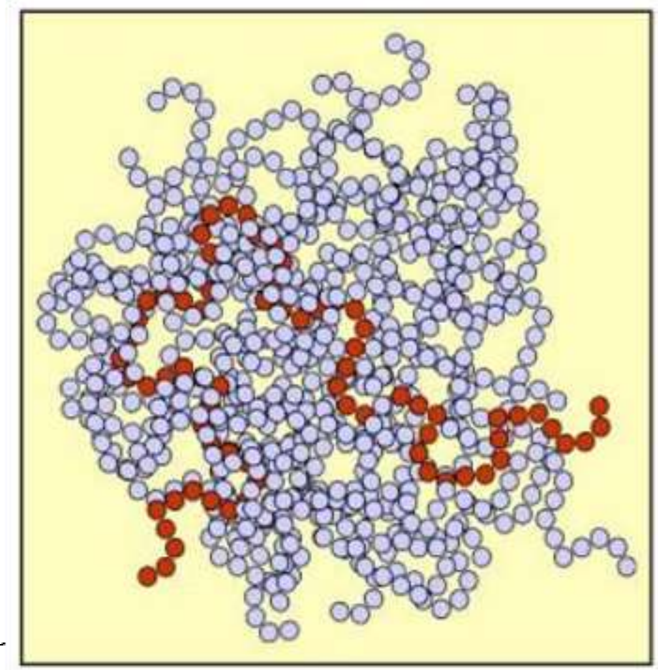
Change repeat units
Some repeat units are stronger, stiffer or have different chemistry

Change interlinking
Chains can be tethered together by strong covalent bond

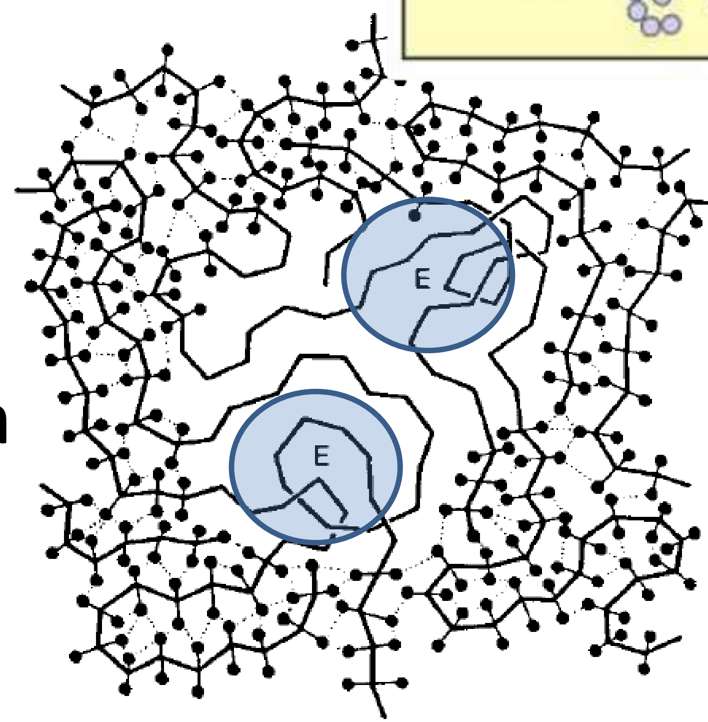
Change architecture
Macroscopic changes in shape and form of polymer product (composites and foams)

Change crystallisation
Some polymers can form crystals to varying degrees

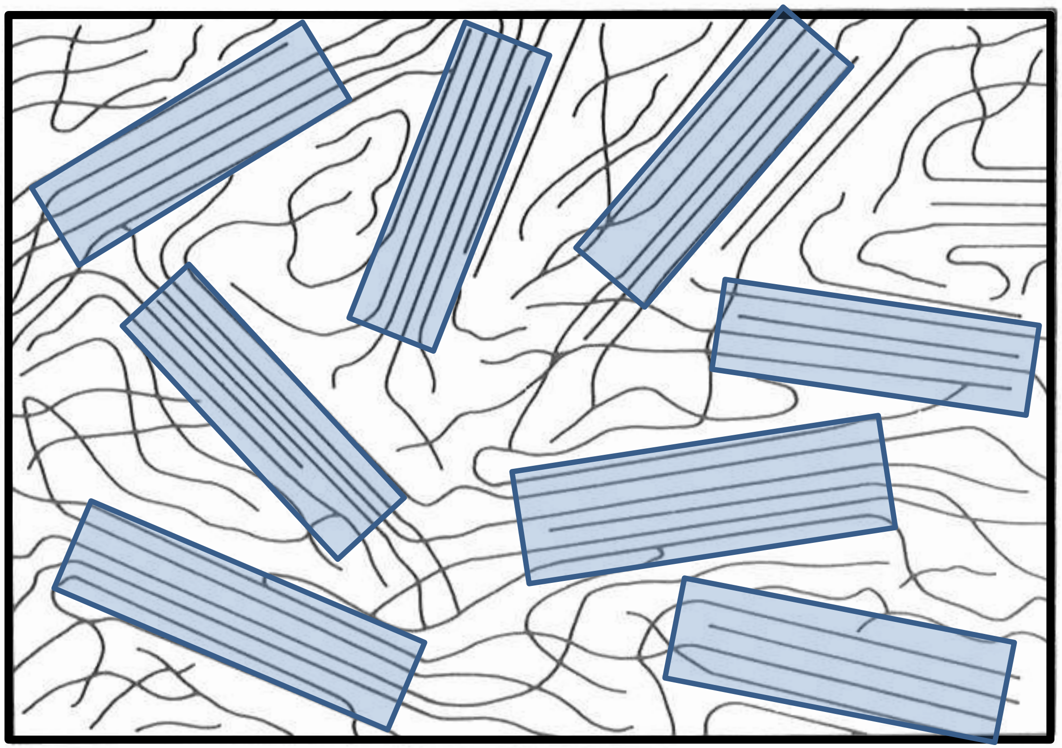
Amorphous Polymers



- Long chains don't pack easily
  - Become entangled and twisted together
- Lack of long range order
  - Amorphous
- Stiffness arises from entanglements of chains

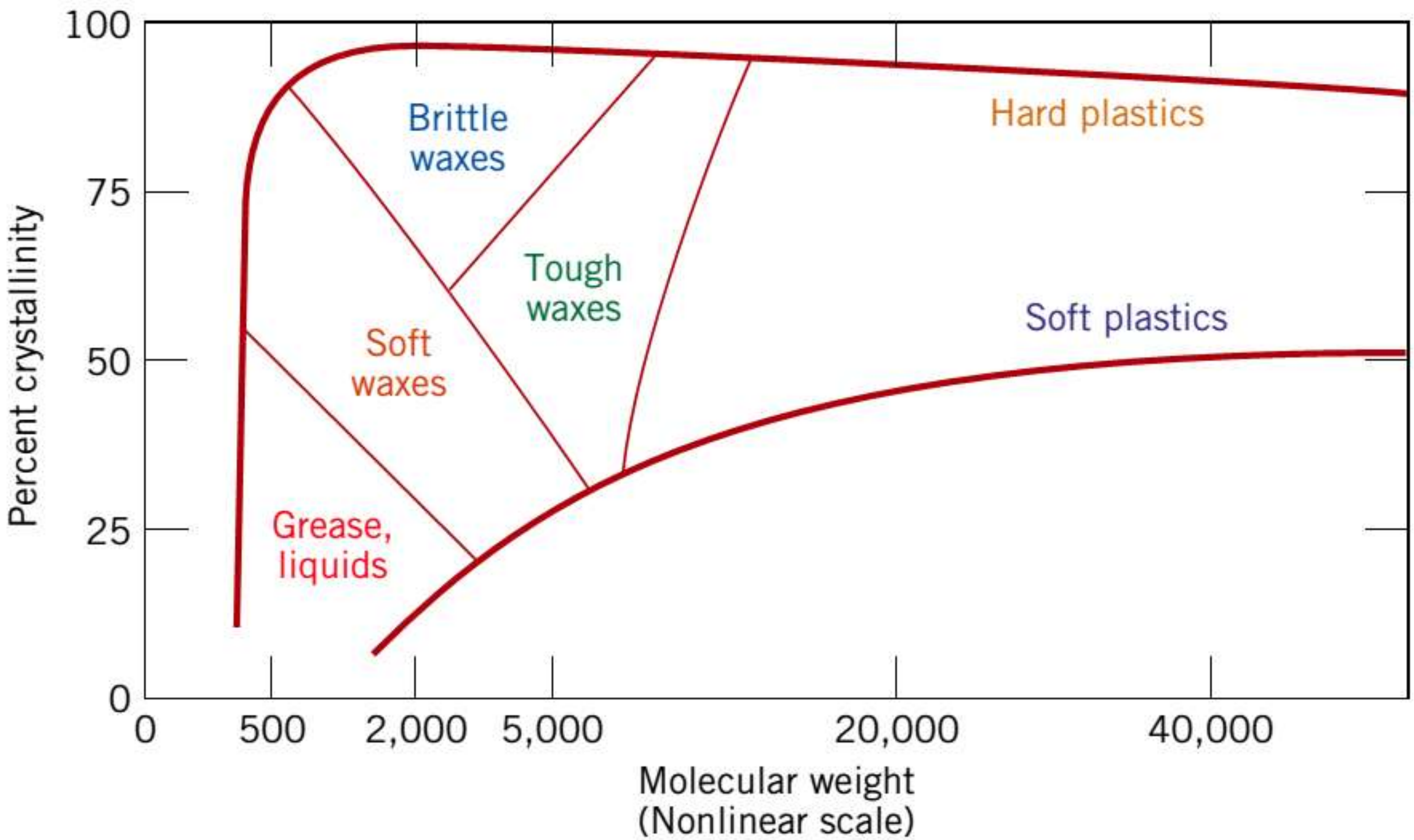


Semi-crystalline



- Hard to get close packing of long chains
  - Small regions of crystals surrounded by amorphous phase
- Additional stiffness derived from close packing

Chain length and Crystallinity



Longer chains, more crystallinity = denser, stiffer, stronger polymer

Amorphous *vs.* crystalline

Amorphous

- Broad softening range
  - Variety of bond strengths due to formless structure
- Usually transparent
  - Loose structure of consistent refractive index

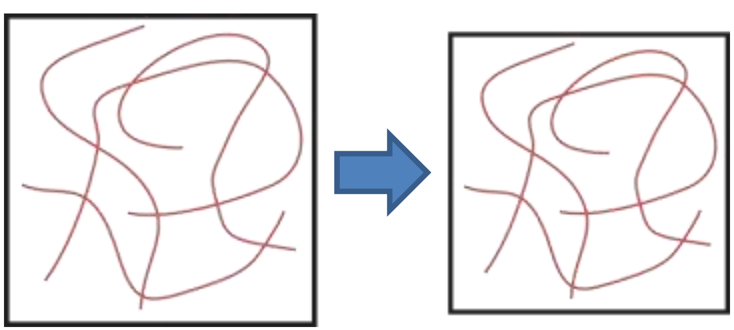
Semi-crystalline

- Sharp melting points
  - Regular structure so bonds have the same strength
- Usually opaque
  - Regions have different refractive index leading to interference

Amorphous *vs.* crystalline

Amorphous

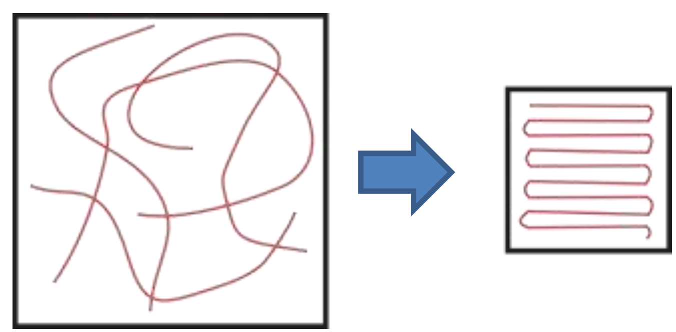
- Low chemical resistance
  - Open random structure allows chemicals to penetrate
- Low shrinkage
  - Processed in amorphous state and remains in this state



liquid solid

Semi-crystalline

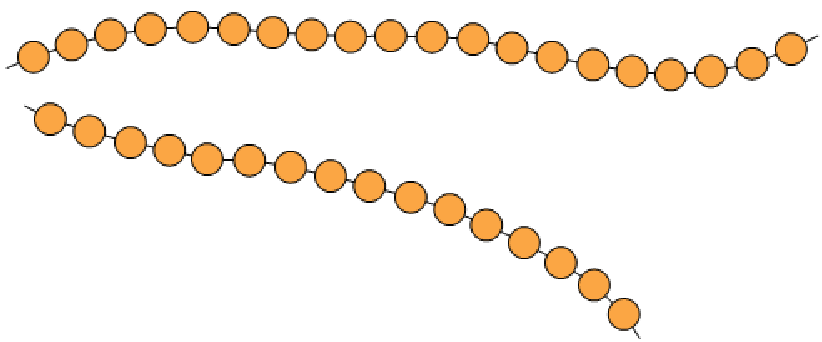
- High chemical resistance
  - Tightly packed structure is harder to infiltrate
- High shrinkage
  - Crystalline regions take up less space than amorphous

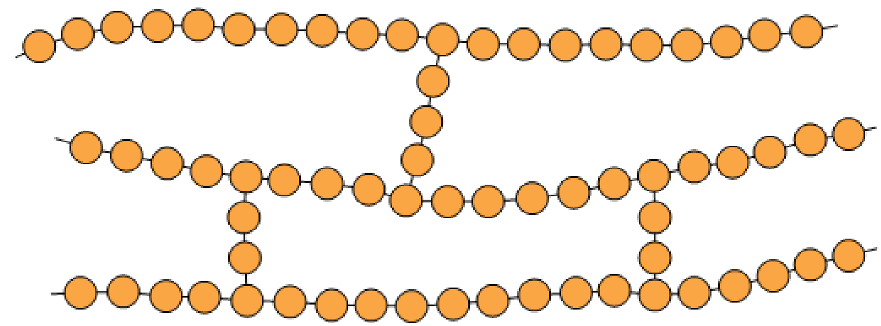


liquid solid

Interlinking

- Chains have thousands of covalent bonds in the chain
- Chains can be linked together by additional covalent bonds
  - Interlinks or cross-links

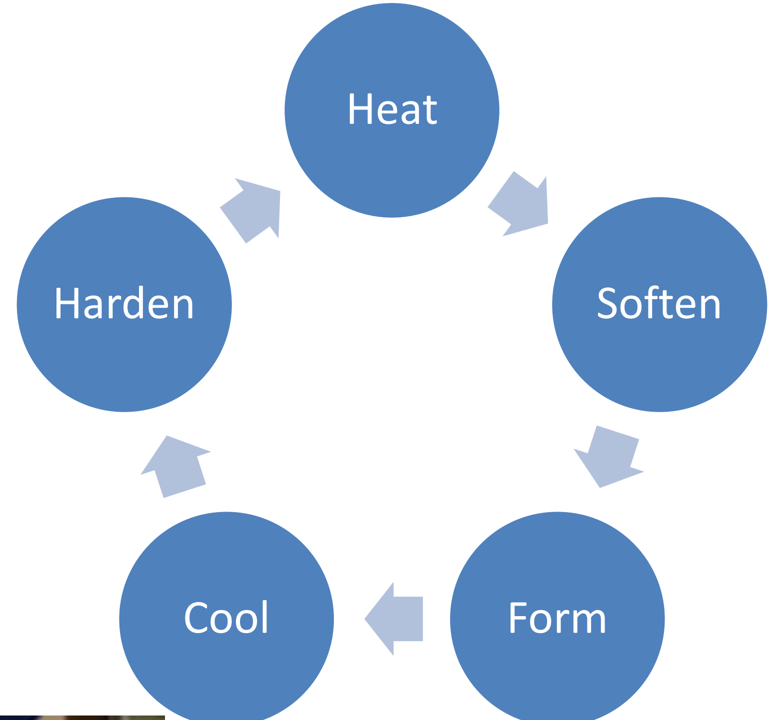




- Thermoplastics
  - Polyethylene
  - Nylon
- Thermosets
  - Epoxy resins

Thermoplastics

- Most common
- Allow mechanised forming methods
  - Heat based
  - Suited to high productivity
- Polymers that melt or soften are thermoplastics



Thermoplastics

Thermosets

- No need for heating/cooling
  - Particularly suited to custom, low productivity
- Automated still easy
  - Need to allow for setting time

Prepare component(s)

↓

Mix, heat, press or irradiate

↓

Final piece

Hand layup of composites

Summary

- Characterised by
  - low density
  - low stiffness/strength
  - Ease of manufacture
- Polymers are highly customisable
  - Monomer, chain length, interlinking, crystallinity

Properties of Materials

Theme: Polymers and Composites

Lecture 2: Deformation of Polymers

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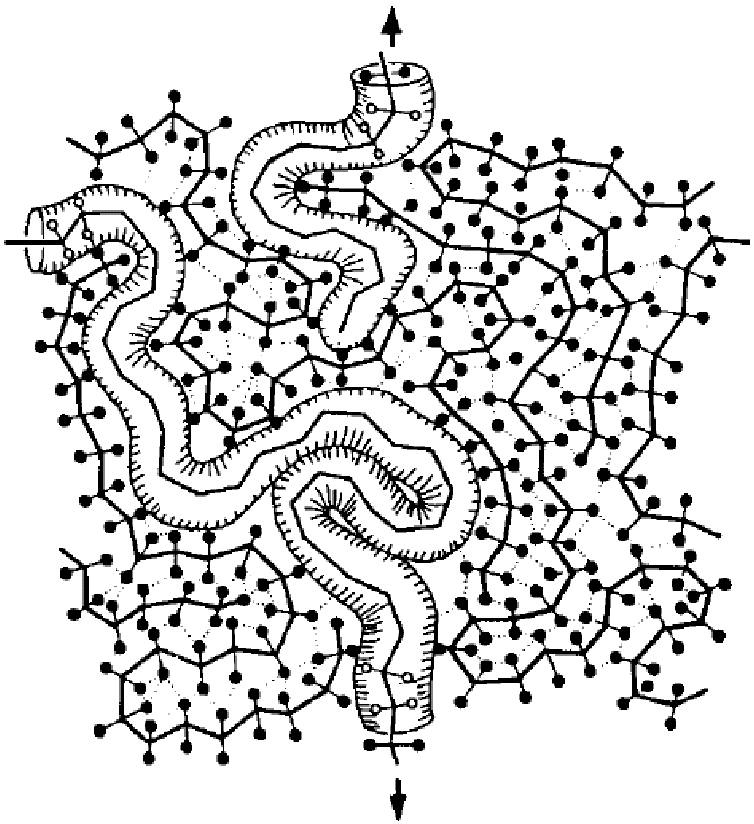
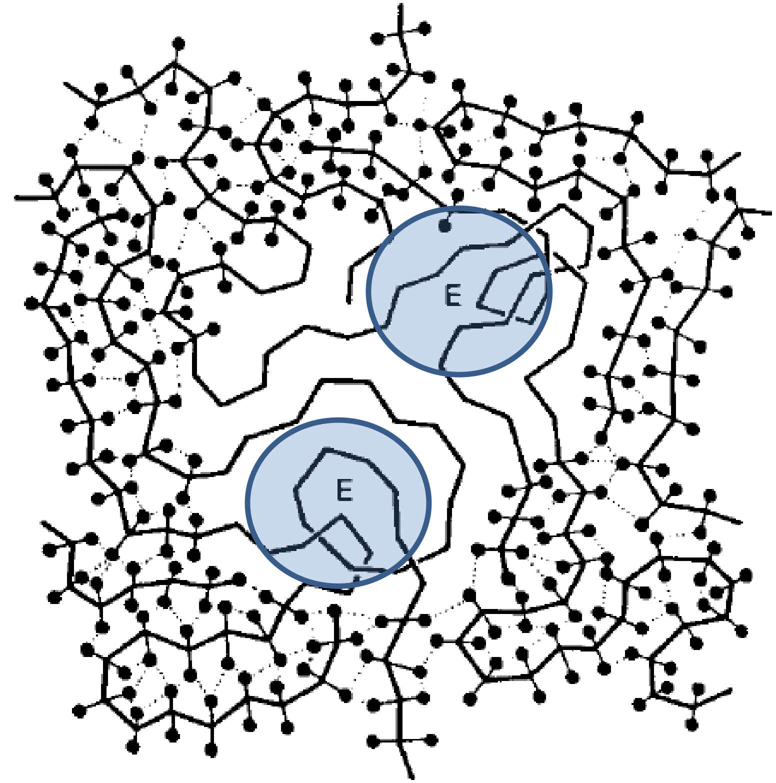
Introduction

- Glass transition temperature
  - Change from brittle to rubbery
- Chain alignment
  - Increasing strength with deformation
- Viscoelasticity
  - Time dependent plastic deformation

Glass Transition



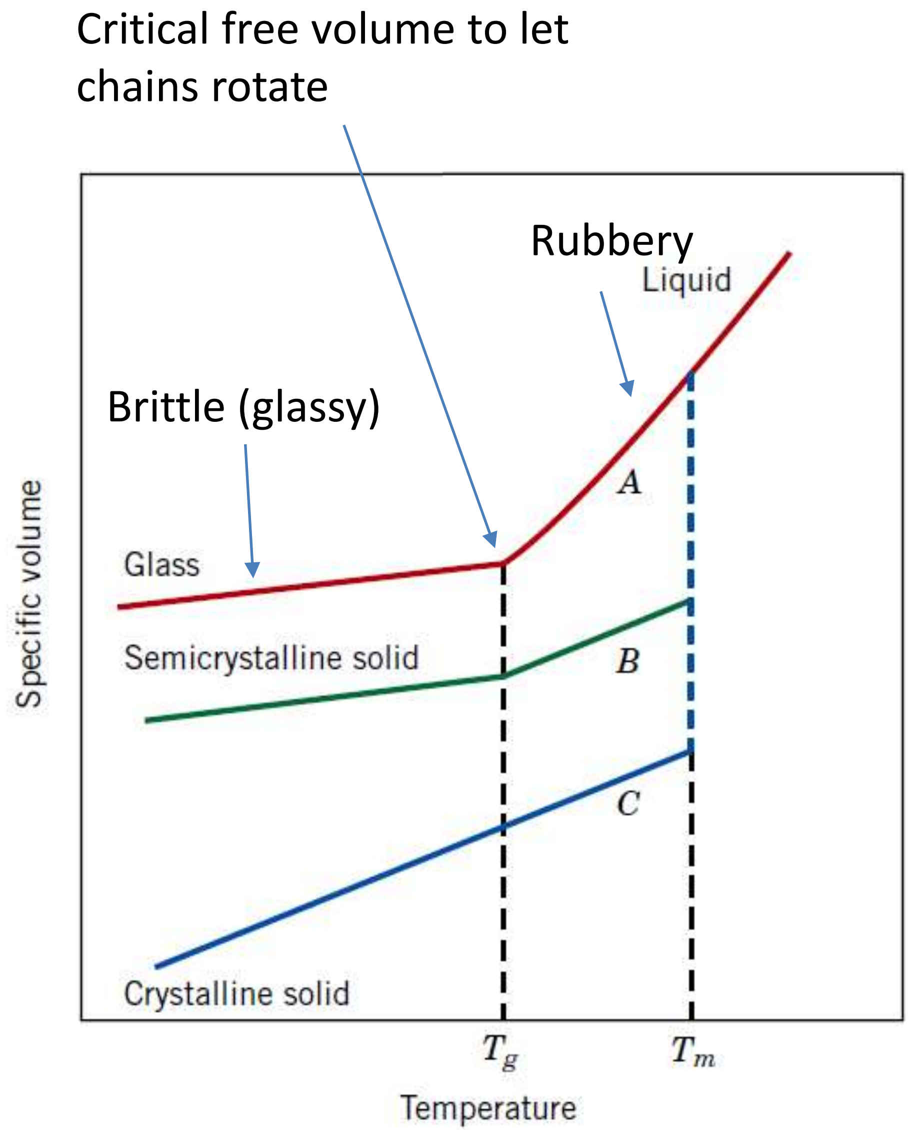
Each chain occupies a tube of **free space** within which it can slide or rotate (and bond with neighbours)



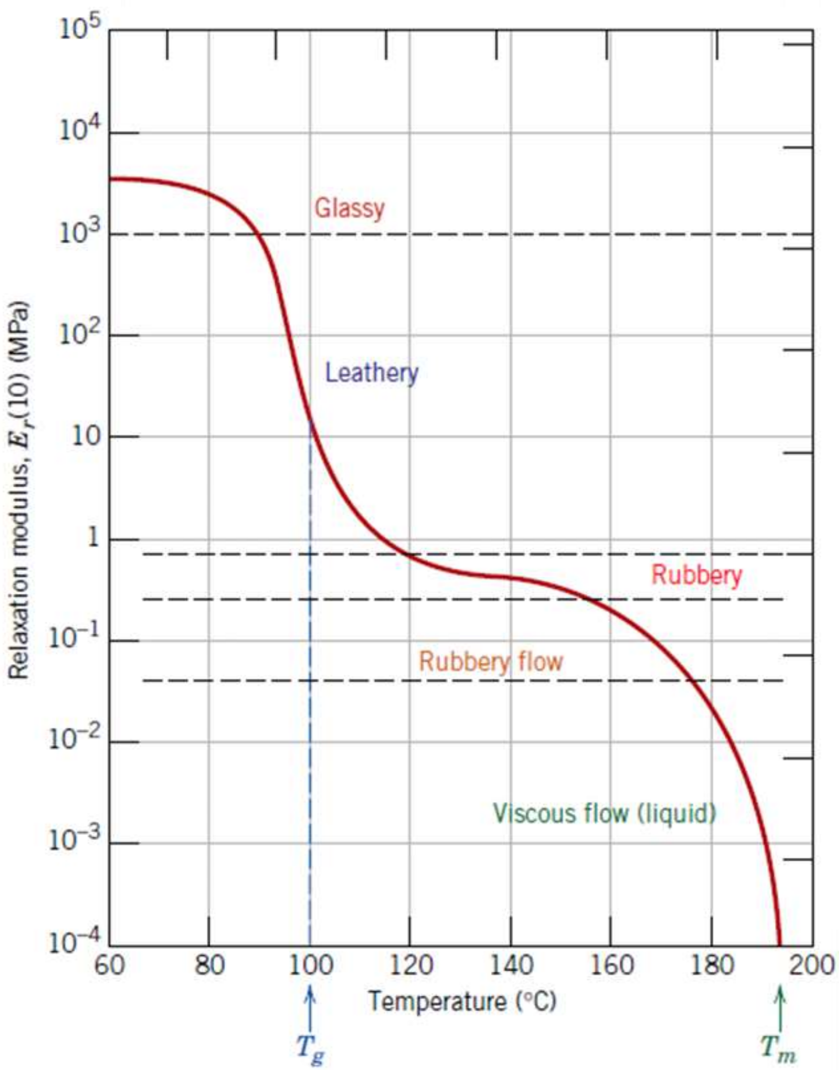
In addition to bonding chains become linked at 'entanglement' points (last lecture)

Glass Transition

- Crystalline
  - Step change in state at melting point
- Glass
  - Change in gradient at glass transition
  - No clear change from solid to liquid



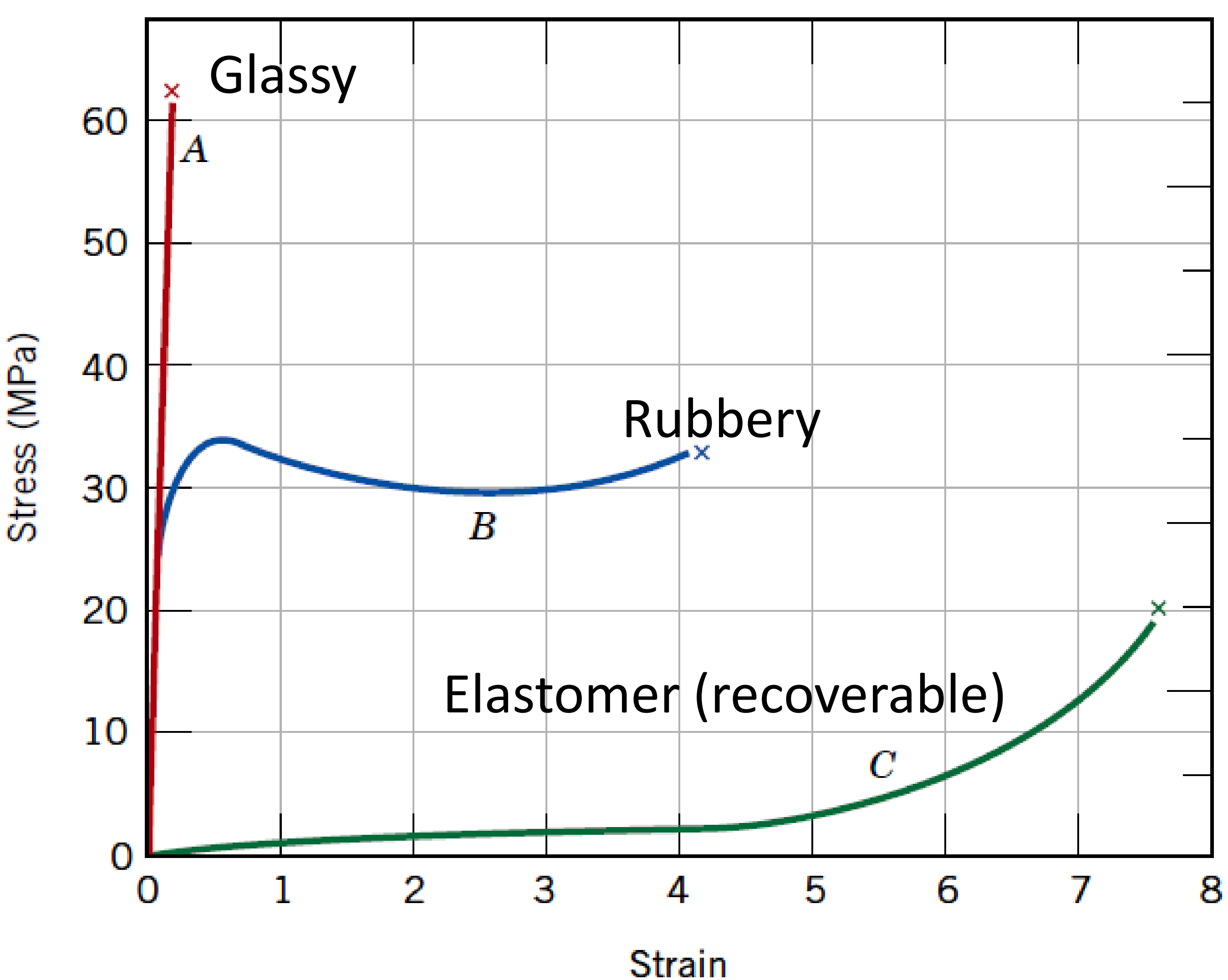
Glass Transition



- One polymer shows different behaviour at different temperatures

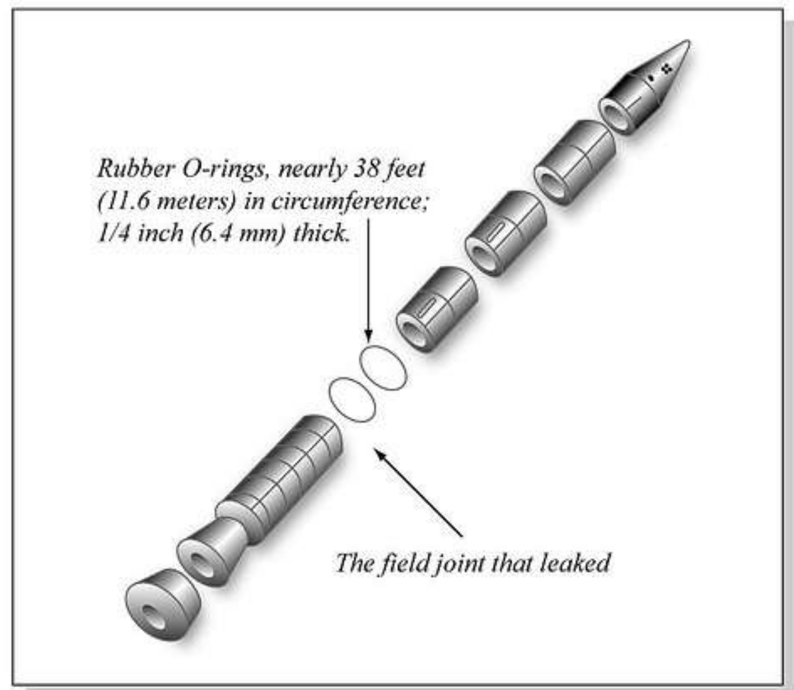
Polymer	GTT (°C)	Melting point (°C)
LDPE	-110	115
PTFE	-97	327
HDPE	-90	137
PP	-18	175
Nylon	57	265
PET	69	265
PVC	87	212
PS	100	240
PC	150	265

Glass Transition



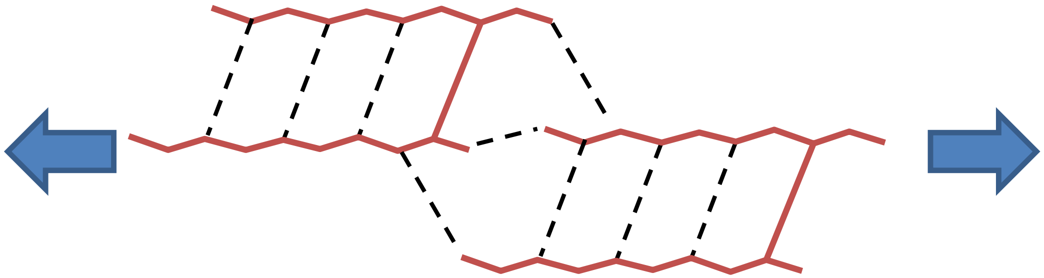
Glass Transition

- Challenger: rubber seals expanded too slowly in low temperatures (below glass transition)

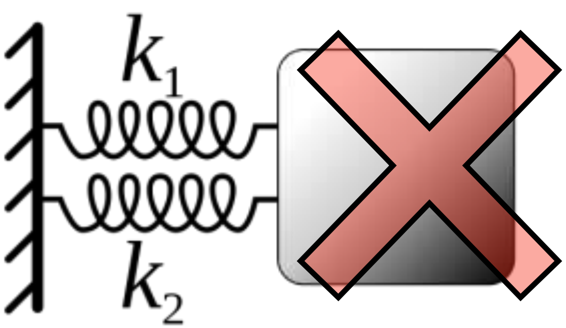


Stiffness (Glassy Polymers)

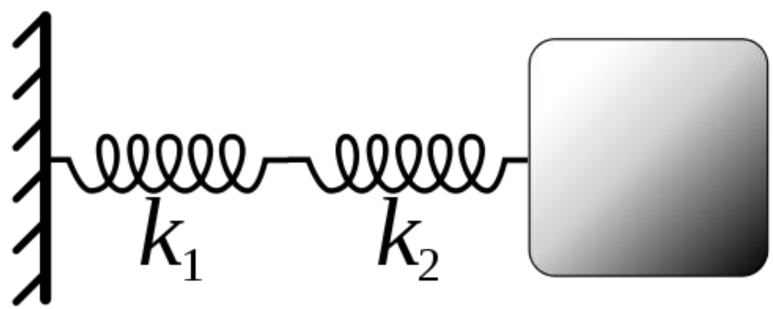
Small distortions of secondary and primary bonding



Some load taken by primary bonds (stiff)
Some load taken by secondary bonds (compliant)



Model: springs in parallel

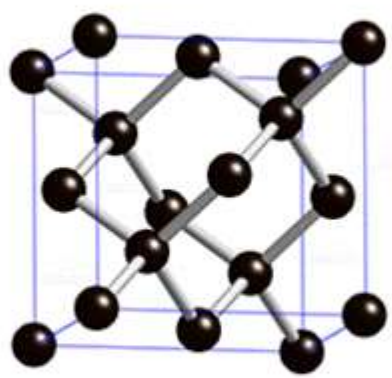


Model: springs in series

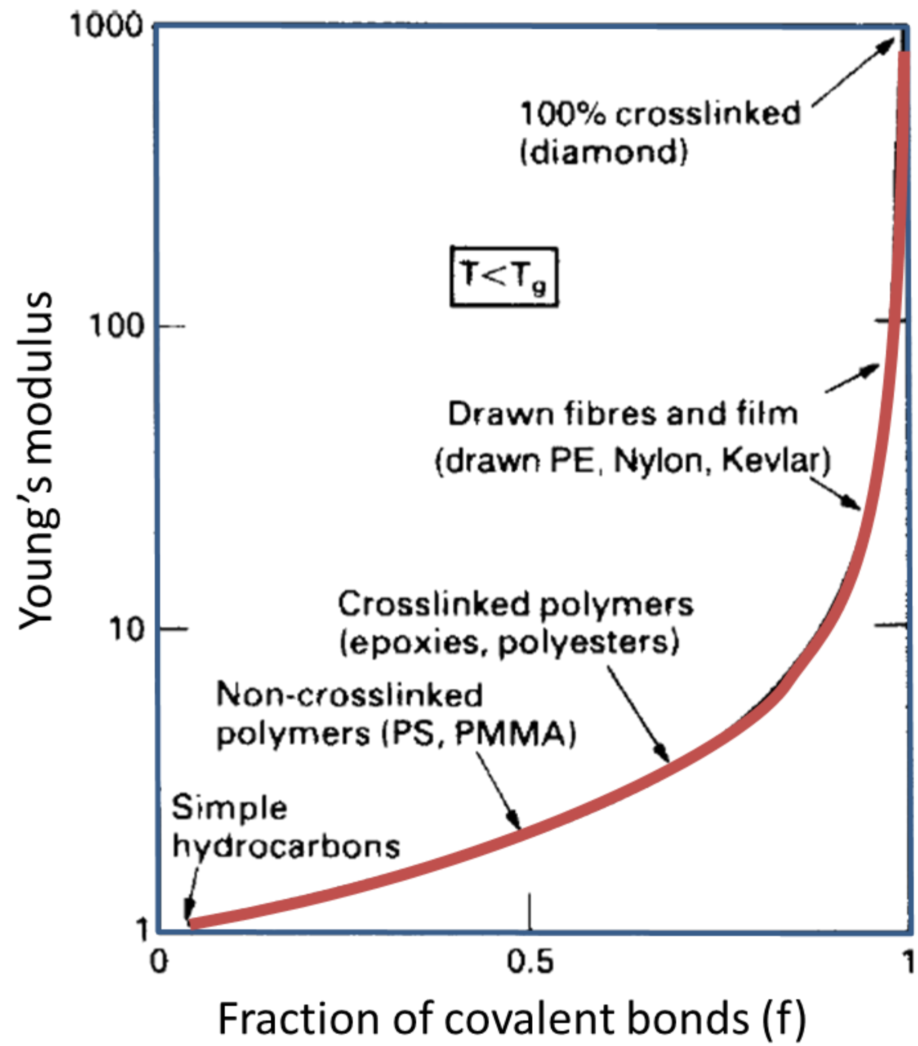
Stiffness (Glassy Polymers)

$$E = \frac{\sigma}{\varepsilon} = \left[\frac{f}{E_1} + \frac{1-f}{E_2}\right]^{-1}$$

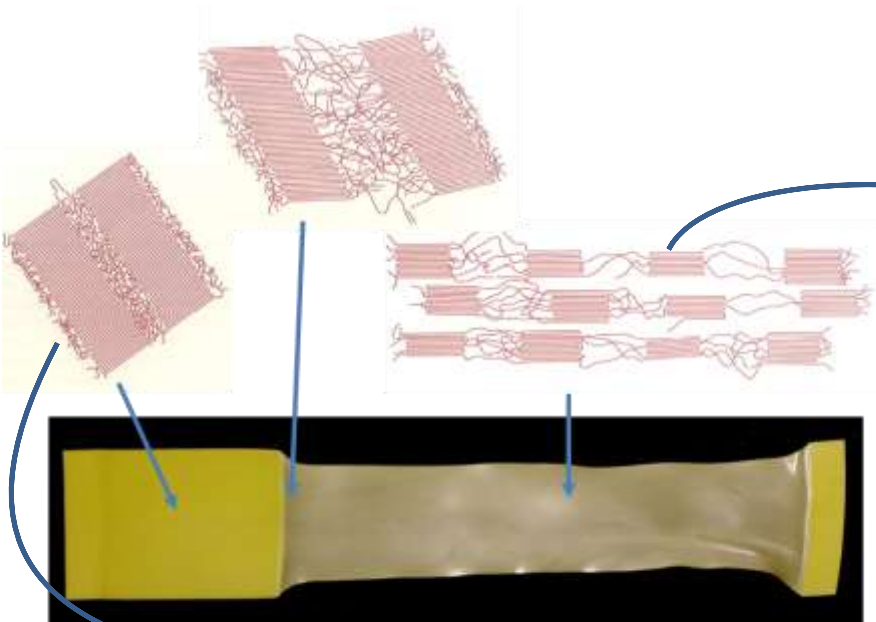
Diamond
100% covalent bonds linking C atoms

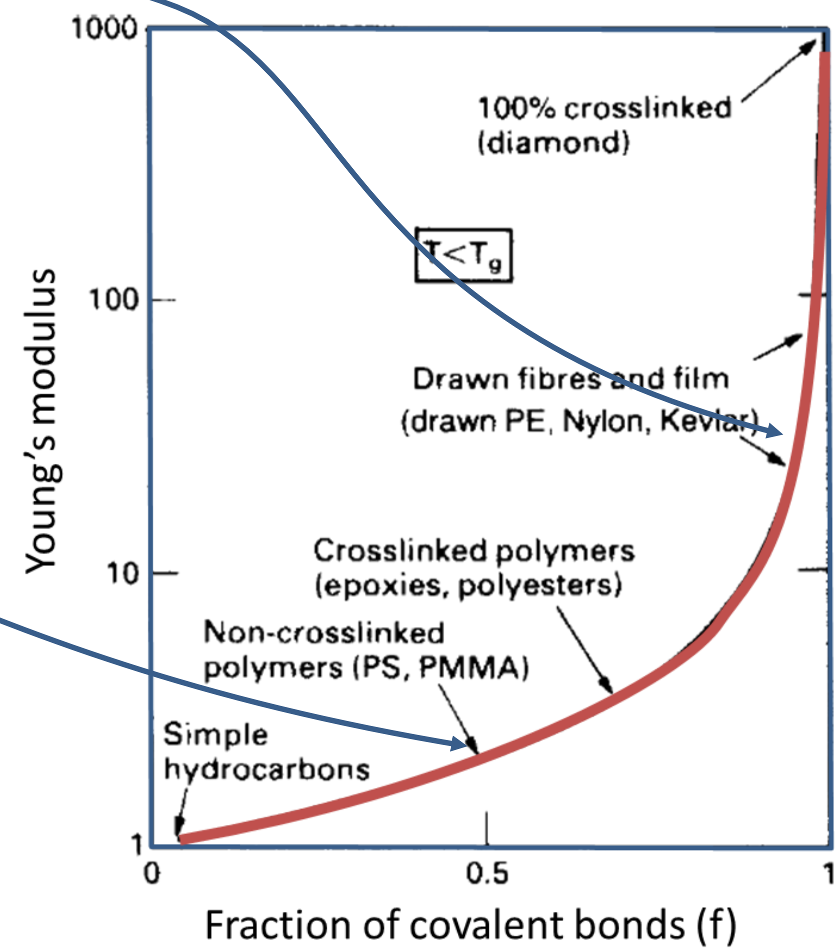


Paraffin wax
Small chains
Lots of secondary bonds



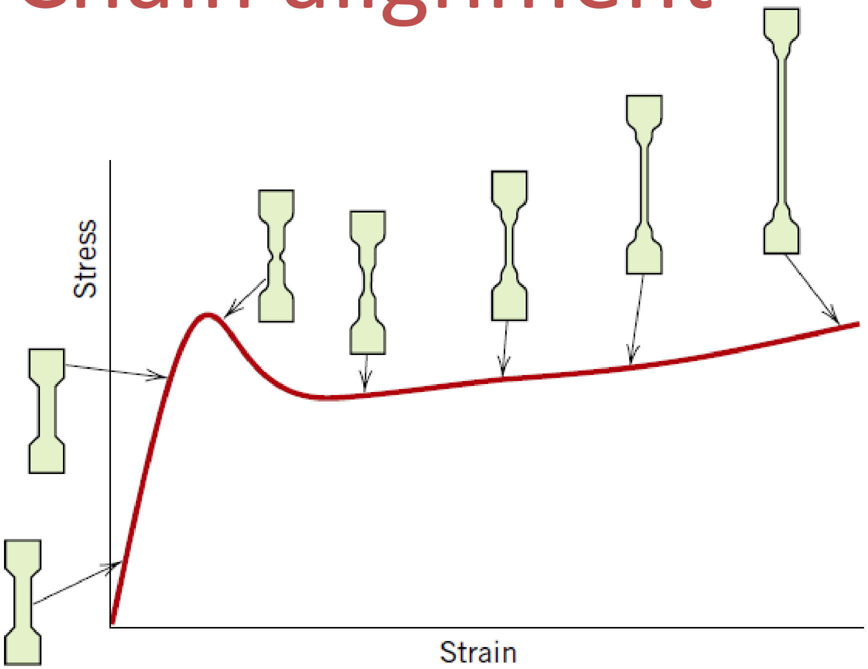
Plastic (permanent) deformation





- Deformation aligns chains
- Locally stronger neck
- Stable!

Chain alignment



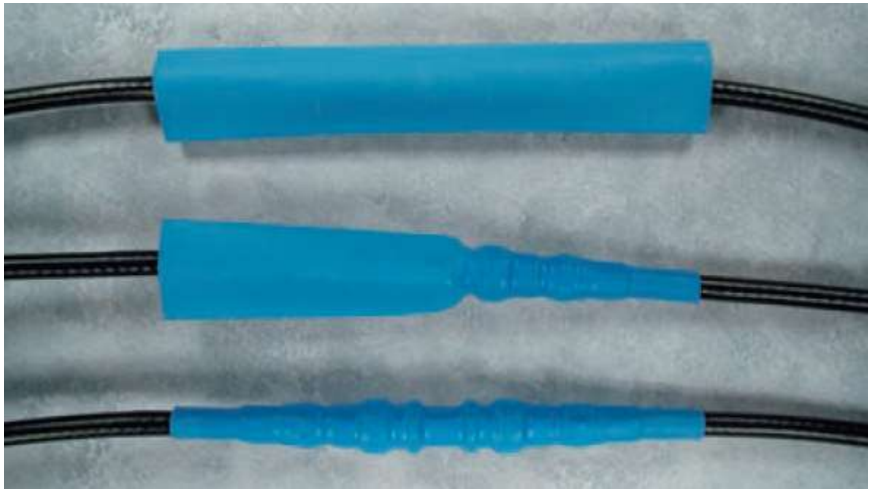
Stable Necking

Unlike metals, polymers form long stable necks as chains are drawn in an align

Memory Effect

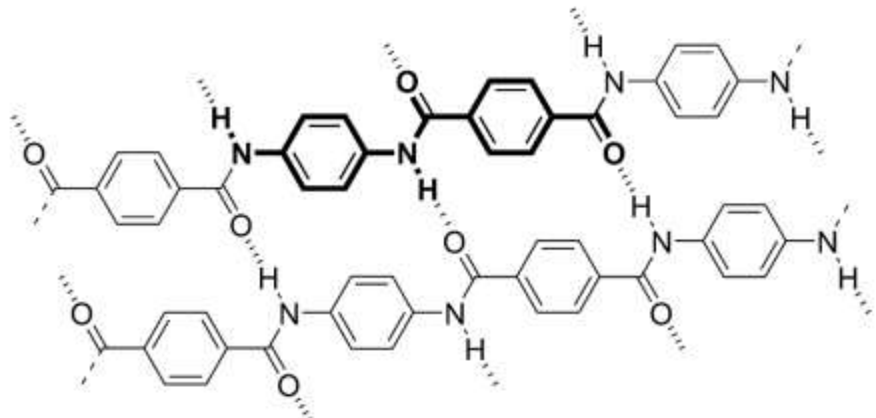
Applying heat lets aligned chains curl up again

Reverses previous plastic strain



Kevlar (aromatic polyamide)

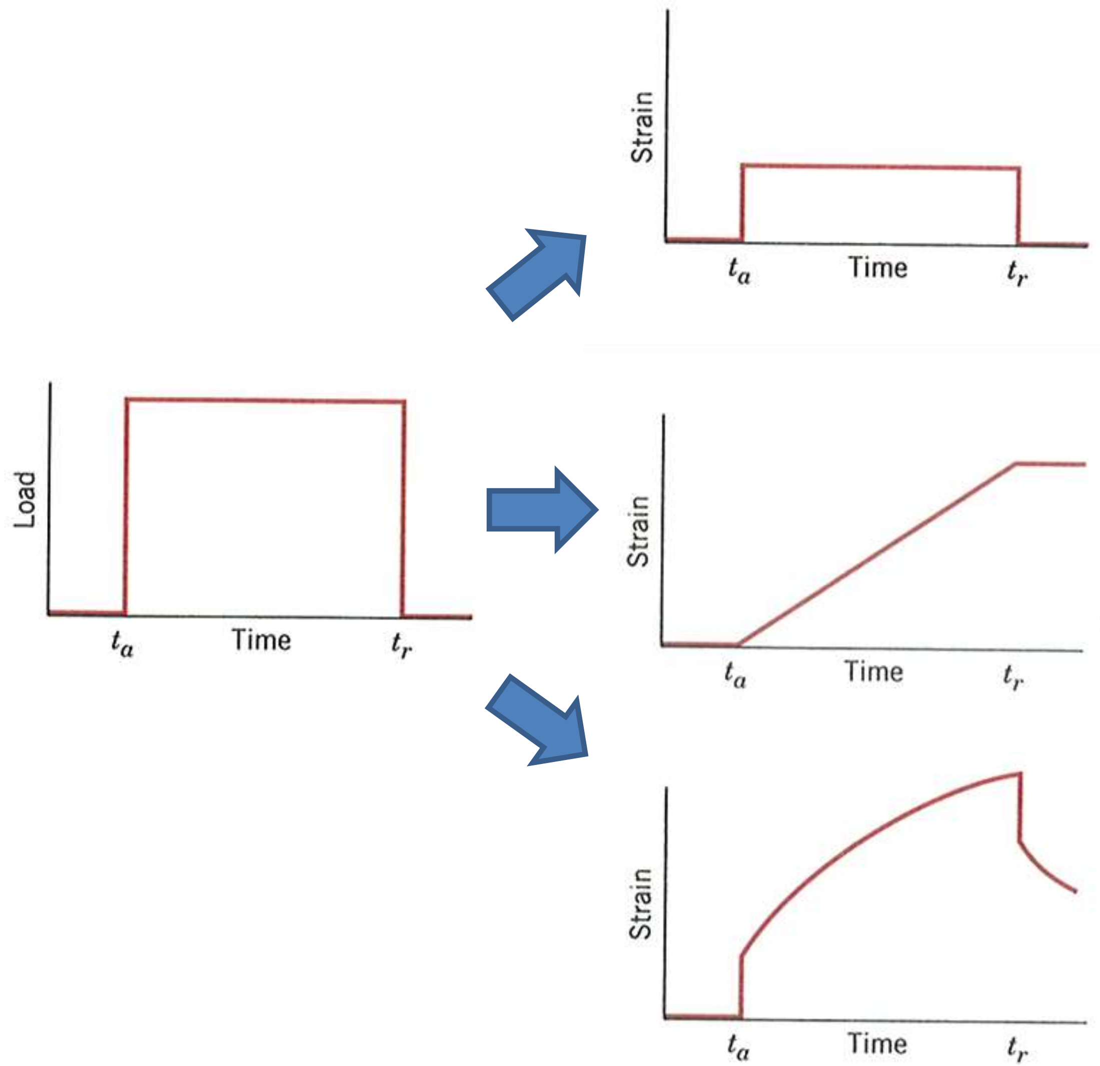
- 5 times higher specific strength than steel



- Straight, immobile repeat units, many secondary bonds
  - Highly aligned in fibres

Viscoelastic Behaviour

Polymers show time-dependent, recoverable strain = viscoelasticity



Pure Elastic Material

- Instantaneous
- Fully reversible on unloading

Pure Viscous Material

- time dependent
- Not reversible on unloading

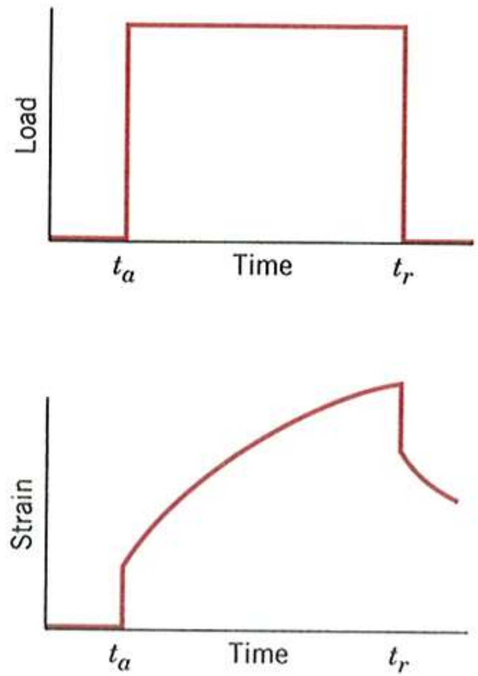
Viscoelastic Material

- Intermediate behaviour
- Partially instantaneous
- Some time dependent strain

Viscoelastic Behaviour

Creep

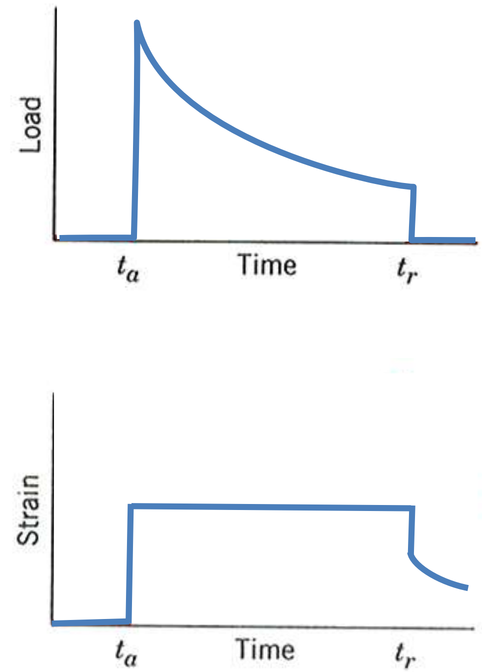
The increase in strain when held at constant stress



Creep Modulus $$E(t) = \frac{\sigma_0}{\varepsilon(t)}$$

Stress relaxation

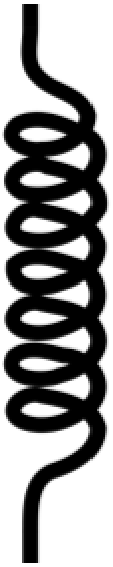
The reduction in stress when held at constant strain



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

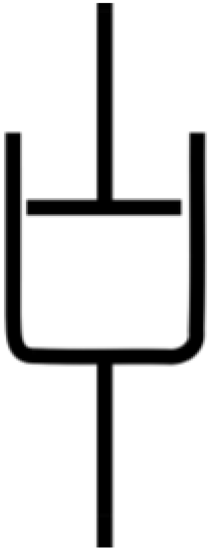
Viscoelastic Behaviour

Try to mimic this behaviour using imaginary elements



Spring
Simple elastic spring following Hooke's law. Instantaneous deformation with force proportional to deformation
Elastic part

$$\sigma = E\varepsilon$$



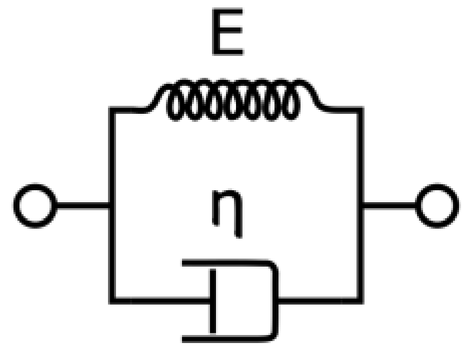
Dashpot
Damping element filled with viscous fluid which resists movement of the piston. Force needed is a function of deformation rate
Viscous part

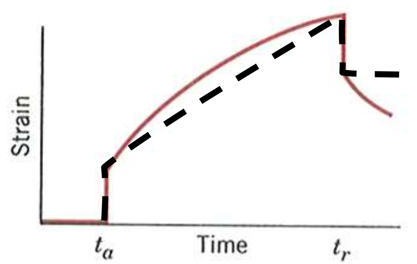
$$\sigma = \eta\frac{d\varepsilon}{dt}$$

Viscoelastic Behaviour

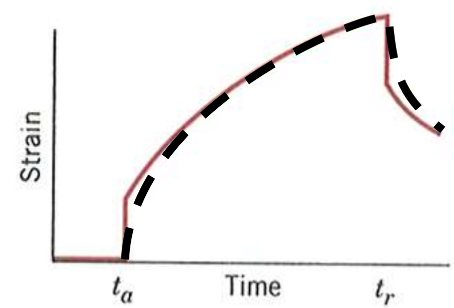
Maxwell unit
(in series)

Voigt unit
(in parallel)

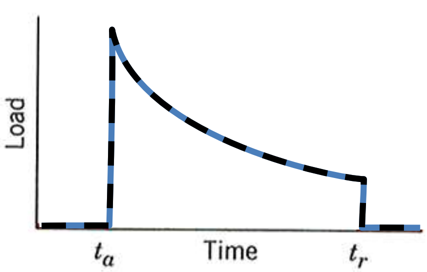




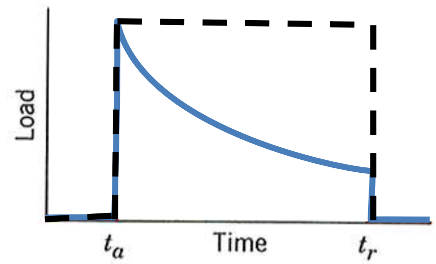
Bad Creep
No retarded strain response



Good Creep
Retarded strain response



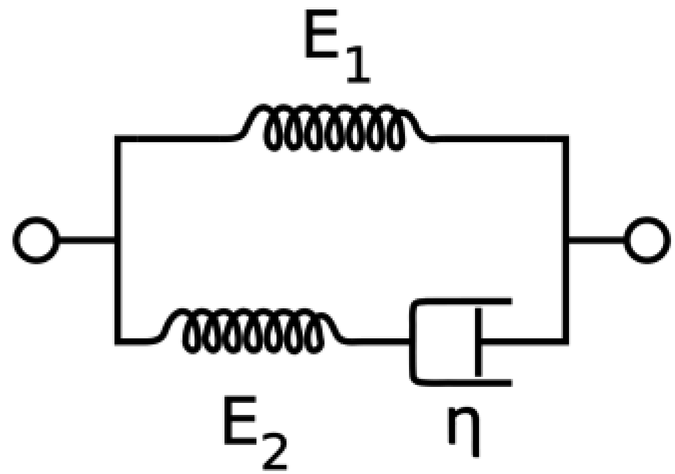
Good Relaxation
Dashpot relieves strain in spring

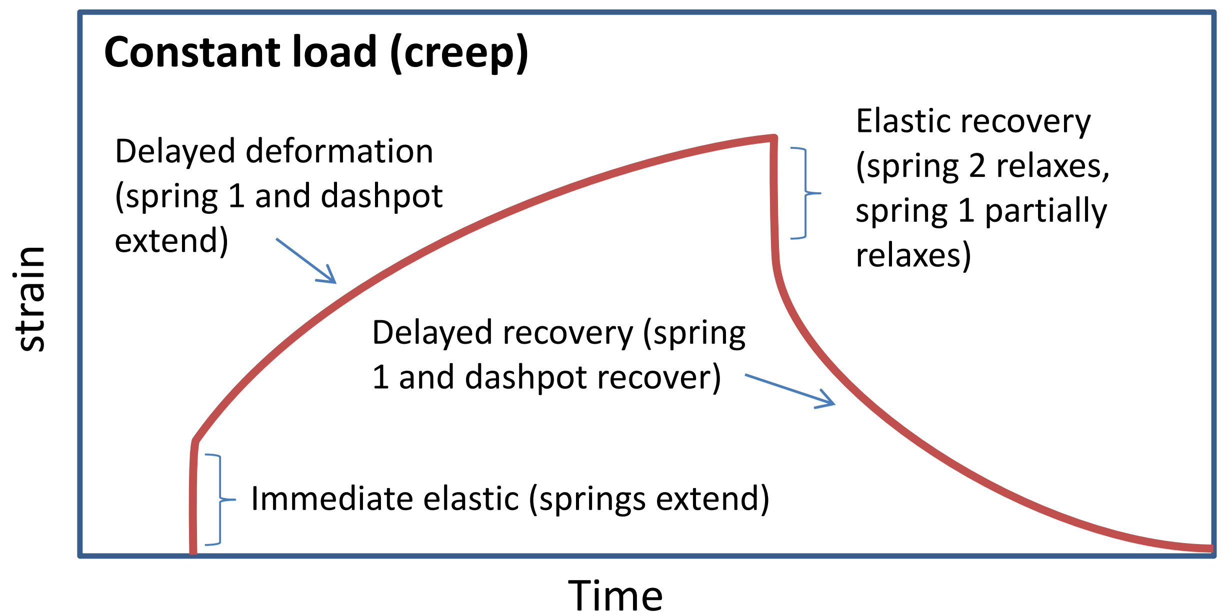


Bad Relaxation
No relaxation at all

Viscoelastic Behaviour

Standard Linear Model
(simplest model that predicts both creep and relaxation)





Predicts 100% recovery

How might permanent deformation be included? (revision question 1)

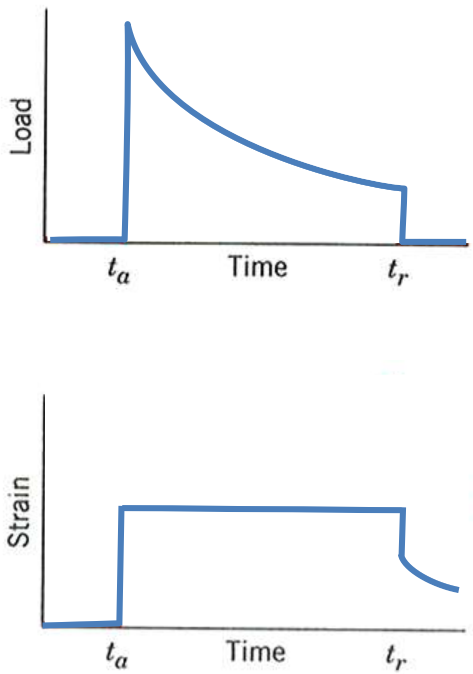
Viscoelastic Behaviour

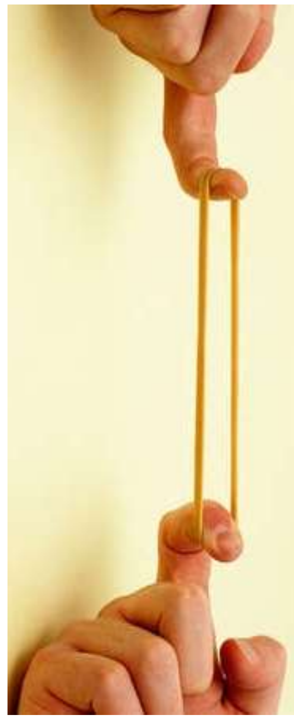
Ear plugs recover shape to fill available space

Cars left for long times develop flat spots (persists for some time)

Maxwell Relaxation Time

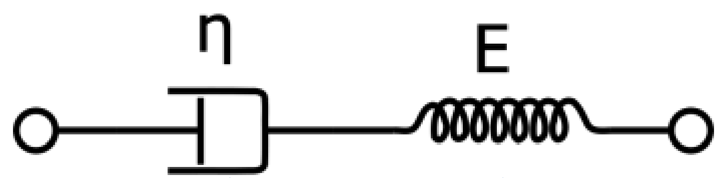
The reduction in stress when held at constant strain





Can use these models to derive mathematical models

Maxwell unit



$$\frac{d\varepsilon_d}{dt} = \frac{\sigma}{\eta}$$

$$\sigma = E\varepsilon$$

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

$$\frac{d\varepsilon_s}{dt} = \frac{1}{E}\frac{d\sigma}{dt} = -\frac{d\varepsilon_d}{dt}$$

Maxwell Relaxation Time

Under conditions of stress relaxation:

$$\frac{d\varepsilon}{dt} = \frac{1}{E}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$

$$\int_0^t \frac{E}{\eta} dt = -\int_{\sigma_0}^{\sigma} \frac{d\sigma}{\sigma}$$

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

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

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

$$\tau = \frac{\eta}{E}$$

Relaxation time
Material parameter

Measured empirically

Long time = dimensionally stable

Maxwell Relaxation Time

These are only semi-empirical models for plastic behaviour

Time (s)	Stress (MPa)
0	8.62
157	2.44

Constant strain = 5%

What is the relaxation modulus after 331 seconds?

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

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

$$\tau = \frac{-\overset{157\text{ s}}{t}}{\ln\left(\underset{2.44\text{ MPa}}{\sigma}/\underset{8.62\text{ MPa}}{\sigma_0}\right)}$$

$$\tau = 124.47s$$

$$\sigma = 8.62\exp\left(-\frac{331}{124.5}\right) = 0.60\text{MPa}$$

$$\boxed{E(t) = \frac{0.6}{0.05} = 12.07\text{MPa}}$$

Summary

- Most of the time we can treat polymer properties the same as metals/ceramics
- Need to be aware of odd differences arising from unique structure
  - Glass transition temperature
  - Chain alignment (increasing strength)
  - Viscoelasticity

Properties of Materials

Theme: Polymers and Composites

Lecture 3: Composites

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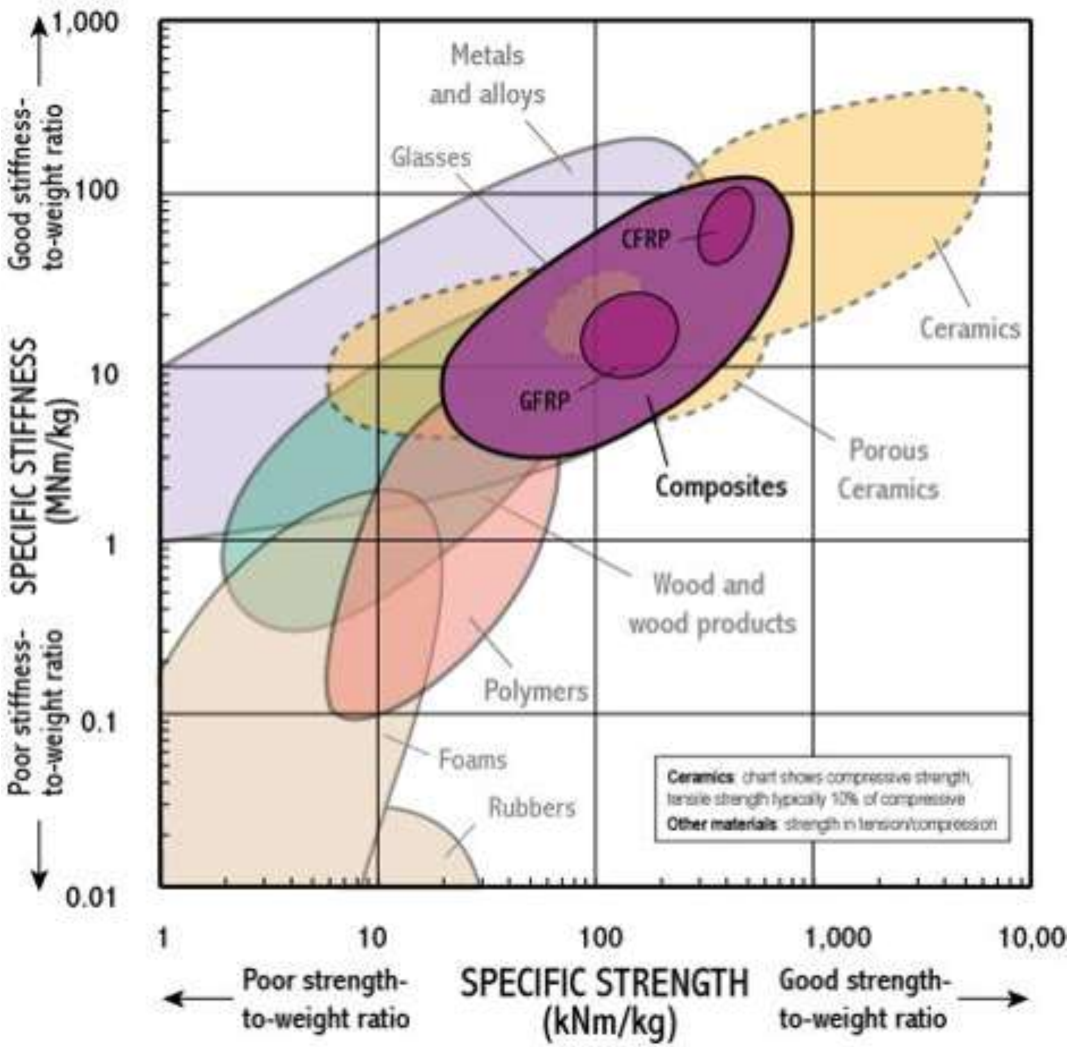
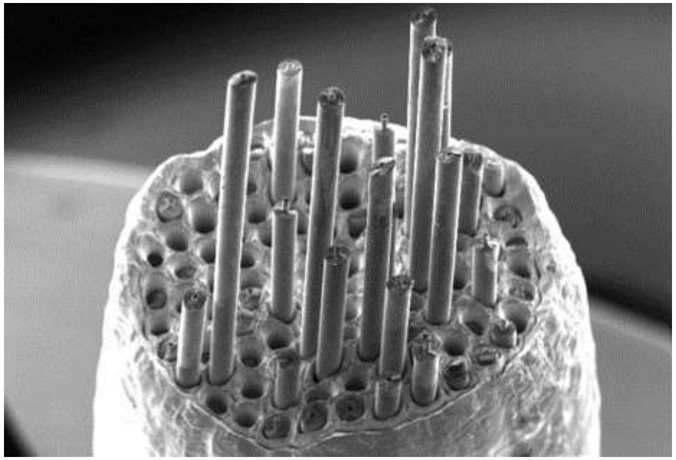
ACCIS Suite, Queen’s Building

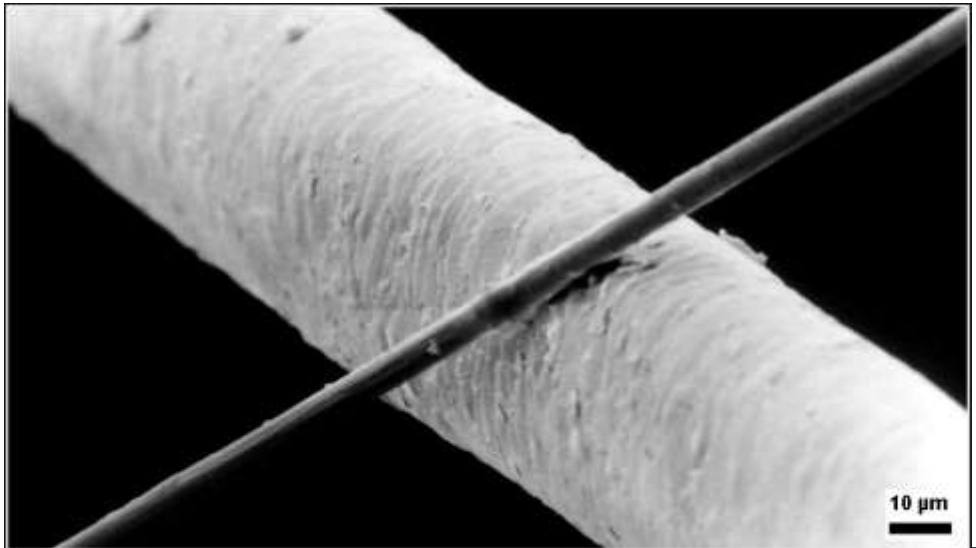
Composites



1,000
100
10
1
0.1
0.01
Good stiffness-to-weight ratio
SPECIFIC STIFFNESS (MNm/kg)
Poor stiffness-to-weight ratio
Metals and alloys
Glasses
CFRP
GFRP
Ceramics
Porous Ceramics
Composites
Wood and wood products
Polymers
Foams
Rubbers
Ceramics: chart shows compressive strength, tensile strength typically 10% of compressive
Other materials: strength in tension/compression
1
10
100
1,000
10,00
Poor strength-to-weight ratio
SPECIFIC STRENGTH (kNm/kg)
Good strength-to-weight ratio



Carbon fibre



- Hard to make bulk strong carbon
- Easy to make high quality fibre

- Fibre strong in tension
- Weave into fibre and cloth for mass use

Carbon fibre + matrix (resin)

- Fibre provides strength and stiffness
- Resin provides protection (wear, chemical) and holds shape

Properties

Expect to see volume fraction dependent properties

E.g. Carbon-epoxy

$$\rho_c = V_f \rho_f + (1 - V_f)\rho_m$$

2.2 GPa

390 GPa

$$\sigma_f = E_f \varepsilon_f$$

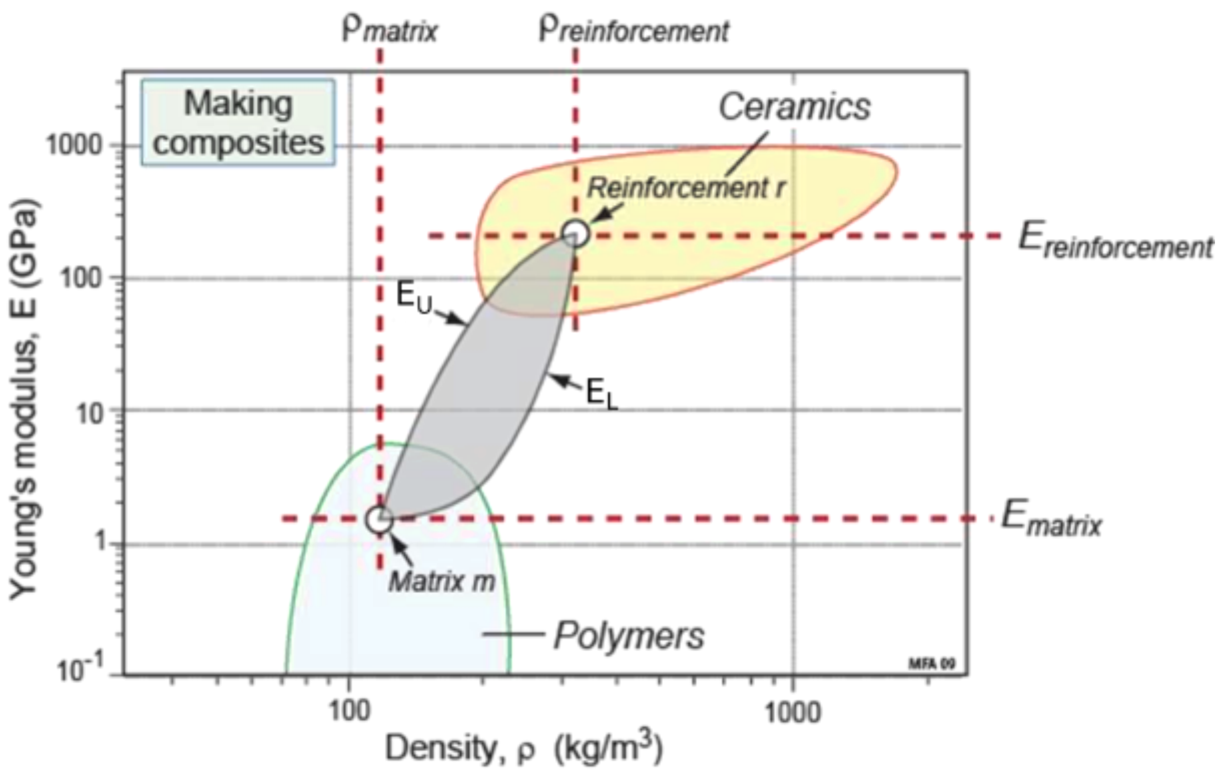
0.0056

0.06 GPa

3.5 GPa

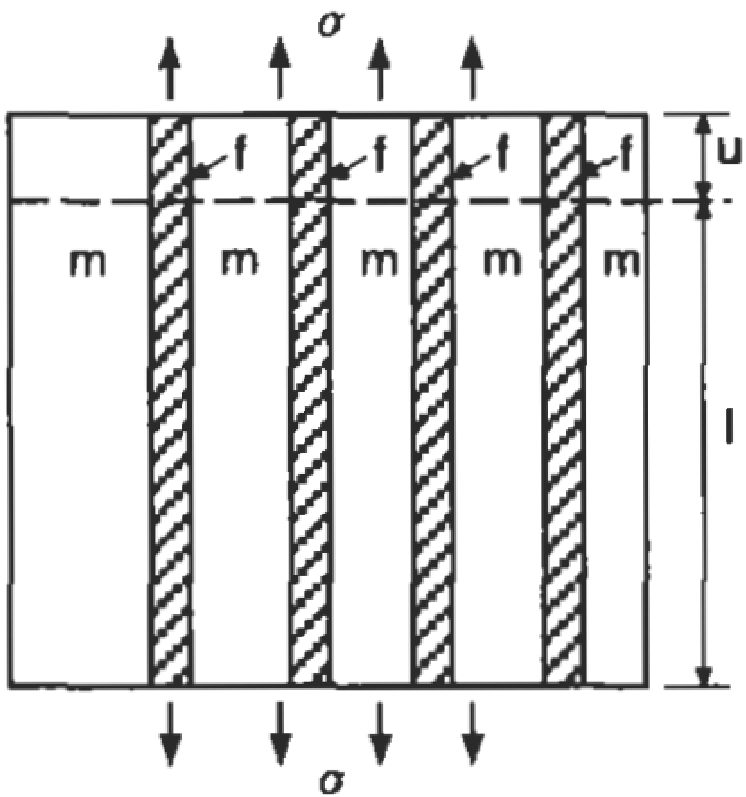
$$\sigma_m = E_m \varepsilon_m$$

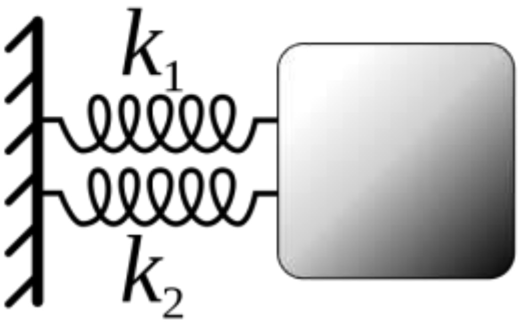
0.017



Modulus Aligned fibres

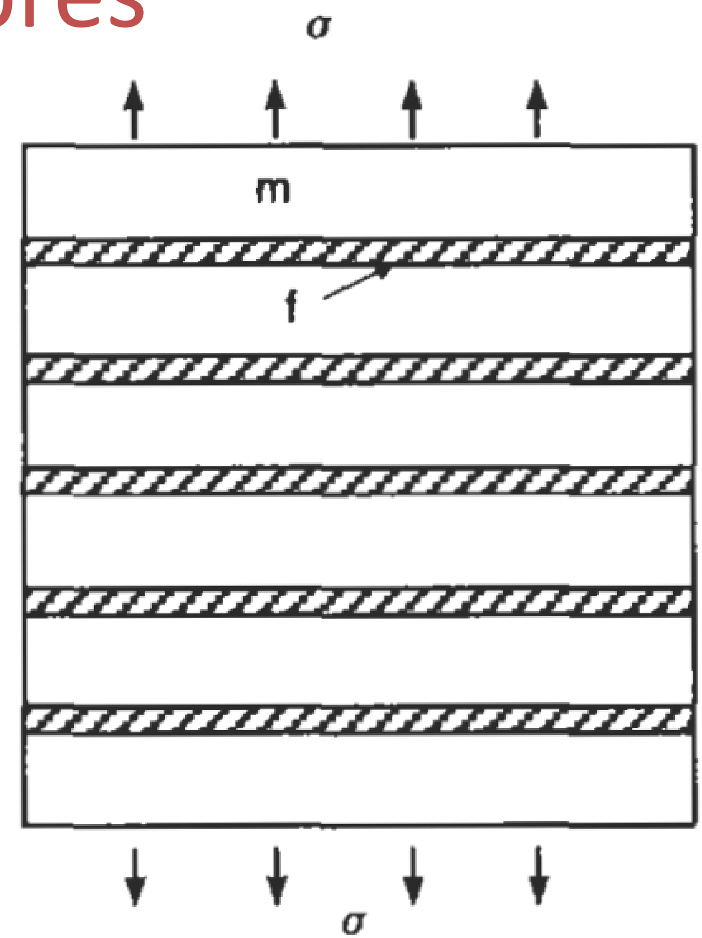
- Same **strain** in both components
  - $\varepsilon_c = \varepsilon_f = \varepsilon_m$
  - Otherwise continuity breaks
- Fibre higher modulus
  - Same strain, high E = high fibre stress
  - Load partitioning
  - Load shedding

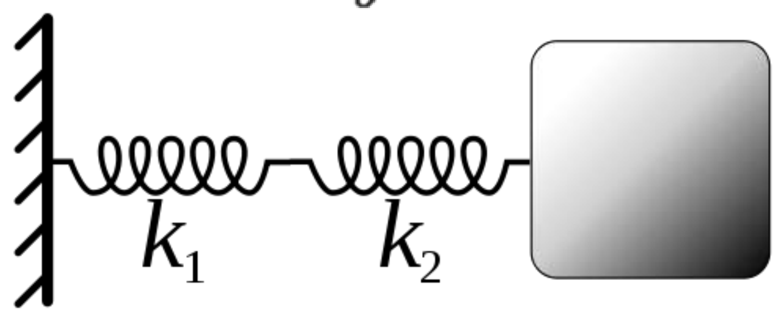




Modulus Unaligned fibres

- Same **stress** in both components
  - $\sigma_c = \sigma_f = \sigma_m$
  - No need for continuity
- Strain function of E
  - Matrix: low E, high strain
  - Fibre: high E, low strain
- Fibres provide no restraint on matrix strain
  - limited reinforcement





Modulus

Aligned (Voigt)

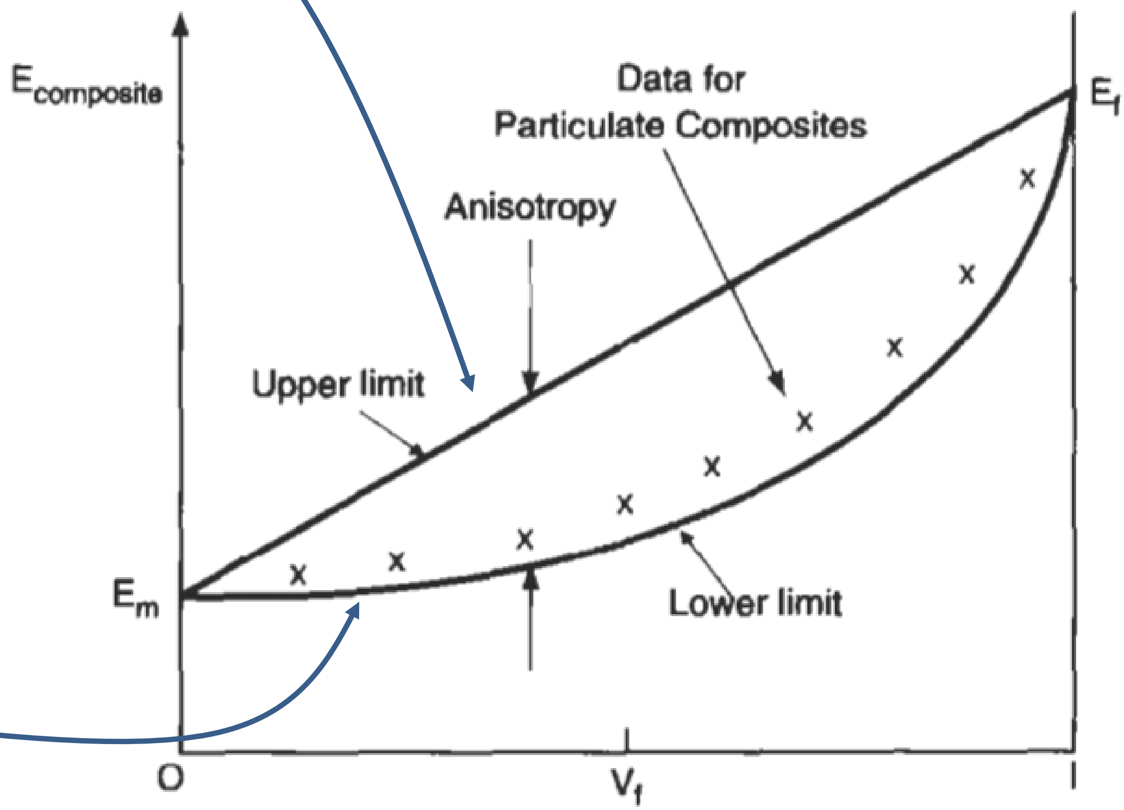
$$E_c = V_f E_f + (1 - V_f) E_m$$

Upper limit

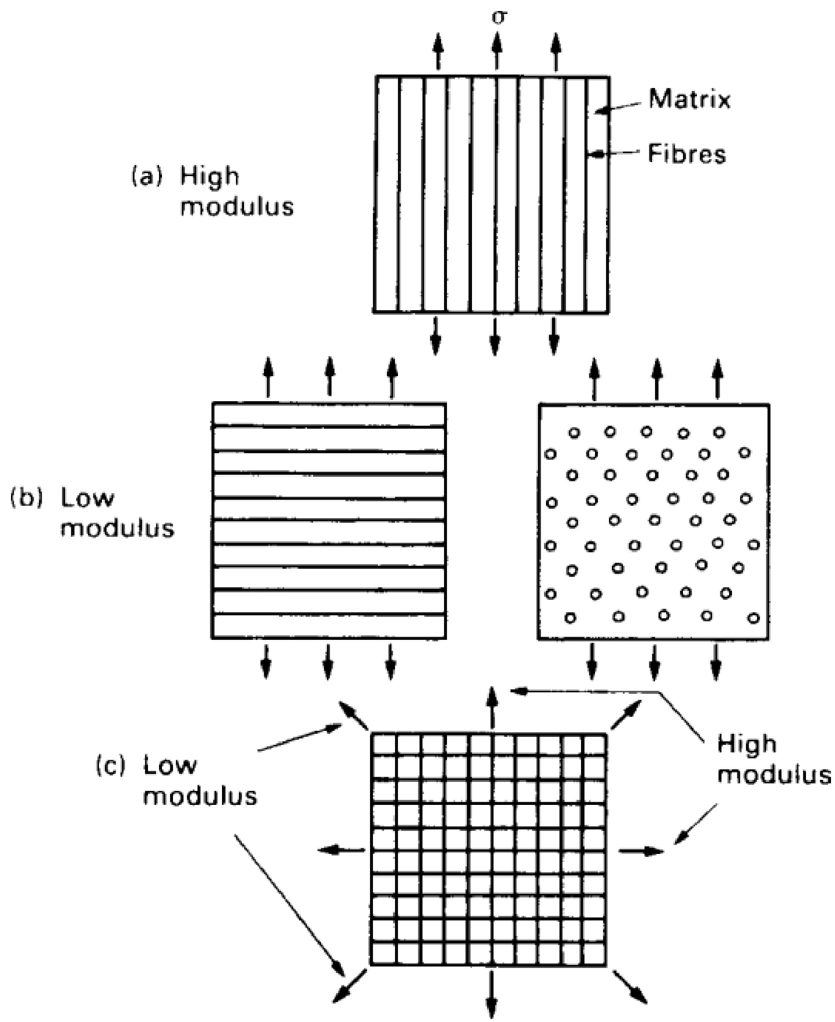
Unaligned (Reuss)

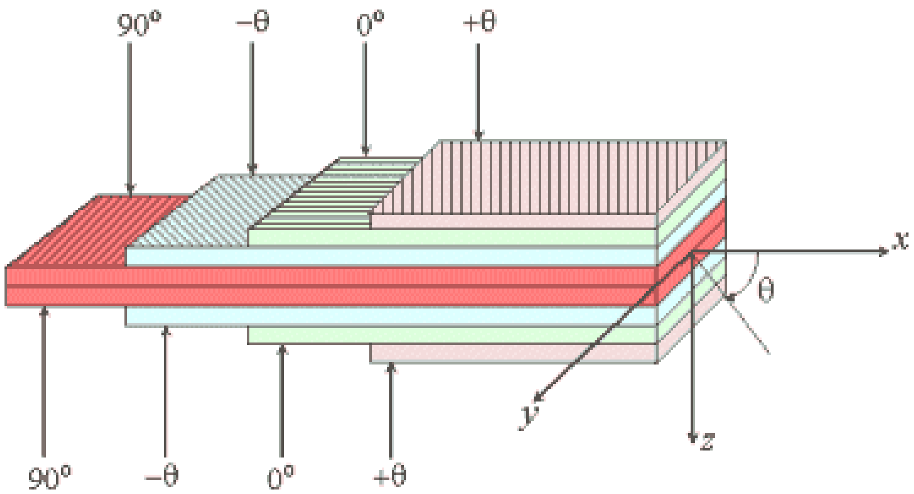
$$\frac{1}{E_c} = \frac{V_f}{E_f} + \frac{(1 - V_f)}{E_m}$$

Lower limit

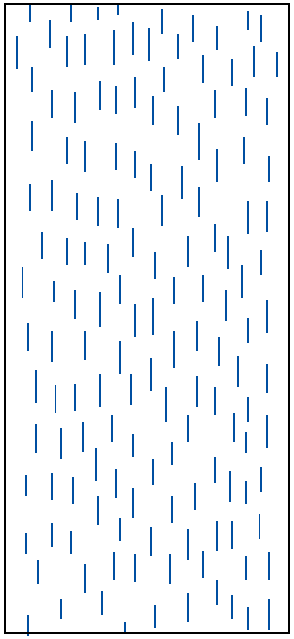


Anisotropy

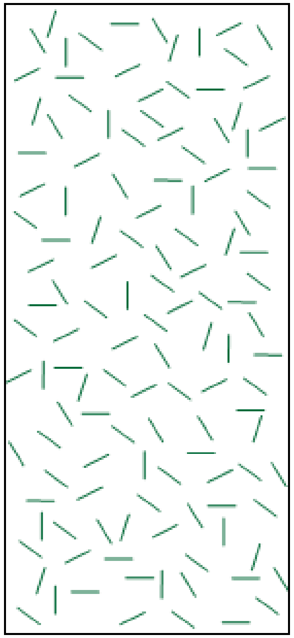

σ
Matrix
Fibres
(a) High modulus
(b) Low modulus
(c) Low modulus
High modulus


90°
−θ
0°
+θ
x
y
z
θ
90°
−θ
0°
+θ

Anisotropy

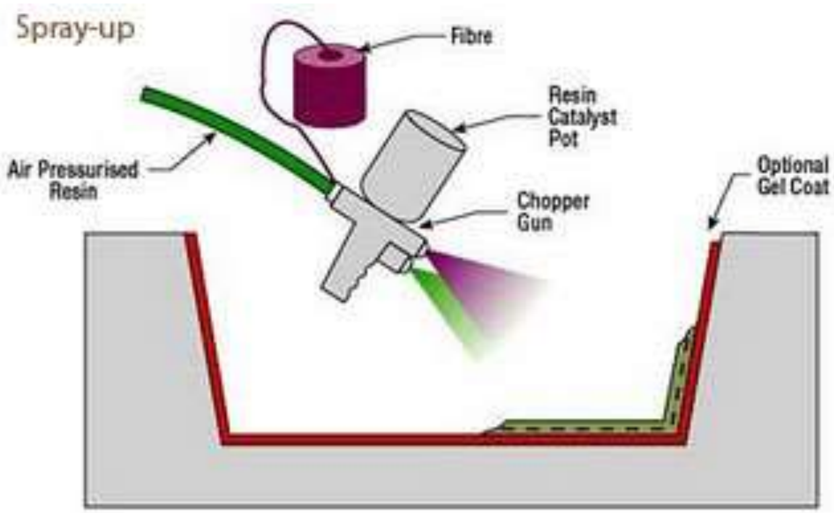


Aligned short
fibres
High peak E
High anisotropy



Random short
fibres
Lower peak E
Low anisotropy

$$E_c \approx \frac{(E_u+E_l)}{2}$$



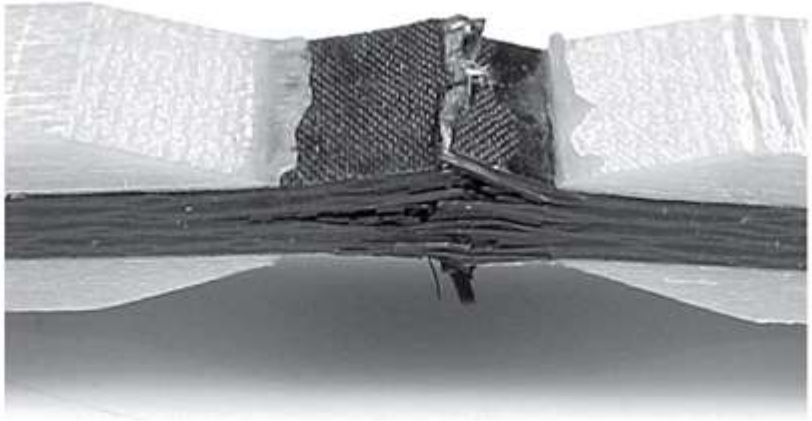
Anisotropy

Opportunity to customise modulus to be high in specified directions

Potential for failure due to unexpected loading!

Strength

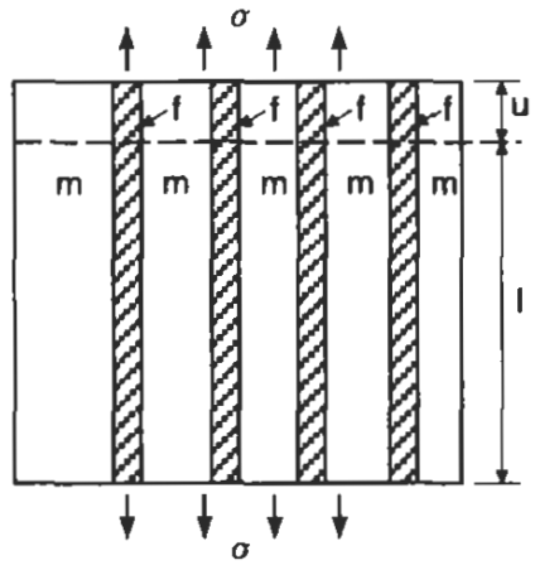
- Much more complex than modulus
- Multiple failure mechanisms
- Hard to predict compared to metals
  - Major limit on uptake



Strength

Assume linear elastic fibres and matrix

$$\sigma_c = V_f \sigma_f + (1 - V_f)\sigma_m$$



2.2 GPa

390 GPa

$$\sigma_f = E_f \varepsilon_f$$

0.0056

0.06 GPa

3.5 GPa

$$\sigma_m = E_m \varepsilon_m$$

0.017

- High fibre fraction
  - Controlled by stiff fibres
  - Fibres fail, matrix fails

$$\varepsilon_m = \varepsilon_f$$

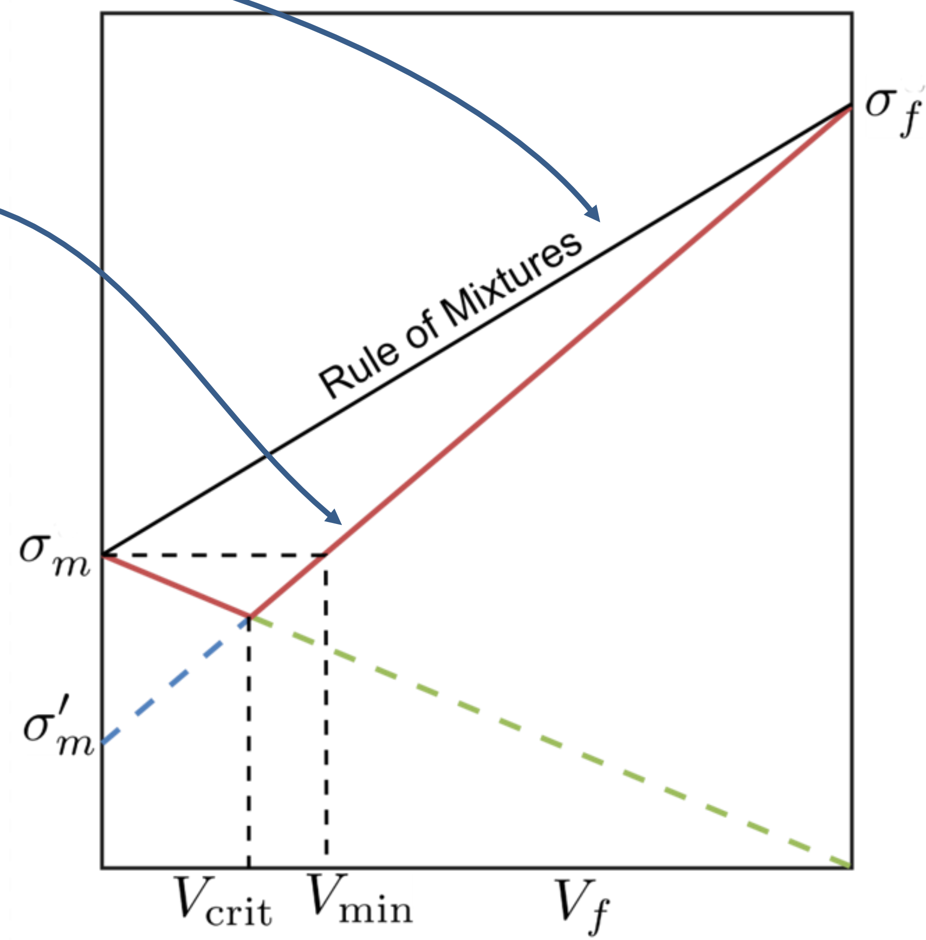
$$\sigma_m{}' = E_m \varepsilon_f$$

  - Reduced matrix contribution

Strength

$$\sigma_c = V_f \sigma_f + (1 - V_f)\sigma_m$$

$$\sigma_c = V_f \sigma_f + (1 - V_f)\sigma_m'$$

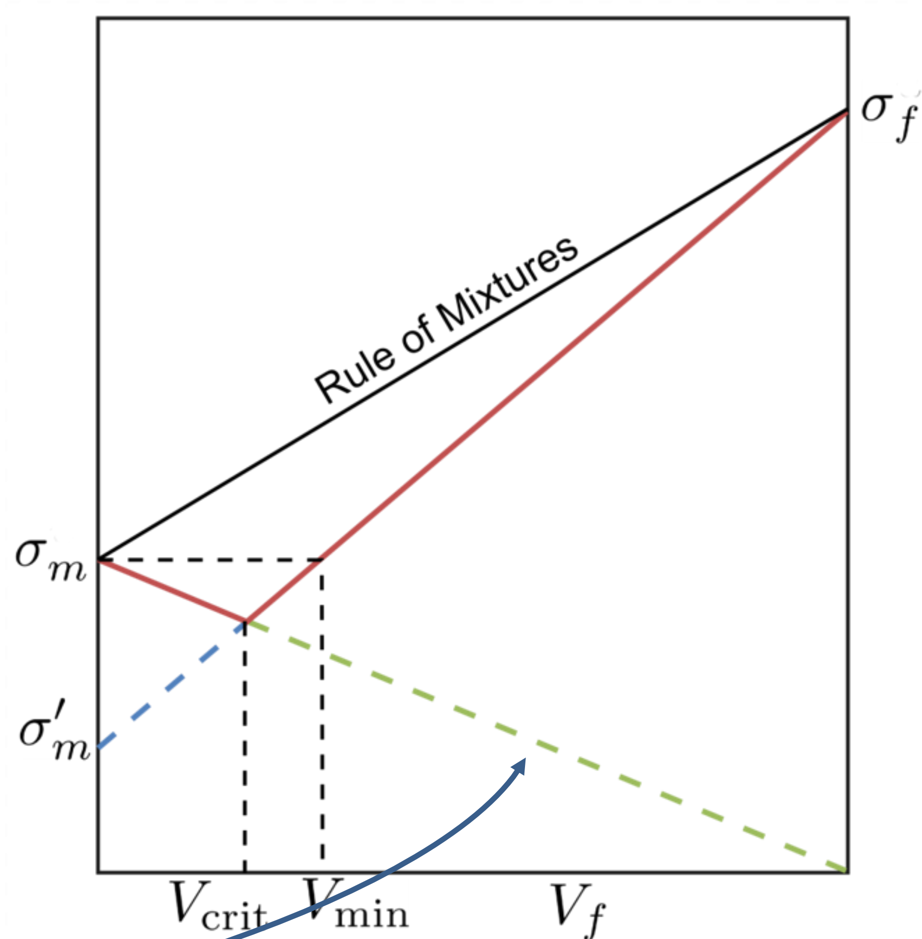


Strength

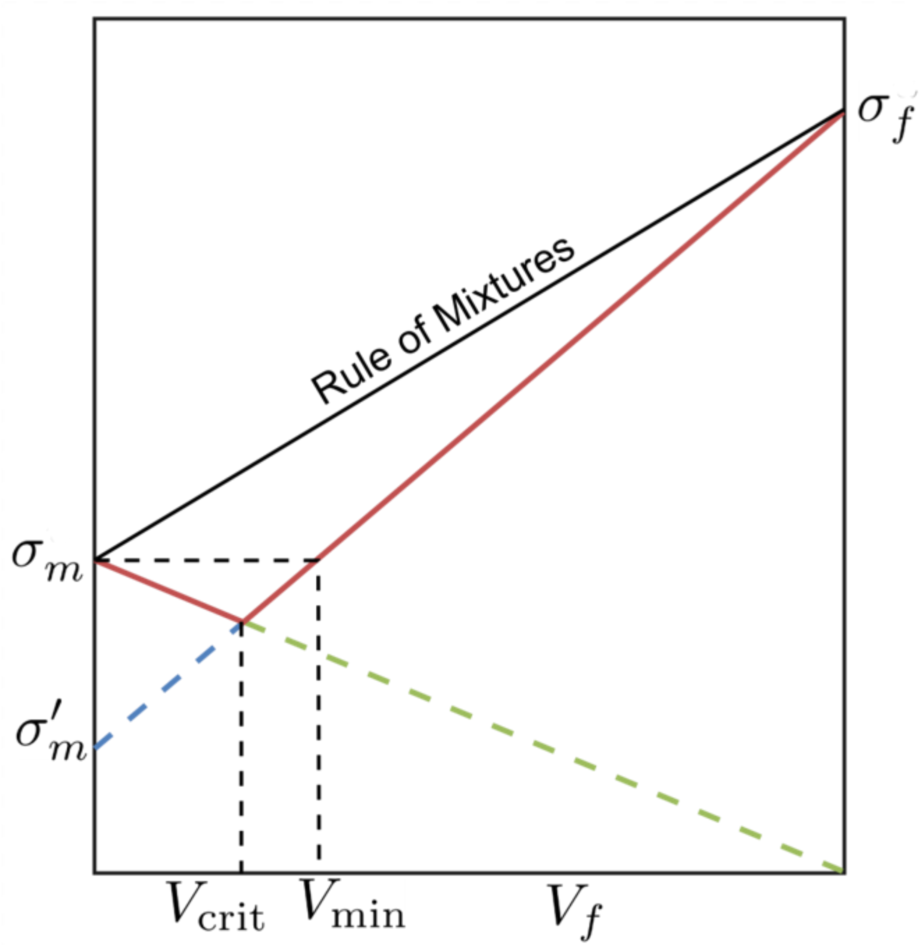
- Low fibre fraction
  - Controlled by matrix
  - matrix fails, fibres fail
  - $\varepsilon_c \approx \varepsilon_m$
  - Fibres already fractured by the time the matrix reaches failure strain
  - Fibres effectively hole

$$\sigma_c = V_f \sigma_f + (1 - V_f)\sigma_m$$

$$\sigma_c = (1 - V_f)\sigma_m$$

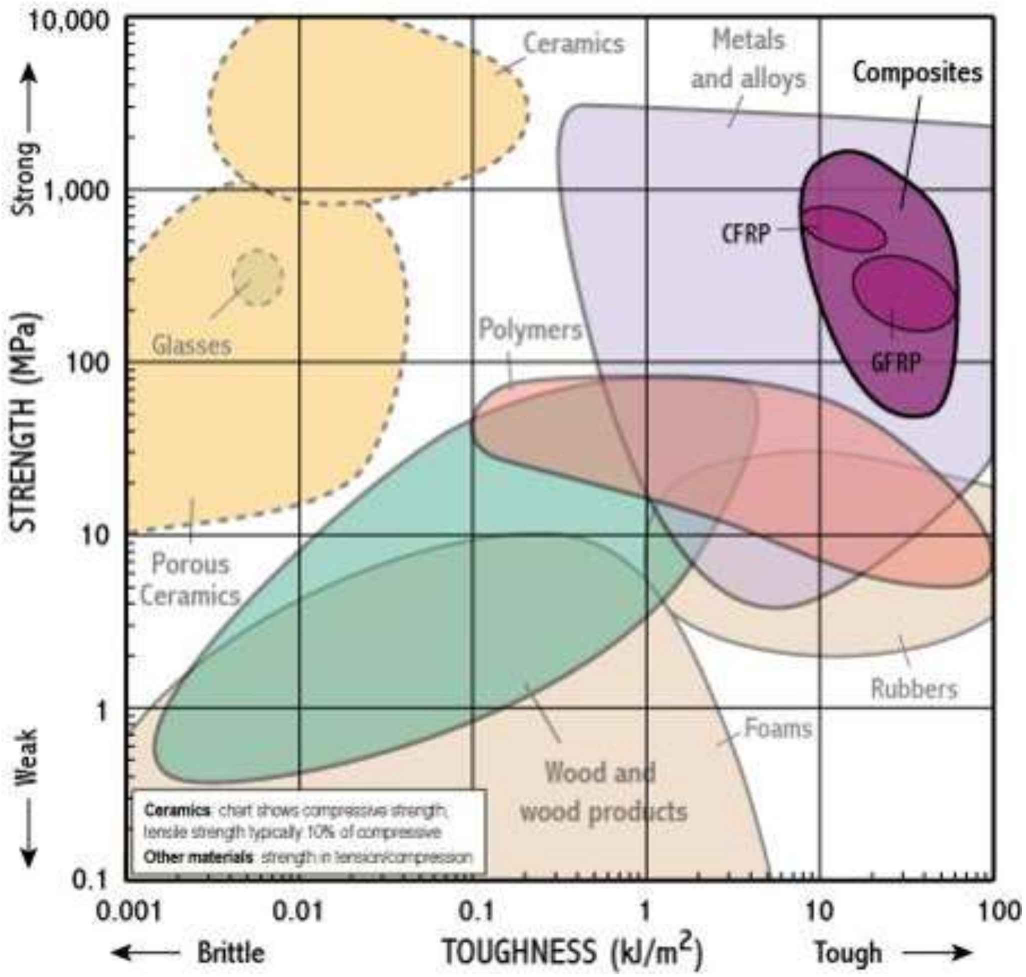


Strength



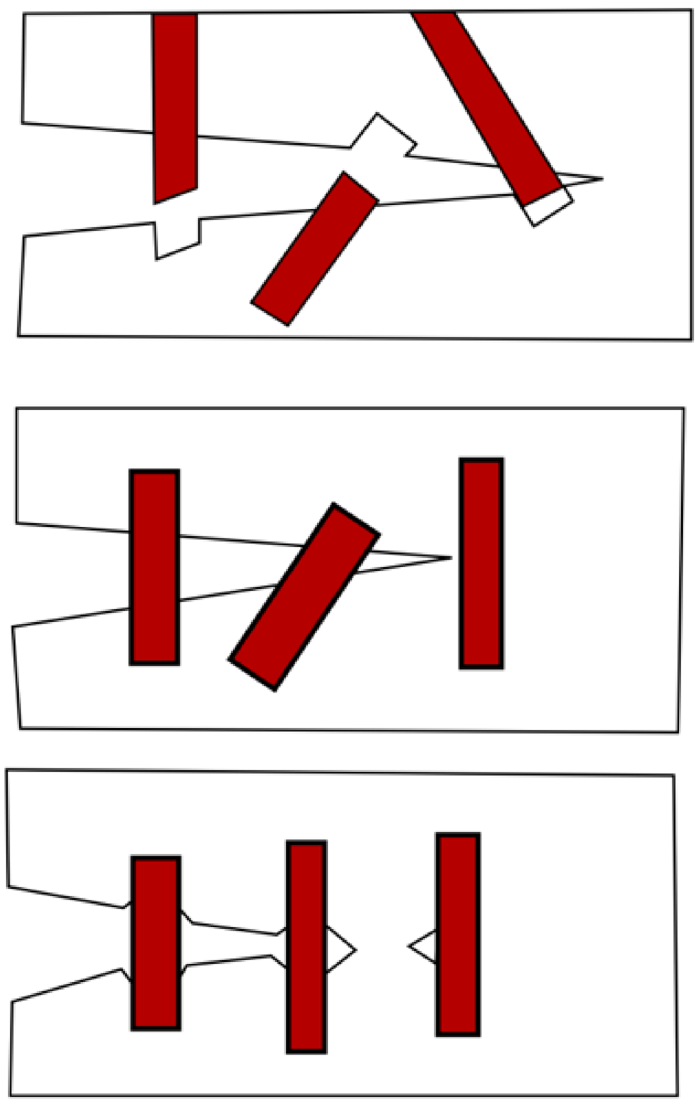
- Less benefit than expected
- Need minimum V_f to improve compared to matrix
- Actually compromise strength prior to V_{min}
  - Very low for strong fibres/weak matrix
  - Worst strength at V_{crit}

Toughness



- Composites give E and σ_f of ceramic without the brittleness (much)
- Small, high quality fibres
- Protection by matrix
- Complex fracture mechanisms

Toughness



- Fibre pull out
  - Drag fibres from matrix
- Crack bridging
  - Fibres hold crack together and prevent it growing
- Deflection
  - Fibres get in way of crack

Summary

- Composites (and other hybrids) get strengths of both phases and mitigate weaknesses of both
- Potential game changer in design
  - Not properly exploited?
- Introduce new set of complications
  - Either component can fail
  - Multiple failure modes
  - New failure modes
  - Anisotropy in modulus and strength