Properties of Materials

Theme: Polymers and Composites

Lecture 1: Introduction to Materials and Processes

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Intended Learning Objectives

- Describe the main manufacturing processes for aerospace composite materials
- Describe different types of aerospace polymer
- Identify techniques to measure property development
- Explain the effect of temperature on processing cycles
- Identify when polymers transitions from liquid to solid
- Name process induced defects that arise during processing of polymer composites
- Describe the effect crystallisation processes that occur in thermoplastic composite materials

Overview

Lecture 1: Introduction to composite materials and manufacturing processes

Lecture 2: Curing kinetics of thermosetting polymers

Lecture 3: Gelation and vitrification

Lecture 4: Residual stress development

Lecture 5: Solidification of thermoplastic polymers

Lecture 6: Review a previous exam question

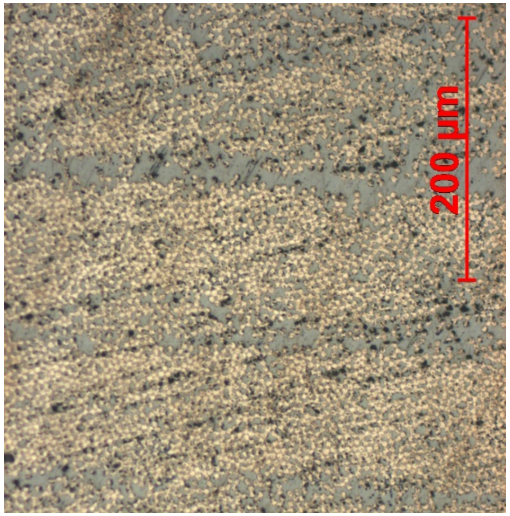
Today's Lecture Contents

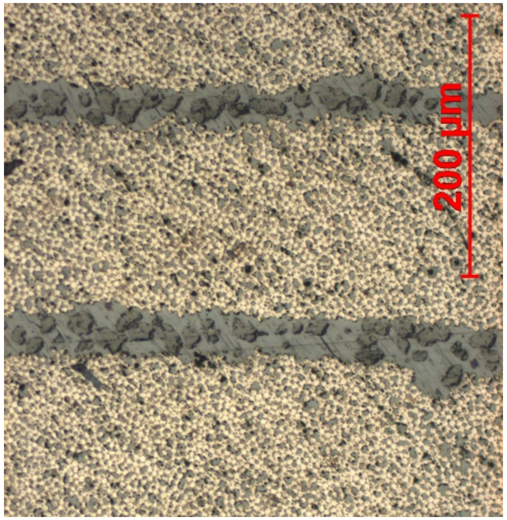
- Introduction to the most important process parameters that influence manufacturing of composite materials
- Activity: Propose a material and potential risks for a new wing.

Next single aisle (CGI concept plane)

Aerospace Composite Materials

- Highly packed long slender fibres oriented to obtain a wide range of material properties
  - Target fibre volume fraction of 55-60% (aerospace)
- High-temperature polymer matrix
- Recently: interleaf particles for toughness





Micrograph of a carbon-fibre/epoxy composite material (left) and particle interleaf toughened variant (right)

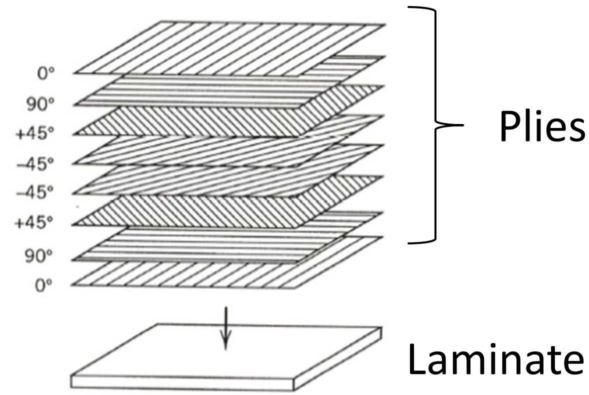
Fibre Reinforced Polymers (FRPs)

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

$$E_{max} = V_f E_f + (1 - V_f) E_m$$

fibre: 240-280 GPa

matrix: 3-3.5 GPa



A unidirectional laminate [0]

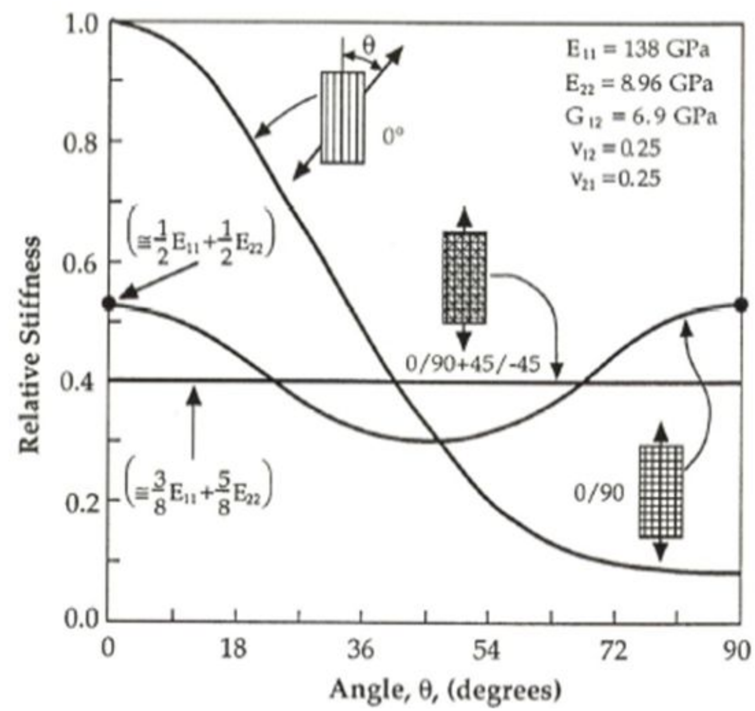
$$E_{max} \sim V_f E_f$$

A cross-ply laminate [0/90]

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

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

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



Images: T Gutowski, Advanced Composites Manufacturing, Wiley, 1997.

Why Study Polymer Processing?

Usually a deviation between ‘as designed’ and ‘as made’

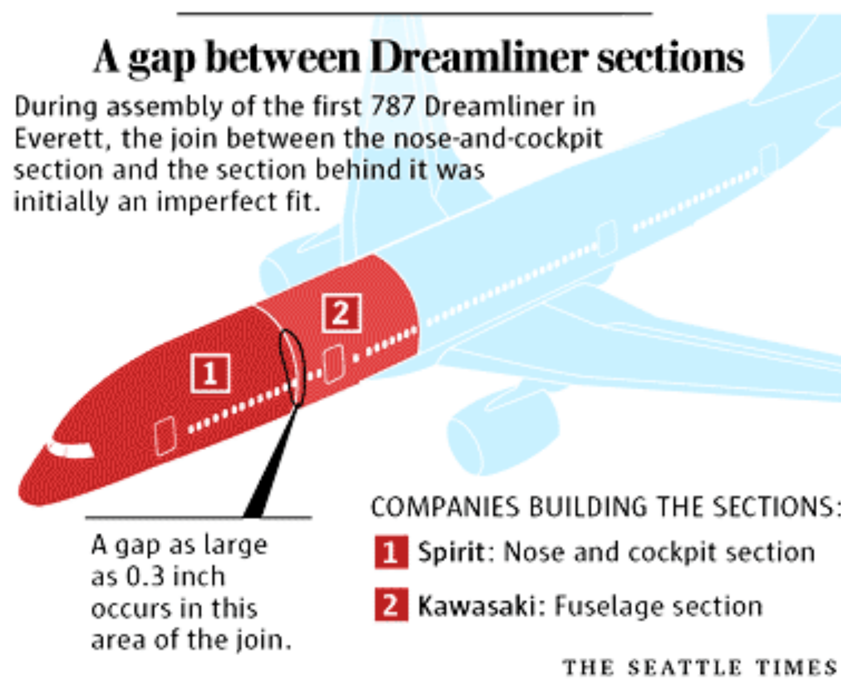
Boeing & Aerospace | Business

Boeing finds 787 pieces aren’t quite a perfect fit

Originally published June 12, 2007 at 12:00 am | *Updated June 28, 2007 at 4:14 pm*

1 of 2 *On the left-hand side of the Dreamliner fuselage, a gap of 0.3 inch appeared du joining of the nose-and-cockpit section to the section behind it. Through the ga ceiling is visible. The photo, which appears to be an...* **More**

Photos of the final-assembly process show the jet's first two f sections did not fit properly when initially joined. On one sid was a gap wide enough to stick a finger in.



Why did this happen?

Making Composites is Like Baking

Combine ingredients

Making Composites is Like Baking

Creating the material and the shape simultaneously

Oven
- Temperature control
- Temperature distribution
- Heat transfer coefficient

Material
- Heat generated
- Density
- Heat capacity
- Thermal conductivity

Muffin baking

Mould
- Thickness
- Heat capacity
- Thermal conductivity
- Thermal expansion

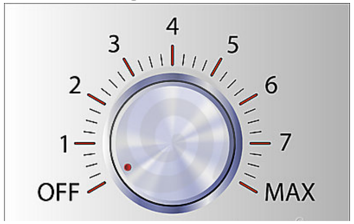
Why do **fan assisted ovens** bake faster than **conventional ovens**?

Advantage of Process Modelling

Quickly adapt to changes in the process:

1. Material
2. Mould
3. Oven
4. Mould placement

Temperature



Evenly baked composite
every time, in any oven!

➢ Faster and cheaper than trial-and-error!

Aerospace Polymers

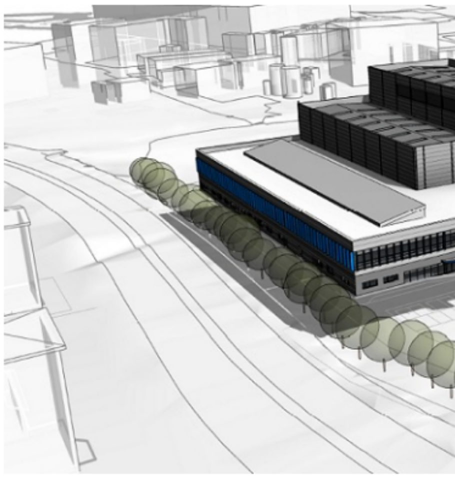
- TS: Thermosets (Epoxies)
  - Processed al low molecular-weight (viscosity low)
  - Easily wet fibres
  - React to form a high-molecular-weight glassy solid
  - Add energy (heat) to form irreversible crosslinks

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

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

Airbus Wing Development and Test Centre

AEROSPACE TECHNOLOGY INSTITUTE



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/ JANUARY '16

CHANCELLOR ANNOUN INTEGRATION CENTRE

Posted by jwarehand

Chancellor of the Exchequer Georg **Williams CBE** to announce a £37 m Airbus site in Filton, Bristol.

The new ATI-funded facility will be components. It will enable Airbus a helping underpin the UK as one of

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News story

Chancellor and Airbus announce cutting edge research facility

From: HM Treasury and The Rt Hon George Osborne MP
First published: 28 January 2016

New £37 million aircraft technology centre will safeguard hundreds of jobs in the South West.

Hundreds of highly skilled manufacturing and engineering jobs will be safeguarded in the South West thanks to a new £37 million research facility, the Chancellor has announced today (Thursday 28 Jan).

On a visit to Airbus in Filton, George Osborne joined the company's COO Tom Williams to announce a £37 million investment in a new Wing Integration Centre to develop and test the aerospace technology of the future, ensuring that hundreds of highly skilled jobs remain in Britain for years to come.

Chancellor of the Exchequer George Osborne said:

> " When it comes to aerospace design Britain is the innovator of Europe and I want to see us going even further and becoming the global leader.

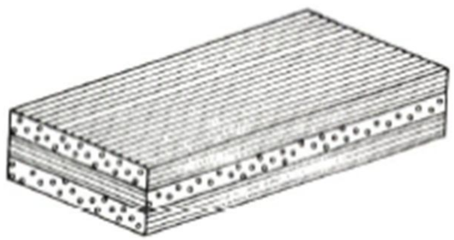
Activity: Material for a Composite Wing

- New single aisle (A320/737 replacement) wings could be made from metal or composite
- In groups of 2-3, take 4 minutes and discuss the material you would propose for a composite wing?

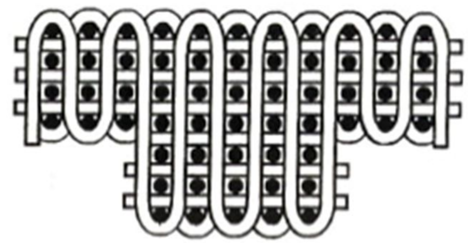
Composite Manufacturing Processes

Overview (a lot more covered in Composite Design and Manufacture Y4)

- Fabricate an intricate fibre network



Linear fibre structure



Interlaced fibre structure

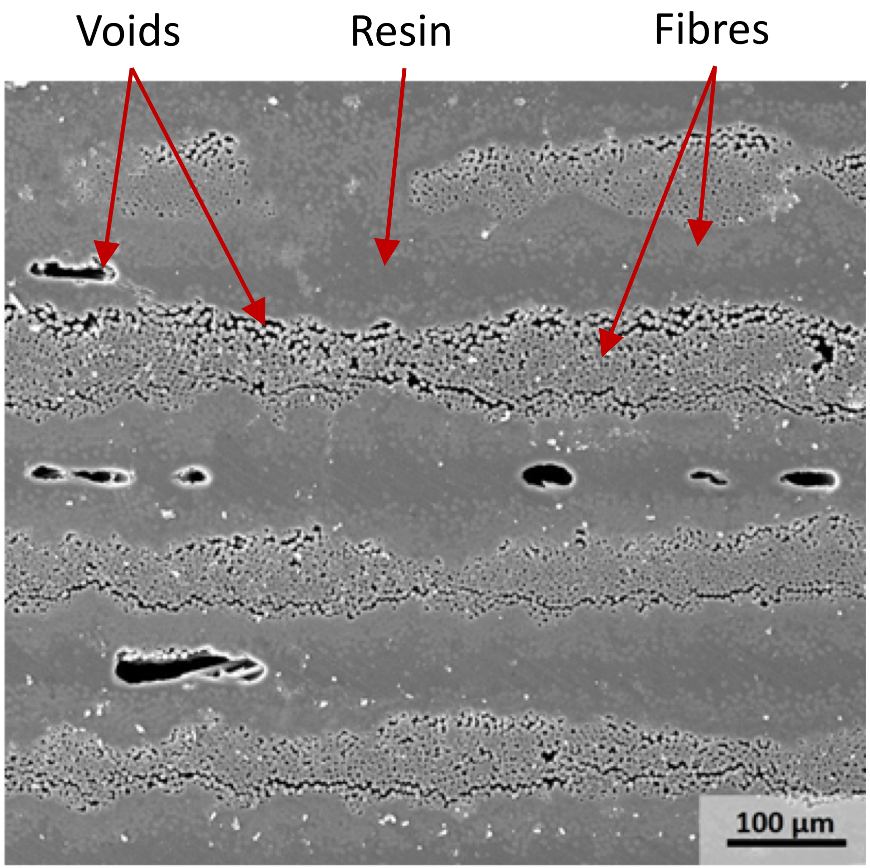
- Wet-out fibres with matrix polymer
  - Prepreg: prior to generation of complete fibre structure
  - Infusion: at the time of processing dry fibre structure
- Fibre and polymer must be supported by rigid tooling

Images: T Gutowski, Advanced Composites Manufacturing, Wiley, 1997.

Composite Manufacturing Processes

Prepreg Materials

(Resin pre-impregnated into fibre)



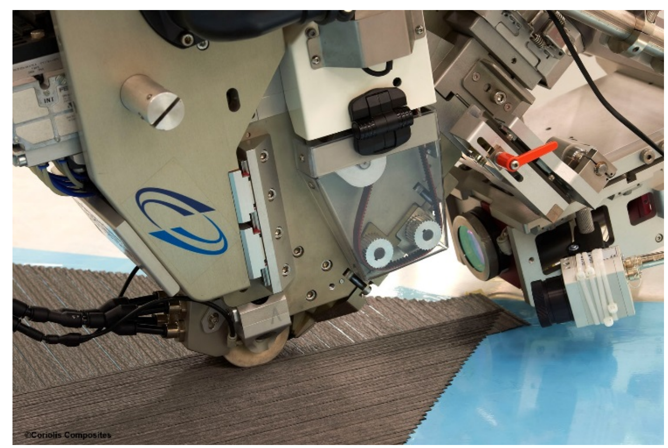
SEM micrograph of prepreg

Image: Lessa Grunefelder (USC)

Deposition Methods

Hand lay-up

Image: Easy Composites

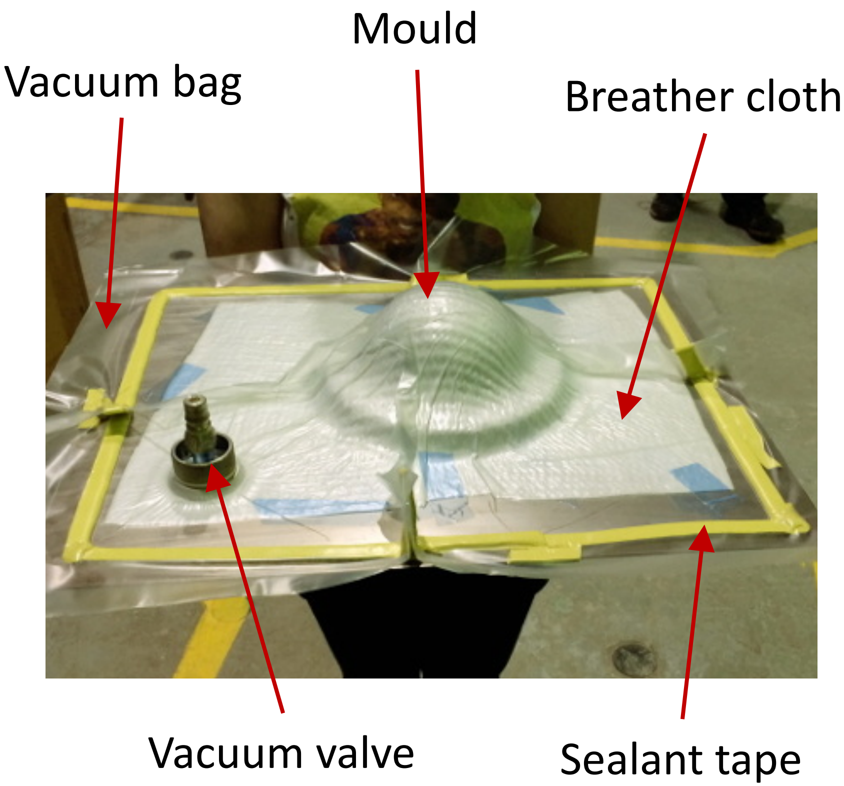


Automated fibre placement (AFP)

Image: Coriolis Composites

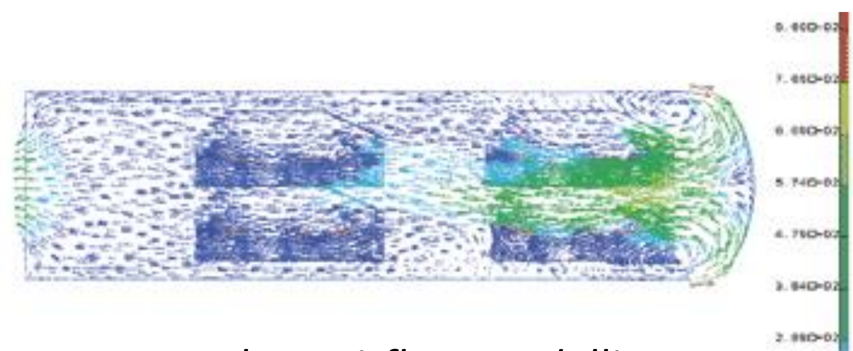
Composite Manufacturing Processes

Vacuum Bagging



Autoclave Consolidation

Autoclave loading
Image: Italmatic

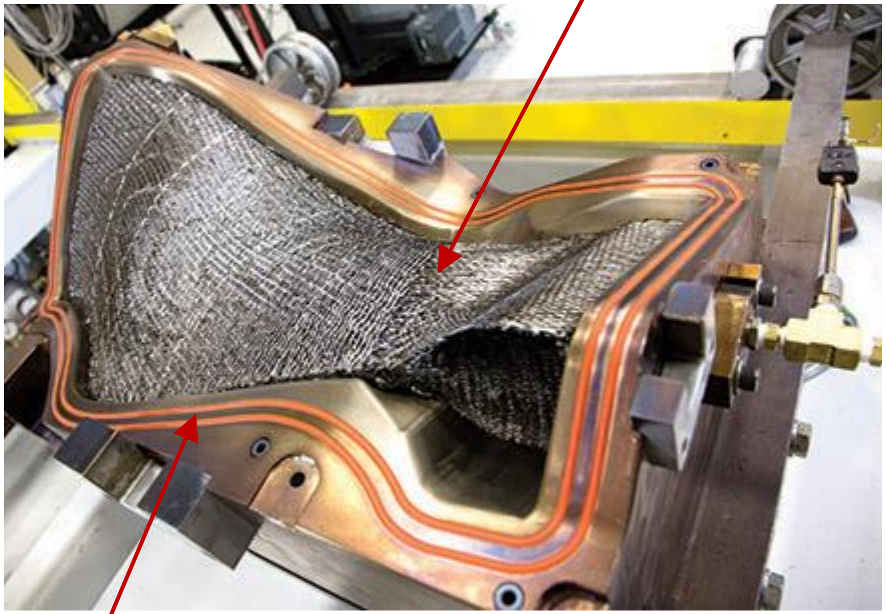


Autoclave airflow modelling
Image: Quartus Engineering

Composite Manufacturing Processes

Resin Infusion (RI)

Dry continuous fibre preform



Fan blade form in mould

Image: Albany Engineering Composites

Seals

Chopped glass fibre preform

Image: Ford/ Aston Martin

Boat hull infusion

Image: Maccaferri

Summary

- Composite materials: material and shape are manufactured at the same time
- Two categories of aerospace polymers. Thermosets react to form an irreversible cross-linked network. Thermoplastics can be melted, shaped, and cooled to form a solid.
- A wide range of processes are available but follow three basic steps.
    1. Create fibre network
    2. Wet fibre network with polymer matrix
    3. Tooling to support part while polymer converted from liquid to solid

Properties of Materials

Theme: Polymers and Composites

Lecture 2: Curing Kinetics

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Previously – Aerospace Polymers

<u>Thermosets</u>

- Flow easily
- Cross-link
- Glassy solids

<u>Thermoplastics</u>

- Melt
- Flow less
- Cool to solidify

<u>Deposition Methods</u>

- Hand
- Machine

<u>Wetting Methods</u>

- Prepreg (off-line)
- Resin infusion (on-line)

Today's Lecture Contents

- Cure Kinetics models:
  1. Measurement technique
  2. Models to describe the cure reaction rate to degree of cure
- Activity: manufacture of tennis racquets

Heat Transfer Equation

Heat **ABSORBED** by the composite

Heat **TRANSFERRED** by the composite

Heat **GENERATED** by curing resin

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

Density

Specific heat capacity

Thermal conductivity

Fibre volume fraction

Heat of reaction

Cure rate
or
*Cure **kinetics***

Did you know? *Kinetic* comes from the Greek word *kinētikos, and refers to* the motion of material bodies and the forces/ energy associated with this motion

- Chemical potential energy in a resin is converted into heat during curing

Definitions

Term	Symbol	Physical Meaning	Units
Heat of reaction	ΔH_T	Total heat released by the chemical reaction when liquid resin becomes a glassy solid. Calculated by integrating the heat flow when full cure is achieved.	J/g
Degree of cure	α	Resin degree-of-cure at time t	%
Cure kinetics	$d\alpha/dt$	Change in degree-of-cure	s^{-1}
Specific heat capacity	C_p	Heat required to change a unit mass of a substance by one degree in temperature	$\frac{kJ}{kg \cdot K}$
Density	ρ	Mass in a given volume of space	kg/m^3
Thermal conductivity	κ	Heat transmitted through a unit thickness of a material	$\frac{W}{m \cdot K}$
Fibre volume fraction	V_f	Space occupied by fibres in a volume of composite (fibre, polymer, void, other stuff….)	%
Chemical cure shrinkage	CCS	Reduction in the free volume (material becomes denser) as cross-linking progresses	%

Curing of Thermosetting Polymers

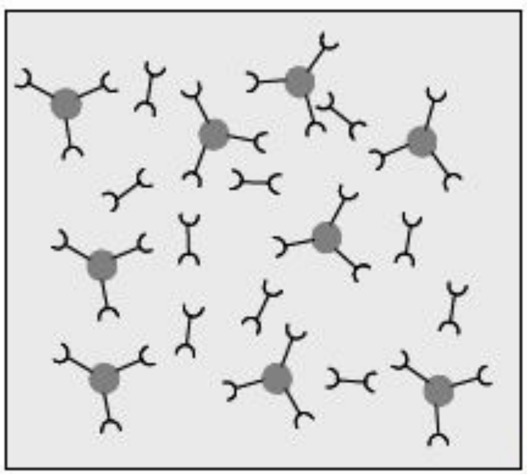
Reaction of monomers or oligomers into a three-dimensional cross-linked network

Gelation: sufficient network formation to maintain shape

A: Mixing

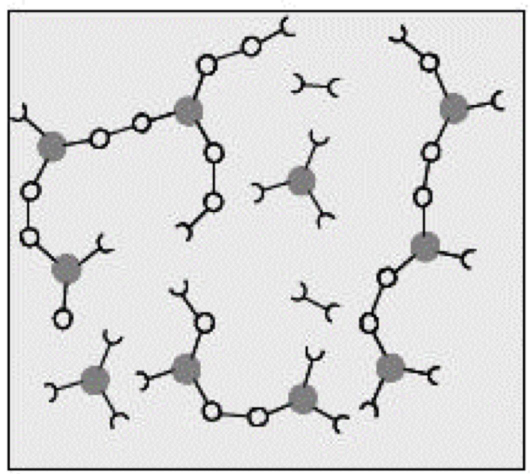
B: Prepregging/Curing

C: Cured



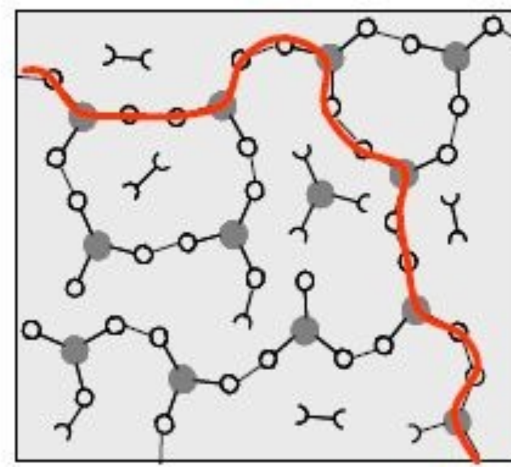
Unreacted monomers

- Soluble



Small branched molecules

- Partially soluble



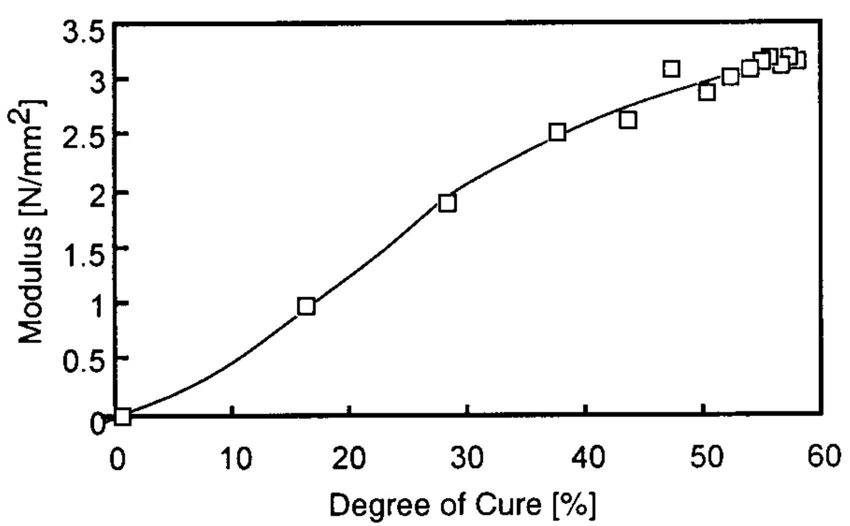
Cross-lined polymer

- Insoluble
- Some unreacted groups remain

Images: Franck A. Understanding rheology of thermosets. TA instruments, 2004.

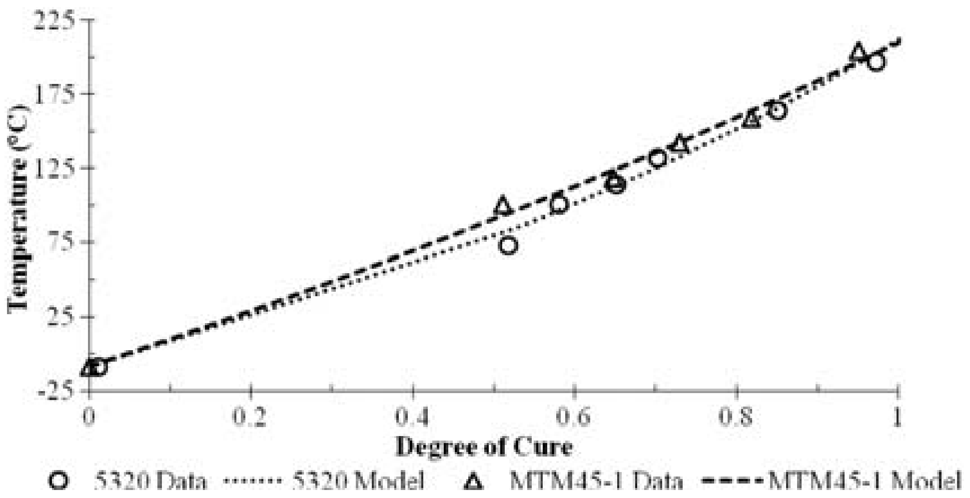
Degree-of-Cure Influence on Properties

- Advancement in degree-of-cure influences all mechanical and physical properties



Polymer matrix modulus development

Reference: Theriault R, et al. Properties of thermosetting polymers during cure. ANTEC 97, 1997.



Glass transition temperature development

Reference: Kratz J, et al. Thermal models for MTM45-1 and Cycom 5320 out-of-autoclave prepreg resins. Journal of Composite Materials. 2013;47(3):341-52..

Cure Kinetics

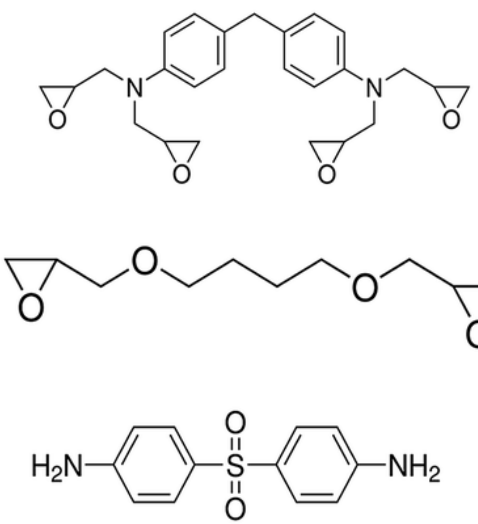
- Describe the time dependent process of cure advancement for a given temperature

Phenomenological models

- Macroscopic level
- One reaction represents the whole process
- No knowledge or details of the chemical species are required

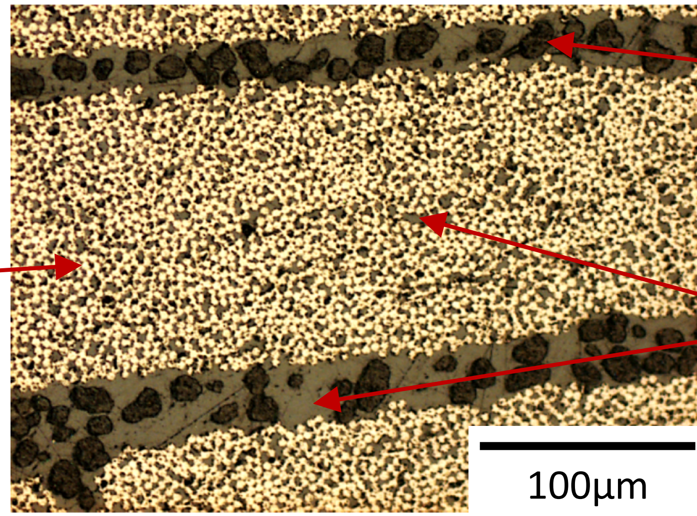
Mechanistic models

- Microscopic level



➢ In composites, users rarely know the resin composition

What’s in My Composite?



Laminate cross-section

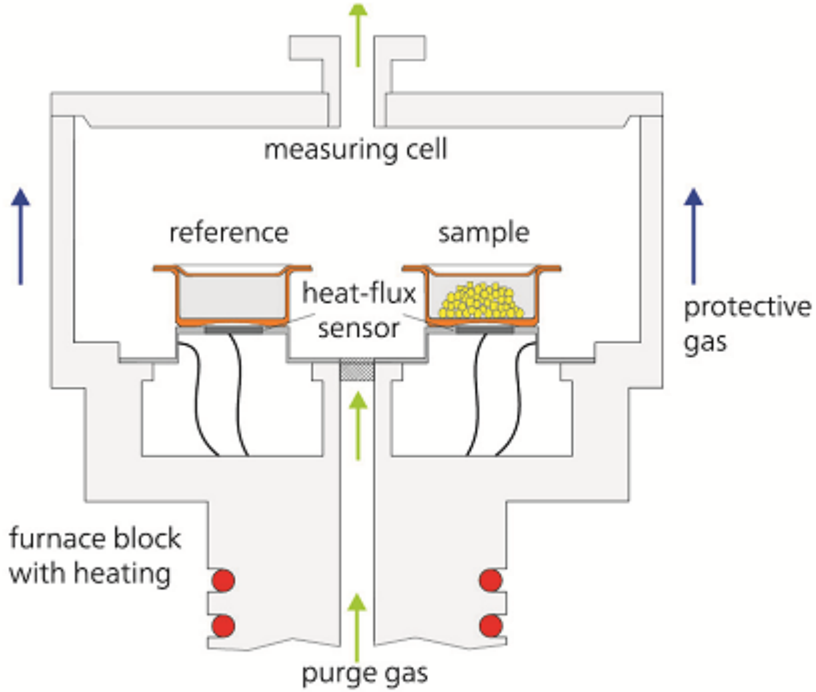
3 COMPOSITION/INFORMATION ON INGREDIENTS				
Name	EC No.	CAS-No.	Content	Classificatio
BISPHENOL F EPOXY RESIN	500-006-8	9003-36-5	10-30%	Xi;R36/38. N
DAPSONE	201-248-4	80-08-0	10-30%	Xn;R22
TETRAGLYCIDYL METHYLENE DIANILINE	249-204-3	28768-32-3	10-30%	Xn;R21/22.
TRIGLYCIDYL-P-AMINOPHENOL	225-716-2	5026-74-4	10-30%	Xn;R21/22. R43.

Information about the resin matrix from safety data sheets

Differential Scanning Calorimetry (DSC)

- Measure the heat flow from small (6-8mg) samples
- Can be heated or cooled at rates up to 100°C/min to evaluate temperature transitions in materials

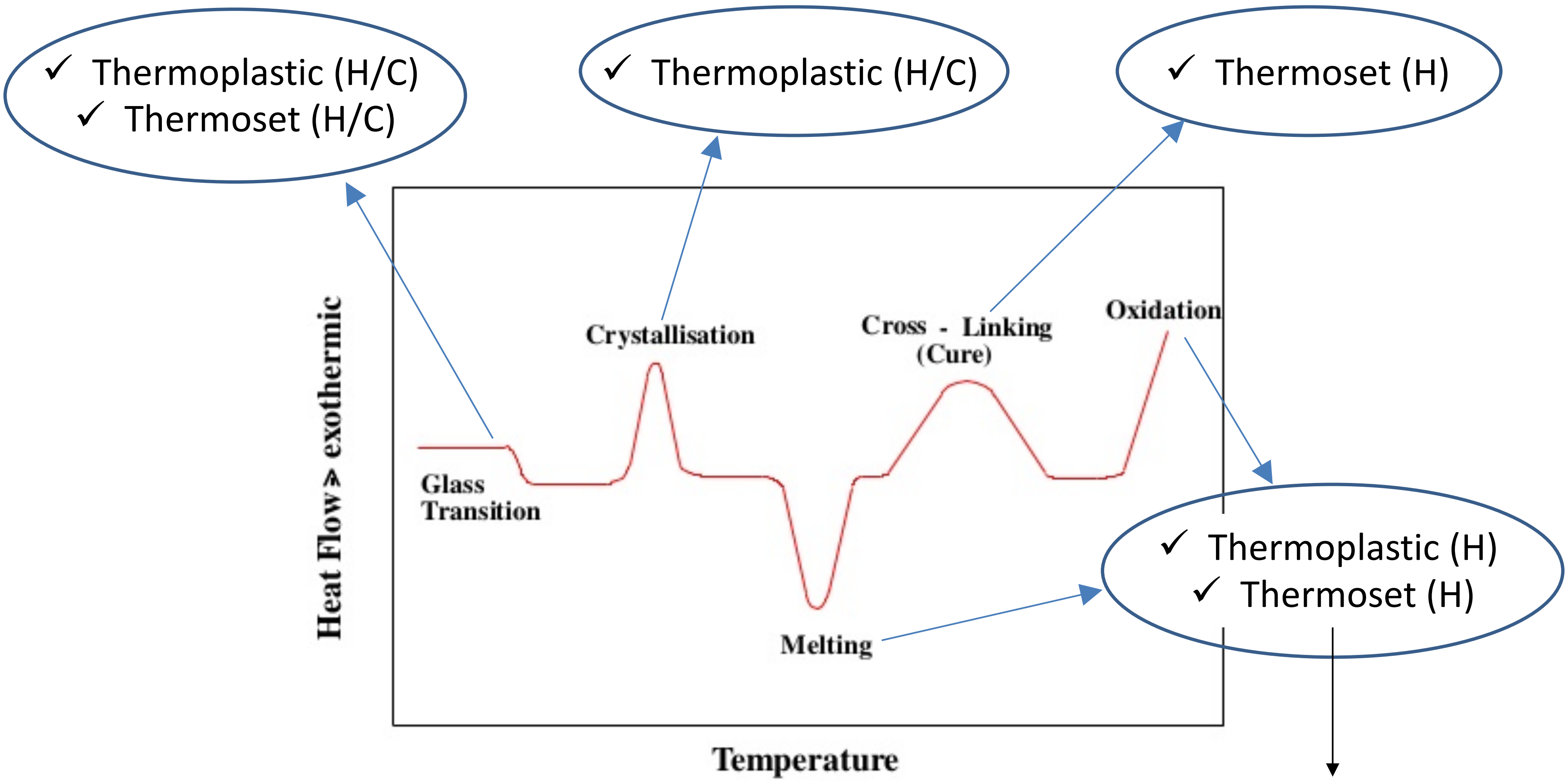
DSC measurement cell



DSC cell cross-section

Images: Netzsch Thermal Analysis

Heat Flow Signals



Typical DSC signals

Image: TA Instruments

H: heating event only

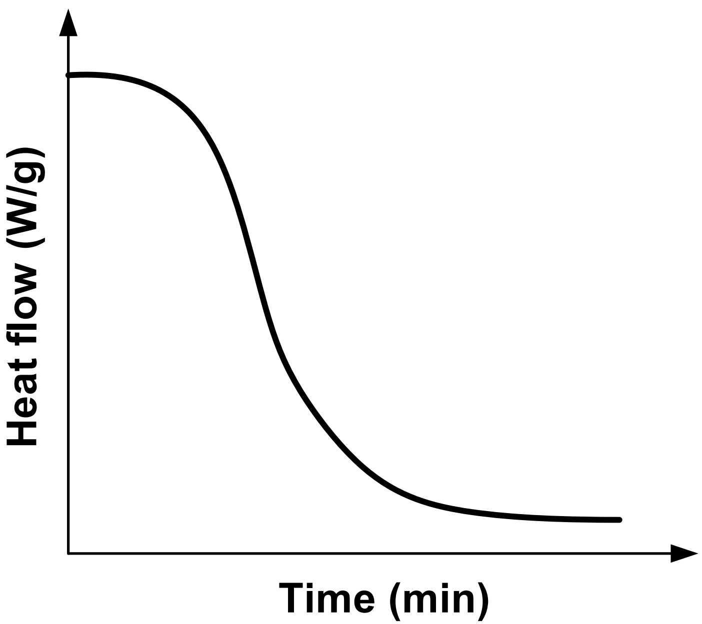
C: cooling event only

H/C: observed in both heating and cooling events

Thermosetting Cure Reaction Types

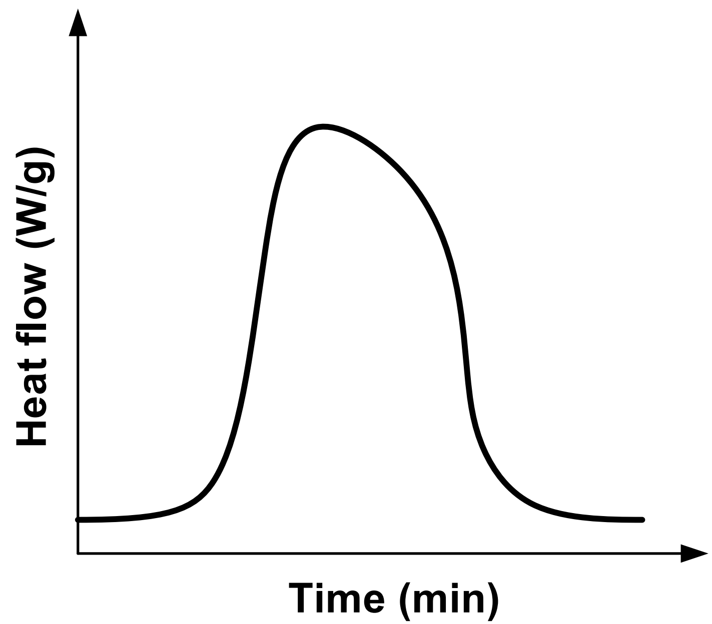
n^{th} order reaction

- Maximum reaction rate at t = 0
- Single reactions
- 'Mix' initiated



Autocatalytic reaction

- Maximum reaction rate at 30-50% conversion
- Multiple reactions
- 'Temperature' initiated

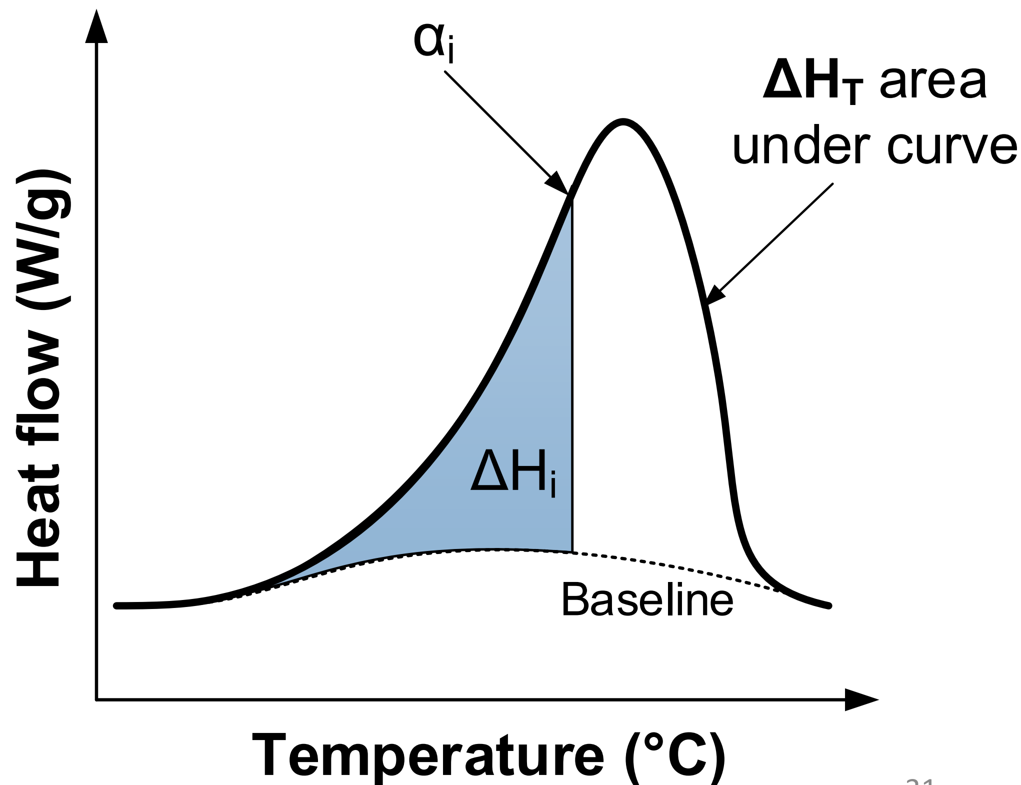


Converting Heat Flow to Cure

- Assumption: since the cure of thermosetting resins is an exothermic process, the **degree-of-cure**, **α**, can be related to the heat released

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

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



Cure Kinetics (or Cure Rate)

- Derivative of the degree-of-cure with time

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_T}\frac{dH_i}{dt}$$

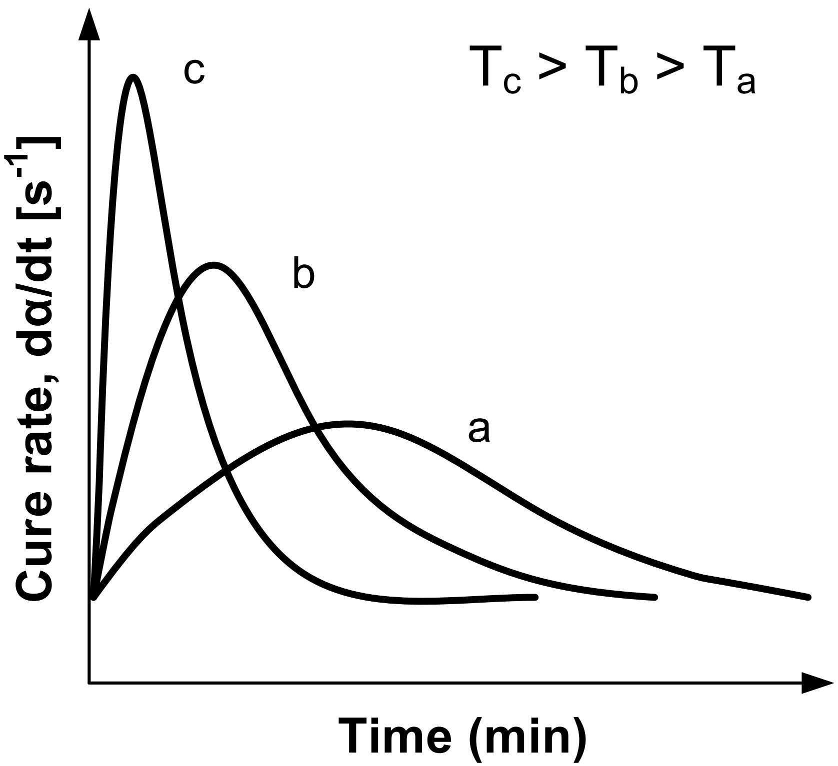
- Often modelled using an Arrhenius relationship

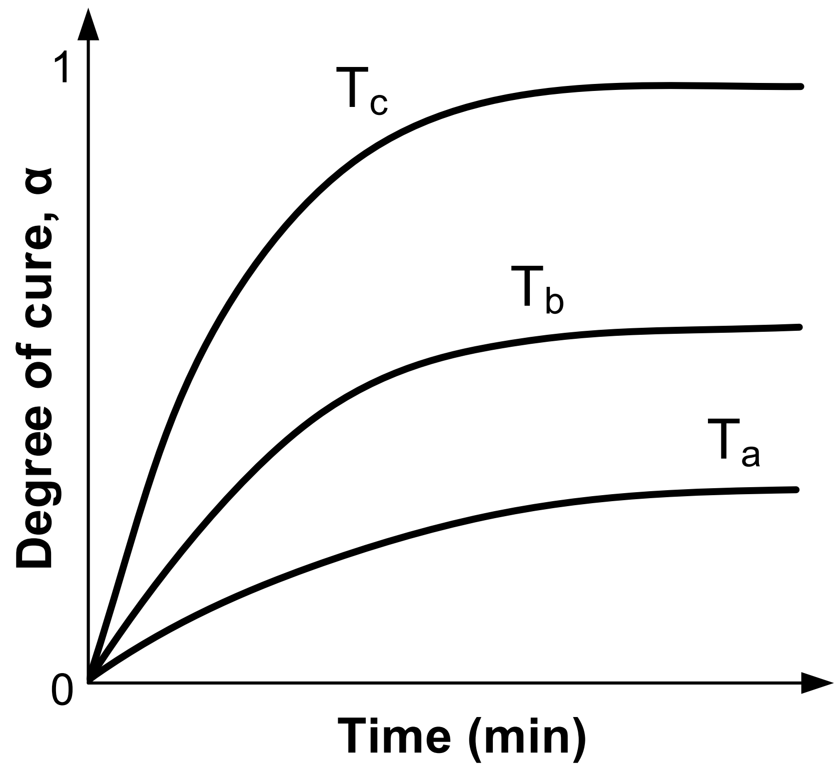
$$\frac{d\alpha}{dt} = A\,exp\left(-\frac{E_a}{RT}\right)\alpha^m(1-\alpha)^n$$

A: pre-exponential constant [s^{-1}]
Ea: activation energy [J/mol]
T: temperature in Kelvin [K]
R: Universal gas constant, 8.314 [J/(mol·K)]
m,n: constants
note: m = 0 for an n^{th} order reaction & m ≠ 0 for an autocatalytic reaction

Effect of Temperature on Cure

- Faster cure rate and a higher degree-of-cure is achieved as process temperature increased





Activity

You are a production engineering at Head responsible for the manufacture of tennis racquets. The marketing department has done an amazing job advertising this new racquet and as a result, they are flying off the shelves 25% faster than current production capacity. Your manager wants to increase production and together your team has identified the following options:

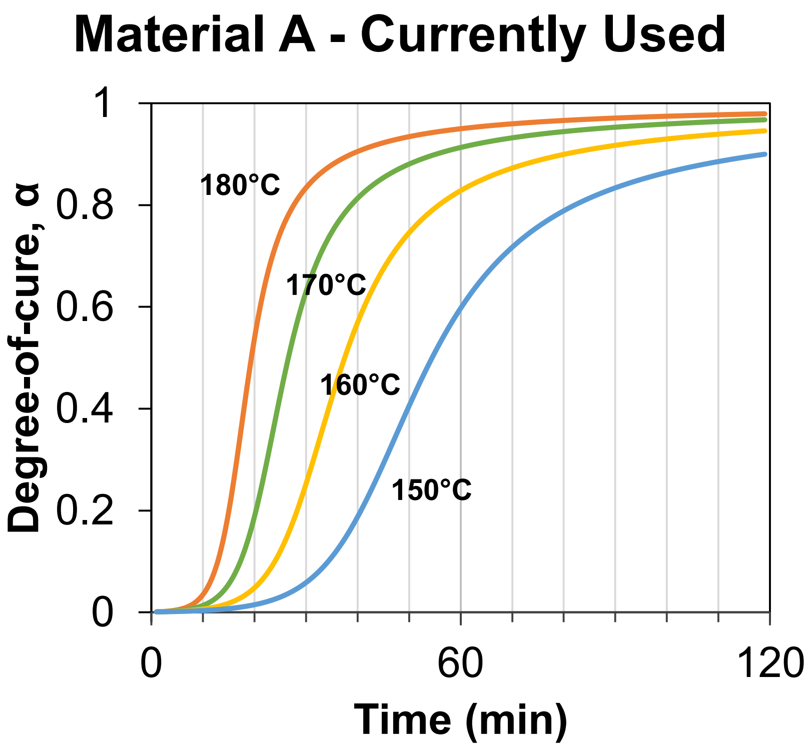
i. Increase production temperature
ii. Change materials
iii. Create a second production line

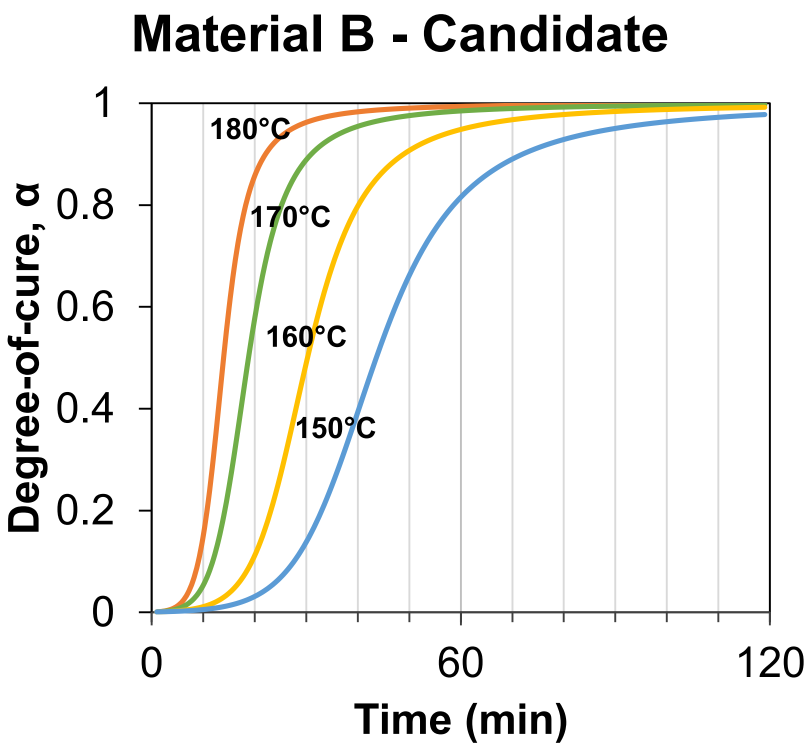
In teams of 3-4, take 7 minutes and identify the advantages and disadvantages of each option. Which option would you propose to your manager?

Material data are available on the following slide

Video: https://www.youtube.com/watch?v=PqaEOf-Ysyc

Racquet Materials





Both materials follow this semi-empirical relationship

$$\frac{d\alpha}{dt} = A\,exp\left(-\frac{E_a}{RT}\right)\alpha^m(1-\alpha)^n$$

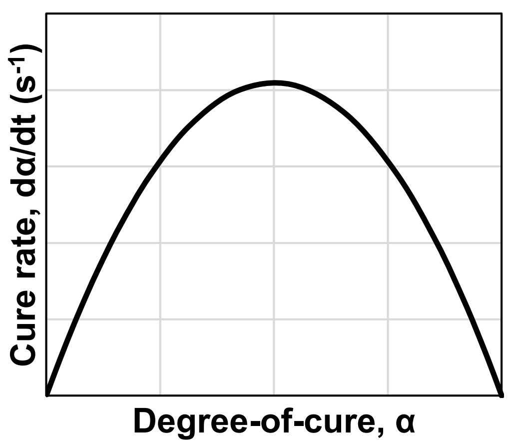
Effect of Reaction Type

What changed between candidate materials A & B to shorten the time needed to reach an equivalent degree-of-cure?

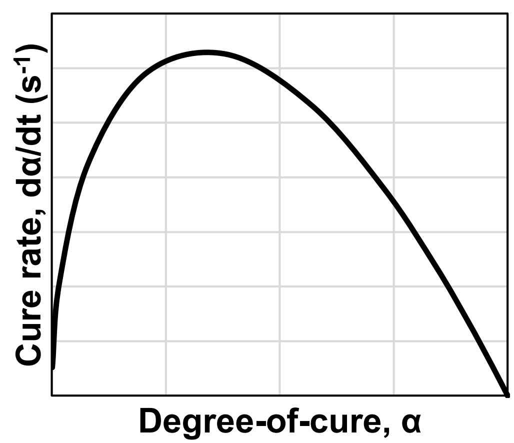
<u>Going back to our cure kinetics equation:</u>

$$\frac{d\alpha}{dt} = A\, exp\left(-\frac{E_a}{RT}\right)\alpha^m(1-\alpha)^n$$

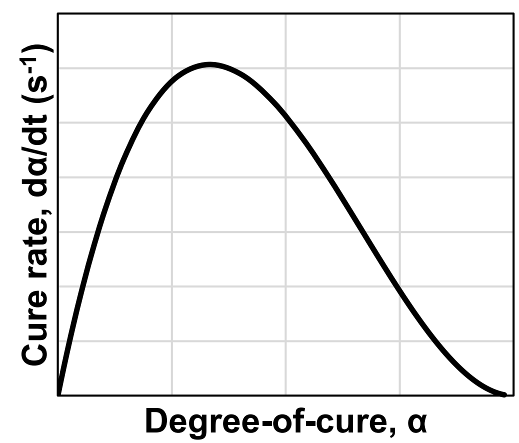
m = 1, n = 1



m = 0.5, n = 1



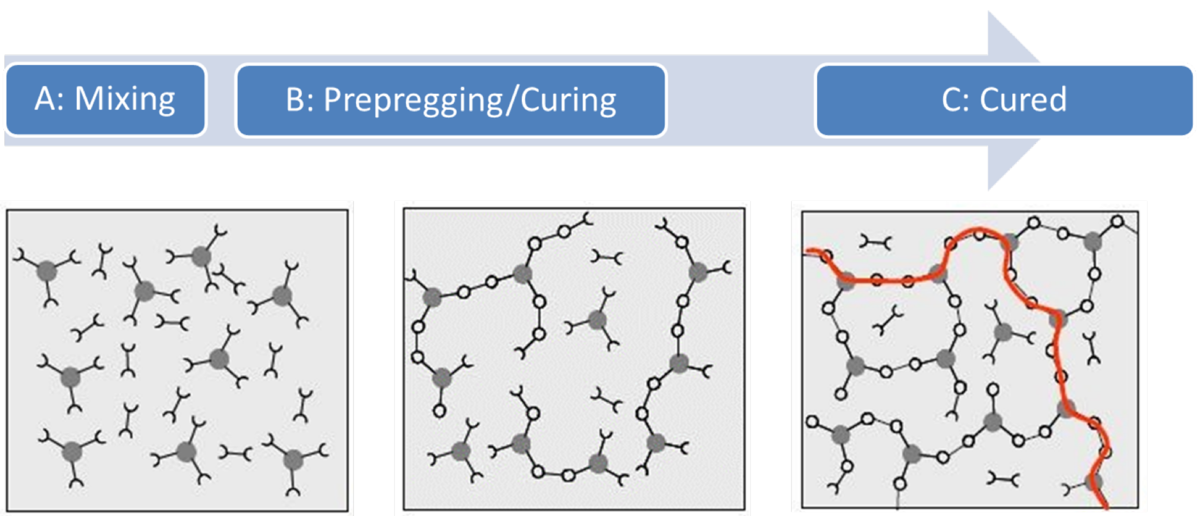
m = 1, n = 2

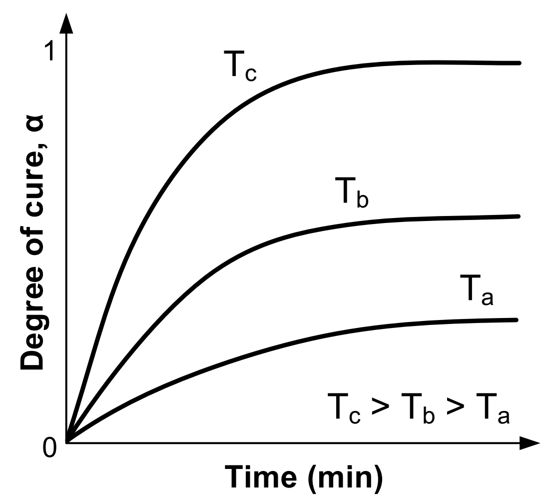


- Pure autocatalytic
- n^{th} order biased
- n^{th} order biased

Summary

- Energy released during the curing reaction can be measured by a differential scanning calorimeter (DSC)
- A model can be used to describe the cure kinetics and deployed to predict the time needed to reach a target conversion at any temperature





Properties of Materials

Theme: Polymers and Composites

Lecture 3: Gelation and Vitrification

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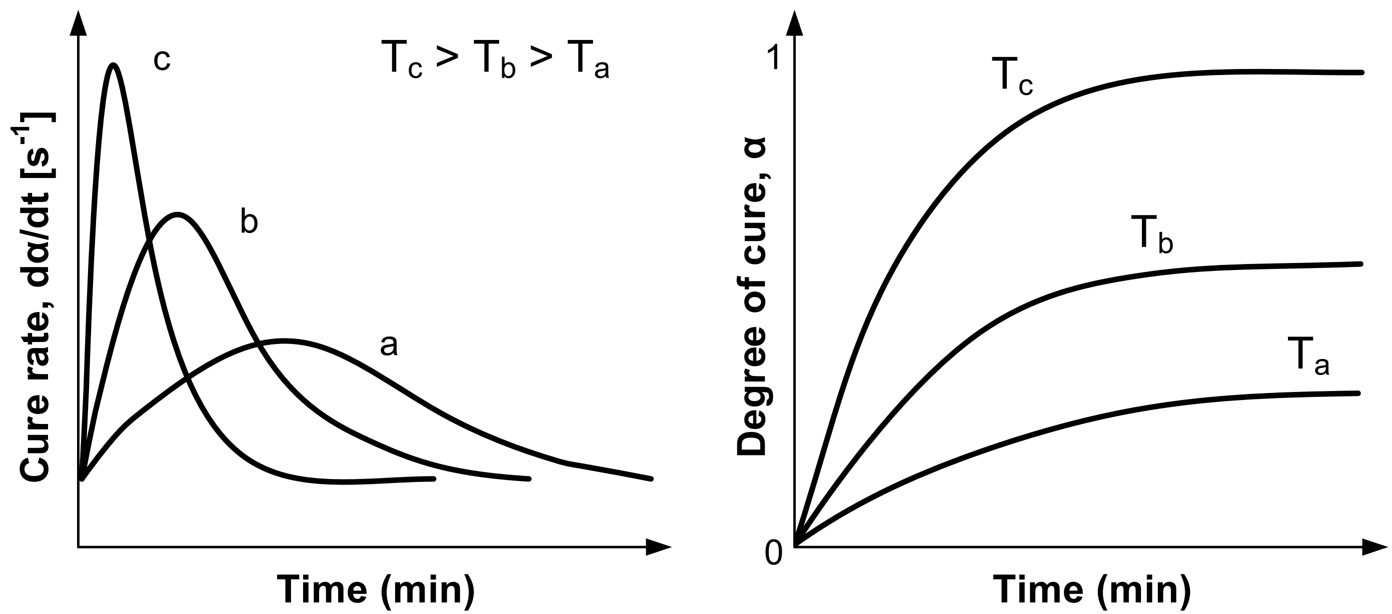
Review

Effect of Temperature on Cure

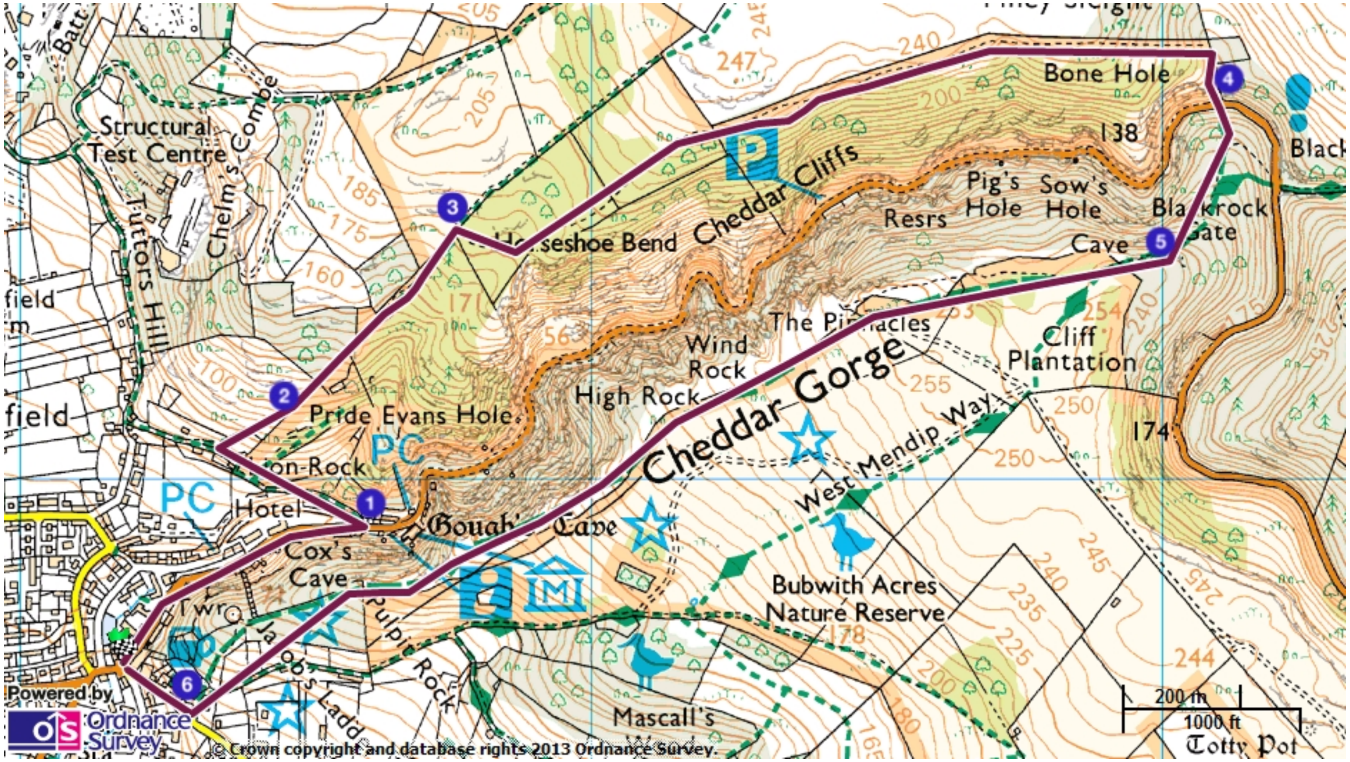
- Faster cure rate and a higher degree-of-cure is achieved as process temperature increased



➢ Today: why the degree-of-cure is more limited at some temperatures?

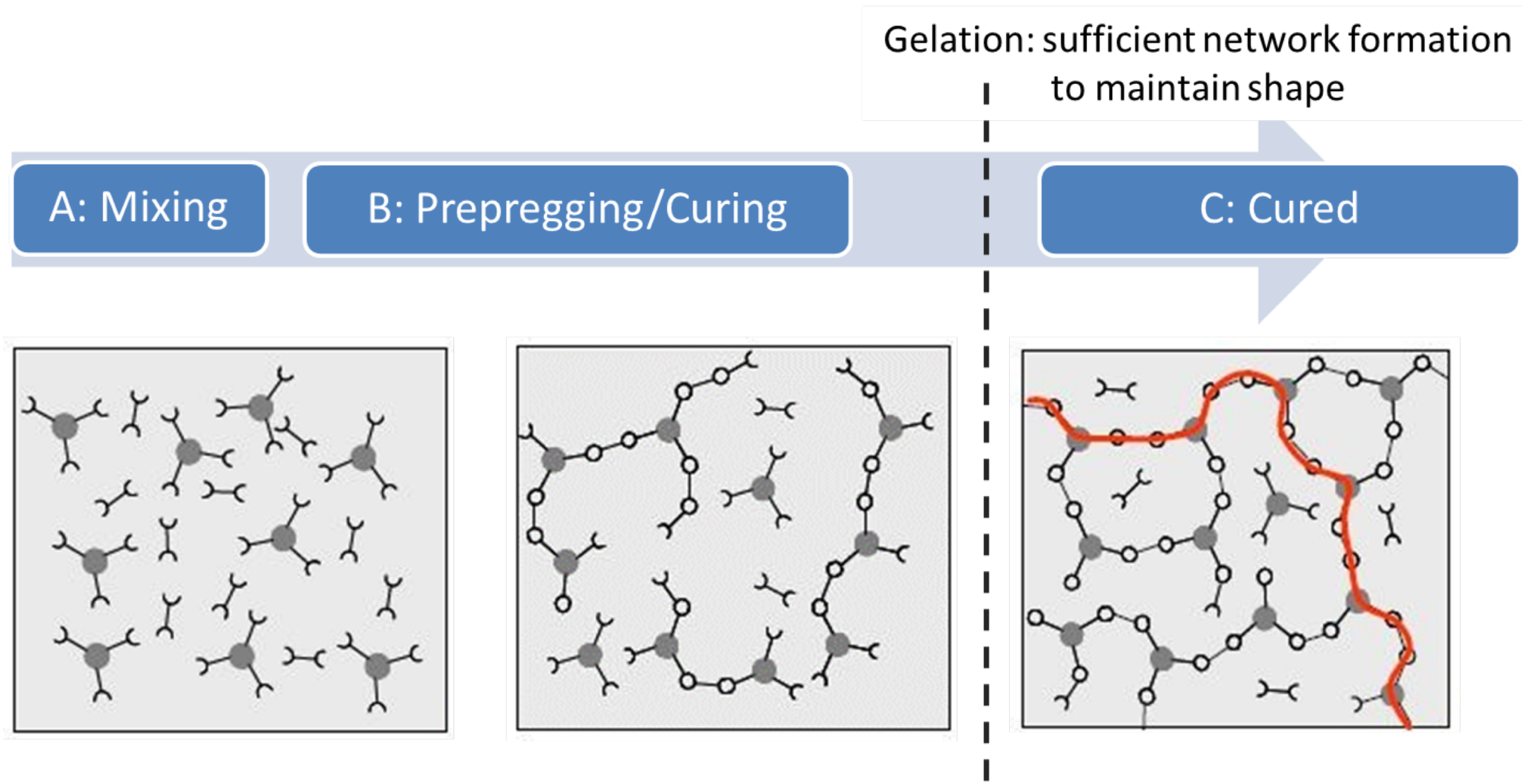
Today's Lecture Contents

- Gelation, viscosity testing and viscosity models
- Glass transition temperature
- Activity: TTT Diagrams (a curing map)



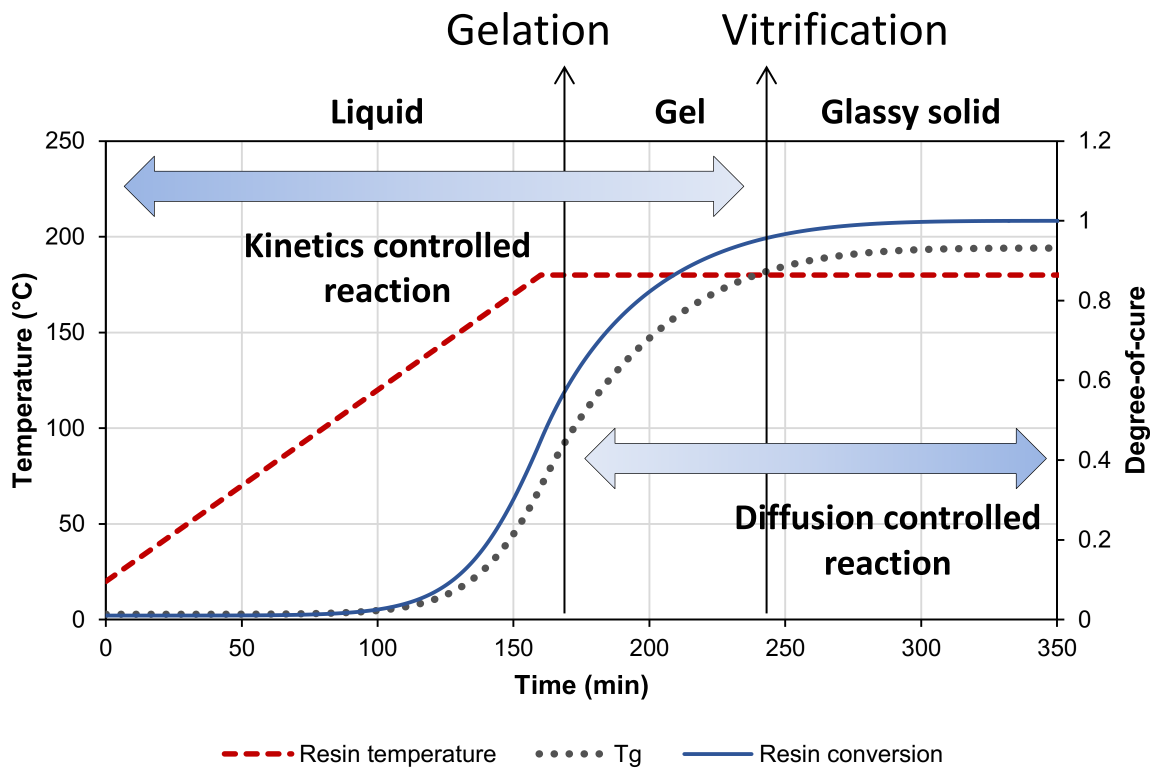
Polymer Physical Changes

- During the curing reaction, the molecular weight increases and flow is no longer possible
- Can now eject a part from a mould

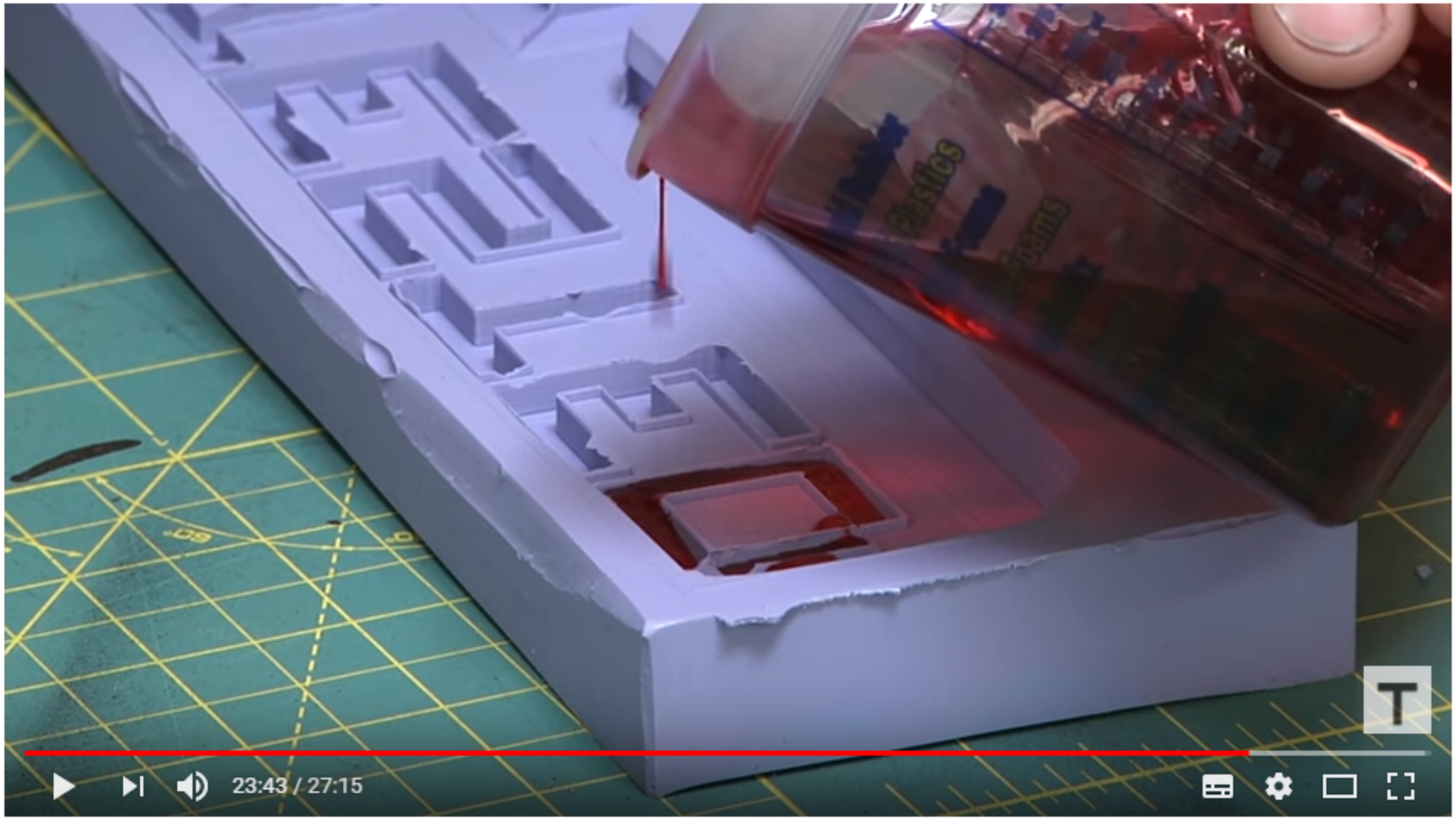


Gelation and Vitrification

- Gelation: transformation of the resin from a liquid to a **rubbery** state
- Vitrification: transformation to a gelled **glass** when the glass transition temperature exceeds the cure temp.



Pot Life



https://www.youtube.com/watch?v=J1jDaZX6PCk&feature=youtu.be&t=1424

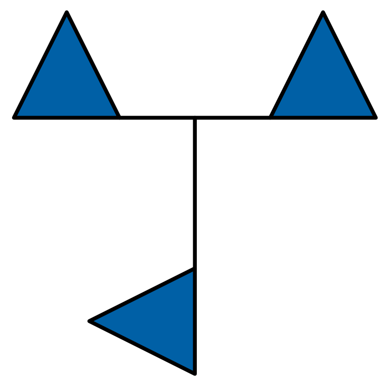
23:30

Effect of Functionality

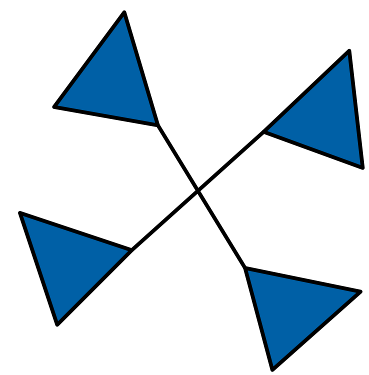
- Material branching will happen more rapidly when you increase functionality

Di-functional

Tri-functional



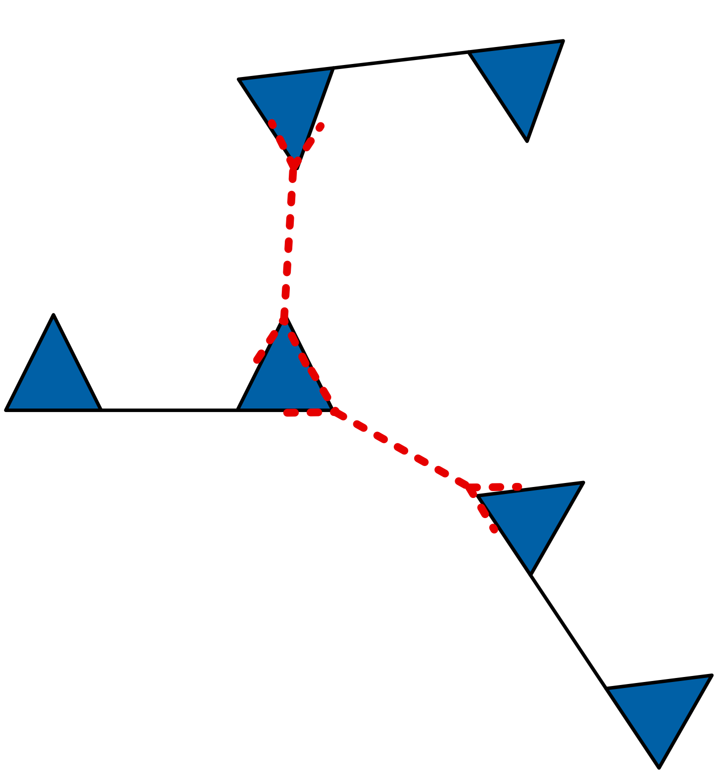
Tetra-functional



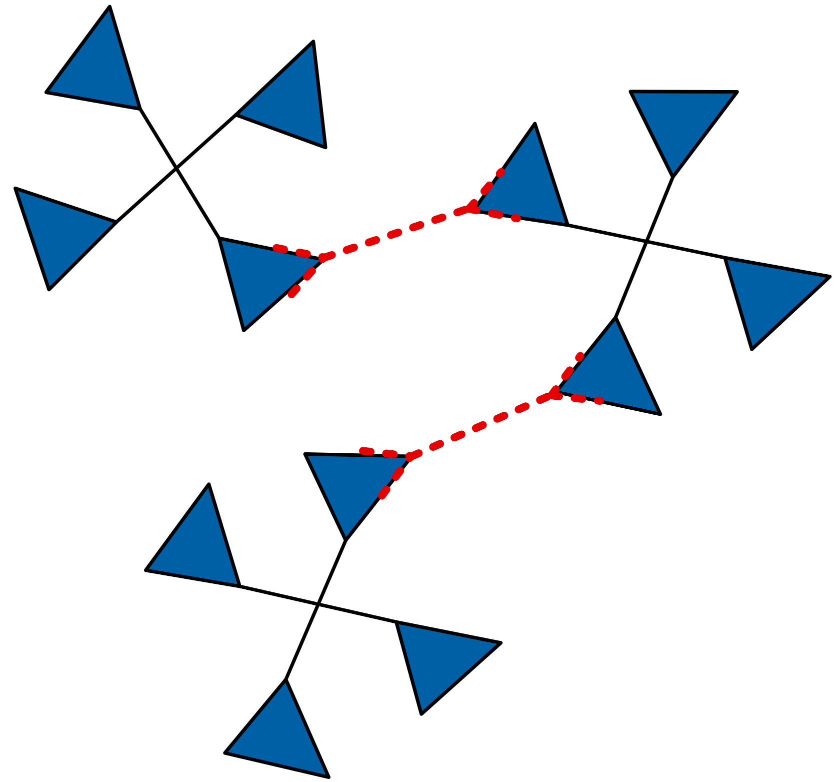
Curing agent (hardener)

Network Formation of 3 Monomers

Di-functional



Tetra-functional



- Two cross-links create very different network densities
- Can we predict when each network will gel?

Onset of Gelation

- Flory–Stockmayer theory

$$\alpha_{gel} = \frac{1}{[r + rs(f-2)]^{1/2}}$$

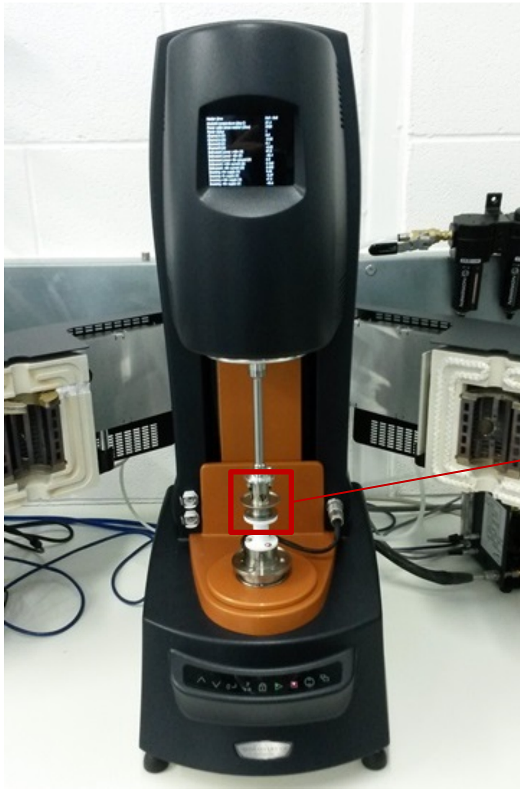
f is the functionality of the cross-linking groups
r is the molar ratio of epoxy group to amine hydrogen
s is the fraction of the amine hydrogen in the reactants

- Let's consider a common case of di-amine and tetrafunctional epoxy (TGDDM), *f* = 1, *r* =1, and *s* = 1.

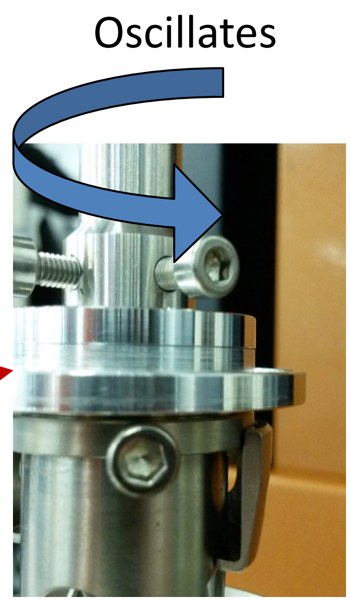
$$\alpha_{gel} = 0.577 \longrightarrow \text{In practice, } 0.6 \pm 0.02$$

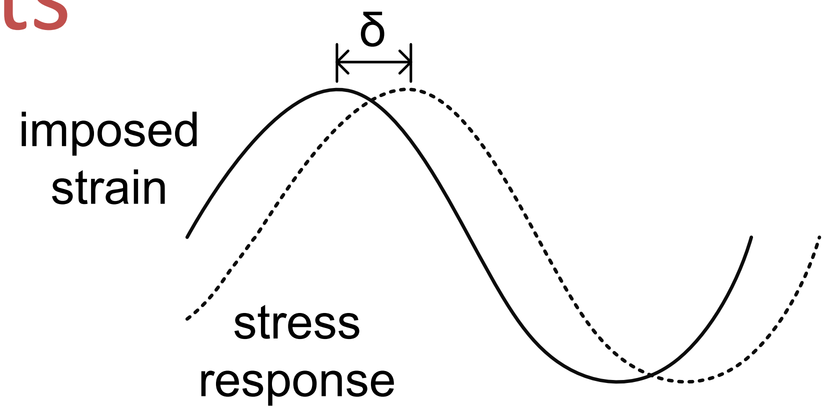
- Above this value, molecule mobility reduces and the cure reaction switches from a kinetics dominated reaction to a diffusion dominated reaction.

Viscosity Measurements



Rotational Rheometer





Strain in fluid:

$$\hat{\gamma} = \gamma_0 \sin \omega t$$

Resulting stress in fluid:

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

Complex viscosity:

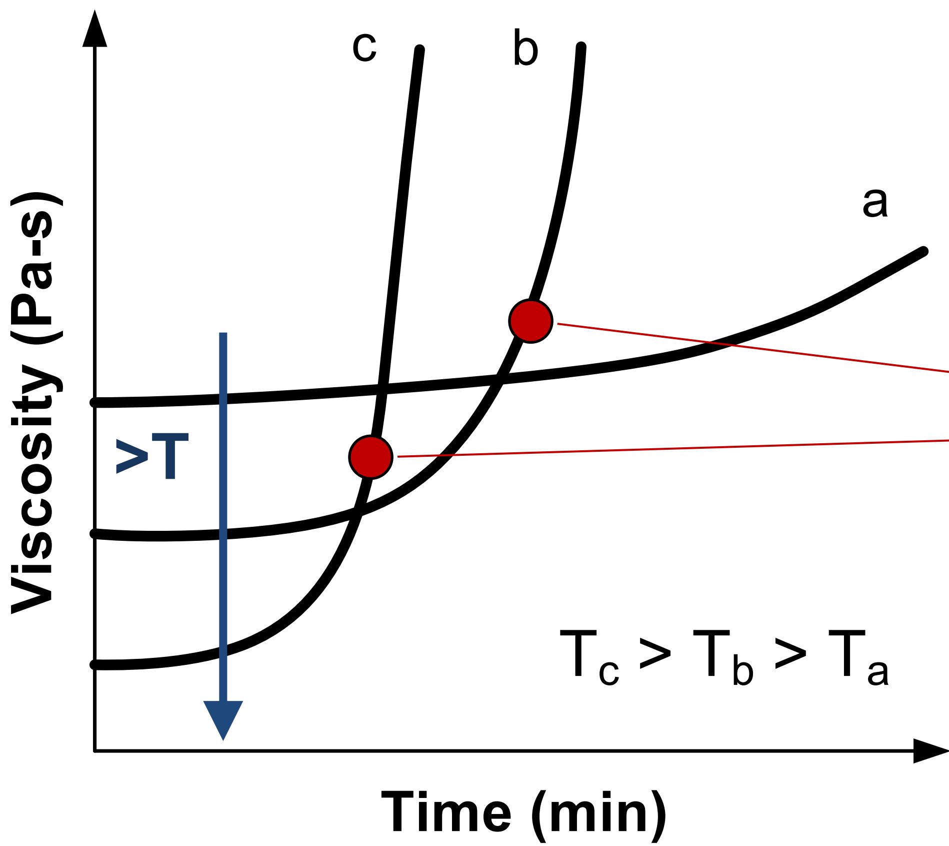
$$\eta^* = \eta' + i\eta'' \qquad \eta' = \frac{G''}{\omega} \quad \& \quad \eta'' = \frac{G'}{\omega}$$

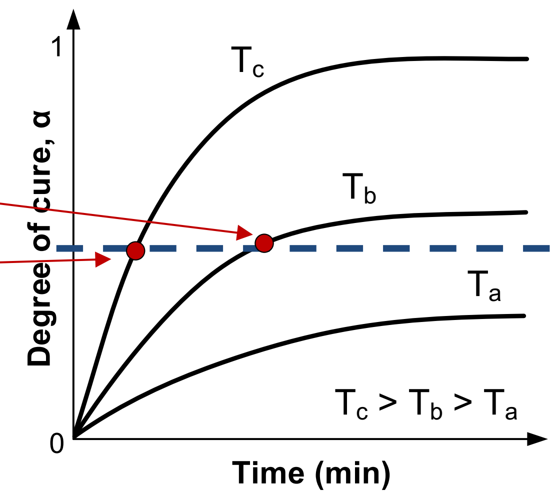
Where physically:
G’: elastic storage modulus, in-phase
G”: viscous loss modulus, out-of-phase
ω: is the angular frequency

Gelation: tan(δ) = 1
Elastic and viscous response equal

Effect of Temperature on Viscosity

- Increasing processing temperature reduces viscosity and shortens time to gelation





Resin Viscosity Model

- Castro and Macosko[1] model:

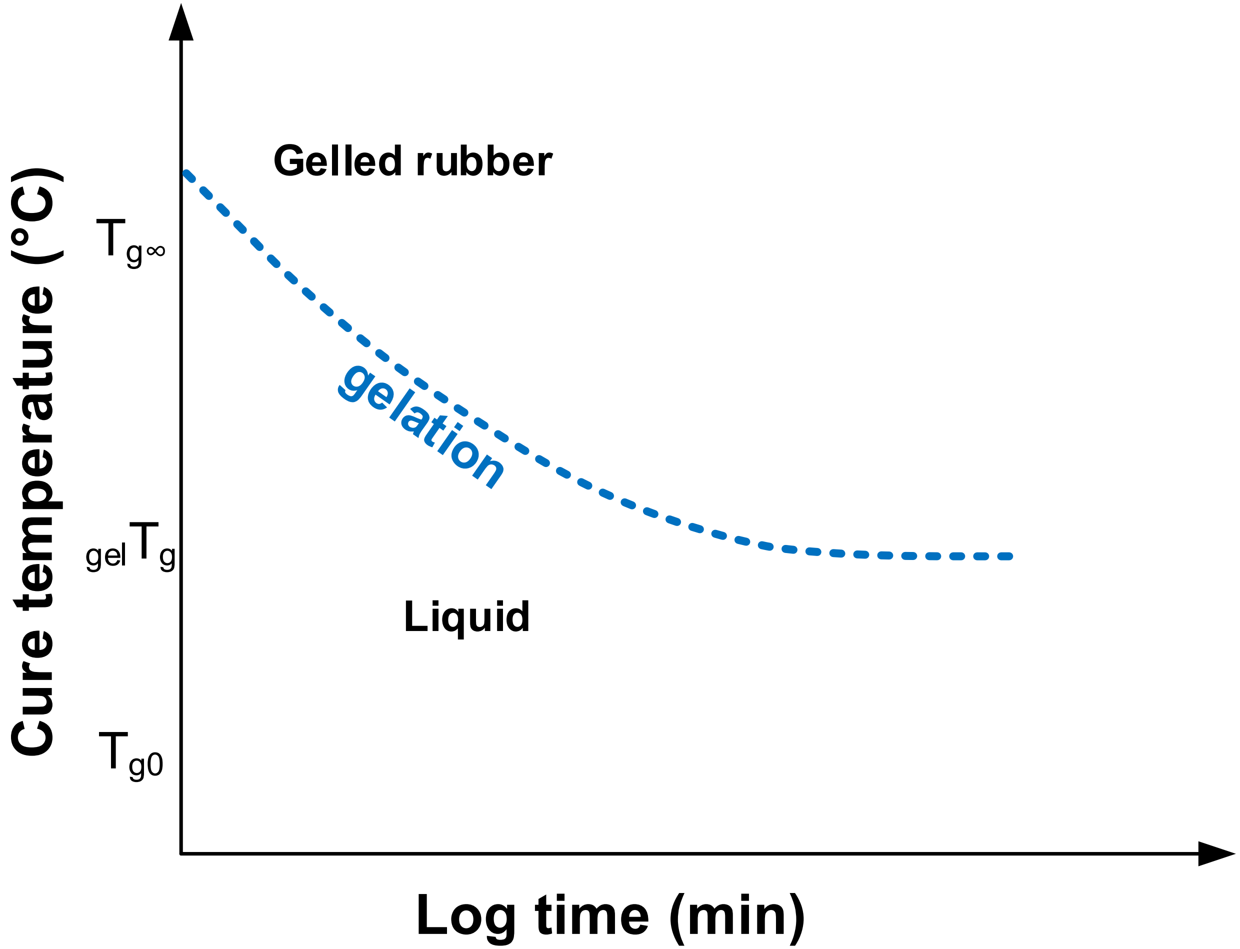
$$\eta = A_\eta \, exp\left(\frac{-E_\eta}{RT}\right)\left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha}\right)^{A+B\alpha}$$

A_η: pre-exponential constant [Pa·s]
E_η : activation energy [J/mol]
T: temperature in Kelvin [K]
R: Universal gas constant, 8.314 [J/(mol·K)]
α: instantaneous degree-of-cure
α_{gel}: degree-of-cure at gelation
A, B: constants

[1]Castro JM and Macosko CW. Kinetics and rheology of typical polyurethane reaction injection molding systems. Society of Plastics Engineers (Technical Papers), 434–438, 1980.

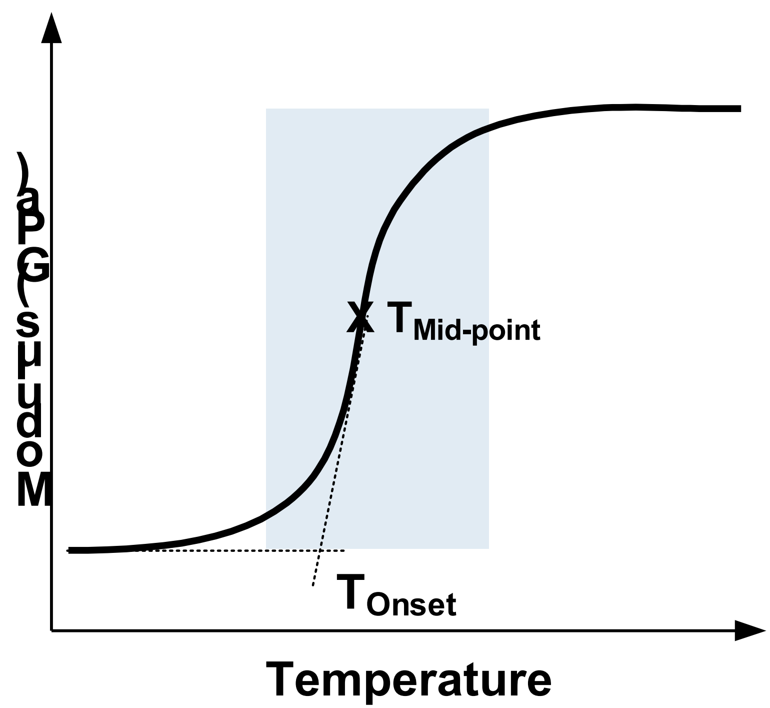
Time-Temperature-Transformation (TTT) Cure Diagram

- Time to reach gelation



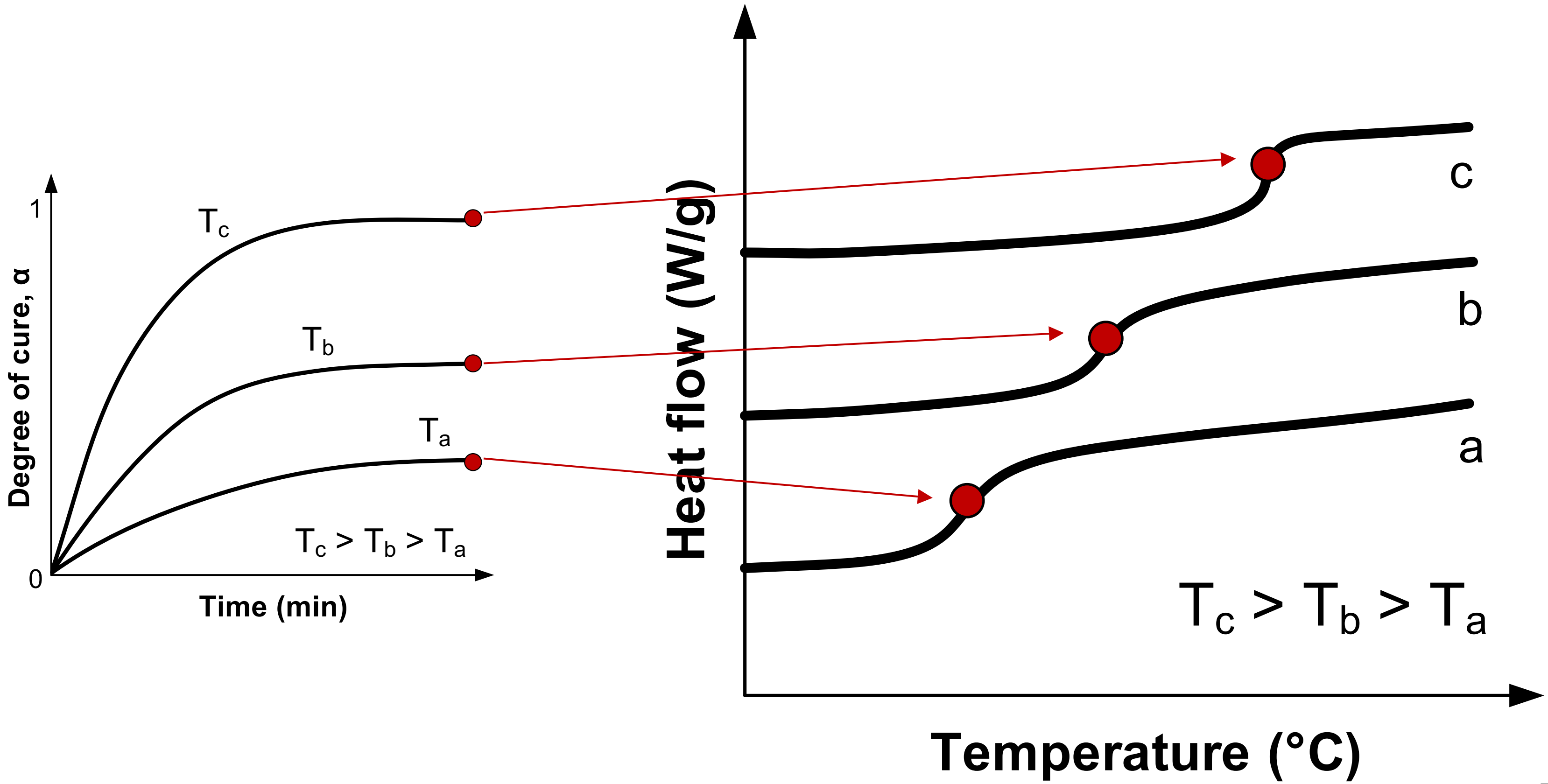
Glass Transition Temperature (T_g)

- "The reversible change from (or to) a viscous or rubbery condition to (or from) a hard and relatively brittle state." –ISO 11357-2
- A range rather than a specific temperature



Effect of Temperature on T_g

- Increasing processing temperature increases glass transition temperature (T_g)

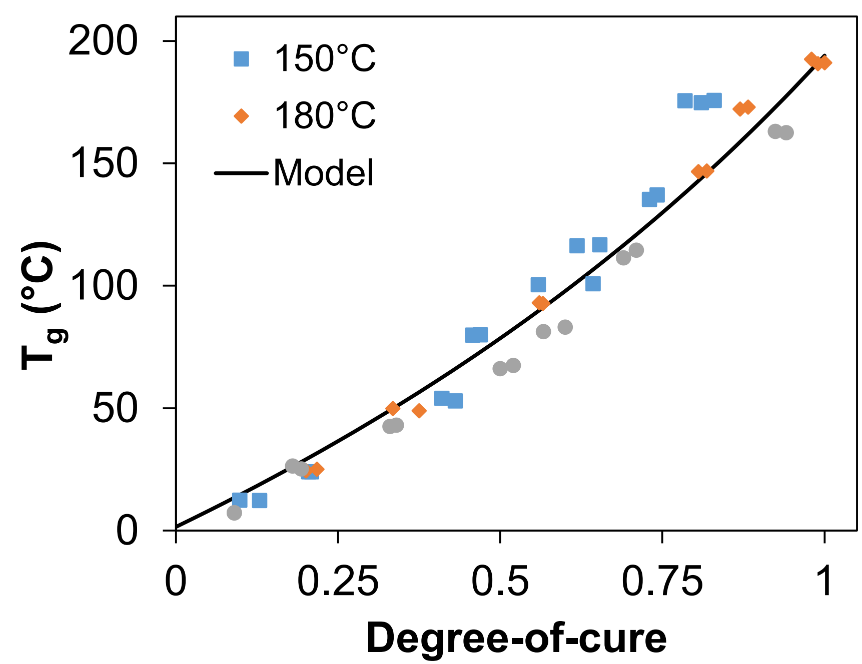


Glass Transition Temperature (T_g)

- Depends on the degree-of-cure (α) and described by the DiBenedetto equation

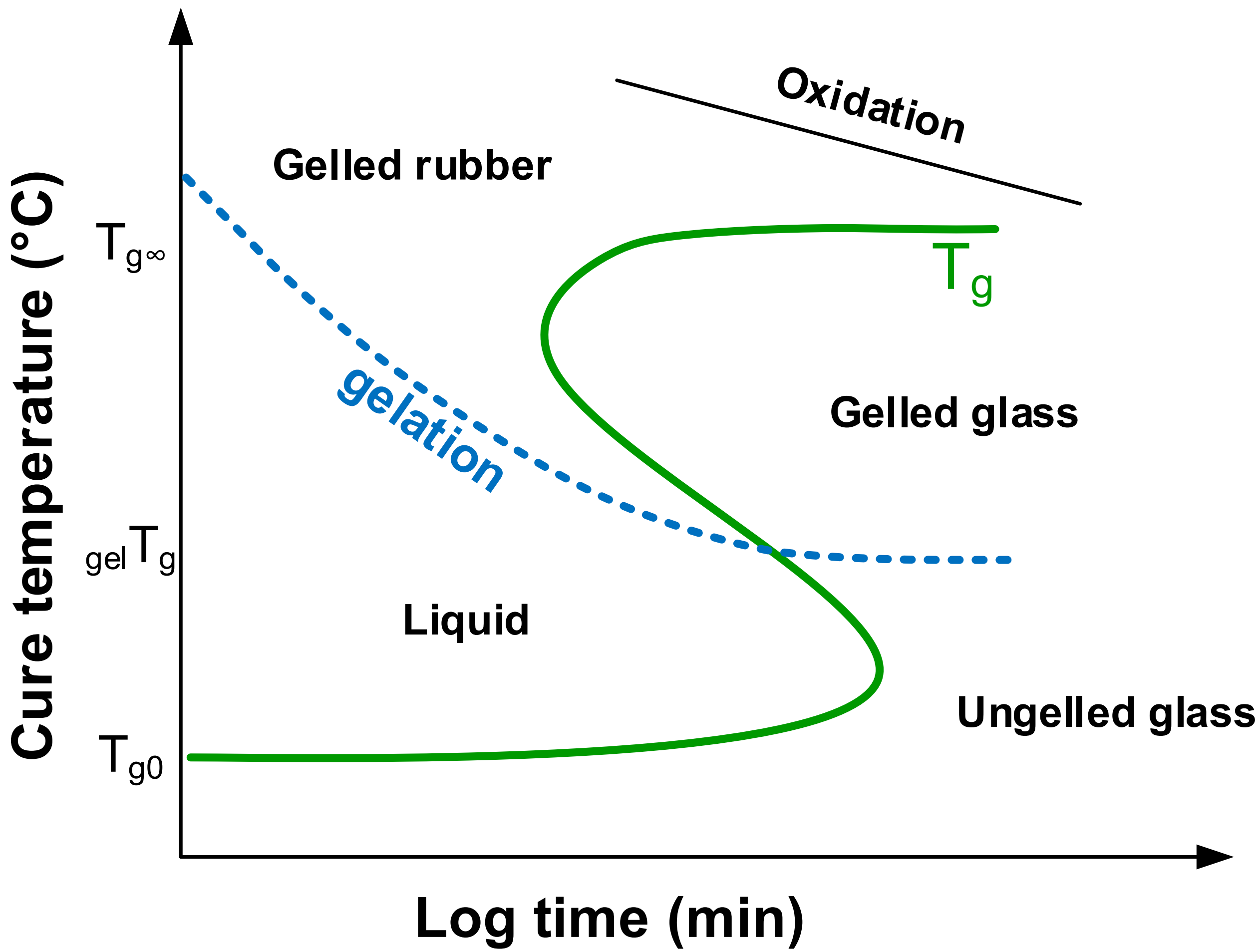
$$T_g = T_{g0} + \frac{\left(T_{g\infty} - T_{g0}\right)\alpha\,\lambda}{1-(1-\lambda)\,\alpha}$$

T_{g0}: uncured glass transition temperature
$T_{g\infty}$: final glass transition temperature
λ: fitting parameter



Time-Temperature-Transformation (TTT) Cure Diagram

- Time to reach gelation and vitrification



Describing cure with a TTT diagram

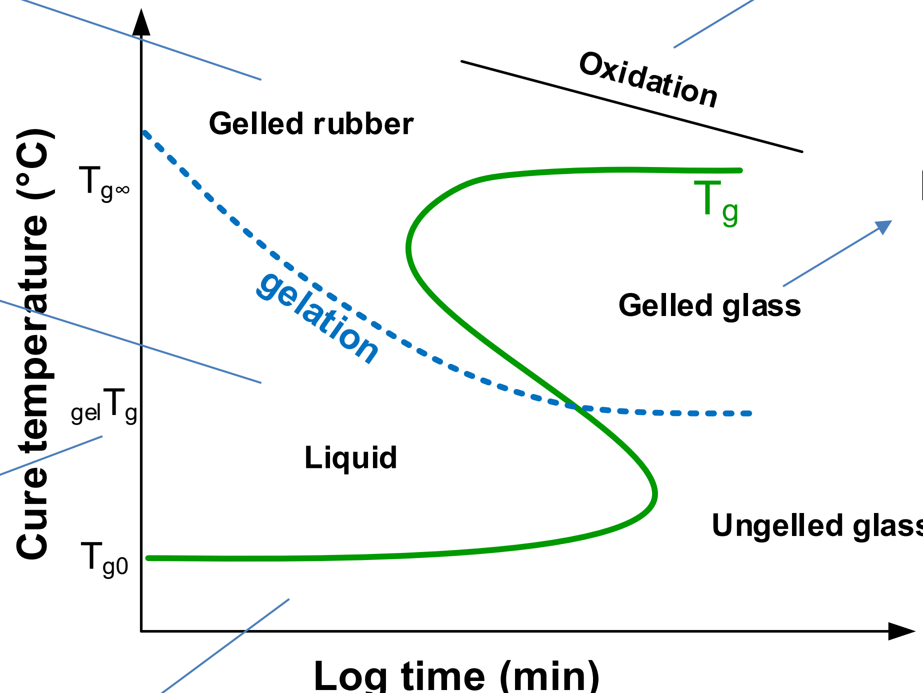
Reaction slows as a network of cross-linked polymer molecules forms

Material degradation

Resin is fluid and remains processable

Reaction slows considerably

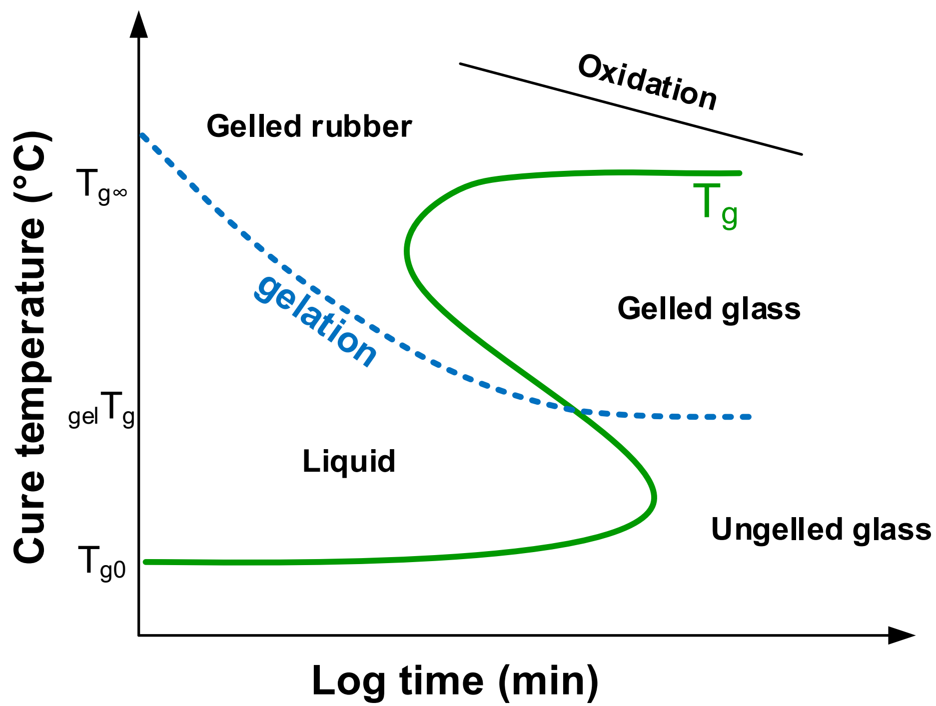
Temperature when the time to gel is the same as the time to vitrify



No reaction occurs because the monomers are immobilised in the glassy state

Activity

- In groups of 2-3, identify the isothermal processing temperature you would propose to get the best material properties. Justify your reasoning.
- How does your choice influence the manufacturing process?



Summary

- Viscosity: captures material fluidity by thermal and curing effects (often in competition with eachother)
- Energy (Temperature for curing) increasing mobility of monomers to cross-linking into a gelled rubber and eventually a glassy solid
  - Transition between a gelled rubber and glassy solid is measured by the Glass Transition Temperature (T_g)
- You can map gelation and T_g on a TTT diagram to find a favourable processing route while avoiding problems

Properties of Materials

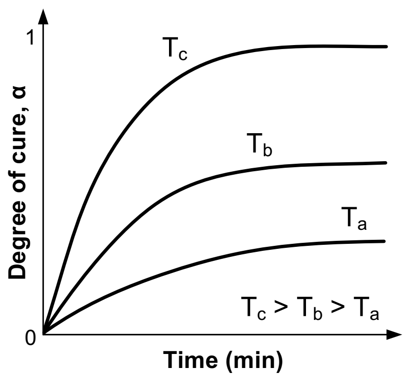
Theme: Polymers and Composites

Lecture 4: Residual Stresses

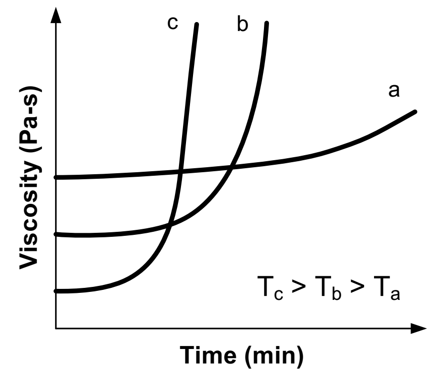
Prof. Ian Hamerton
ian.hamerton@bristol.ac.uk
Room 0.106 Queen's Building

Review

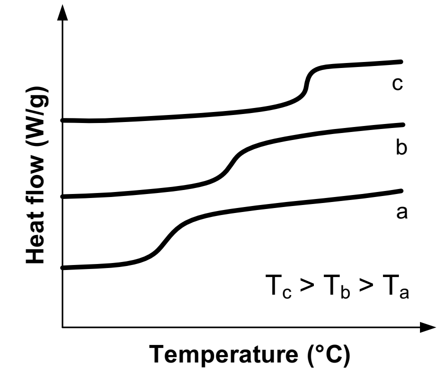
Cure kinetics



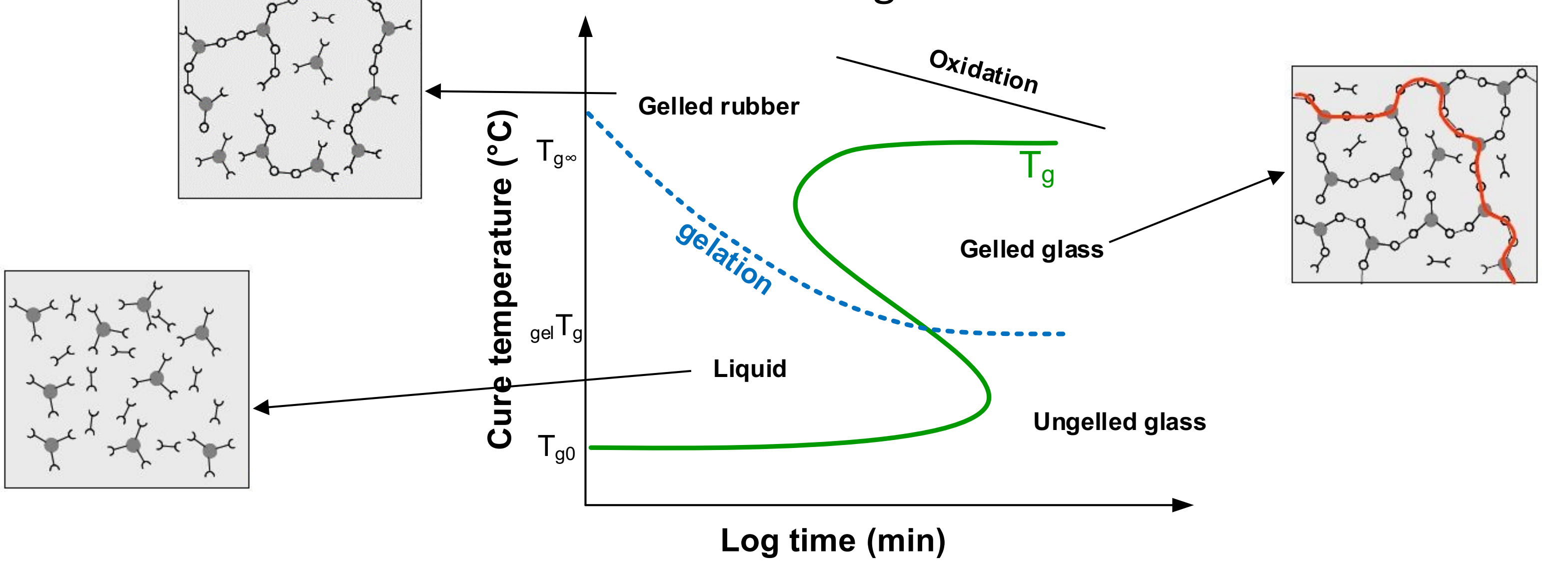
Viscosity and Gelation



Glass Transition Temperature

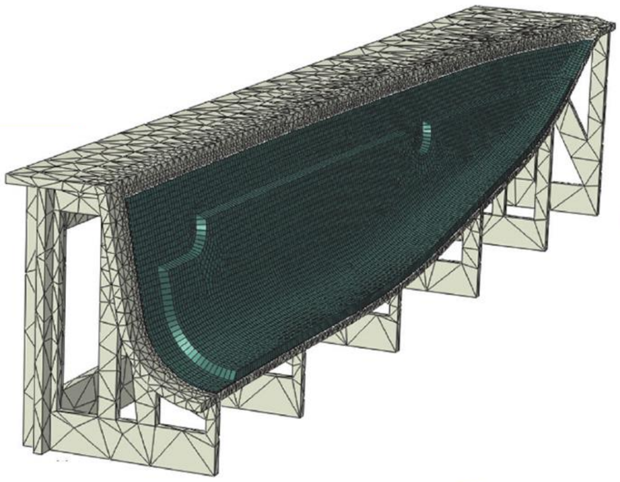


TTT Diagram

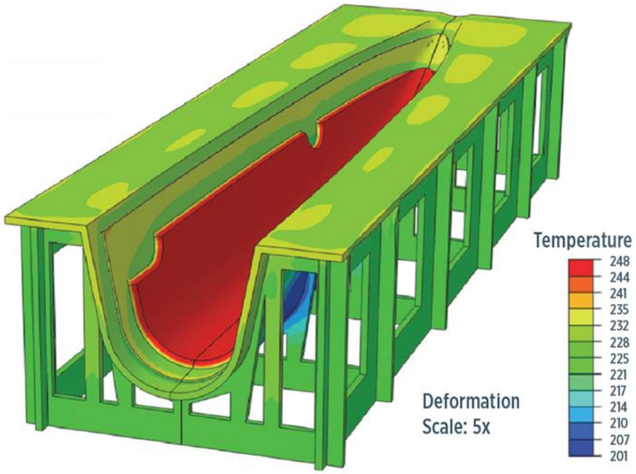


Today’s Lecture

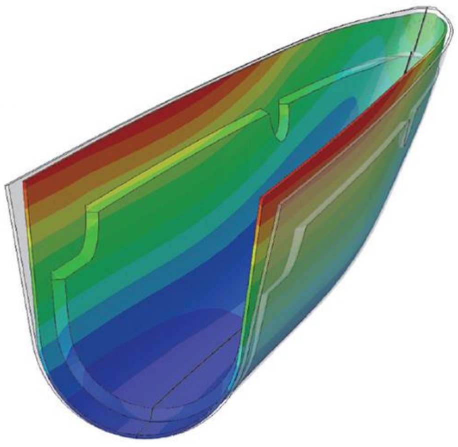
- Process induced deformation and residual stresses that form during curing
- Can be simulated of you know your oven, part shape, tooling material, and material properties.



Finite element mesh



Temperature simulation



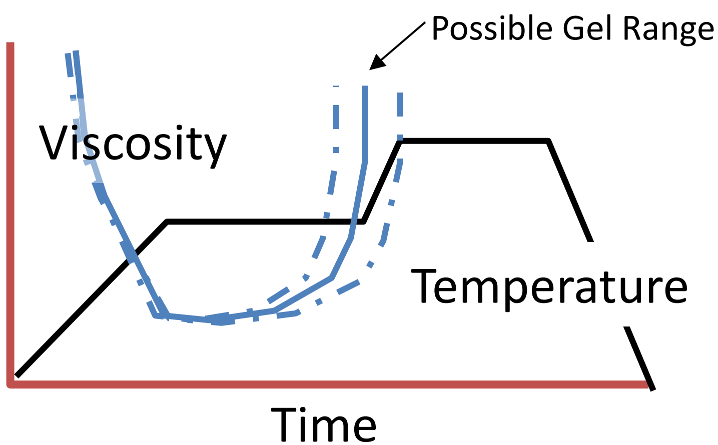
Dimensional change

Images: Fernlund G. and Poursartip A. Getting part dimensions right in composites molding. Composites World, 2015.

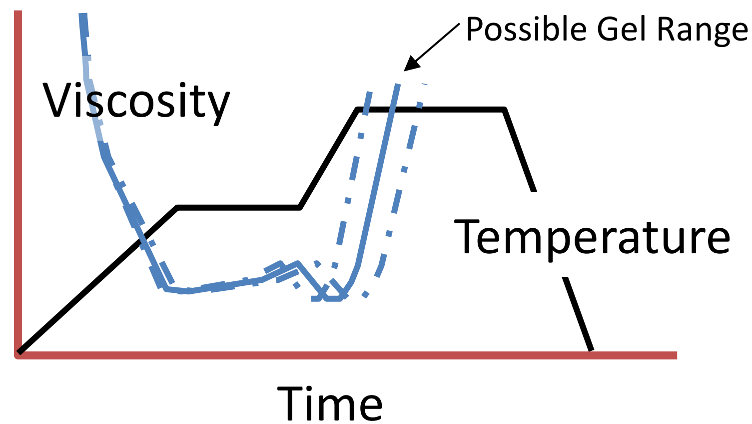
Processing Effects

Dimensional Control may be improved through processing:

- Gel part at final hold temperature
- Use tooling with CTE matched to part
- Reduce thermal mass of tooling and improve temperature uniformity



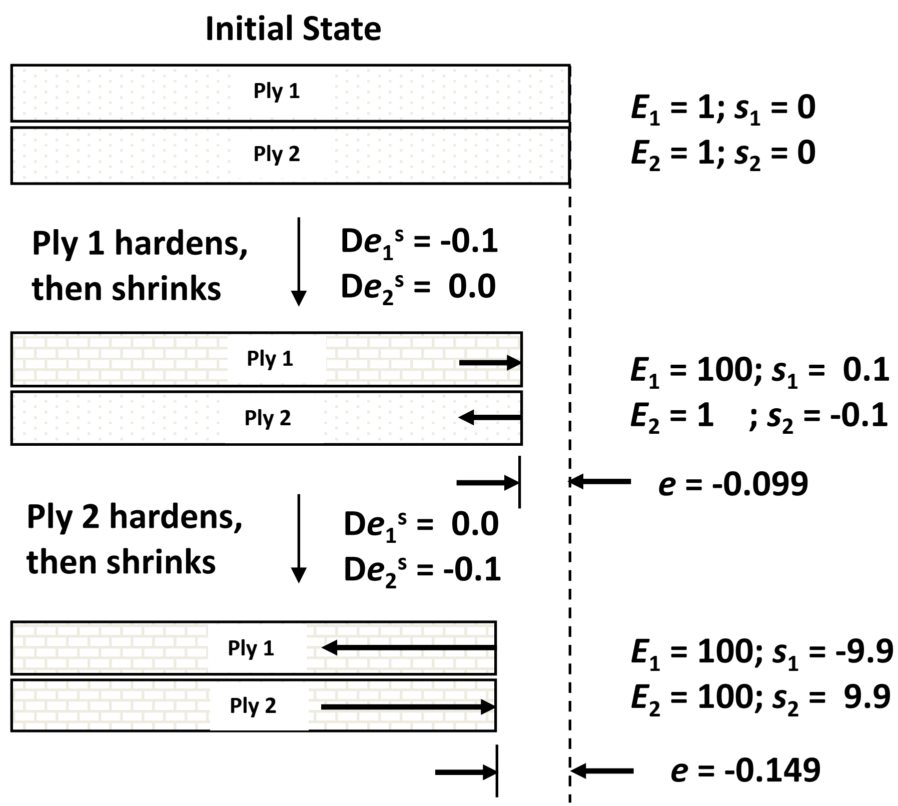
Part gelled during first hold or in second ramp, tool grows during heat-up



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

Reduced variability

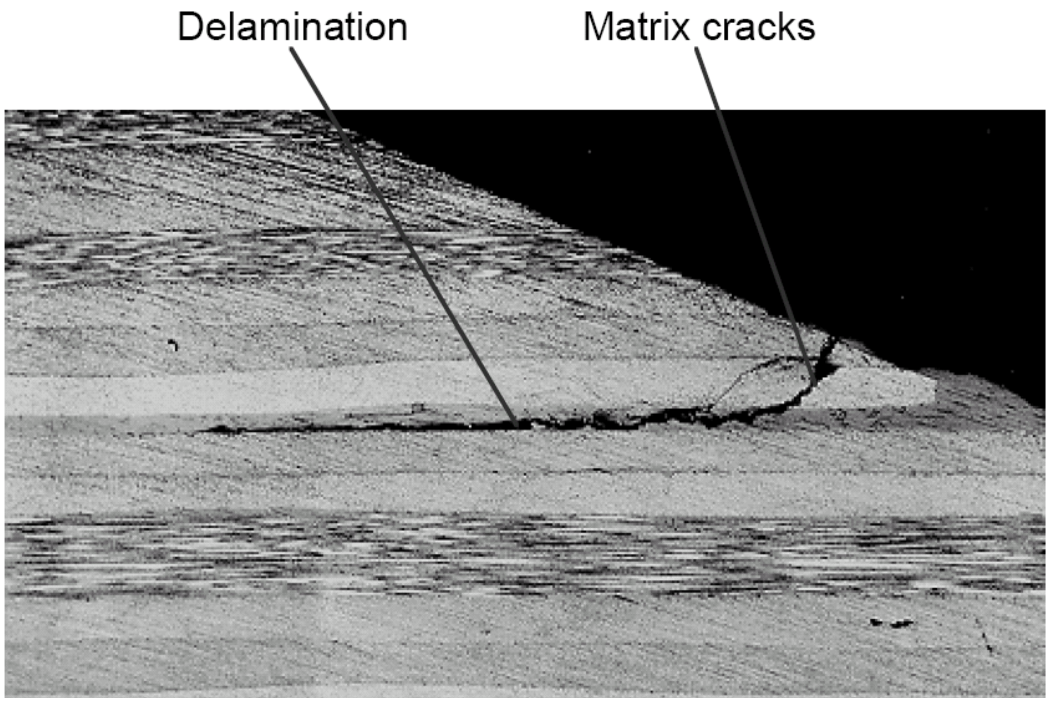
Cure and Temperature Gradients



Result: both cured equally, non-zero stress state

Residual Stresses

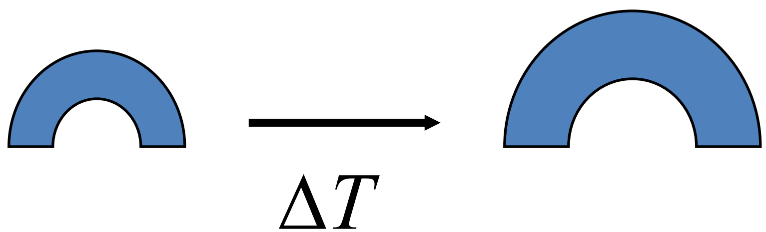
- Residual stress is a stress which exist in the bulk of a material without application of an external load
- Generated during processing of polymer matrix composites
- Residual stress can cause matrix cracking, delamination, warpage, and even failure of a composite component



Thermal Dimensional Change

Simple Materials: isotropic, homogeneous material (aluminium)

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



- Governed by the CTE

(Coefficient of Thermal Expansion)

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

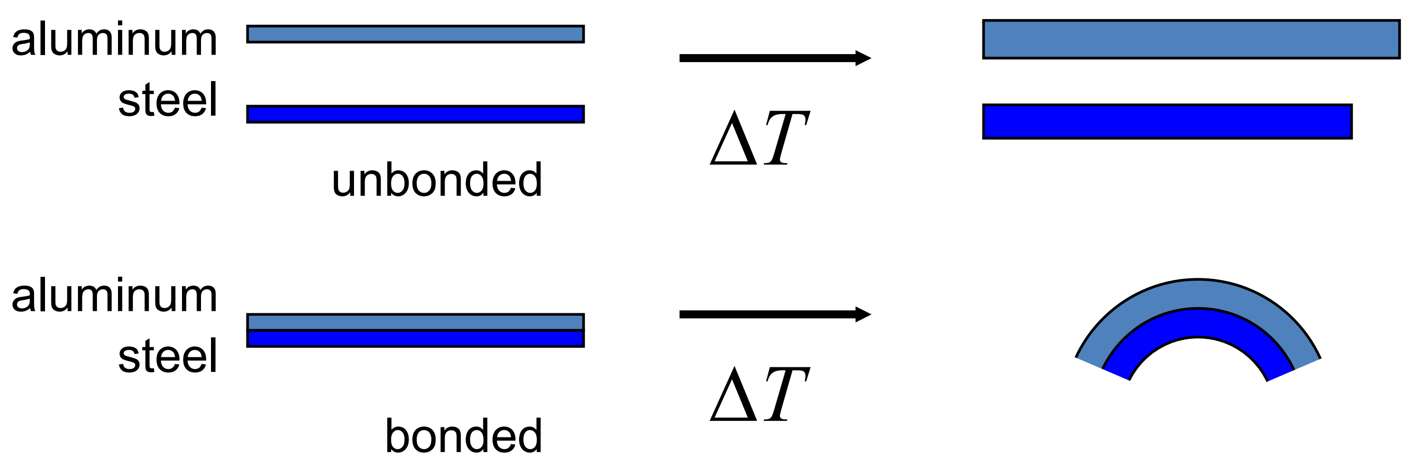
L_2 and L_1 refer to the length of the specimen at temperatures of T_2 and T_1, respectively

L_0 is the original length of the specimen at ambient temperature

Thermal Dimensional Change

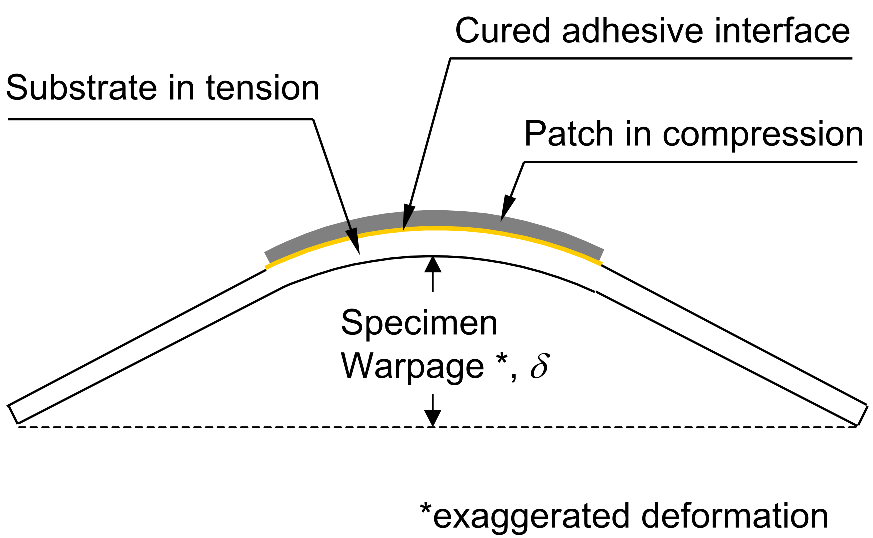
Complex Systems: Bi-metallic strip, composite laminate

- 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

Warpage



Warpage in single-sided bonded patch repair due to difference in CTE of the aluminium substrate and the composite patch

Timoshenko's beam theory

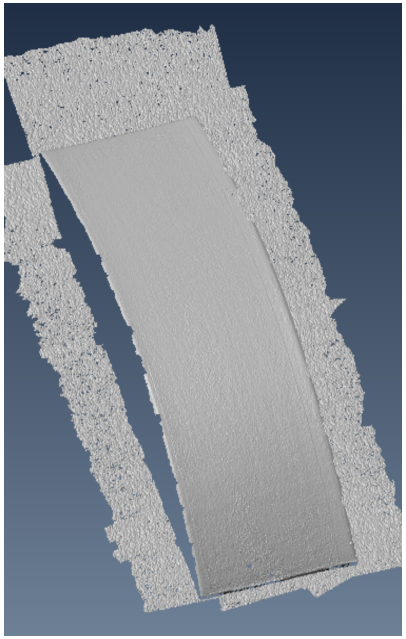
$$\frac{1}{r} = 6 * (CTE_p - CTE_s) \times dT \times (1+m)^2 \times \left\{ (t_p + t_s) \times \left[3 \times (1+m)^2 + (1+mn) \times (m^2 + \frac{1}{mn} \right] \right\}$$

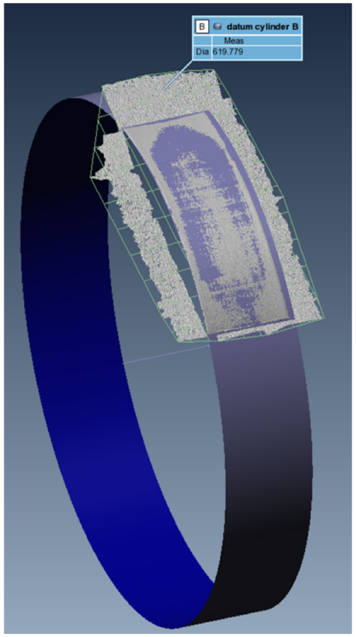
$m = \dfrac{t_p}{t_s}$ Ratio of patch-to-substrate thickness

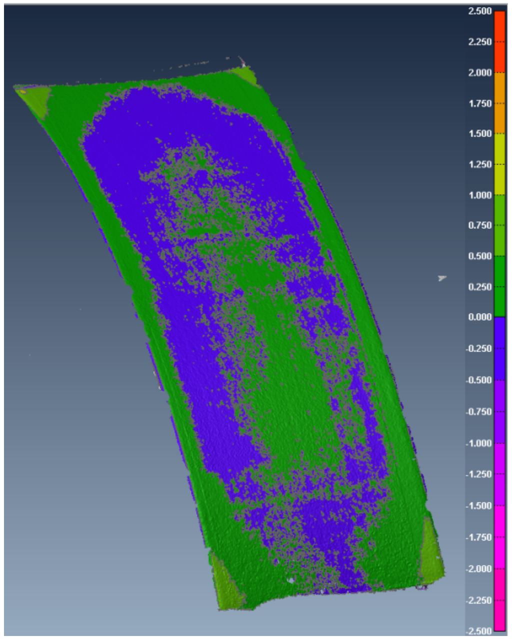
$n = \dfrac{E_p}{E_s}$ Ratio of patch-to-substrate modulus

Measurement of a Curved Panel

- The radius of a curved part can be measured by fitting a cylinder to laser scan data, the radius of this part being 309.916mm
- The surface profile deviation from the nominal cylinder can also be measured and ranges from -0.103mm to 1.042mm





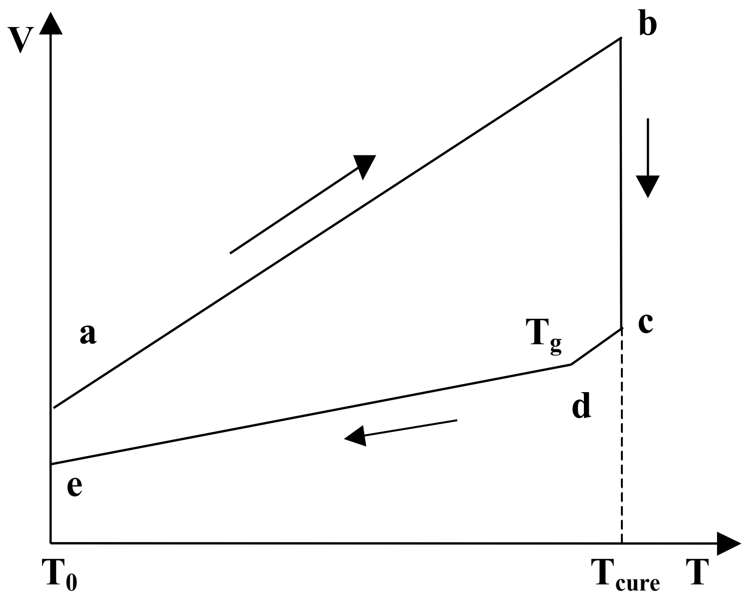


Chemical Shrinkage

The volumetric change due to crosslinking reaction

- Thermosetting resins increase in density during cure
  - This densification is called cure shrinkage
- Chemical shrinkage is NOT thermal contraction
- Chemical shrinkage could contribute to residual stresses and thus resin cracking, delamination….
- Stress due to shrinkage depends on when gelation occurs
  - Stress from shrinkage while in a viscous state quickly relaxes.
- Typical total shrinkage values range from 4 to 10% by volume

Measurement of Chemical Shrinkage



Schematic of volume change of epoxy resins during cure

<u>Stage a-b</u>: Step heat-up from reference (room) temperature, T_0, to a curing temperature, T_c

<u>Stage b-c</u>: Hold at a constant curing temperature until full cure

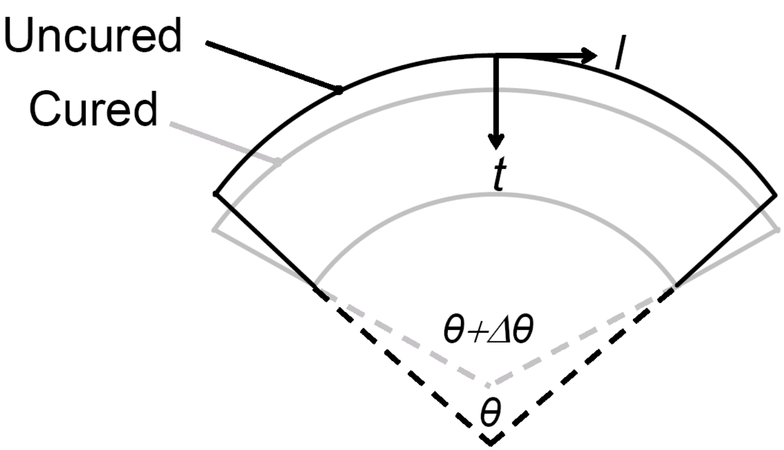
<u>Stage c-e:</u> Cool down to room temperature.

<u>Point *d*</u>: glass transition

Dimensional change b-c: Real chemical shrinkage

Spring-Back/ Spring-In

- Spring-back is defined as a reduction of closed angles due to process-induced residual stress
- For anisotropic material, spring-back is inevitable



Geometry of spring-in of an enclosed angle

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

Where

θ = part initial angle

$\Delta\theta$ = spring-in

ΔT = change in temperature

ϕ_l = longitudinal CS

ϕ_t = through-thickness CS

α_l = longitudinal composite CTE

α_t = through thickness composite CTE

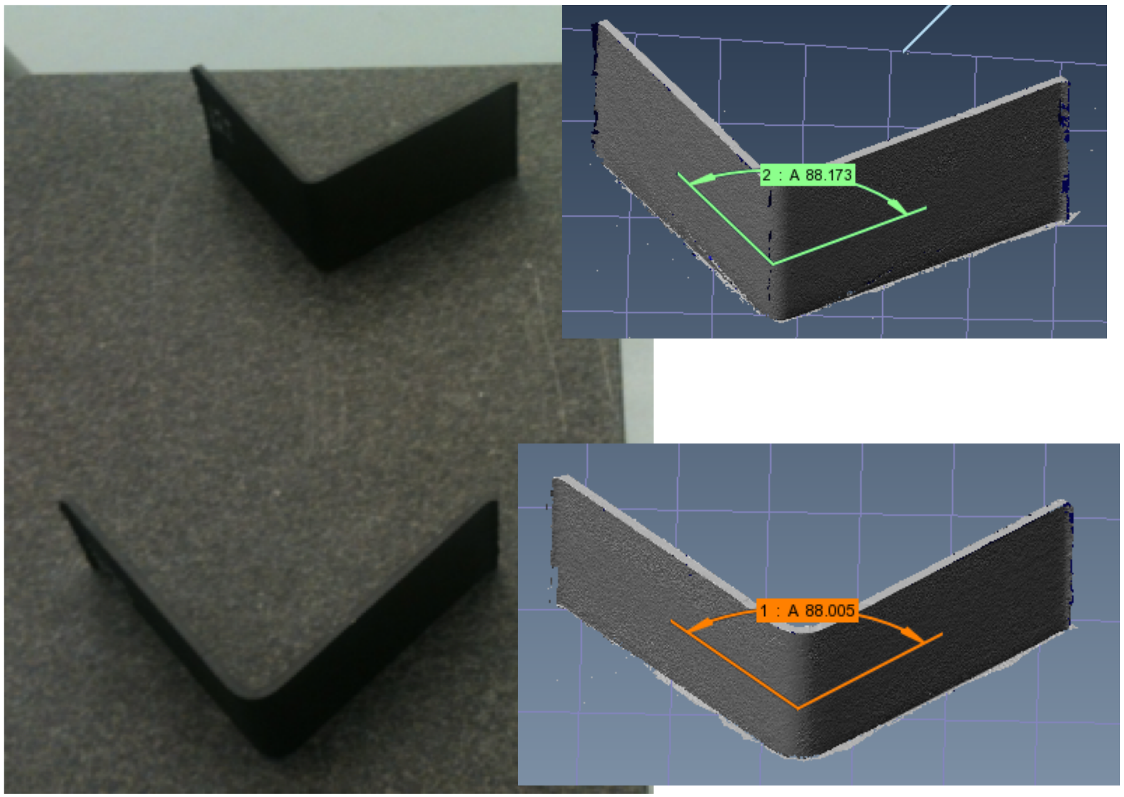
Example

Consider a 4.2 mm thick angle bracket cured on a steel tool at 180°C. What would be the expected spring-in at room temperature?

Parameter	0°/45°/-45°/90° Laminate
α_l	2.3×10^{-6} (m/m/°C)
α_t	5.4×10^{-5} (m/m/°C)
ϕ_l	2.5×10^{-4} (m/m)
ϕ_t	5.1×10^{-3} (m/m)
Cure temperature	180°C
Room temperature	20°C

Measurement of an Angle Bracket

Consider a 4.2 mm thick angle bracket cured on steel tools with radius 5mm and 10mm at 180°C.



- The spring-back of a part can be measured by creating 2 intersecting lines and measuring the angle between the lines.
- In this case the nominal 90° angle was measured to 88.173° and 88.005°
- This information can be used to adjust the spring back allowance in the mould tool

Summary

- Differences between CTE of fibre and matrix, and between the plies is an important source for residual stresses in composites
- Residual stress can cause matrix cracking, delamination, warpage, and even failure of a composite component
- During curing, thermosetting resins increase in density during cure, resulting in a volumetric change
  - This is called cure shrinkage
- Stress due to shrinkage depends on when gelation occurs
  - Stress from shrinkage while in a viscous state quickly relaxes

Properties of Materials

Theme: Polymers and Composites

Lecture 5: Solidification of Thermoplastic Polymers

Prof. Ian Hamerton
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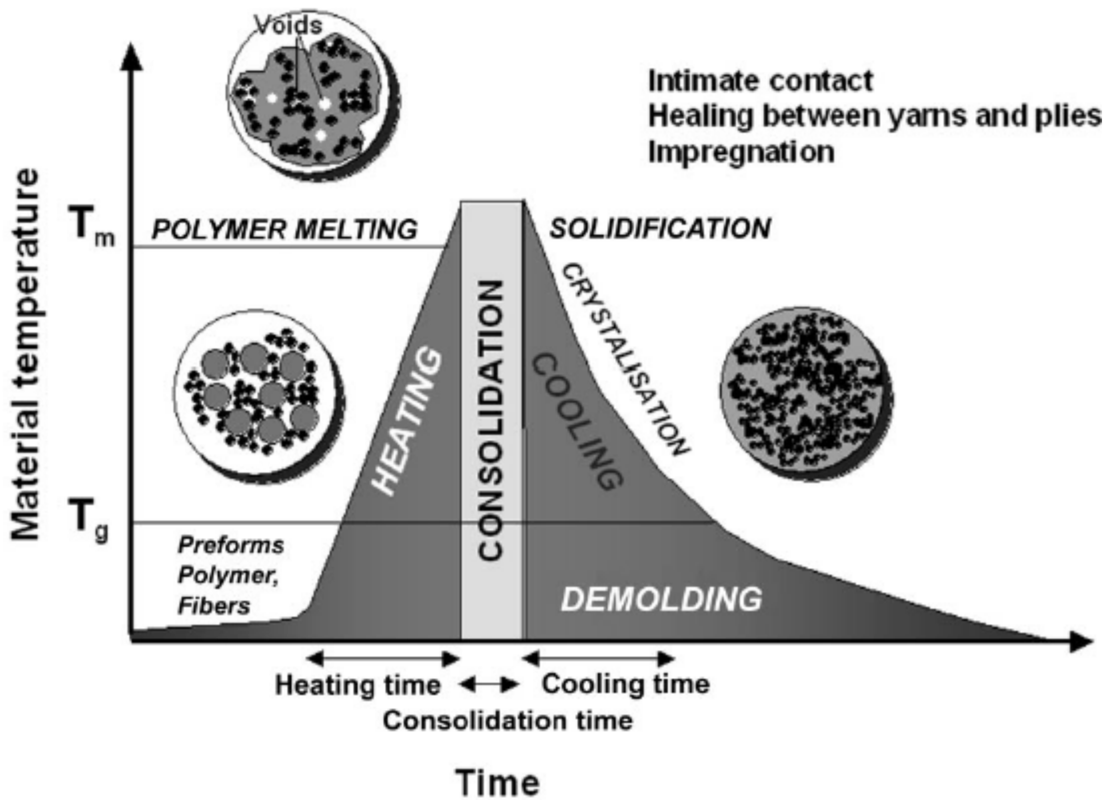
Room 0.106 Queen's Building

Review

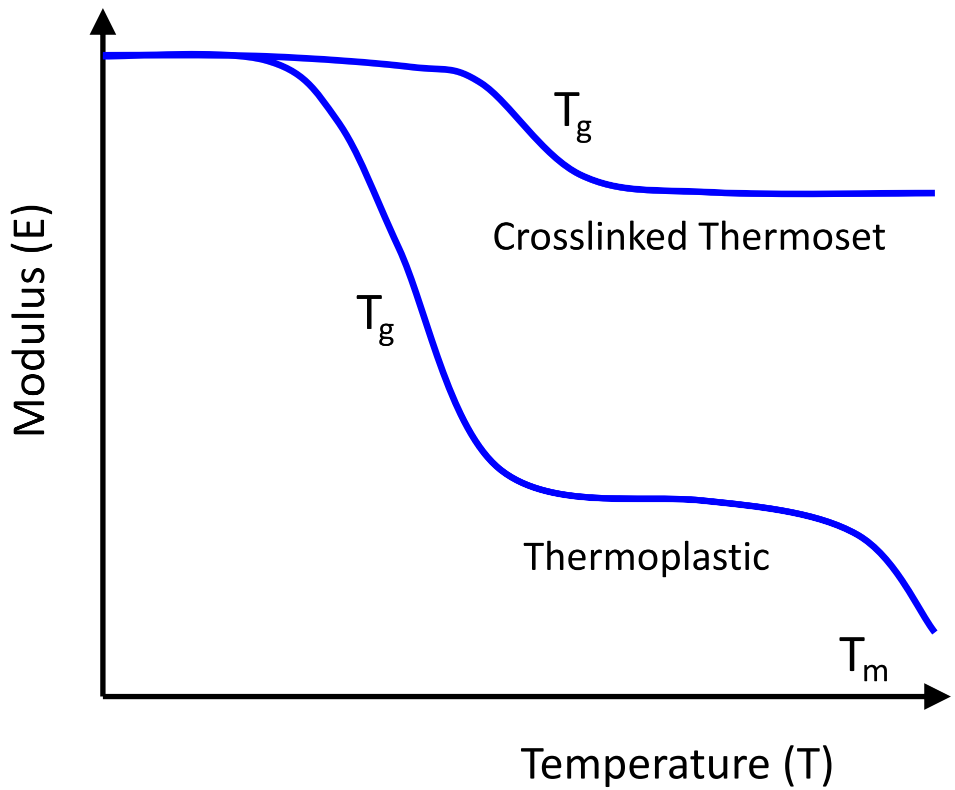
- Composite materials: material and shape are manufactured at the same time
- Thermosets react to form an irreversible cross-linked network.
  - Curing: releases heat during cross-linking
  - Gelation: liquid to rubbery
  - Vitrification: rubbery to glassy
  - Cure shrinkage: change in volume after gel
  - CTE: residual stresses that form during cooling

Today’s Lecture

- Thermoplastic materials that can be melted, shaped, and cooled to form a solid.



Temperature Transitions in Polymers



- Thermal limits for polymer composites identified by T_g and T_m
- Properties (stiffness and strength) drop rapidly as T_g is approached
- Thermoplastics eventually melt, thermosets eventually degrade

Melting and Crystallisation

<u>Melting</u>: Transition from a solid to liquid state of crystalline polymer

- Melting is a characteristic of crystalline
- The chains that melt are not the chains that undergo the glass transition
- Thermosets do not melt

When a crystalline polymer melts:

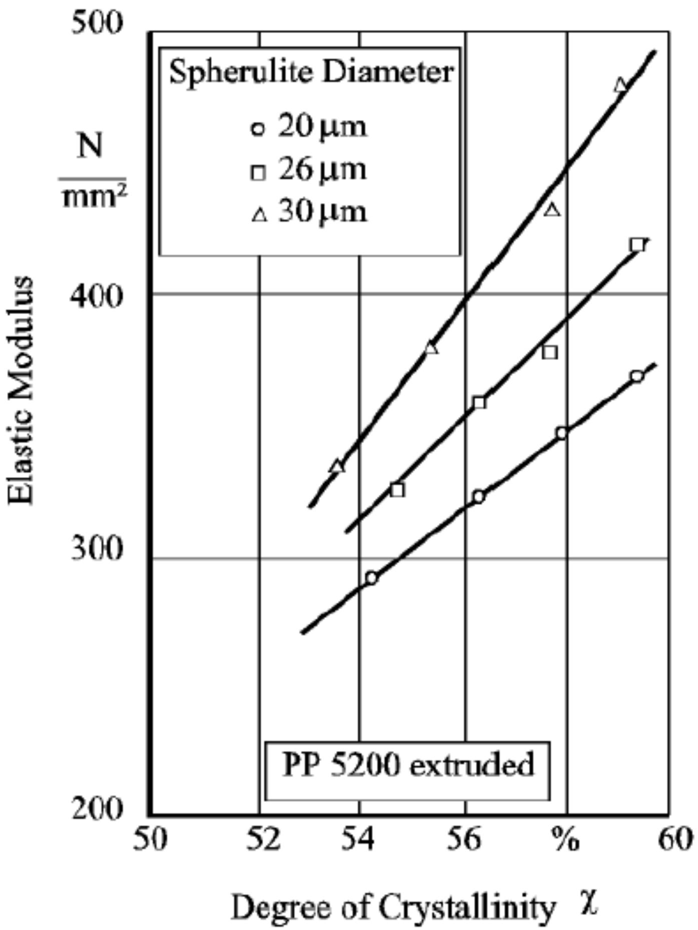
- It absorbs heat
- Undergoes a change in heat capacity

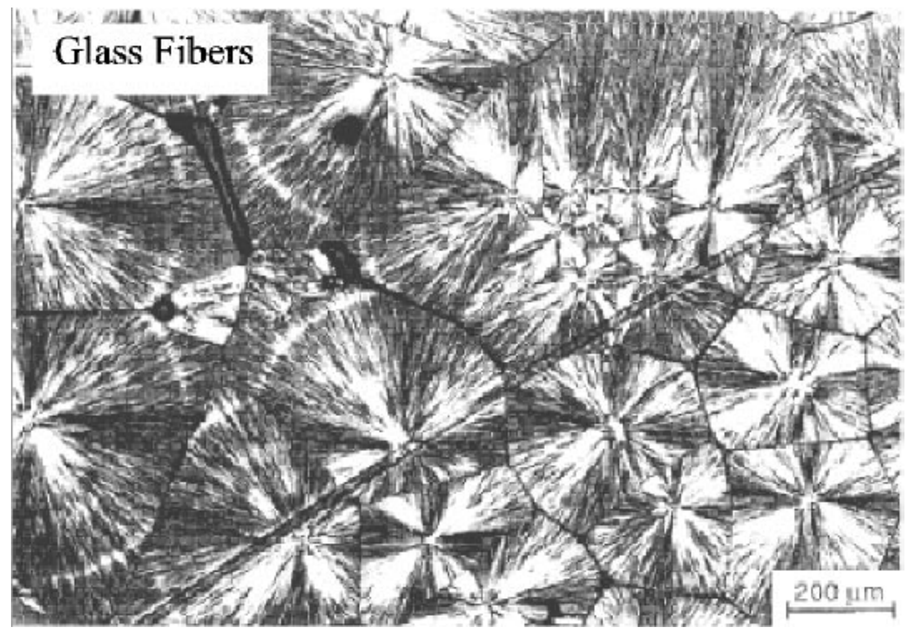
<u>Crystallization:</u> The atoms in a molecular structure in are arranged in an orderly, three dimensional pattern.

- Heat is released (like curing in a Thermoset)
- Undergoes a change in heat capacity

Effect of Crystallisation

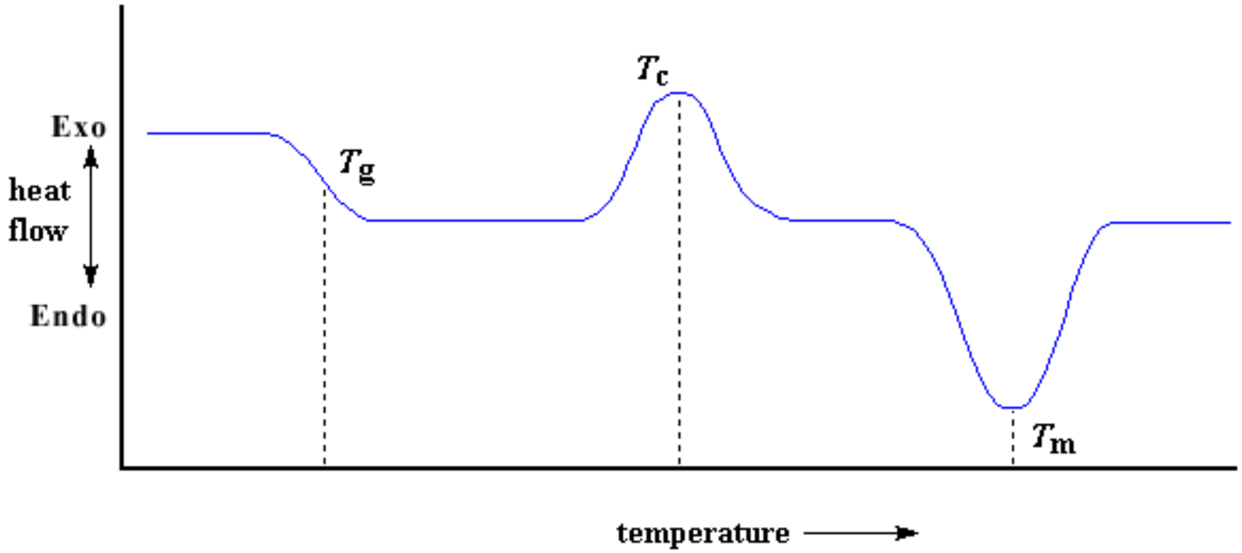
- Increasing Crystallisation increases Modulus





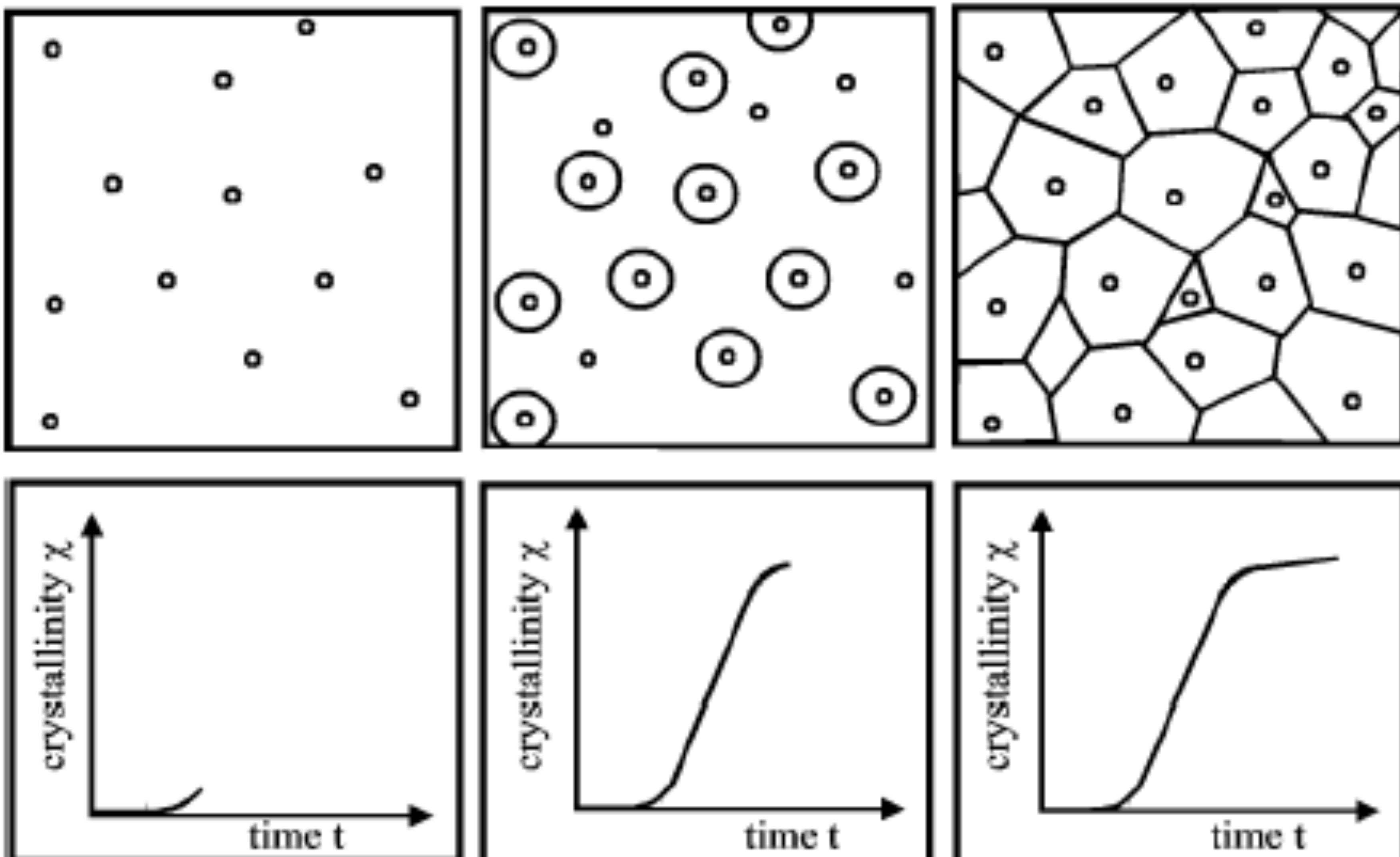
Spherulite structures in a glass fibre composite (glass fibre not shown)

Crystallisation Measurements by DSC



- At the glass transition, $\mathbf{T_g}$, the polymers absorb energy and have more mobility
- At the crystallization temperature, $\mathbf{T_c}$, they will have gained enough energy to move into very ordered arrangements, called crystals. They release heat.
- At the melting temperature, $\mathbf{T_m}$, the polymer crystals begin to fall apart. The chains absorb heat, come out of their ordered arrangements, and begin to move around freely.

Crystallisation Process

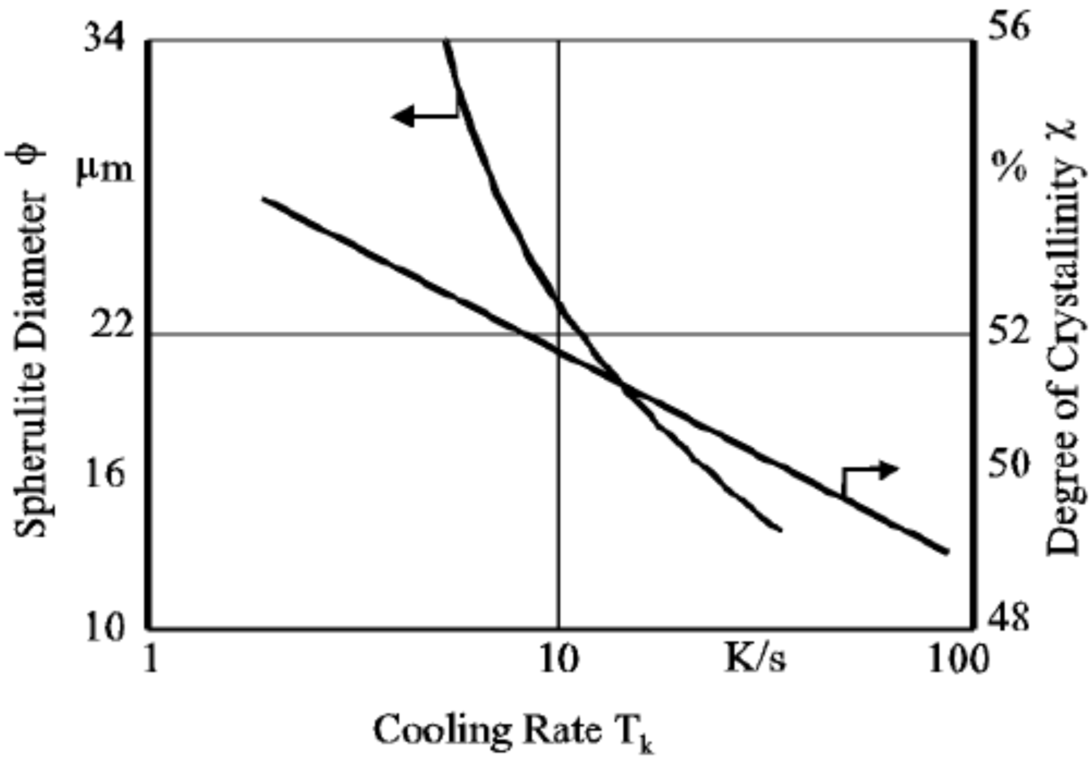


Nucleation Crystal growth Secondary crystallization

Effect of Cooling Rate

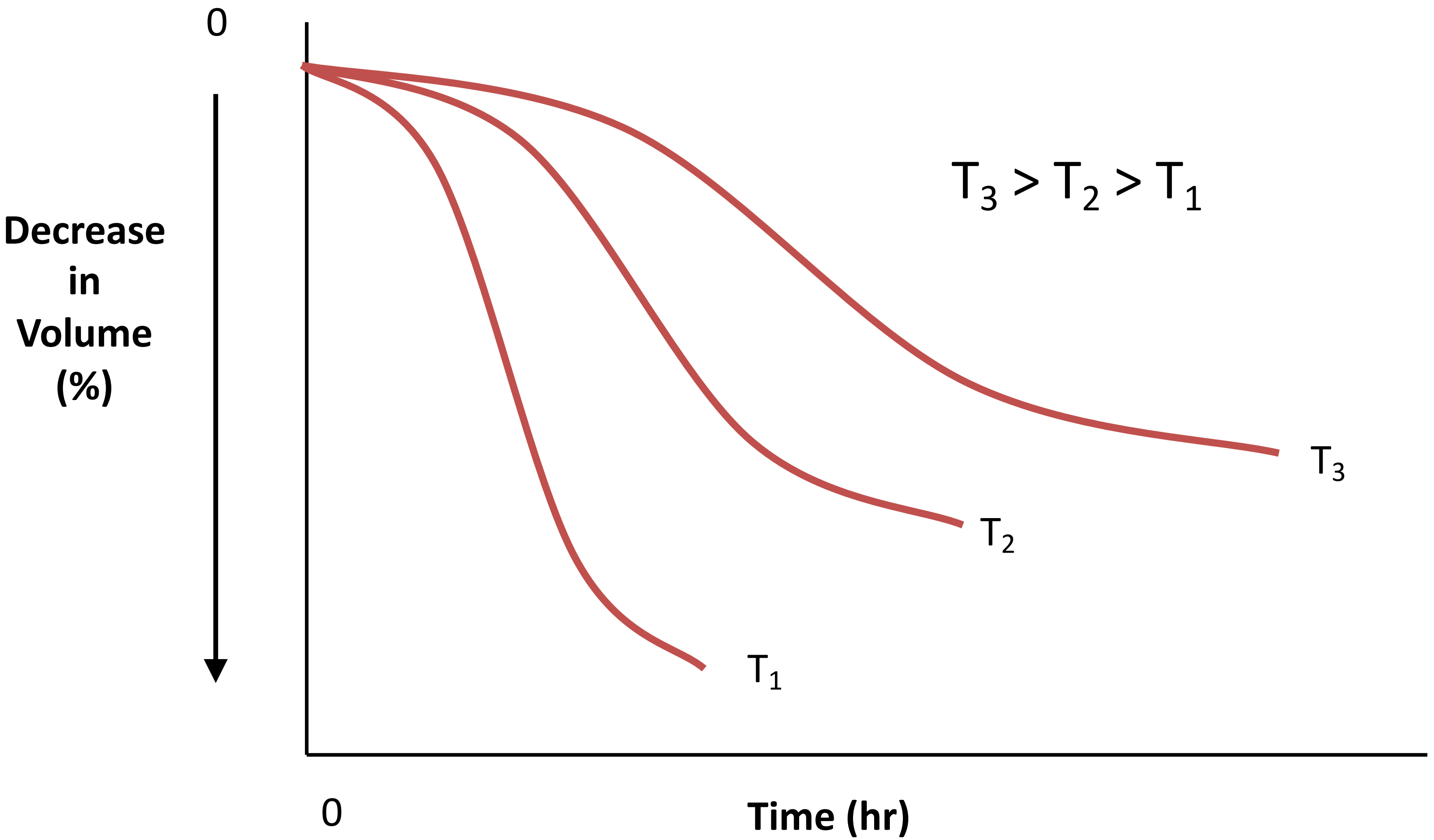
As the cooling rate increases, the degree-of-crystallinity decreases and the average diameter of the spherulite also decreases

- Higher crystallinity and larger spherules gives better properties



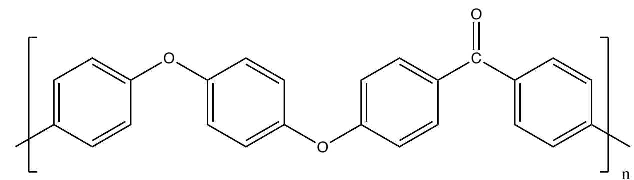
Crystallisation Shrinkage

Below $\mathbf{T_m}$, the crystallization rate increases due to increasing concentration of stable nuclei



Crystallisation of Aerospace Polymer

PEEK: Polyether Ether Ketone



- 30-70% of polymer remain amorphous
- Density of amorphous phase 1.26 g/cm^3, crystalline 1.38 g/cm^3

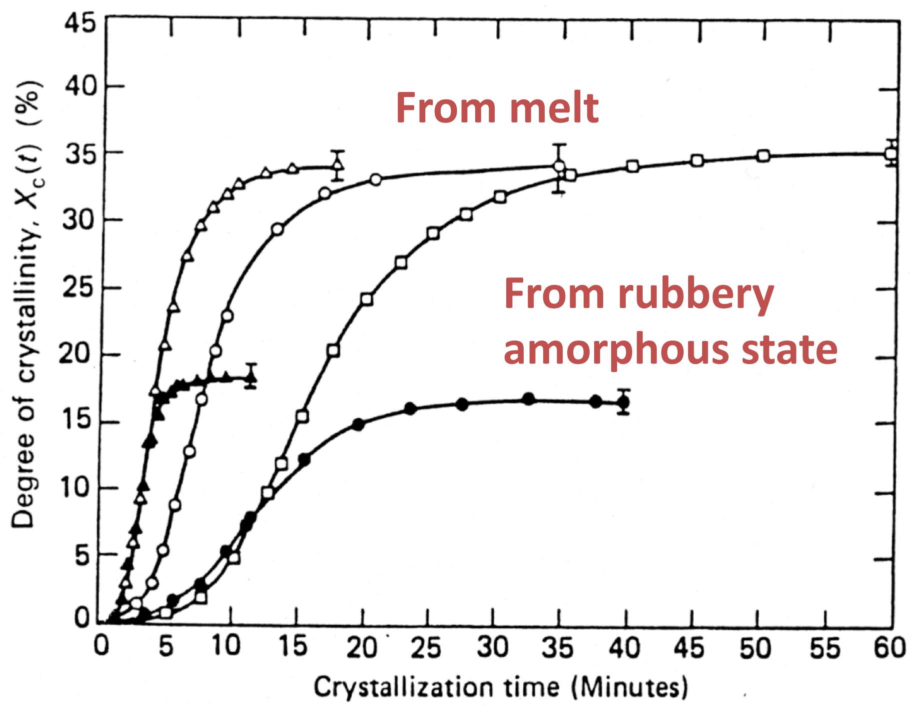


Figure 4 Development of absolute crystallinity with time for isothermal crystallization at 315 C (□), 312 C (○), 308 C (△), 164°C (▲) and 160 C (●)

Welding Thermoplastic Composites

- Fusion Bonding (Welding)
  - Melting the polymer at the weld interface
  - Diffusion of polymer chains across the weld interface
  - Development of the ability to transfer load
- Advantages
  - Little or no undesirable stress concentration
  - Little or no weight penalty
  - Smooth external surfaces at the joint
  - Short processing time
  - Minor surface preparation
- Disadvantages
  - Induced residual stress
  - Imposes difficulties such as uneven heating, delamination and distortion of the fibres

A380 Leading edge

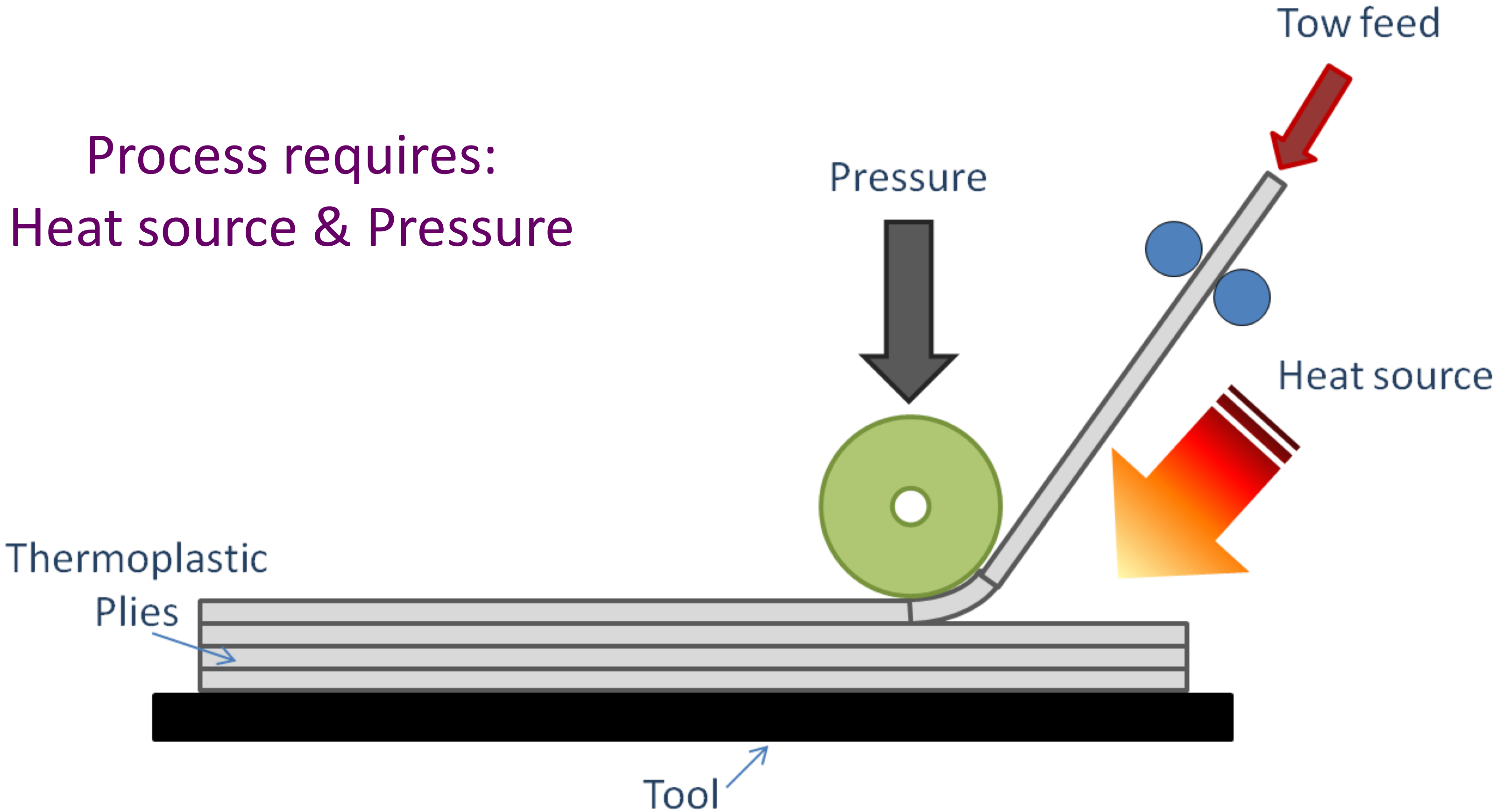
Composite ribs

Internal structure

Deposition of Thermoplastic Tape

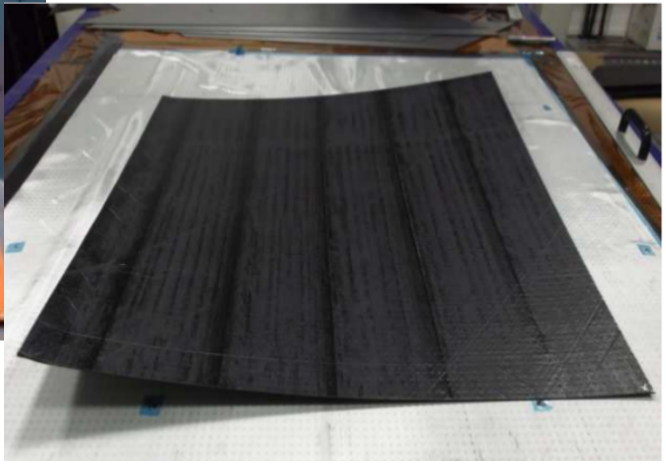
Automated Fibre Placement (AFP)

Process requires:
Heat source & Pressure



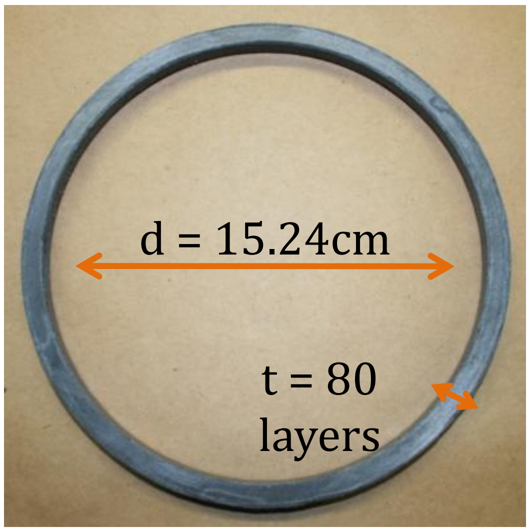
Thermoplastic Composite AFP

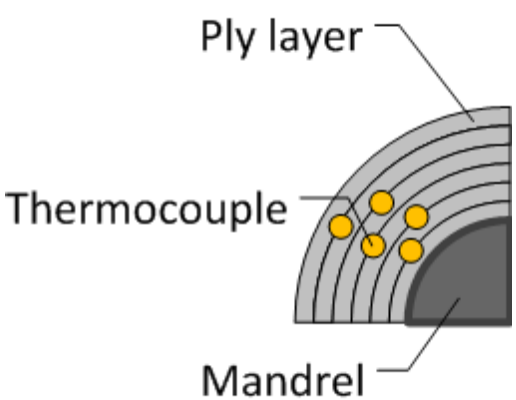
How does the processing affect the crystallinity of the thermoplastic material once the material is solidified?

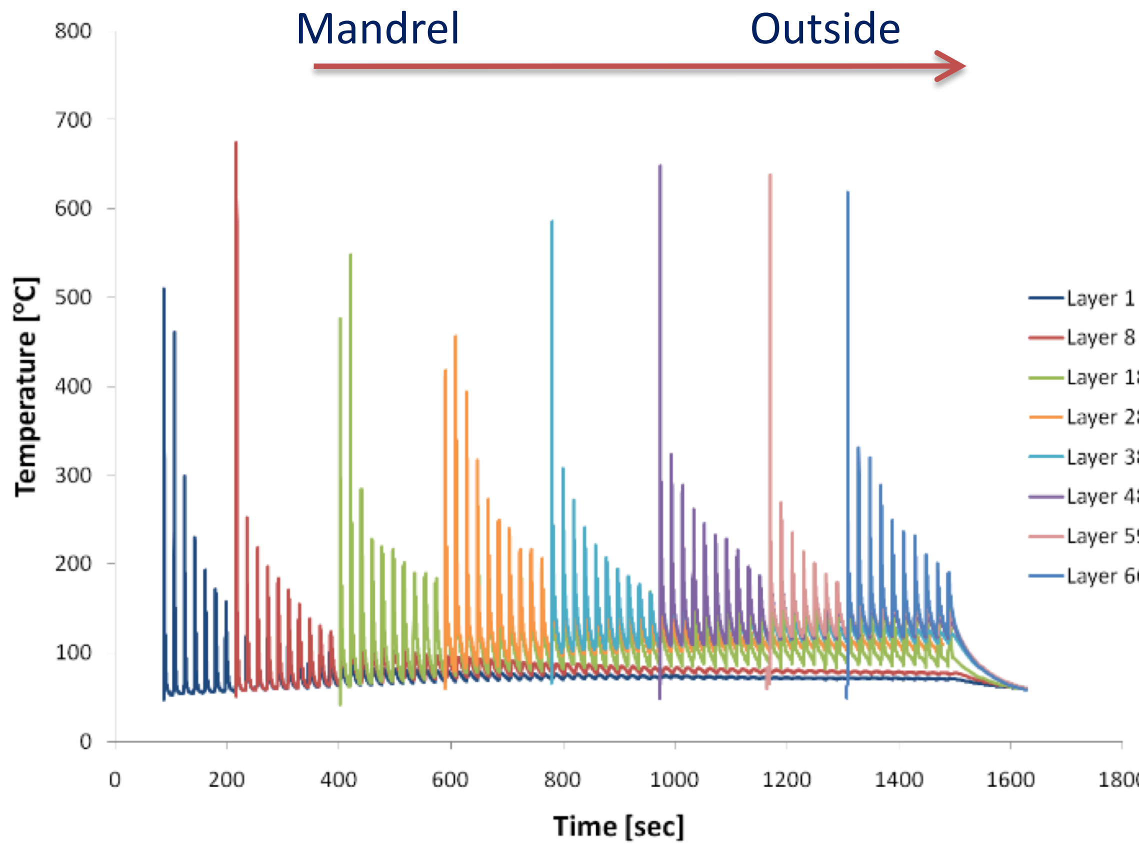


Temperature of PEEK during Processing

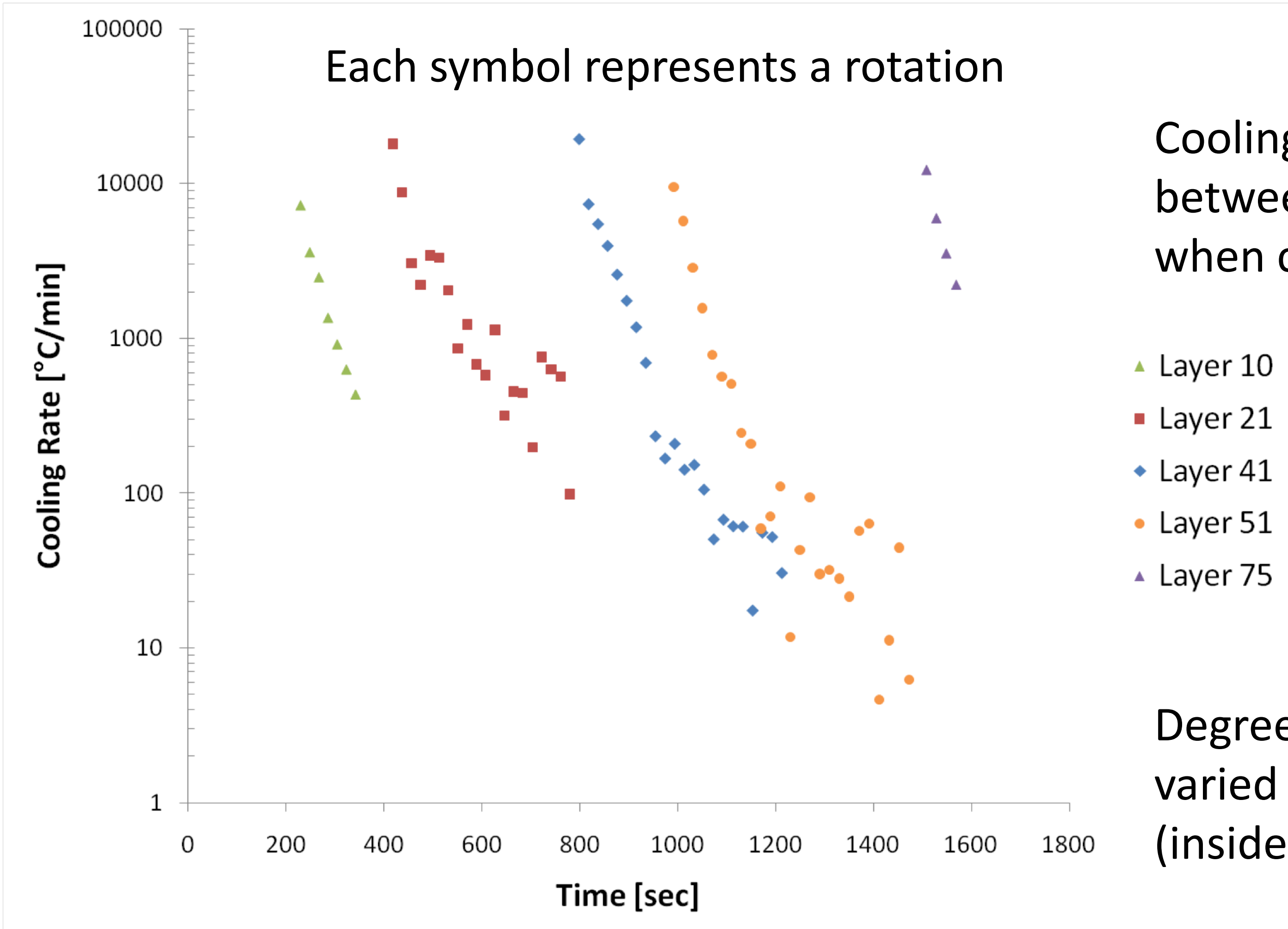
Does the repeated heating influence crystallinity?







Cooling Rates in the PEEK Ring



Cooling rates shown between T_m and T_g, when crystal can form

Degree-of-crystallinity varied from 29-27-29% (inside-middle-outside)

➢ Fairly even crystallinity development in PEEK-carbon composites

Summary

- Crystals form in thermoplastic polymers when the temperature is between glass transition $\mathbf{T_g}$ and melting $\mathbf{T_m}$
  - More, larger crystals = better properties
- An amorphous phase will remain between 30-70%
- In composite processes, crystals form during solidification, when cooling from process temperature to ambient
  - Above T_g, the material can deform if loaded (even under its own weight)
- PEEK is the most common aerospace polymer and shows very consistent degree-of-crystallinity
  - Robust for automated processing, such as AFP