Properties of Materials

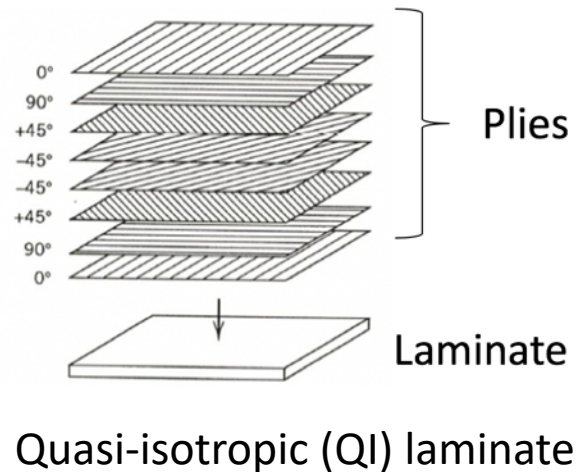## Theme: Polymers and Composites

Revision Tutorial

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Room 0.106 Queen's Building

Lecture 1

Question 1: Which of the following laminate configurations provides the highest stiffness, a cross-ply laminate [0/90], a quasi-isotropic laminate [0/90/+45/-45] or a unidirectional (UD) laminate?

Quasi-isotropic (QI) laminate

The maximum stiffness $\mathbf{E_{max}}$ is found along the fibre direction in each ply.
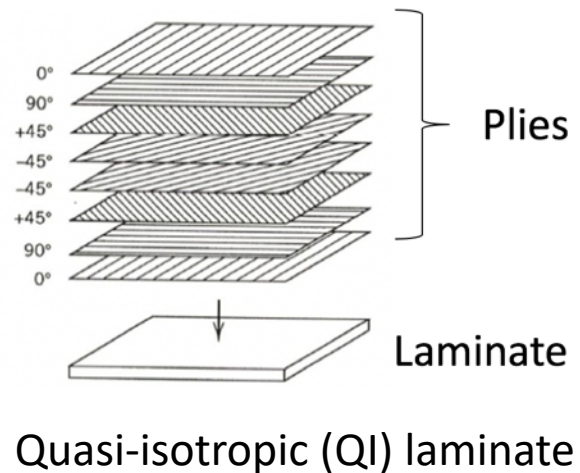
Lecture 1

Question 1: Which of the following laminate configurations provides the highest stiffness, a cross-ply laminate [0/90], a quasi-isotropic laminate [0/90/+45/-45] or a unidirectional (UD) laminate?

Quasi-isotropic (QI) laminate

$E_{11} = 138$ GPa
$E_{22} = 8.96$ GPa
$G_{12} = 6.9$ GPa
$v_{12} = 0.25$
$v_{21} = 0.25$
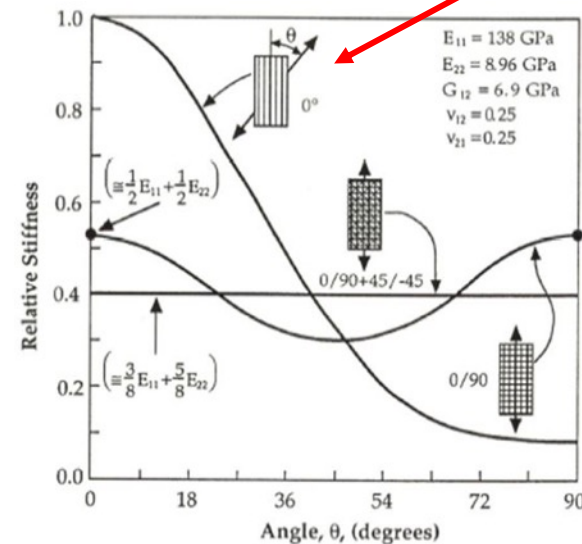
A unidirectional laminate [0]

$$E_{max} \sim V_f E_f$$
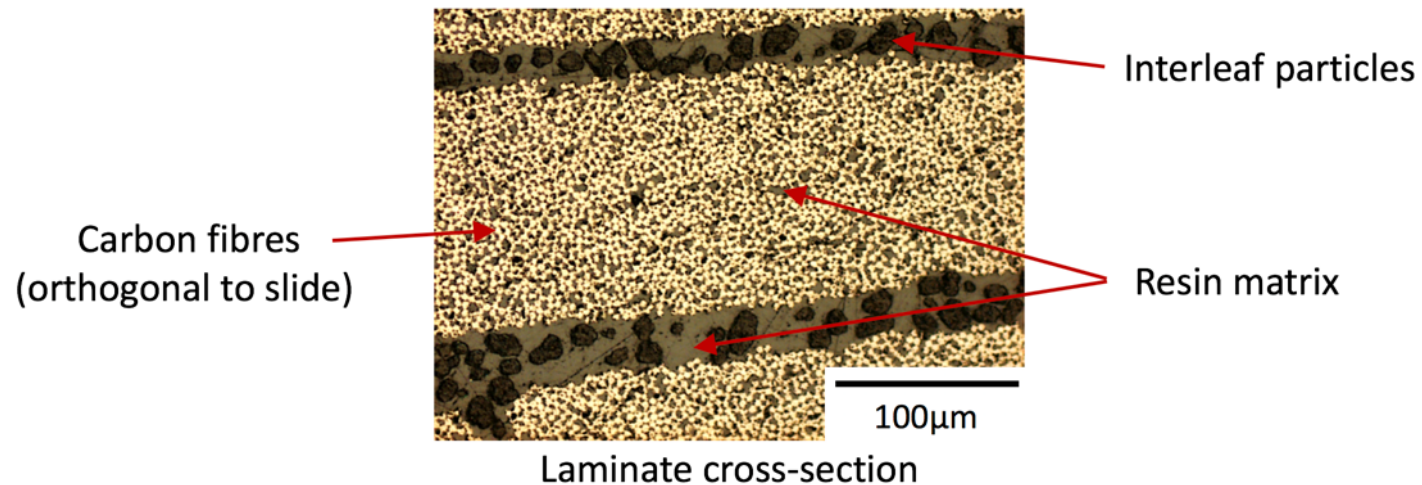
A cross-ply laminate [0/90]

$$E_{max} \sim \frac{1}{2} V_f E_f$$

A quasi-isotropic laminate [0/90/+45/-45]

$$E_{max} \sim \frac{1}{5} V_f E_f$$

Lecture 1

Question 2: In order to calculate the laminate stiffness, which parameters need to be known?

Carbon fibres
(orthogonal to slide)

Interleaf particles

Resin matrix

100μm

Laminate cross-section

Components (resin matrix, fibres, toughening additives) all contribute to total stiffness.

Need to know what is in the laminate (and in what proportion).

Lecture 1

Question 2: In order to calculate the laminate stiffness, which parameters need to be known?
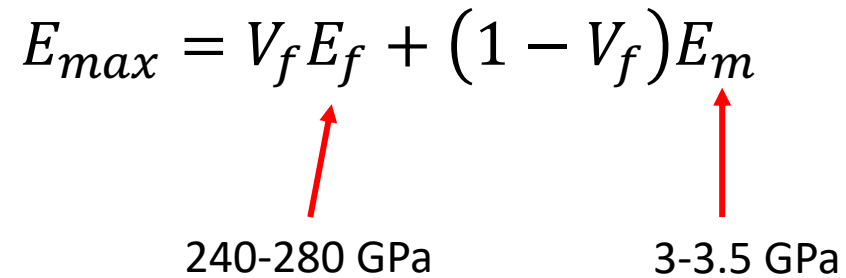
$$E_{max} = V_f E_f + (1 - V_f)E_m$$

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Lecture 1

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$$E_{max} = V_f E_f + (1 - V_f) E_m$$
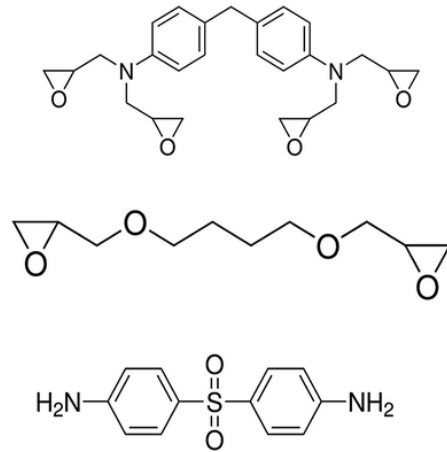
240-280 GPa   3-3.5 GPa

Target V_f = 55-60% (aerospace)

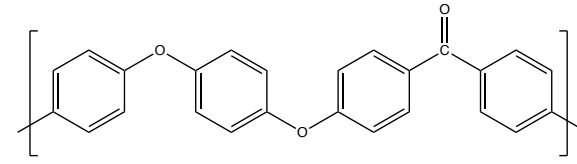Components (fibres, resin matrix, toughening additives) all contribute to total stiffness.

Need to know what is in the laminate (and in what proportion).

Lecture 1

Question 3: What are the main chemical and structural differences between a thermoset and a thermoplastic?

Thermoset – 3D network (crosslinked)
Made up of reactive components (chemistry)

Thermoplastic – linear or branched
Made up of high molecular weight chains
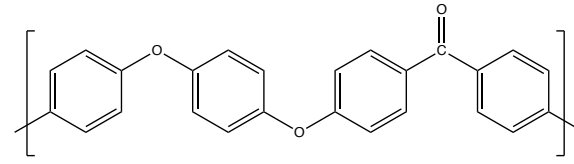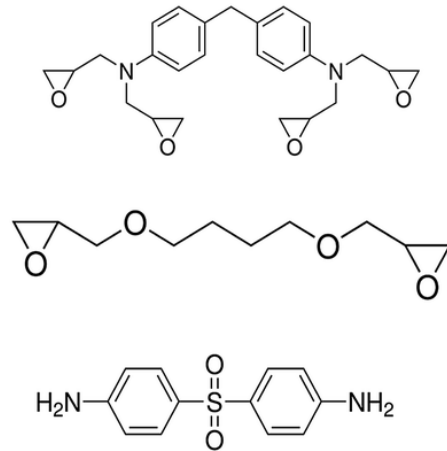
Lecture 1

Question 3: What are the main chemical and structural differences between a thermoset and a thermoplastic?

- TS: Thermosets (Epoxies)
  - Processed al low molecular-weight (viscosity low)
  - Easily wet fibres
  - React to form a high-molecular-weight glassy solid
  - Add energy (heat) to form irreversible crosslinks

- TP: Thermoplastics
  - Processed at high molecular-weight (viscosity 10x > TS)
  - Add energy, shape, and cooled to solidify
  - Reprocessable, weldable, recyclable (?)

Lecture 1

Question 4: What are the typical mechanical differences between a thermoset, such as an epoxy, and a thermoplastic, such as PEEK?

Material	E (GPa)	σ Failure (MPa)	Maximum strain (%)	Density	T_g (°C)	$T_{process}$
Epoxy	3.4	59	3.3	1.2	180	180
PEEK	3.4	100	150	1.3	143	380

Lecture 1

Question 5: Thermoplastics (interleaves and particles) are used to toughen thermosets in modern advanced composites – how does this method operate?
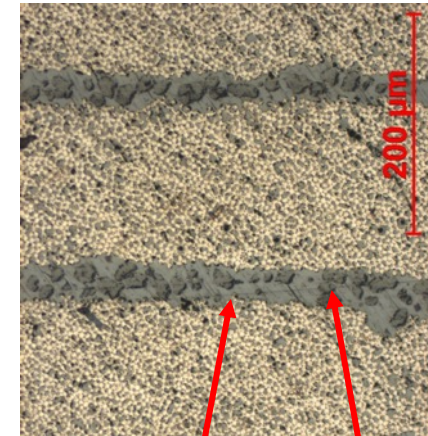
Older generation epoxy

Current epoxy

Thermoplastics present as distributed phase.

Crack path through TP causes cavitation/ distortion and 'pull out' of TP

TPs present as leaves and particles

TP leaves toughen in similar way, but particles deflect cracks and prevent interleaves being crushed

Lecture 1

Question 6: Consider three different laminate deposition methods and fill out the table.
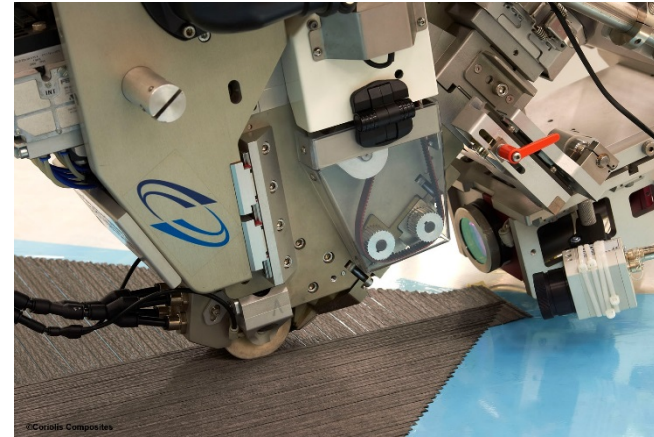
Method	Advantages	Disadvantages
Hand lay up		
Automated fibre placement (AFP)		
Resin infusion		

Lecture 1

Question 6: Consider three different laminate deposition methods and fill out the table.
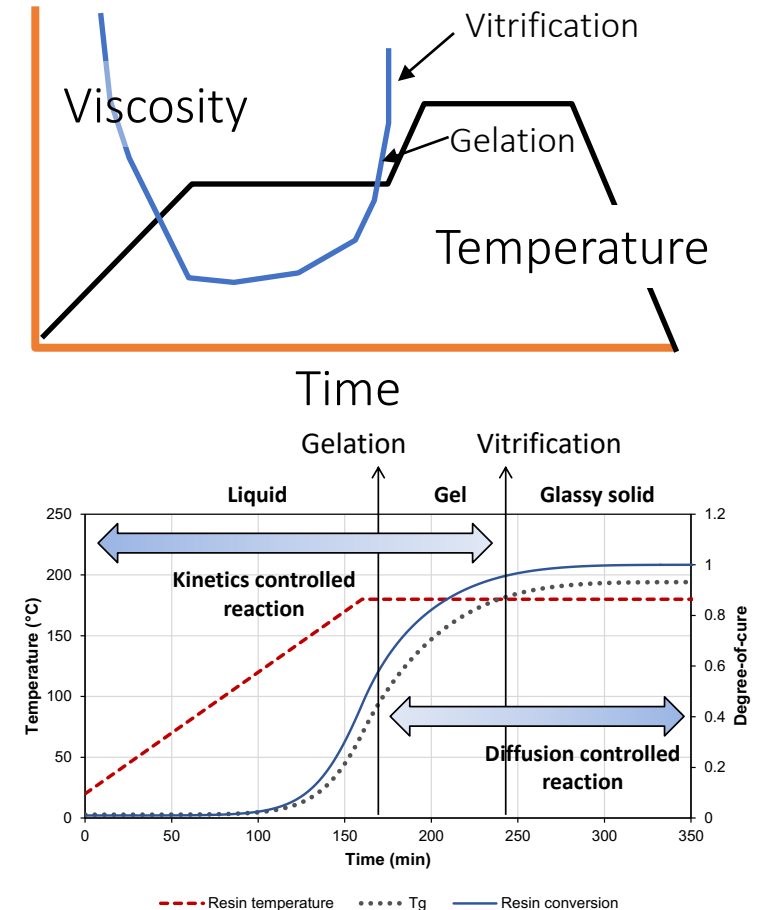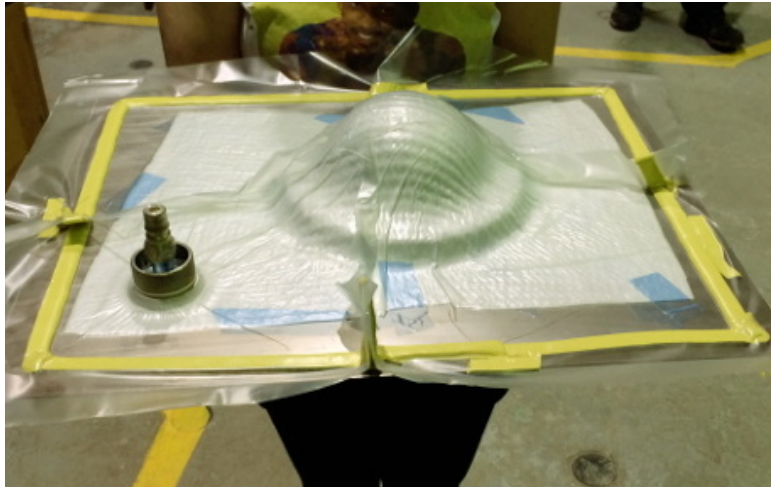

Hand lay up

AFP

Resin infusion

Lecture 1

Question 6: Consider three different laminate deposition methods and fill out the table.

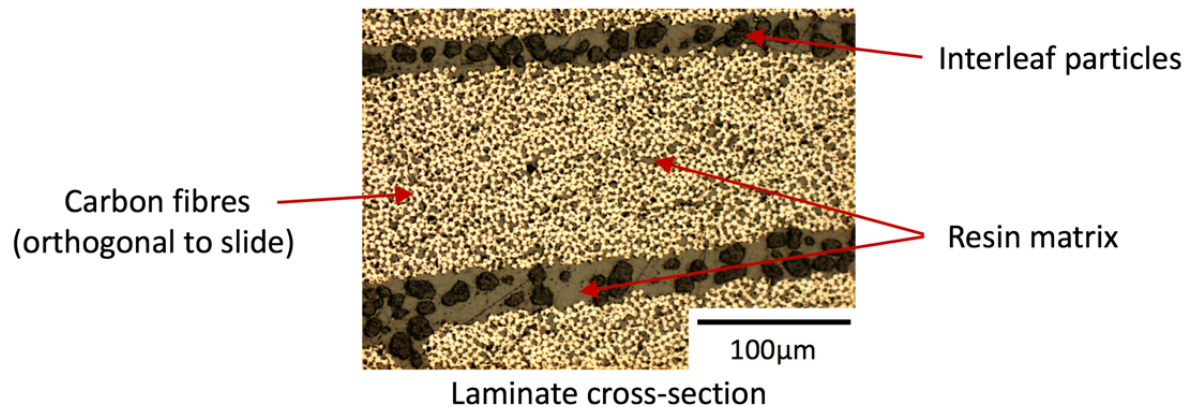| Method	Advantages	Disadvantages
Hand lay up	Relatively cheap Widely available Well suited to complex geometries	Limited in component scale Precision depends on person Labour intensive
Automated fibre placement (AFP)	High orientation precision Not labour intensive	Expensive investment Not well suited to complex geometries
Resin infusion	Well suited to small and large scale manufacture Well suited to complex geometries	Limited to low viscosity matrices May be slow for large components

Lecture 1

Question 7: Assuming that one of the three methods (in the above table) has been used to produce the uncured laminate, what are the basic steps to take in preparing a composite using an autoclave?
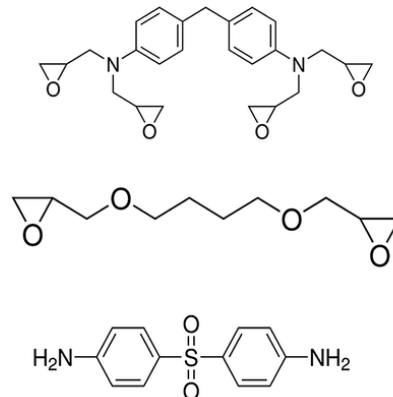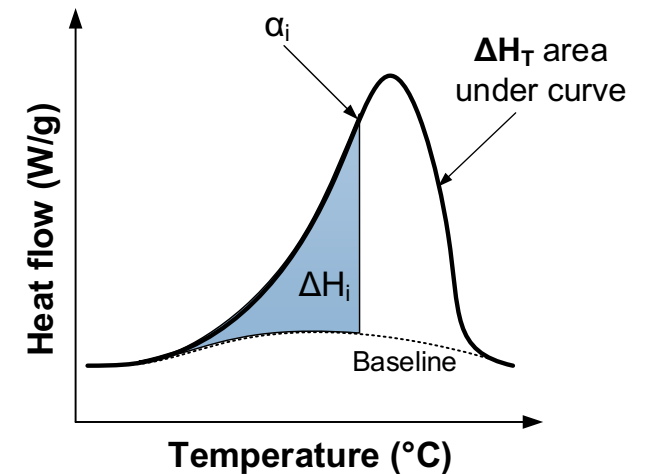
Lecture 2

Question 1: When processing a thermoset resin matrix, heat is evolved in this exothermic reaction. What are individual parameters that determine the heat absorbed by the composite?
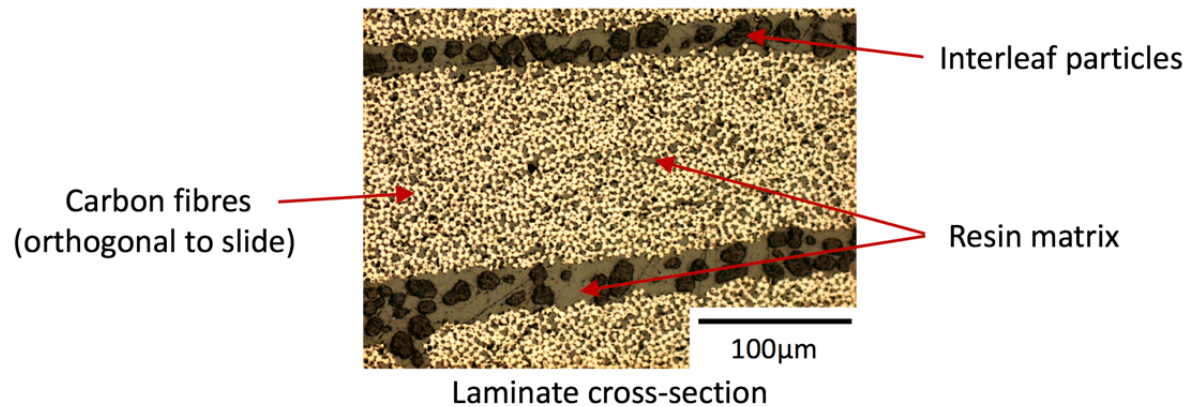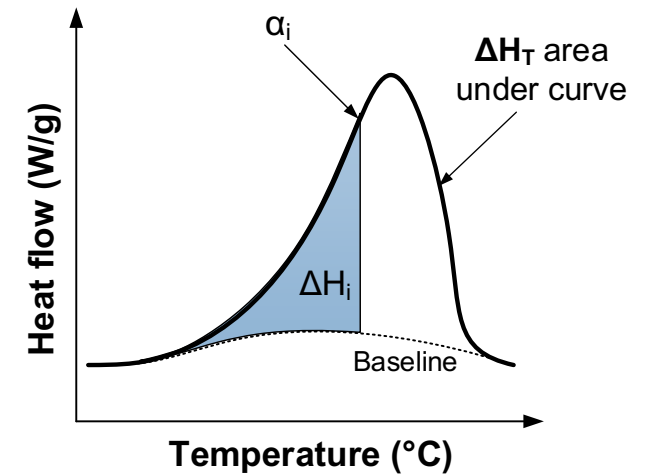

Interleaf particles

Carbon fibres (orthogonal to slide)

Resin matrix

Laminate cross-section

$$\alpha = \frac{\Delta H_i}{\Delta H_T}$$

ΔH_i: enthalpy at a specific time
ΔH_T: total enthalpy of the reaction

α_i

ΔH_T area under curve

Heat flow (W/g)

ΔH_i

Baseline

Temperature (°C)

Lecture 2

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100μm

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Heat flow (W/g)

α_i

$\mathbf{\Delta H_T}$ area under curve

ΔH_i

Baseline

Temperature (°C)

Heat **ABSORBED** by the composite

Heat **TRANSFERRED** by the composite

Heat **GENERATED** by curing resin

$$\rho C_p \frac{\partial T}{\partial t} - \nabla(k_z \nabla T) = \rho(1 - V_f)\Delta H_R \frac{d\alpha}{dt}$$

Density

Specific heat capacity

Thermal conductivity

Fibre volume fraction

Heat of reaction

Cure rate or Cure **kinetics**

16

Lecture 2

Question 2: This is the output from DSC measurements at different temperatures. What is the effect of the process temperature on the extent of reaction (degree of cure, α)?
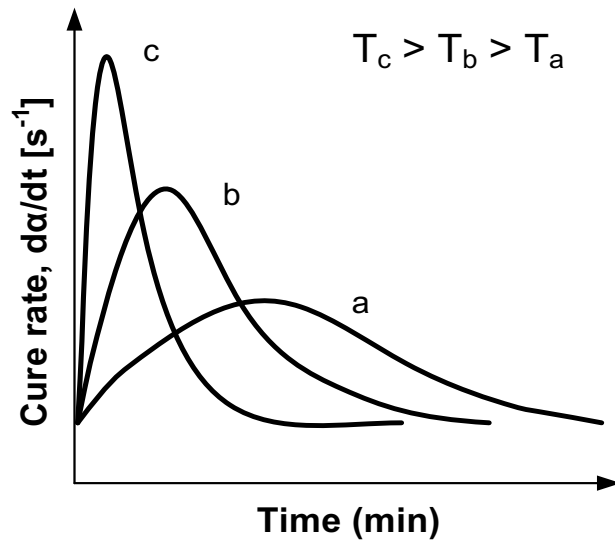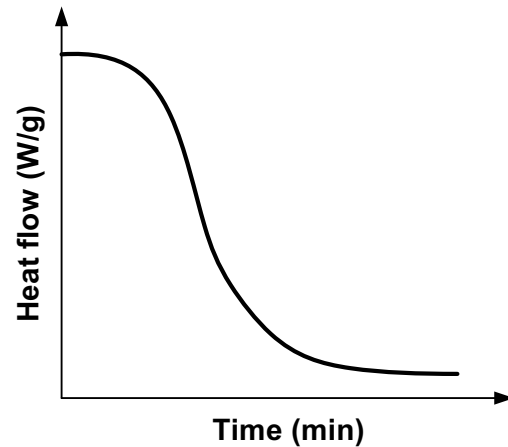

Increasing process temperature increases rate of reaction, increases number of crosslinks formed, increases degree of cure, raises T_g.
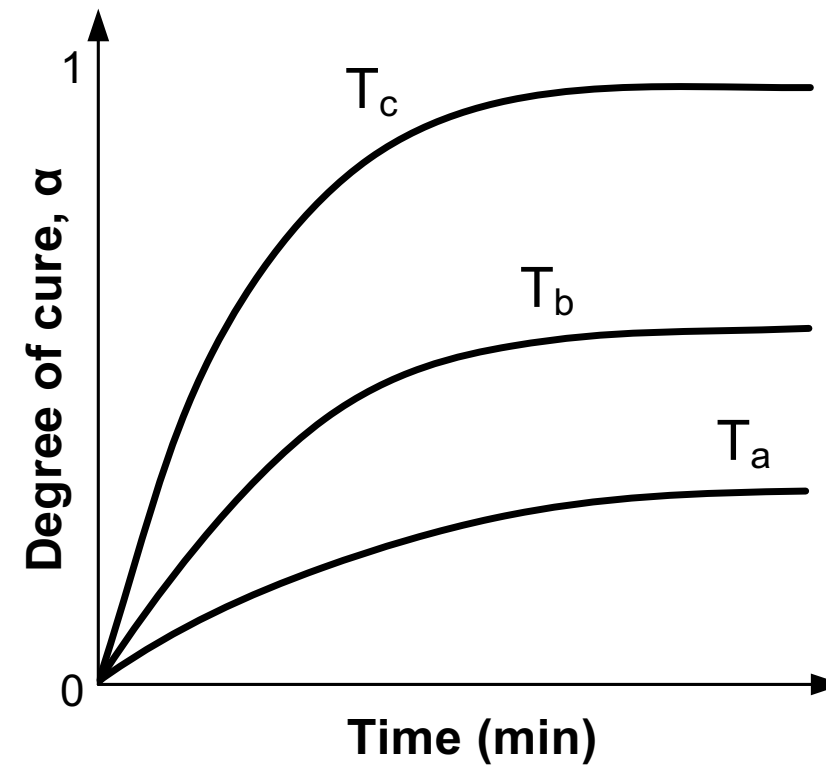
Lecture 2

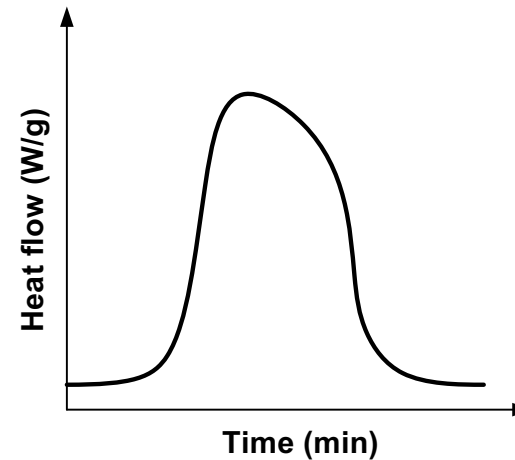Question 3: Sketch the graphs (heat flow versus time) for an nth order and autocatalytic reaction. What are the characteristics of the two types of reaction?

nth order reaction

Maximum reaction rate at t = 0

Single chemical reactions

Reaction starts as soon as components mixed

Autocatalytic reaction

Maximum reaction rate at 30-50% conversion

Multiple chemical reaction types

Reaction starts when curing temperature reached

Lecture 2

Question 4: How does the extent of reaction (degree of cure, α) of a thermosetting resin influence the glass transition temperature (T_g) and the modulus of the polymer network? Whose equation is used to predict the T_g of a polymer from the degree of cure?
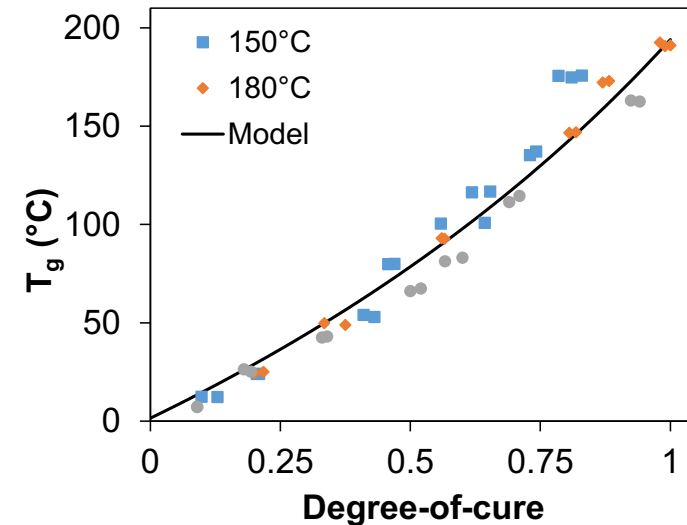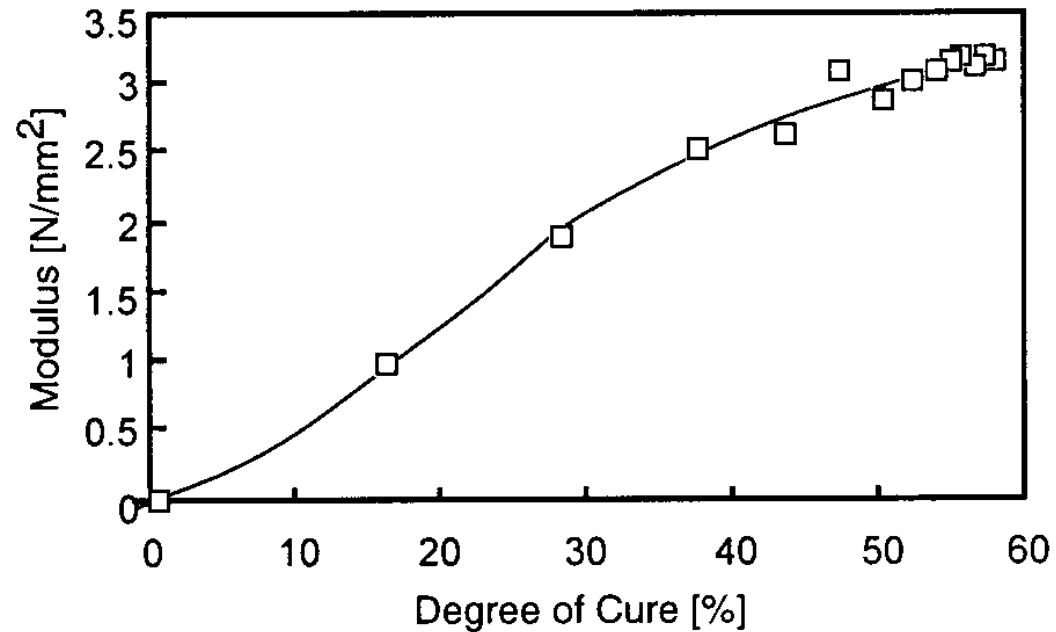
$$T_g = T_{g0} + \frac{\left(T_{g\infty} - T_{g0}\right) \alpha \lambda}{1 - (1 - \lambda) \alpha}$$

DiBenedetto equation

Lecture 3

Question 1: Using the Flory-Stockmayer equation, calculate the predicted polymer conversion at which for the following epoxy formulations (in all cases assume s = 1, as both hydrogens in both amine groups present):

Difunctional epoxy and diamine (f = 2, r = 2/4, s = 1)
Trifunctional epoxy and diamine (f = 3, r = 3/4, s = 1)
Tetrafunctional epoxy and diamine (f = 4, r = 4/4, s = 1)

$$\alpha_{gel} = \frac{1}{[r + rs(f - 2)]^{1/2}}$$
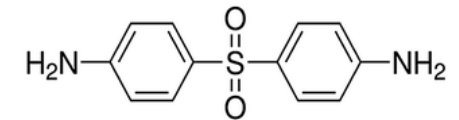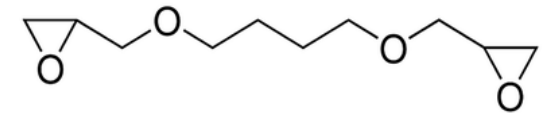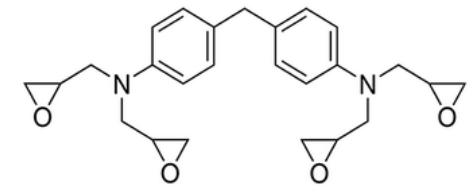
Difunctional epoxy and diamine α_{gel} = 1.41 (*i.e.* model does not represent difunctional/diamine blend well, needs branch point). Typical epoxy formulation contains diepoxy, triepoxy, and diamine

Trifunctional epoxy and diamine α_{gel} = 0.82 (gel point occurs earlier in reaction as functionality is increased).

Tetrafunctional epoxy and diamine α_{gel} = 0.58

Lecture 3

Question 2: What is the effect of monomer functionality (number of reactive groups) on the gelation behaviour (gel point)?
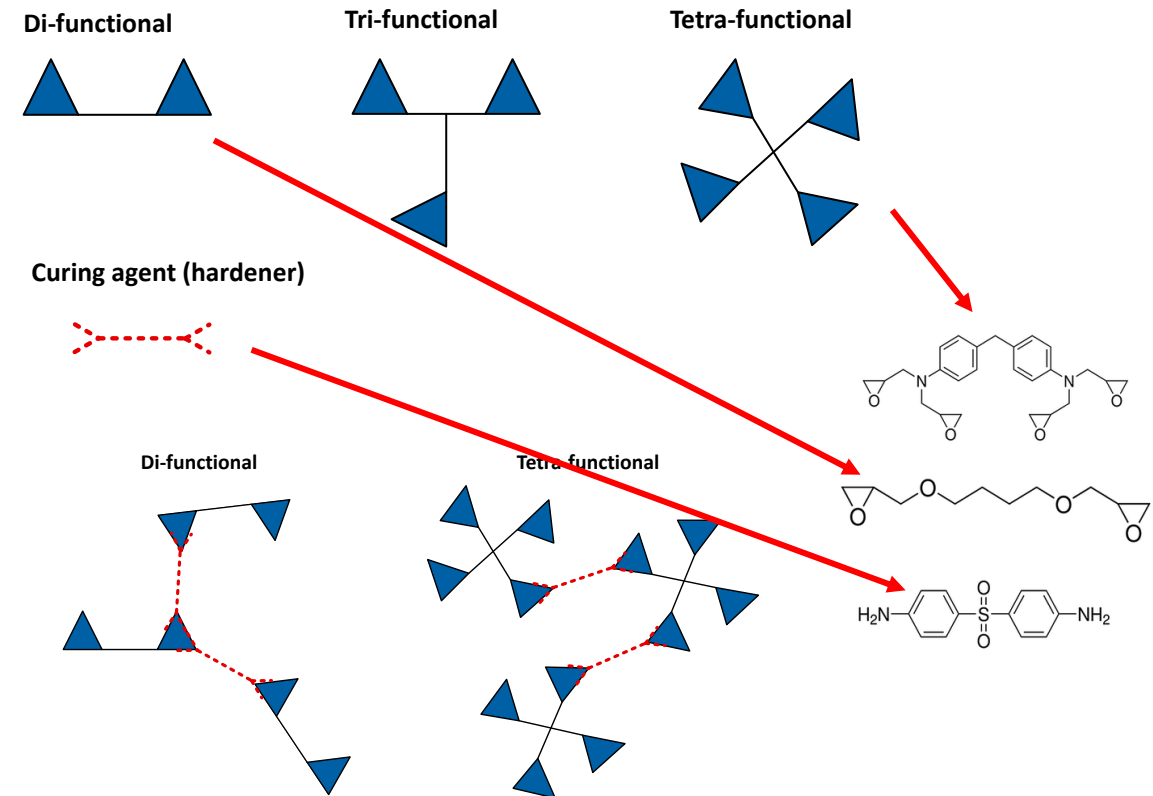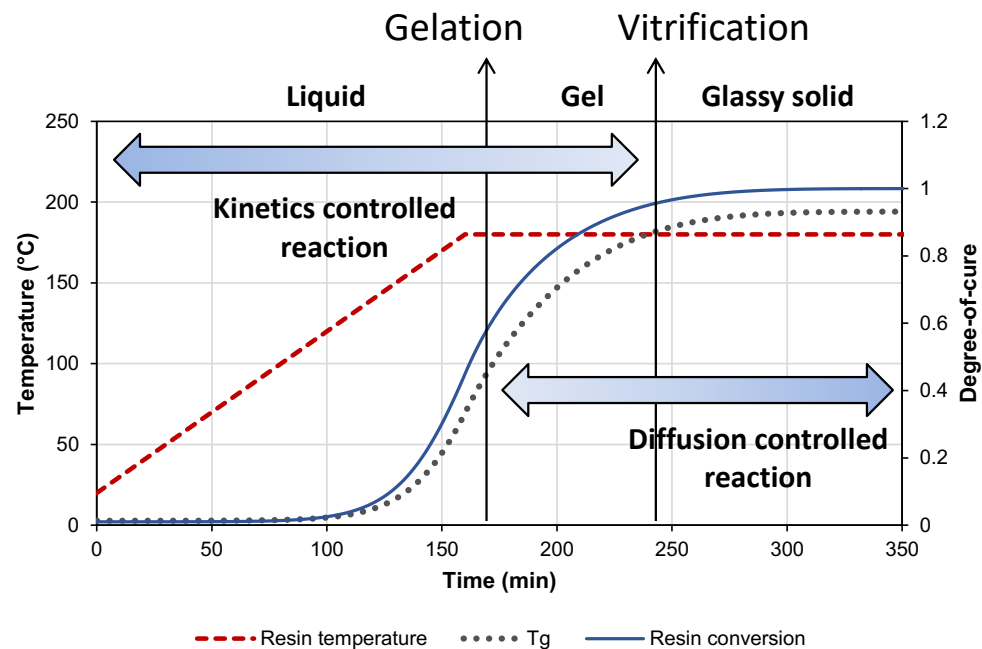
Lecture 3

Question 3: What is the effect of processing temperature on (a) how viscous the polymer blend is, (b) the time taken to reach gel point? Whose equation is used to relate viscosity to conversion?
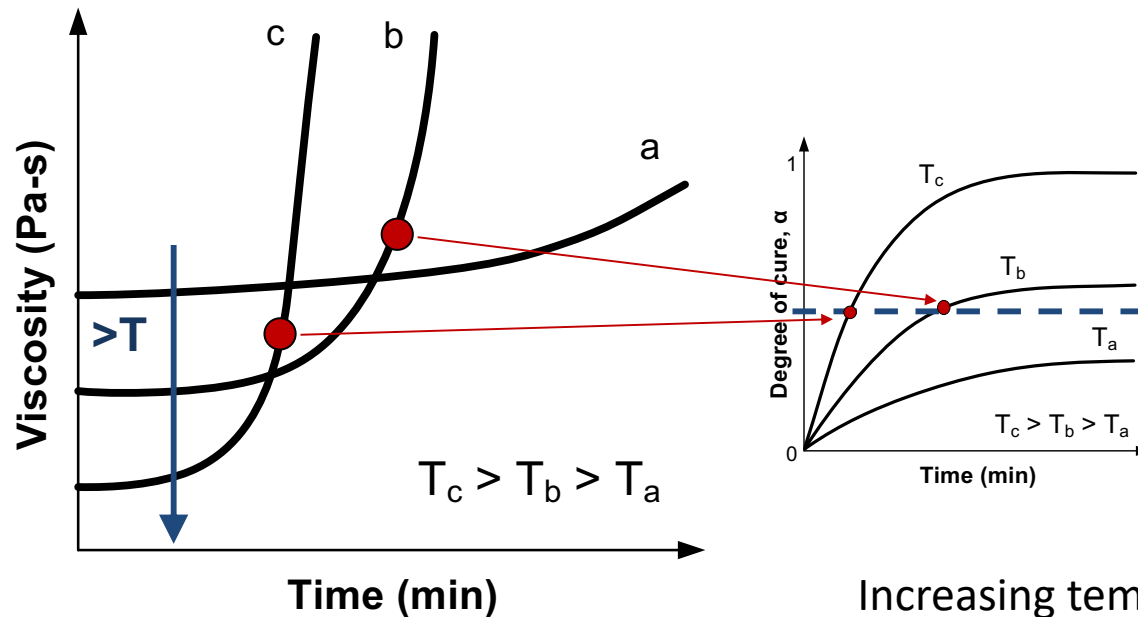

$$\eta = A_\eta \, exp\left(\frac{-E_\eta}{RT}\right)\left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha}\right)^{A+B\alpha}$$

Castro and Macosko model

Increasing temperature reduces viscosity, increases reaction rate, increases numbers of crosslinks formed, shortens time taken to reach gel point.
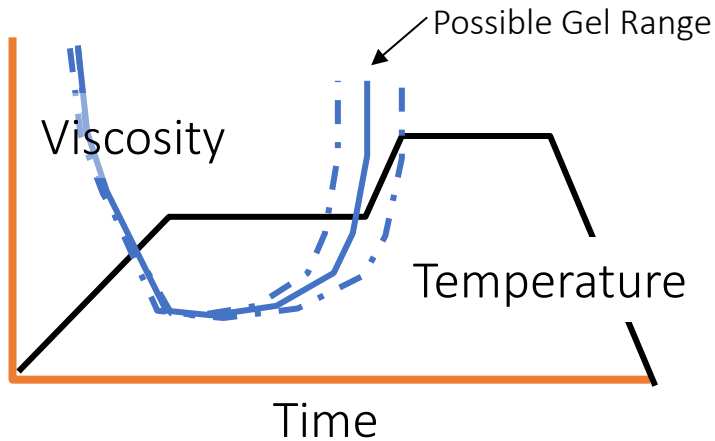
Lecture 3

Question 4: Describe how the different data gathered from DSC and rheology are combined to produce a TTT diagram, and explain how is it used to determine the cure schedule to be used for a thermosetting polymer.
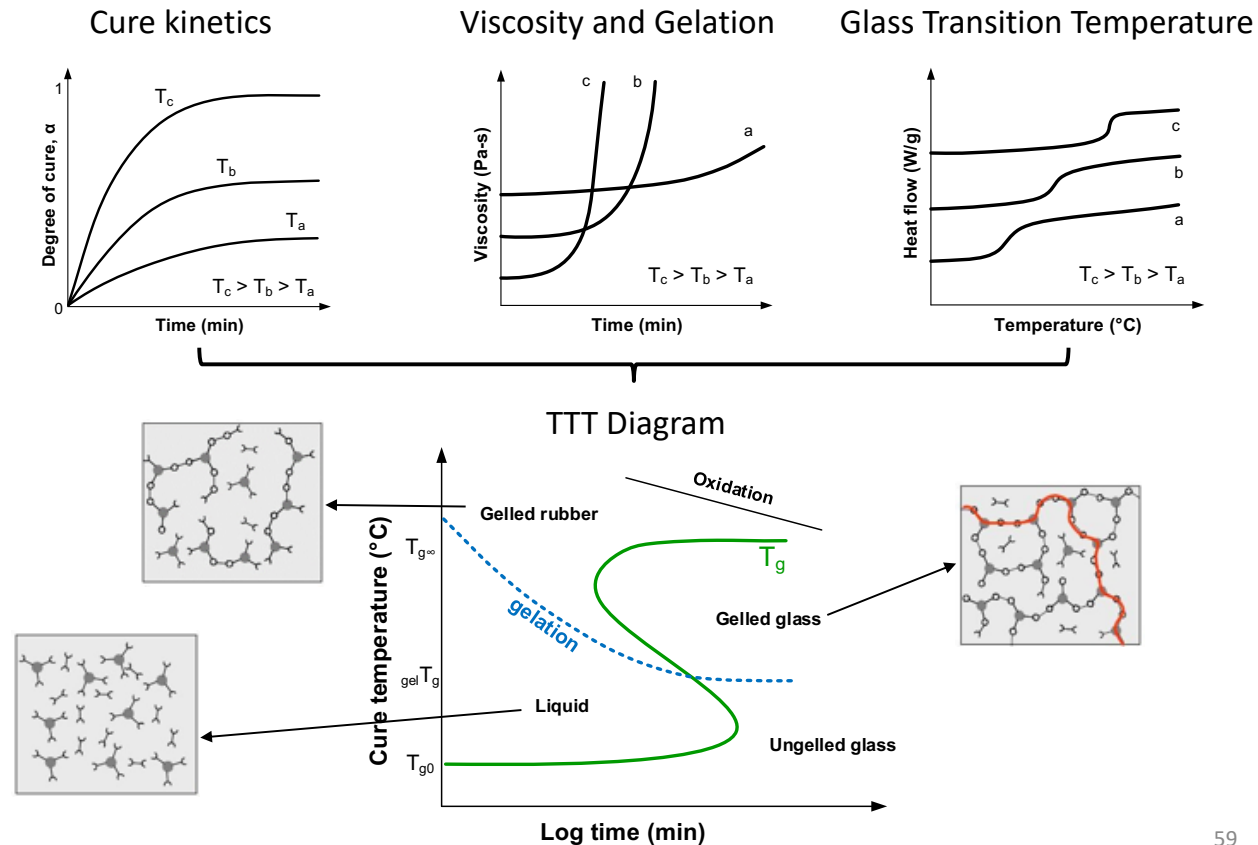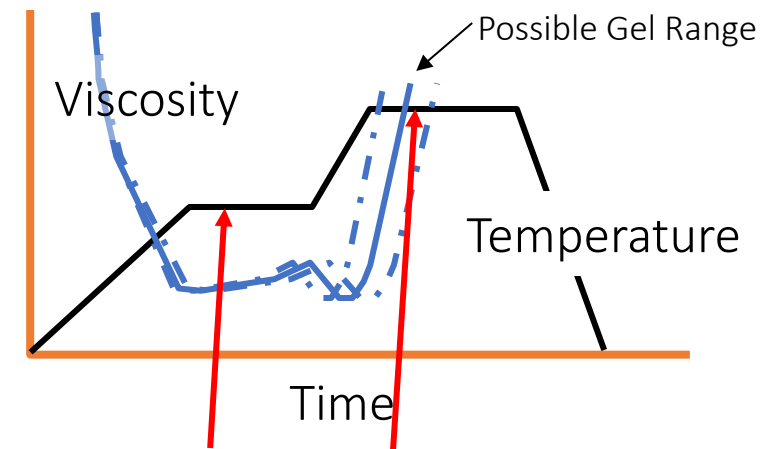
Lecture 4

Question 1: How can processing be modified to improve the dimensional control of the cured composite?

Part gelled during first hold or in second ramp, tool grows during heat-up

Shorter or lower temperature hold allows gelation at final hold temperature
No tool growth during or after gelation

Lecture 4

Question 2: How does dilation differ from distortion and which factors influence whether a material displays either one type of behaviour or the other?

Simple Materials: isotropic, homogeneous material (aluminium)

- A change in temperature causes a change in volume (**dilatation**), but no change in shape (**distortion**)

$$\Delta T$$
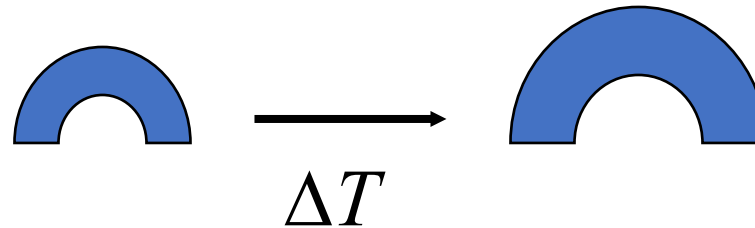
$$\mathrm{CTE} = \frac{(L_2 - L_1)}{L_o(T_2 - T_1)}$$

- Governed by the CTE

  (Coefficient of Thermal Expansion)

Lecture 4

Question 2: How does dilation differ from distortion and which factors influence whether a material disays either one type of behaviour or the other?

Complex Systems: Bi-metallic strip, composite laminate

- A change in temperature additionally leads to **distortion** (shape change)
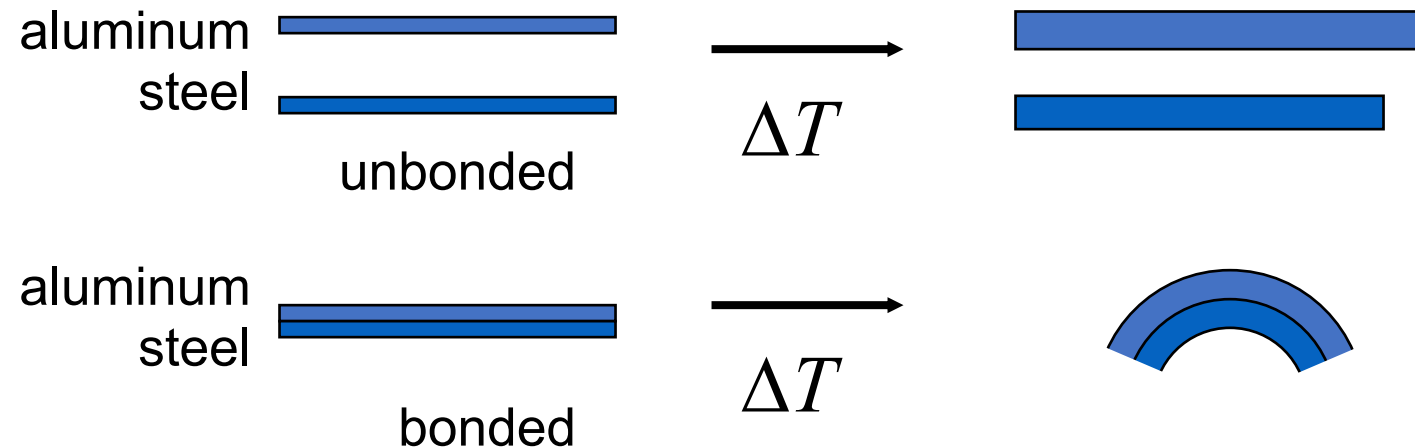
Differences between CTE of fibre and matrix, and between the plies is an important source for residual stresses in composites

Lecture 4

Question 3: How does chemical shrinkage differ from thermal contraction and is chemical shrinkage measured experimentally?
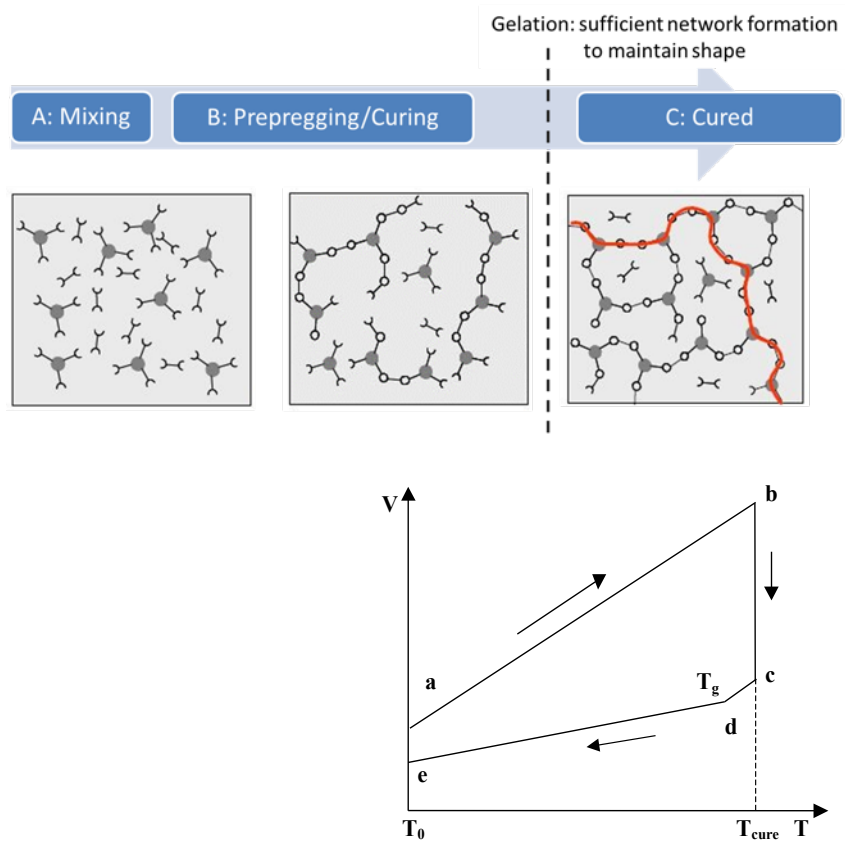
Stage a-b: Step heat-up from reference (room) temperature, T_0, to a curing temperature, T_c

Stage b-c: Hold at a constant curing temperature until full cure

Stage c-e: Cool down to room temperature.

Point *d*: glass transition

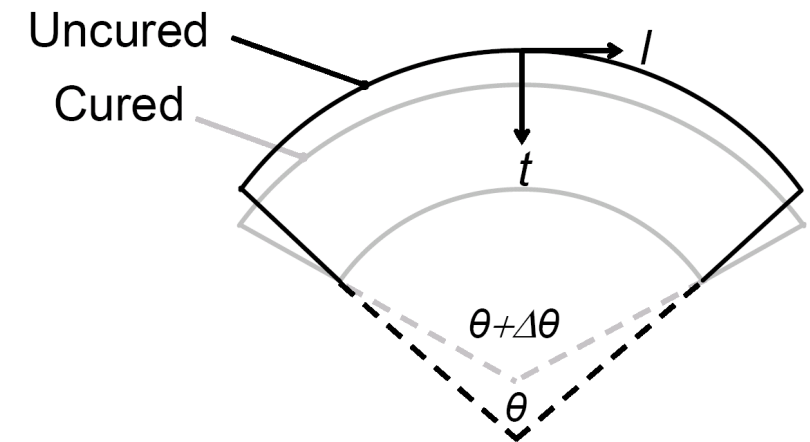Dimensional change b-c: Real chemical shrinkage

Lecture 4

Question 4: For the following quasi-isotropic laminate, consider a 5.0 mm thick angle bracket (90°) cured on a steel tool at 140°C. What would be the expected spring-in at room temperature? How would this be measured?
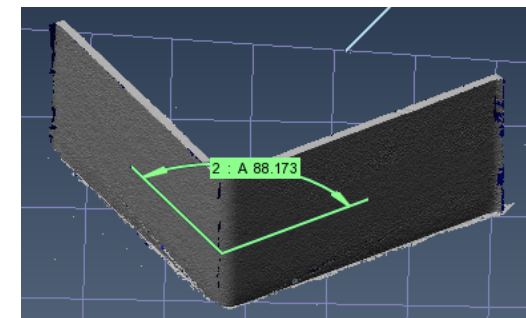
Parameter	0°/45°/-45°/90° Laminate
α_l	2.8 x 10^{-6} (m/m/°C)
α_t	6.3 x 10^{-5} (m/m/°C)
ϕ_l	2.1 x 10^{-4} (m/m)
ϕ_t	4.9 x 10^{-3} (m/m)
Cure temperature	140°C
Room temperature	20°C

Uncured
Cured

l
t
$\theta+\Delta\theta$
θ

$$\Delta\theta = \theta \cdot \left[\left[\frac{(\alpha_l - \alpha_t) \cdot \Delta T}{1 + \alpha_t \cdot \Delta T} \right] + \left(\frac{\phi_l - \phi_t}{1 + \phi_t} \right) \right]$$

Scanned using laser to high precision.
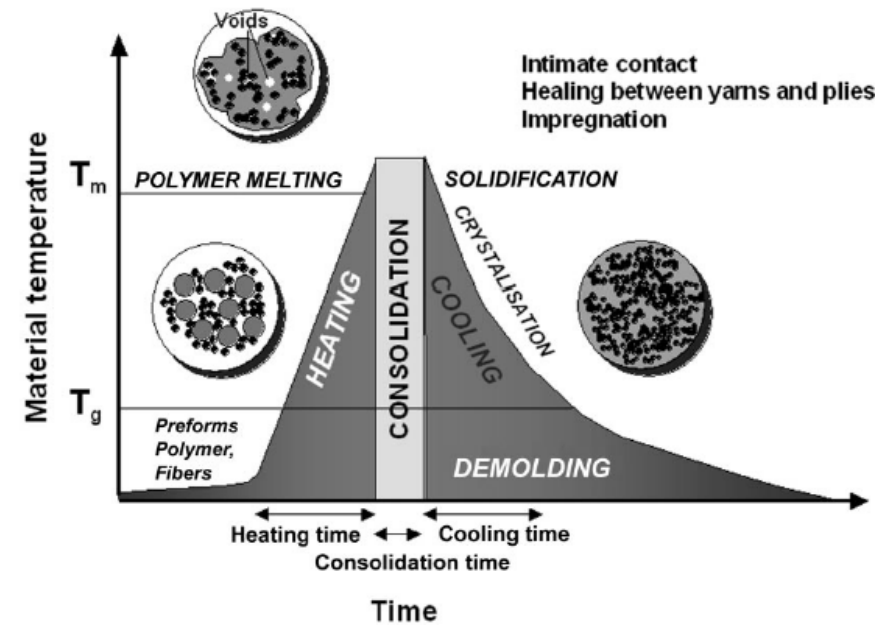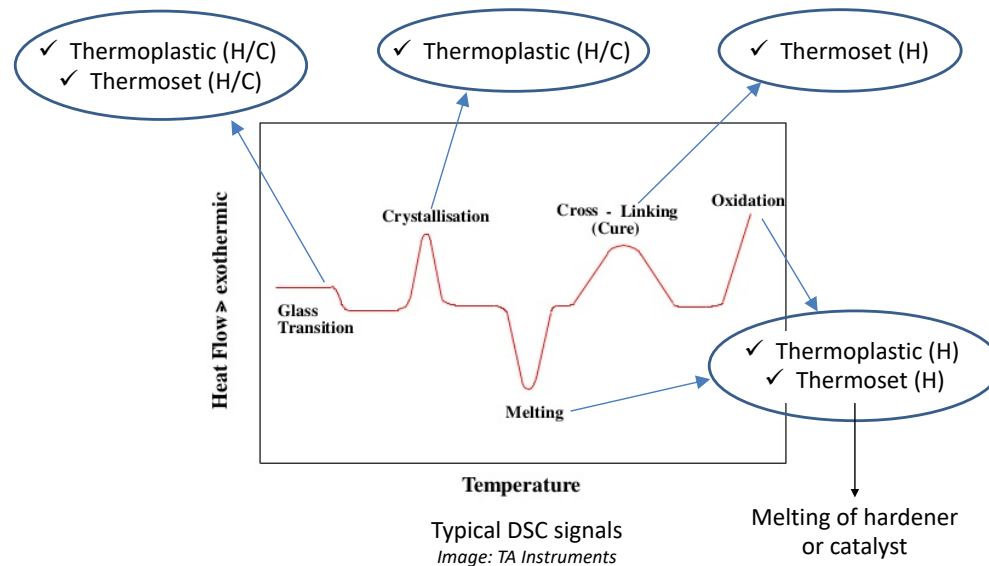

Spring in = (-)1.064 degrees

Lecture 5

Question 1: During the consolidation of a thermoplastic composite, what are the physical processes that take place during the heating and cooling steps?
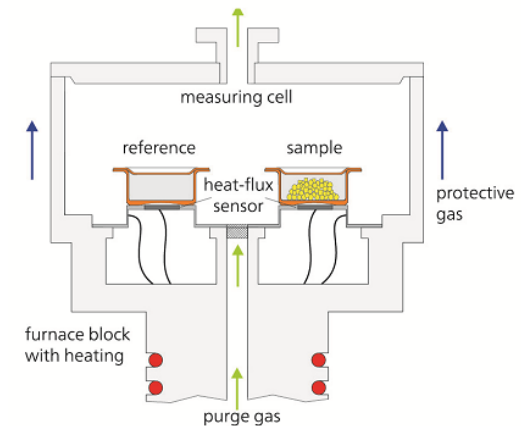

Typical DSC signals
Image: TA Instruments

Lecture 5

Question 2: What does the glass transition temperature, T_g, represent and how is it different from T_m? Which thermal analysis method is commonly used to monitor changes in these parameters?

T_g represents large segments of polymer chain undergoing motion/segmental rotation.
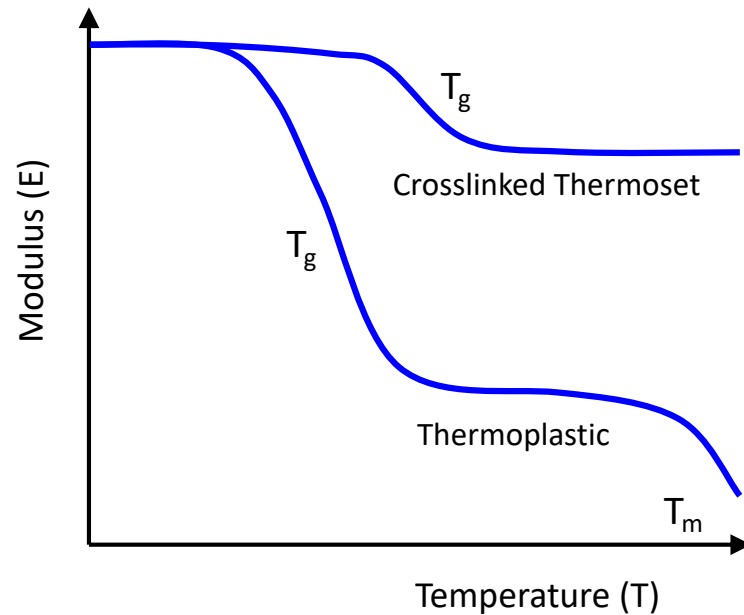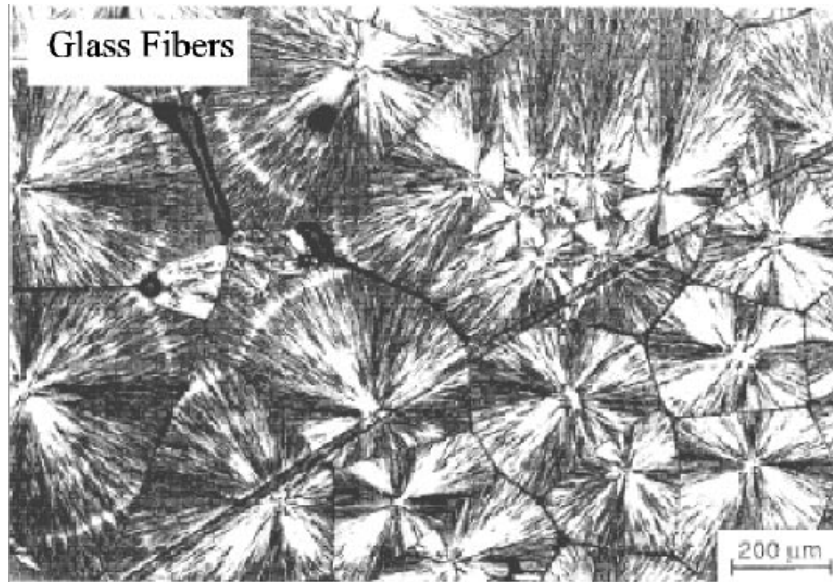

DSC measurement cell

DSC cell cross-section

Lecture 5

Question 3: What is a spherulite and how is the diameter of a spherulite related to modulus?

Spherical semicrystalline regions inside non-branched linear polymers. Their formation is associated with crystallization of polymers from the melt and is controlled by number of nucleation sites, structure of the polymer molecules, cooling rate, etc.
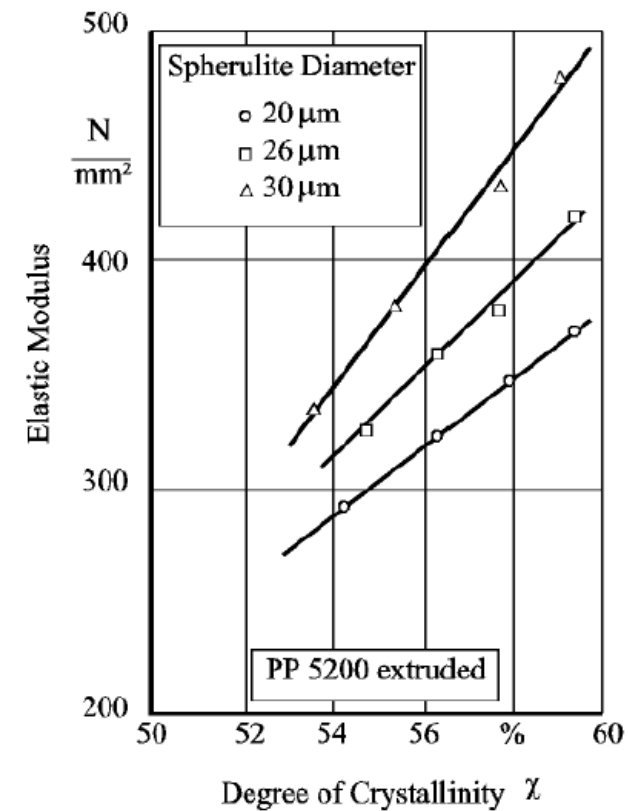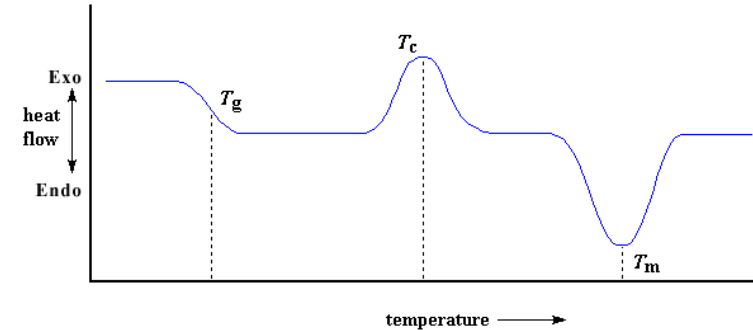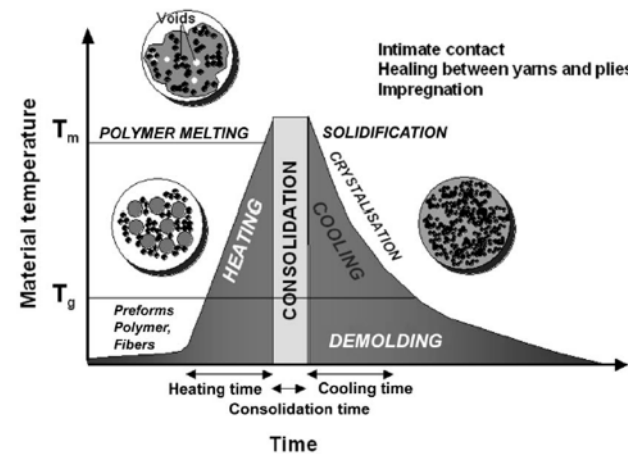
Lecture 5

Question 4: What are the different stages in the crystallisation process and how does cooling rate influence (a) the spherulite diameter and (b) the degree of crystallinity?
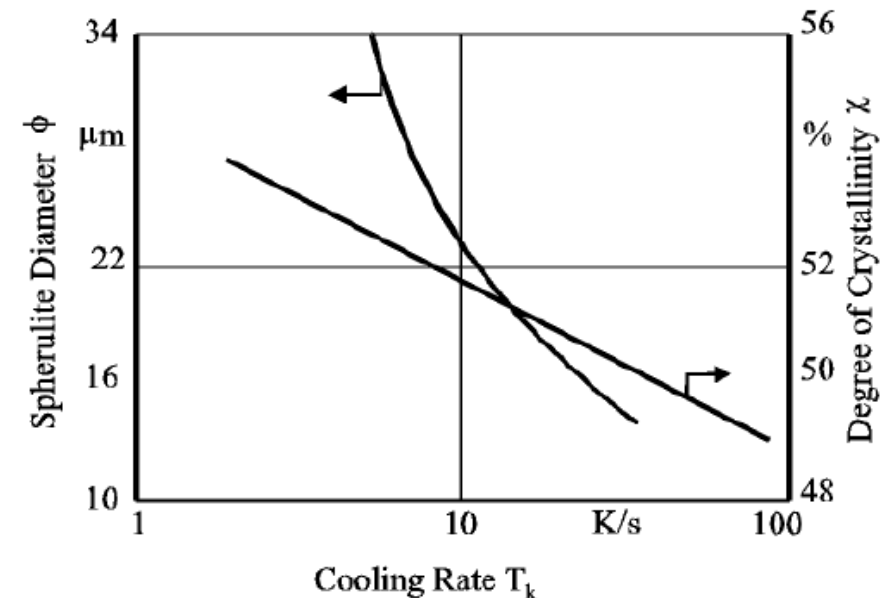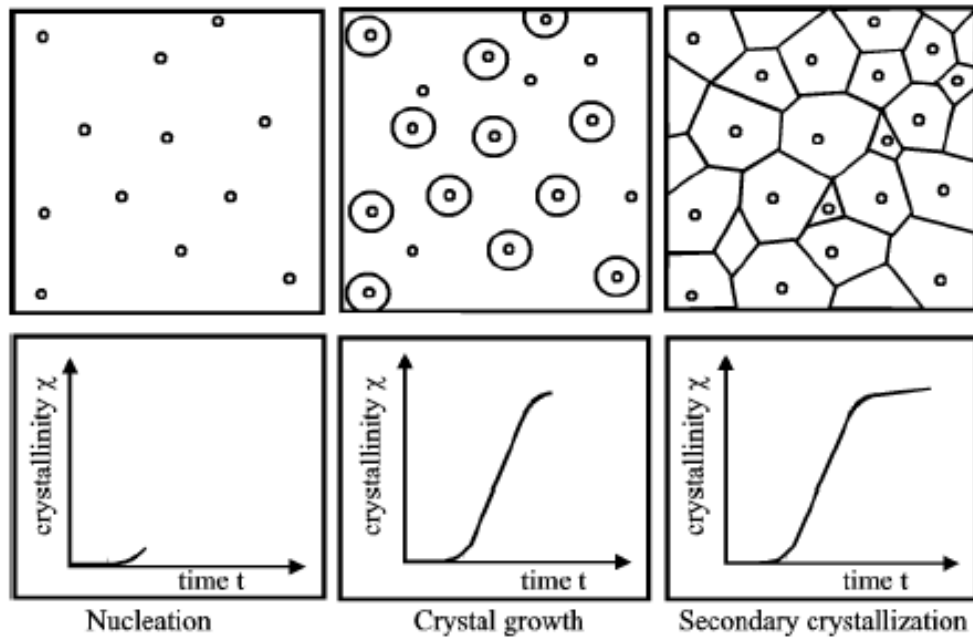
Lecture 5

Question 5: Thermoset polymer composites are typically joined using adhesives, whereas thermoplastics are usually joined using welding. How does thermoplastic welding operate? Fill out the following table.

Method	Advantages	Disadvantages
Thermoplastic welding	Little or no undesirable stress concentration Little or no weight penalty Smooth external surfaces at the joint Short processing time Minor surface preparation	Induced residual stress Imposes difficulties such as uneven heating, delamination and distortion of the fibres