University of BRISTOL
Bristol Composites Institute

Cure path sensitivity of snap-cure pre-pregs for layer-by-layer manufacturing

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Introduction

- Definitions:
- Purpose:

To characterise the reaction kinetics of our chosen snap cure material, and use this to develop a layer by layer manufacturing technique that is:

- Practical
- Industrially applicable

Cure path sensitive materials:

"Materials with mechanical/thermal properties that are sensitive to the cure path"

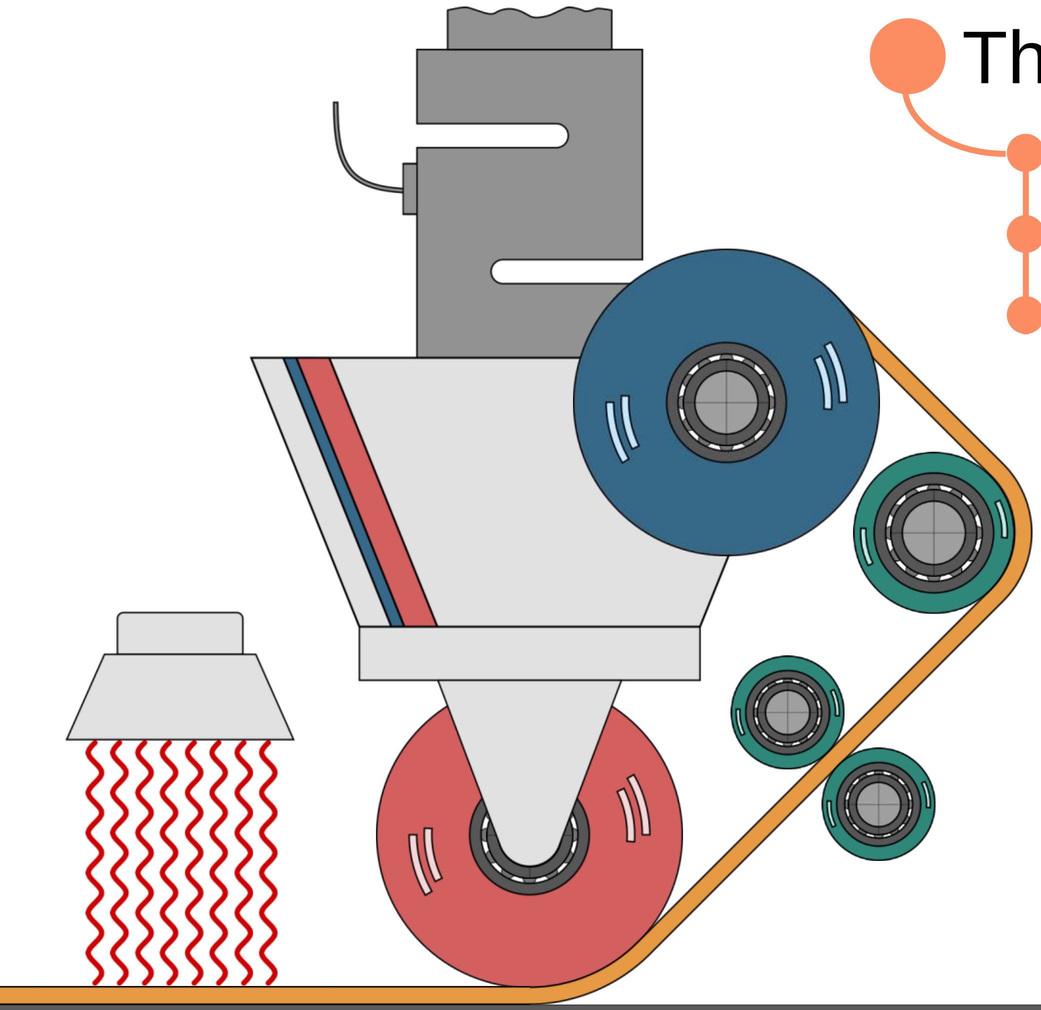
Snap cure material:

"A thermoset that cures an order of magnitude faster (second/minutes) than tradition thermosets (hours)"

Layer by layer manufacturing:

"A CFRP manufacturing method where deposition, consolidation and cure occur simultaneously in a layer by layer manner"

Motivation



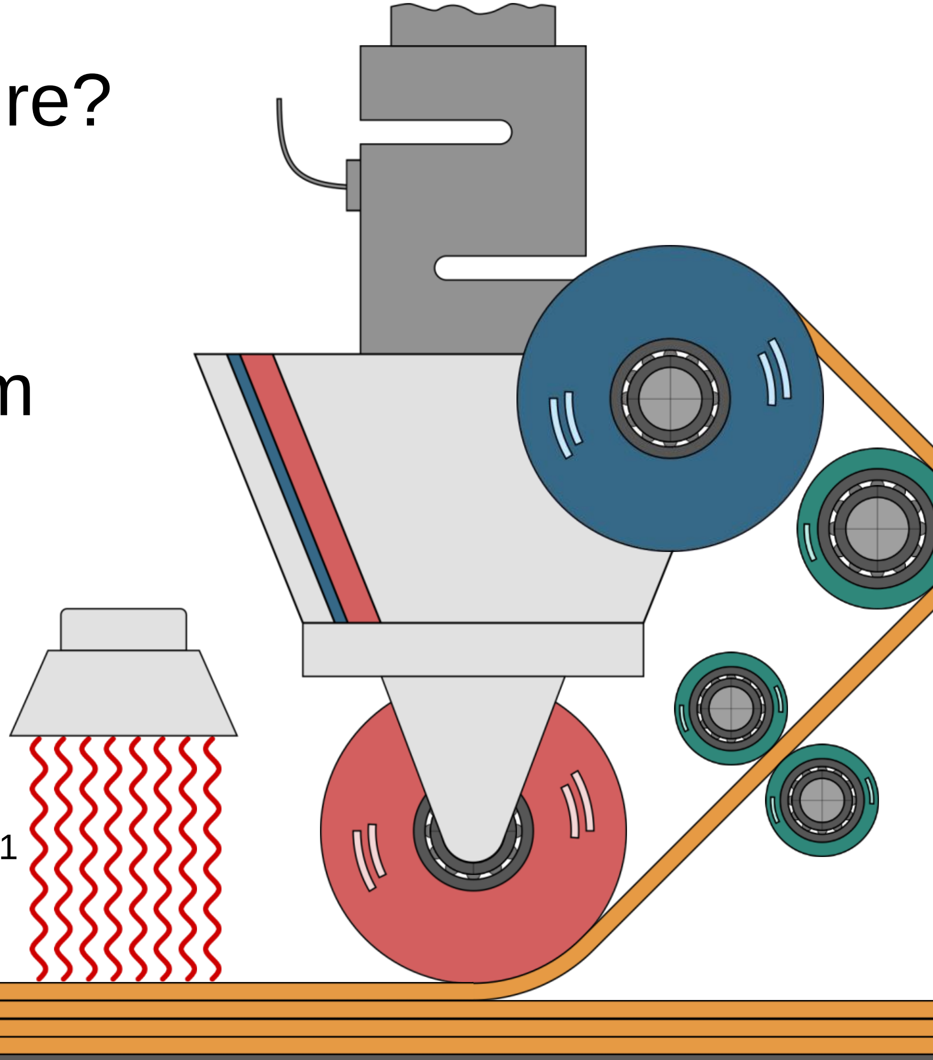
- Three steps of composite processing:
  - Fibre deposition
  - Layer consolidation
  - Matrix curing

Currently discrete. Why?

1. **History** – small parts and low production rates
2. **Technical challenge** – part quality

Motivation

- Why combine deposition, consolidation & cure?
  - Need larger parts at faster rates
  - Large parts = large autoclaves = $$$
- How does layer-by-layer (LbL) combine them
  - AFP style real time deposition/compaction head[1]
  - In-line heating unit to cure composite as it is deposited
- Benefits of layer-by-layer
  - Thick part ≠ exotherm
  - Improved dimensional tolerances with thickness sensing[1]
  - No autoclave



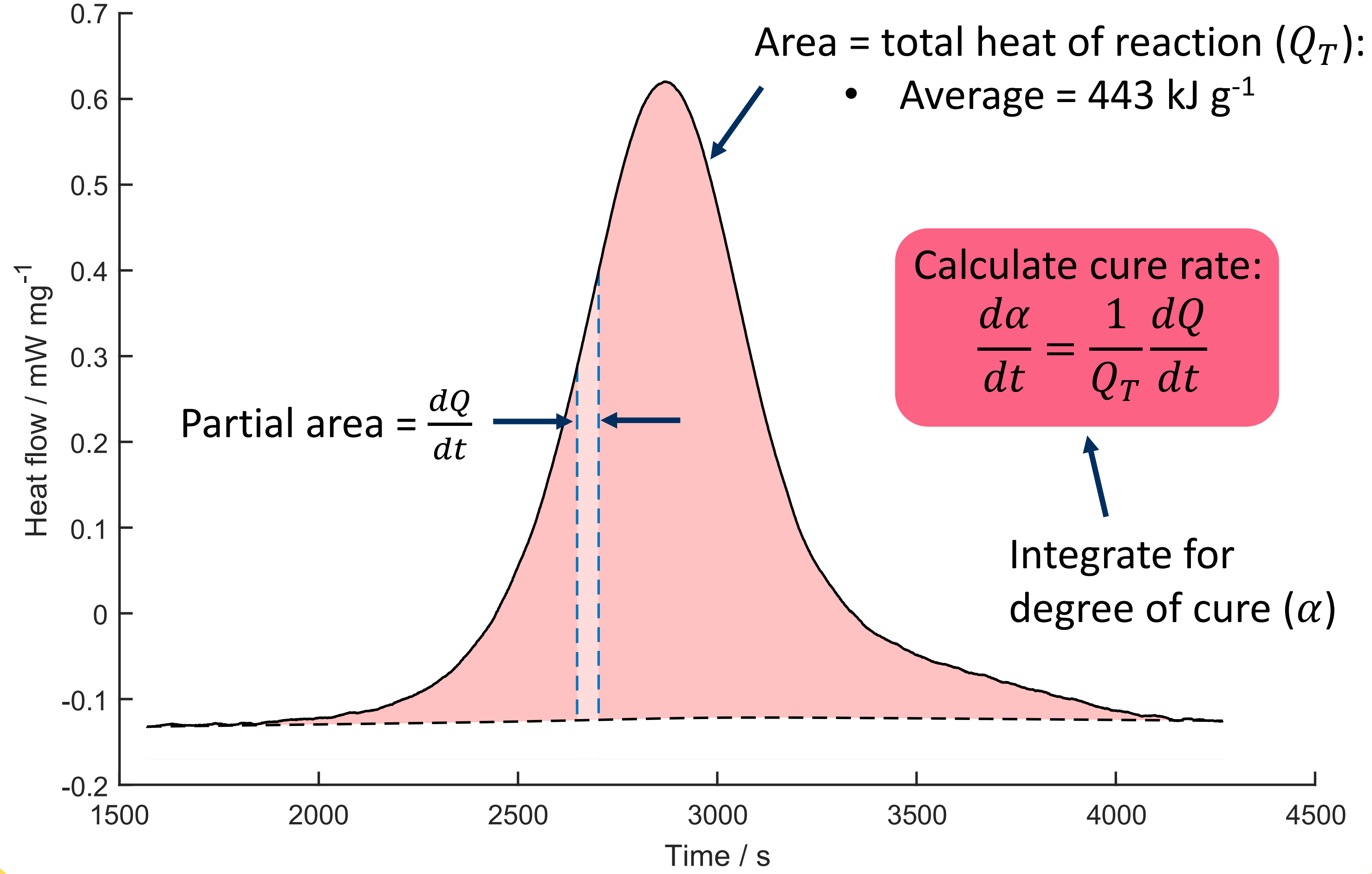
[1] D. Nguyen et. al., *Composites: Part A*, 168 (2023) 107465

Research Questions

- Material selection: Hexcel M78.1 42% UD300
  - Resin content
  - Carbon Fibre: Unidirectional, 300 gsm
  - Resin: Snap-cure epoxy @110 - 160 °C
- Snap-cure behaviour:
  - How does the material cure?
  - Is modelling the kinetics possible?
  - At what degree of cure does it gel?
- Cure path dependency:
  - Are any properties (e.g. T_g) affected by cure path?
  - How does this relate to microstructure?
- Layer-by-layer
  - How can the material behaviour be used to optimise the layer-by-layer process?

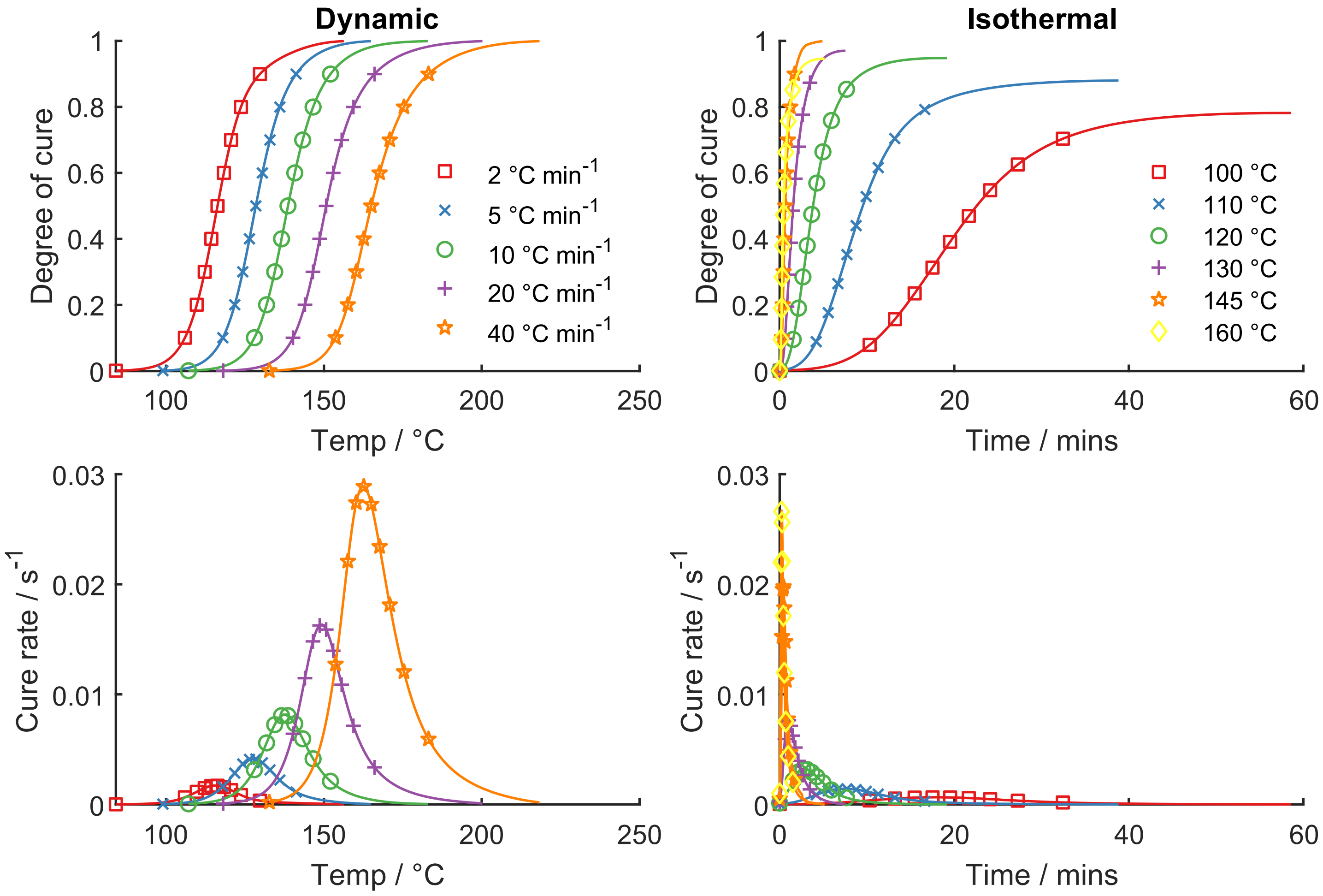
Cure Kinetics Modelling

- Dynamic DSC:
  - 2, 5, 10, 20 & 40 °C min^{-1}
  - Rapid heating in LbL
- Isothermal DSC:
  - 100-160 °C
  - Typical M78.1 cure temps
- Integrate heat flow



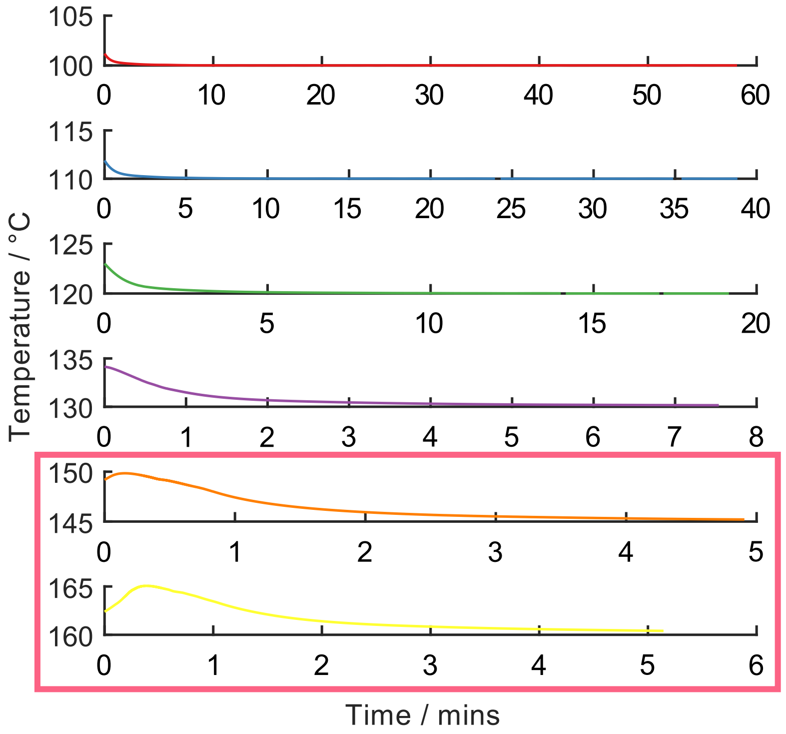
Cure Kinetics Modelling

- M78.1 degree of cure and cure rate:
  - 100 °C - 50 mins
  - 110 °C - 30 mins
  - 120 °C - 15 mins
  - 130 °C - 6 mins
  - 145 °C - 3 mins
  - 160 °C < 3 mins



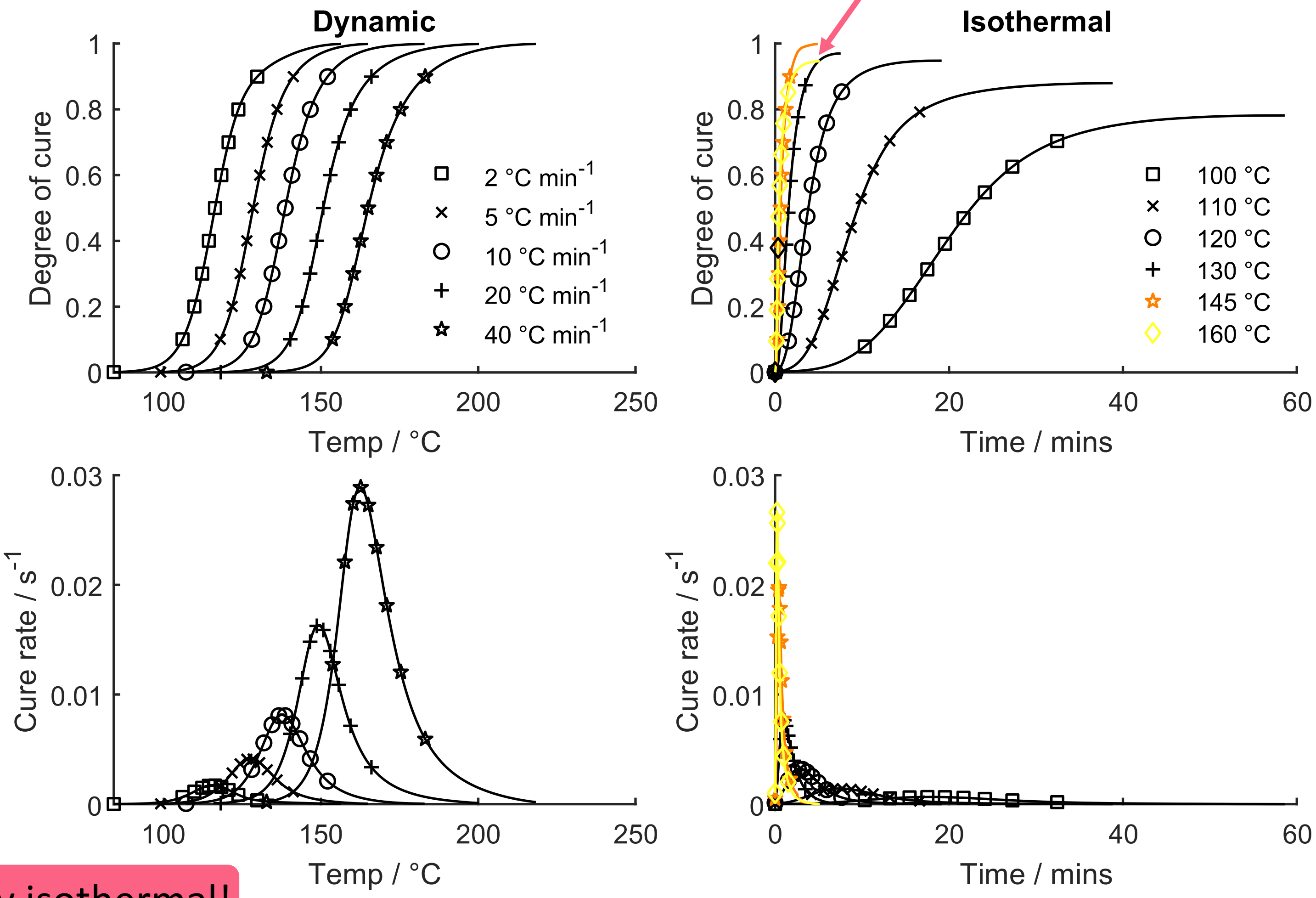
Cure Kinetics Modelling

- 145 °C and 160 °C Iso excluded



Not very isothermal!

Why is final degree of cure at 160 °C lower?

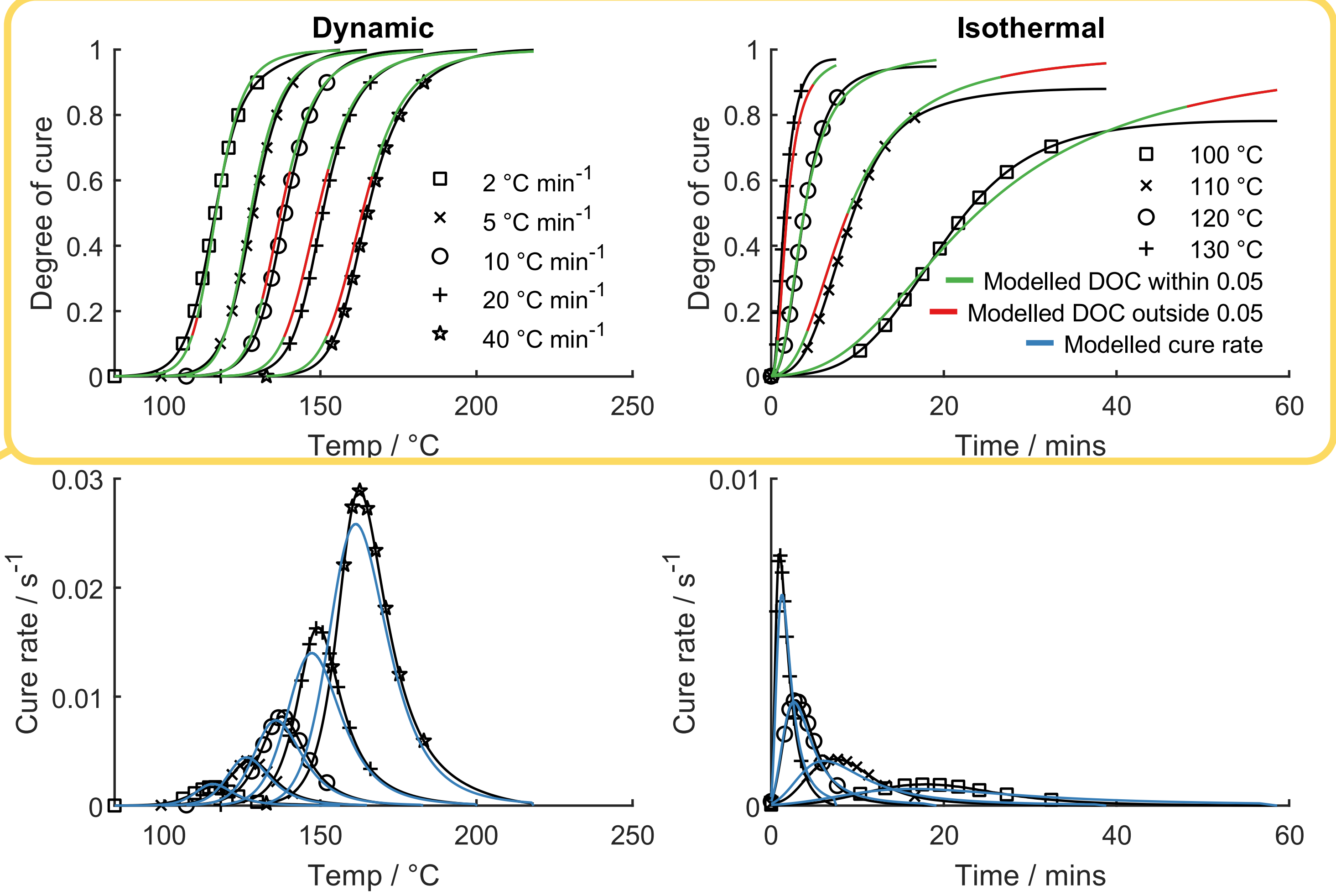


Cure Kinetics Modelling

- Kamal Sourour model:[1]

$$\frac{d\alpha}{dt} = \frac{Ae^{-E_a/RT}\alpha^m(1-\alpha)^n}{1+e^{\left(D(\alpha-(\alpha_{C0}+\alpha_{CT}T))\right)}}$$

Diffusion control term[2]

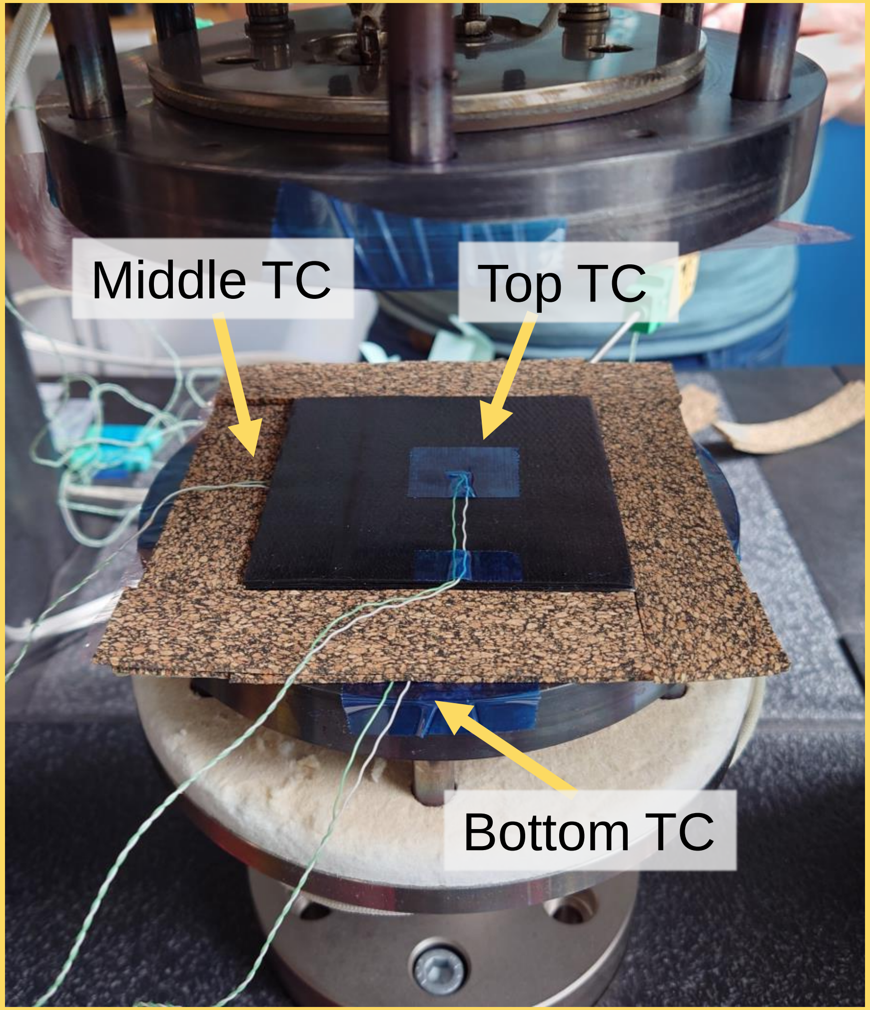


Model fit to both the dynamic and isothermal degree of cure data

[1] Kamal M. R. and Sourour S. *Polym. Eng. Sci*. 1973; 13(1): 59–64.
[2] Cole K. C., Hechler J. J. and Noel D. *Macromolecules* 1991; 24(11): 3098–3110

Cure Kinetics Validation

- Heat transfer/curing experiment
  - 20 plies thick
  - Displacement control (20 × cpt)
  - 5 °C min^{-1} to 110 °C, 40 min hold



- 1D transient heat transfer

$$\rho c_p \frac{\delta T}{dt} = \frac{\delta}{\delta x}\left(k \frac{\delta T}{\delta x}\right) + q_v$$

Solve using finite difference method to get: $T(x, t)$

If cure kinetics are correct then internal heat generation should be accurate

Cure Kinetics Validation

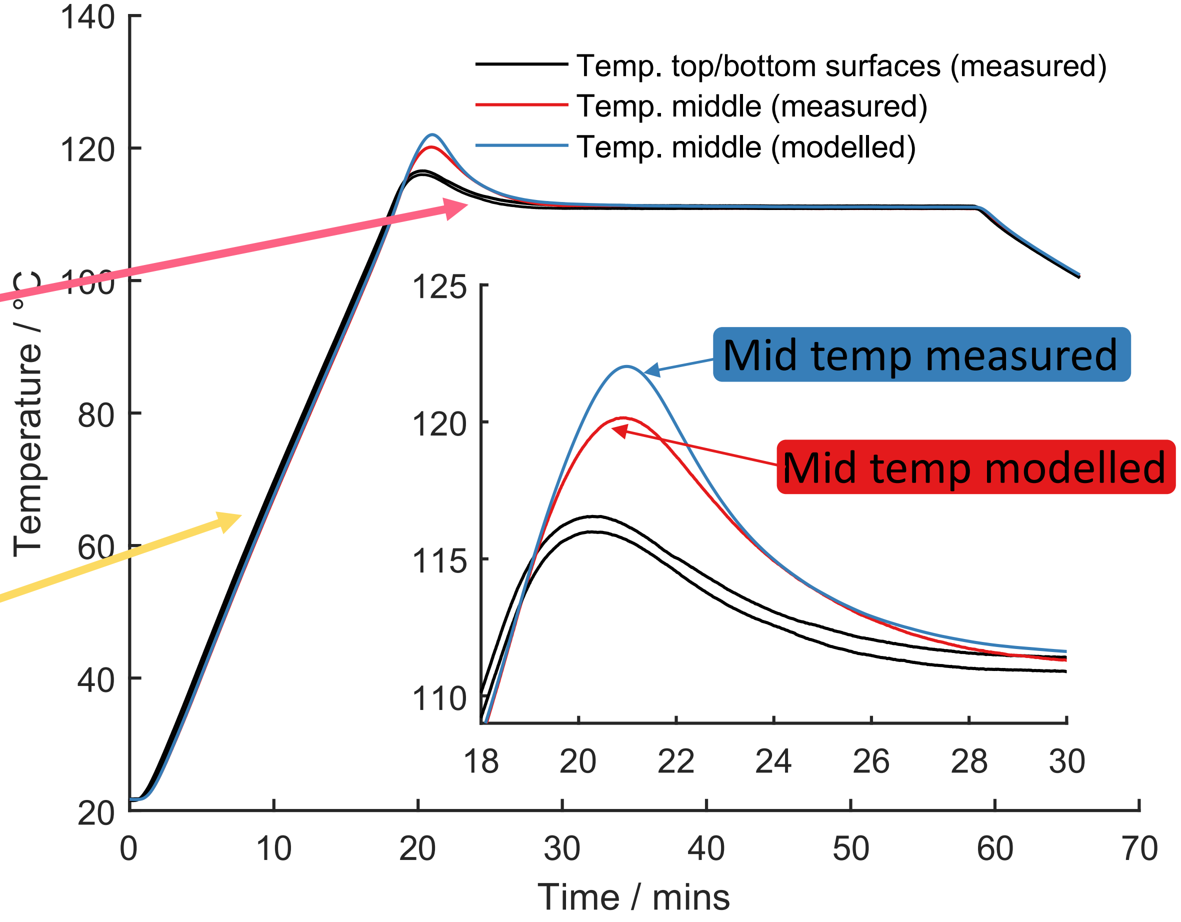
Modelled vs measured T

- Good agreement in both:

Isothermal phase
- Exotherm well represented ∴
  - Total heat of reaction accurate
  - Cure rate accurate

Dynamic phase
- No lag ∴
  - Thermal diffusivity accurate:

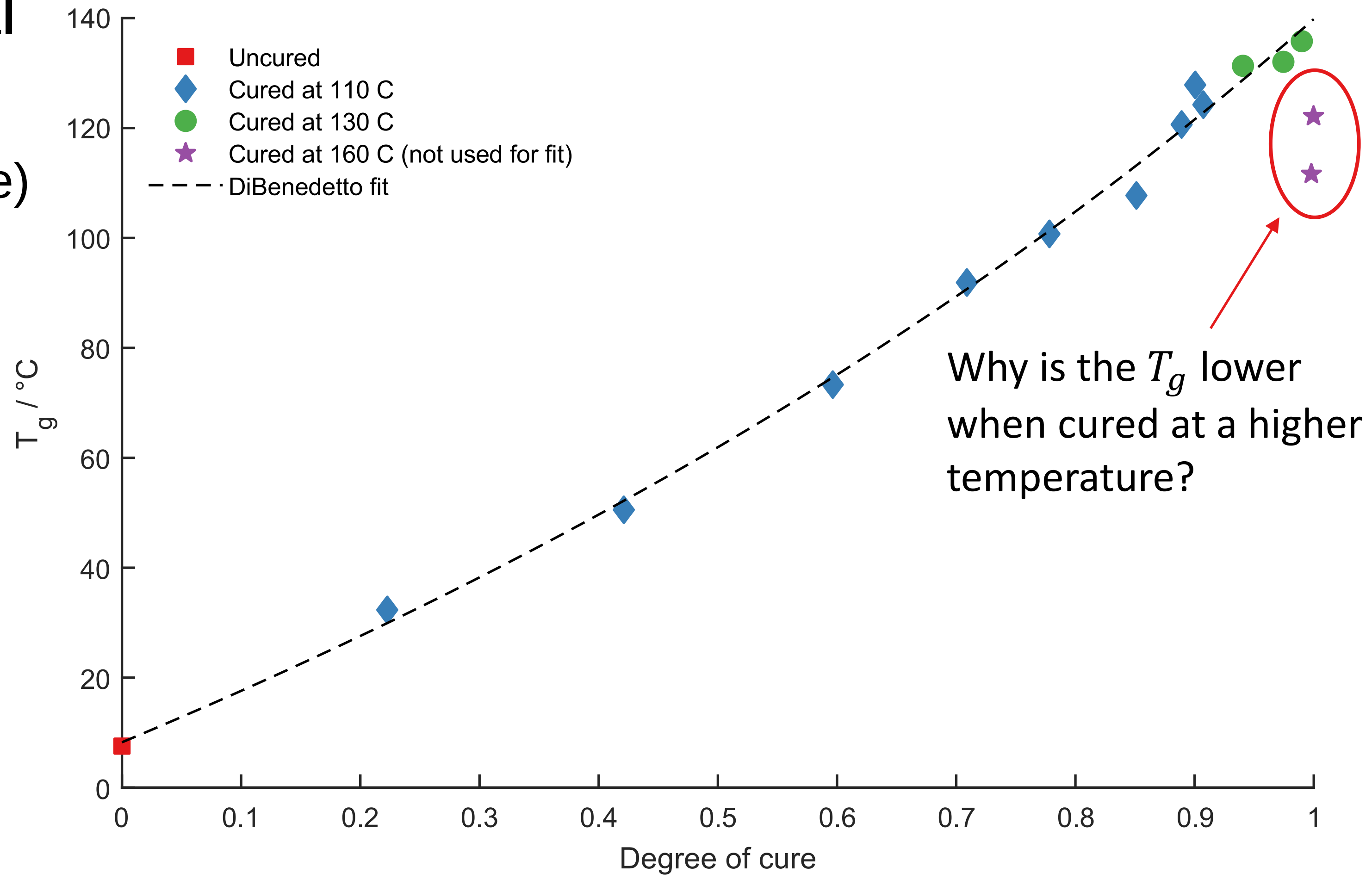
$$\kappa = \frac{k}{pc_p}$$



T_g and Reaction Onset

- Quenched DSC isothermal experiments
  - Cure isothermally (vary hold time)
  - Quench reaction (drop temperature fast)
  - Dynamic ramp to capture resulting T_g and α
  - Fit data using DiBenedetto equation[1] (excluding 160 °C)

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



[1] DiBenedetto A. T., *J Polym. Sci. Part B Polym. Phys.* 1987; 25: 1949–1969

Cure Path Dependency

- Hypothesis:
  - "T_g discrepancy caused by cure path dependency of microstructure"
  - How can this be proved?

Microstructure is locked in at gel. How does curing to gel at different temperatures followed by a post cure at either 130 °C or 160 °C affect the ultimate T_g?

- Experiment:

Stage 1
Partially cure isothermally up to α_{Gel} (0.41) at:
- 100 °C
- 130 °C
- 160°C

→ Measure T_g →

Stage 2
Cure to completion at:
- 130 °C
- 160 °C

→ Measure T_g

Cure Path Dependency

- Results:
  - Higher cure temperature up to gel generally results in higher ultimate T_g
  - Higher stage 2 cure temperature results in lower ultimate T_g
  - Potential causes:
    - Inhomogeneous mixture of epoxy and hardener
    - If entire cure is at 160 °C the two can't inter-diffuse before microstructure is locked in by network formation
    - Results in under crosslinked regions which reduces the ultimate T_g

Stage	Cure temp. / °C	Cure time / s	T_g	Degree of cure
Stage 1	100	1243	44	0.35
	130	107	43	0.35
	160	25	41	0.33
Stage 2: 130 °C	130	600	110	0.84
	130	600	114	0.87
	130	600	130	0.96
Stage 2: 160 °C	160	600	105	0.81
	160	600	107	0.82
	160	600	115	0.87

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Conclusions:

- Cure kinetics can be used to model M78.1 snap cure resin for single step cycles
- The ultimate T_g of the material is dependent on the cure temperature
- Higher temperatures result in rapid cure times but poorer thermal properties (cure path dependency)
- M78.1 is a suitable material system for the proposed layer-by-layer (LbL) manufacturing method
- Care must be taken when developing an M78.1/LbL process to avoid the property cure path dependency problems

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Thank you to the:

Future Composites Manufacturing Research Hub: EP/P006701/1