Crystallisation studies on neat PEKK and carbon fibre/PEKK composites

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- Crystallinity and morphology under different cooling rates
- Crystallisation kinetics during different cooling rates
- Modelling of crystallisation kinetics

All work shown in this presentation is published in:
Pérez-Martín H, Mackenzie P, Baidak A, Ó Brádaigh CM, Ray D. Crystallisation behaviour and morphological studies of PEKK and carbon fibre/PEKK composites. Composites Part A: Applied Science and Manufacturing 2022;159:106992. https://doi.org/10.1016/j.compositesa.2022.106992.

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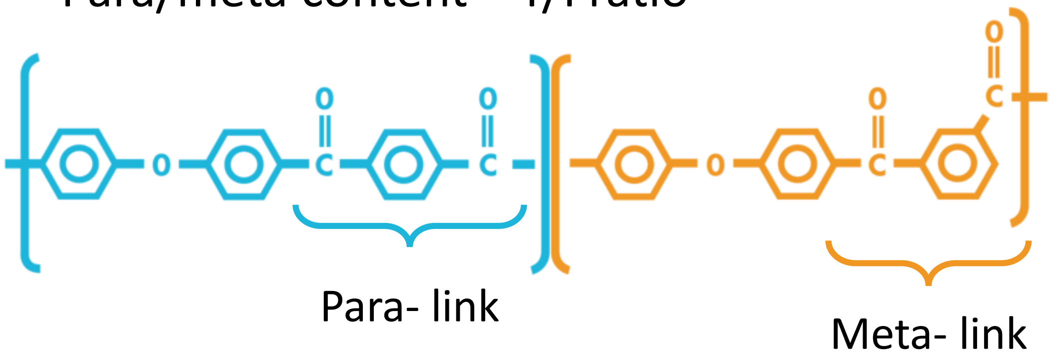
Poly(ether-ketone-ketone), PEKK

- High performance thermoplastic
- Excellent mechanical properties
- Chemically inert
- Resistance to high temperatures

- Tuneable:
  Para/meta content = T/I ratio



	PEKK grade (T/I ratio)			PEEK
	60/40	70/30	80/20	
T_m	**305**	**332**	**358**	**343**
T_g	160	162	165	143

Higher crystallinity →

← Easier processing

Arkema Webinar 2020, “KEPSTAN PEKK, the enabling PAEK”

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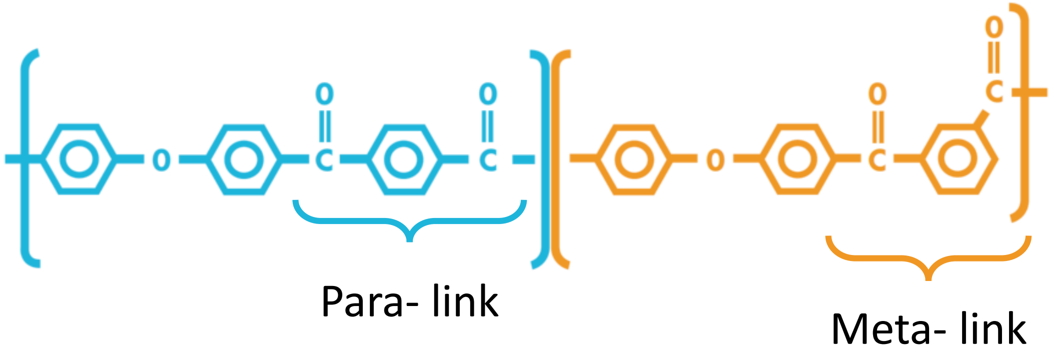
Poly(ether-ketone-ketone), PEKK



- In high-performance applications, it is essential to understand how processing will impact part performance.
- Thermal history plays a key role in thermoplastic composites.
- Crystallisation development of PEKK, and particularly CF/PEKK composites, is not well established.

Aim: to develop understanding of the behaviour of unreinforced PEKK and CF/PEKK composites as a consequence of the thermal cycles it undergoes.

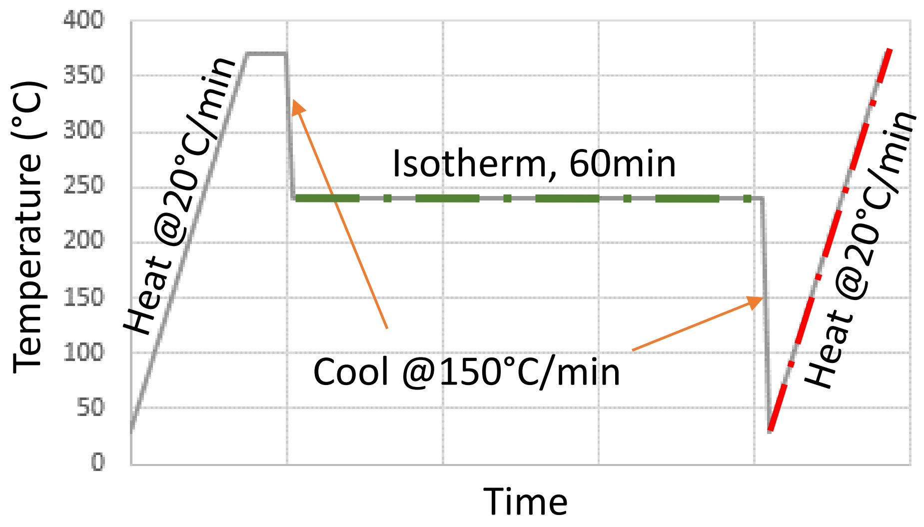
Crystallisation studies: thermal cycles and DSC

Materials: unreinforced PEKK 7002PT (T/I ratio 70/30), AS7 CF/PEKK UD prepreg

Cycle for effect of isothermal holds:

- Heat 30-370°C at 20°/min
- Hold at 370°C for 5min
- Cool 370°C-isotherm at 150°C/min
- Hold at isotherm for 60 min
- Cool isotherm-30°C at 150°C/min
- Heat 30-370°C at 20°/min

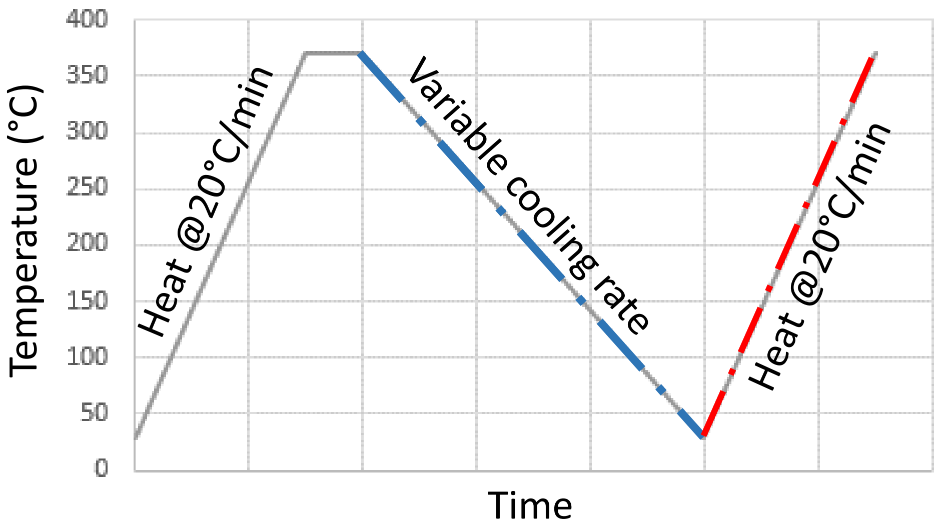
Isotherms: 220, 240, 260, 280, 300°C



Cycle for effect of cooling rates:

- Heat 30-370°C at 20°/min
- Hold at 370°C for 5min
- Cool 370-30°C at the specified cooling rate
- Heat 30-370°C at 20°/min

Cooling rates: 5, 10, 20, 40, 60, 100, 150°C/min



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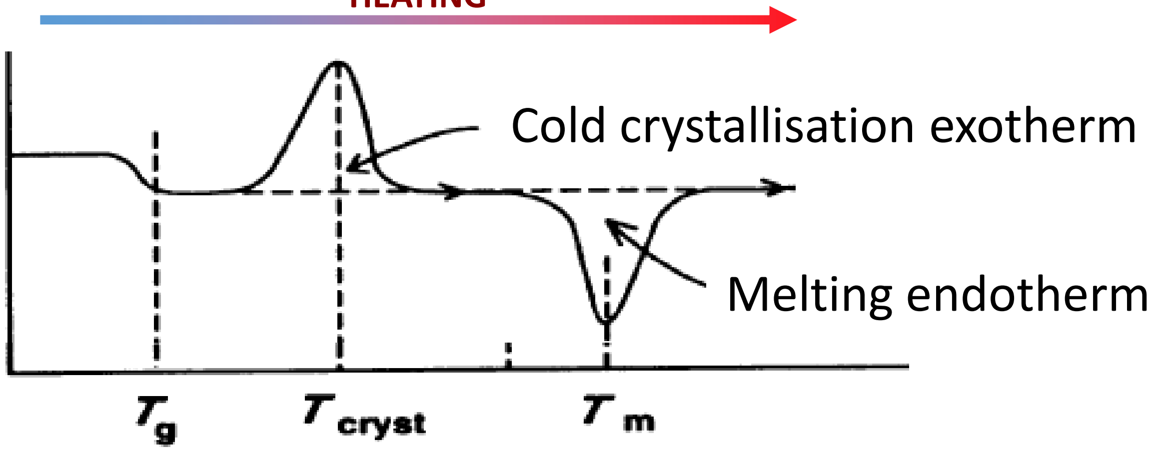
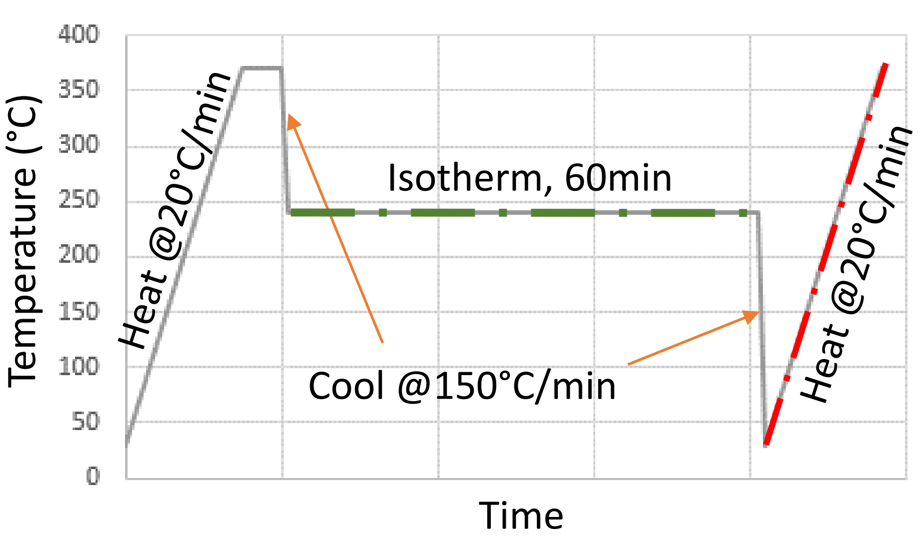
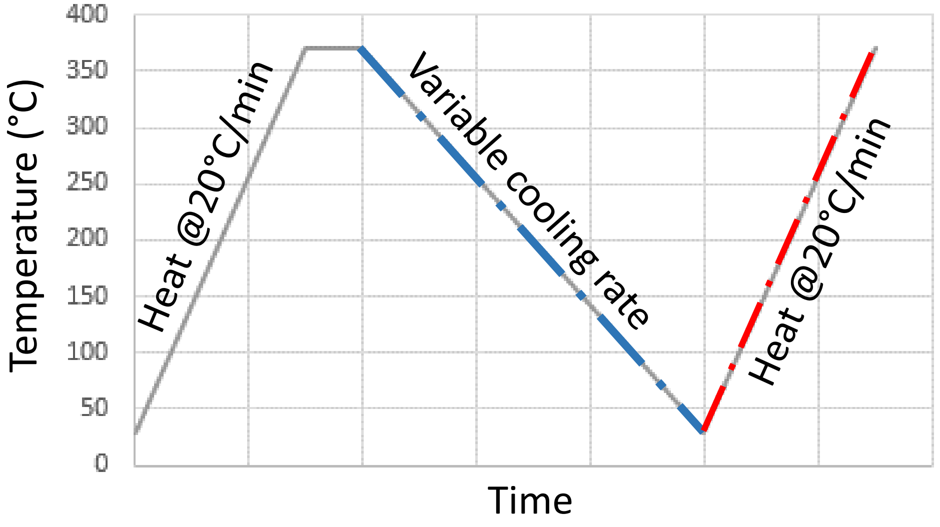
Crystallisation studies: thermal cycles and DSC

Materials: unreinforced PEKK 7002PT (T/I 70/30), AS7 CF/PEKK UD prepreg

Heat scans:
(endo down)







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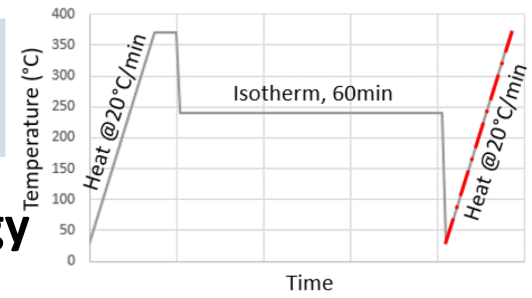
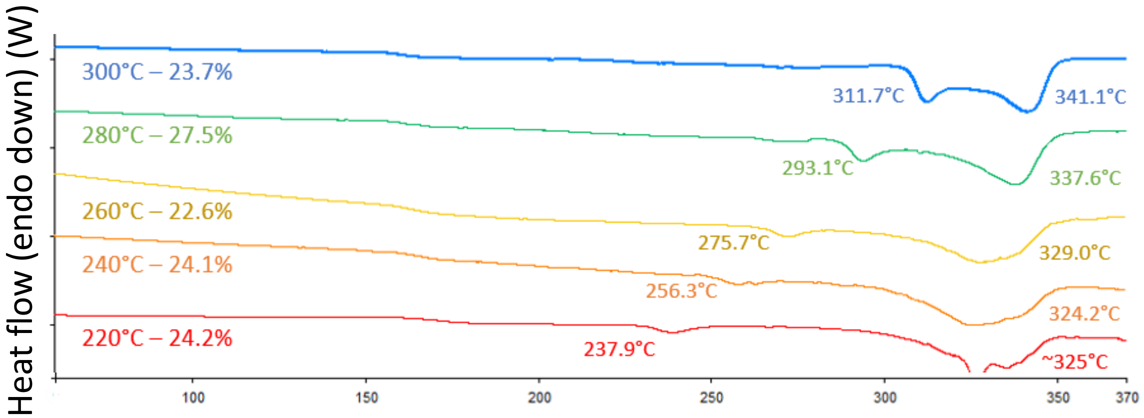
Effect of different isothermal holds on crystallinity

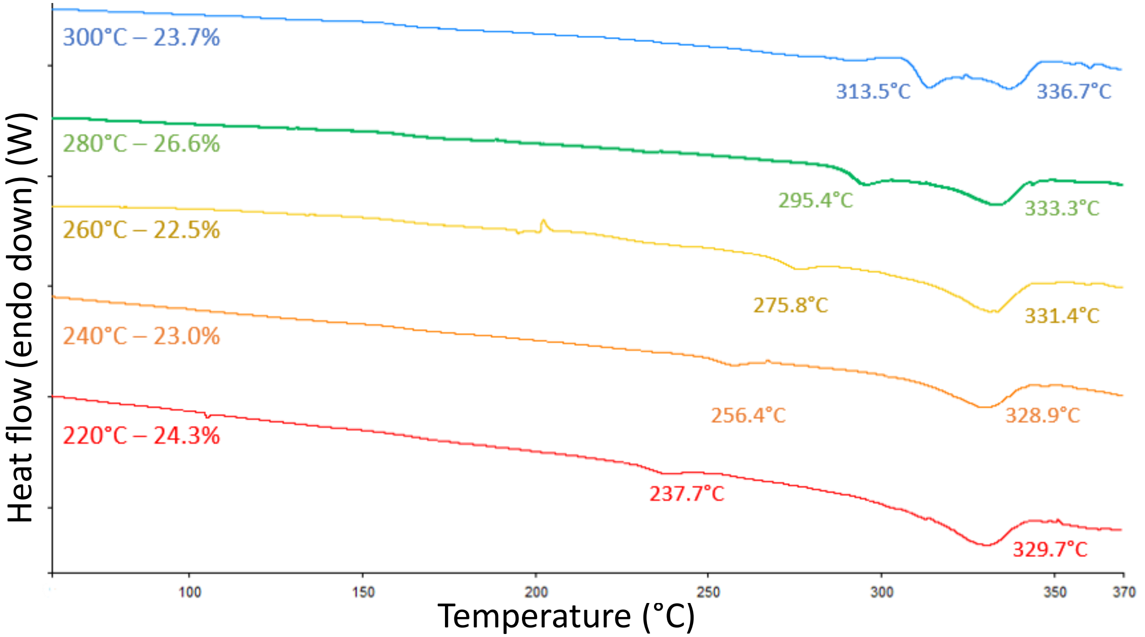


Differential Scanning Calorimetry results

Neat PEKK – heating scans of material after isotherm



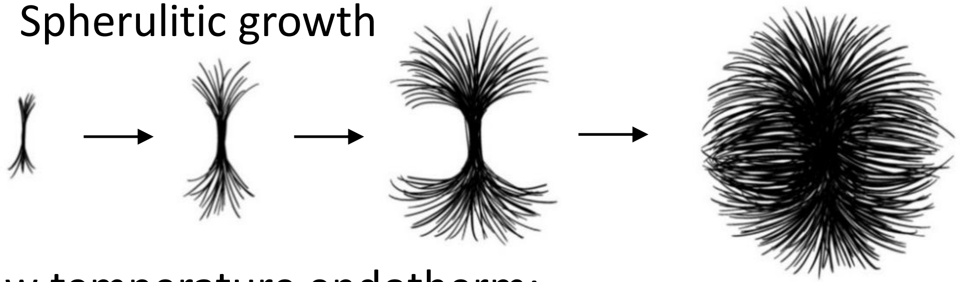
CF/PEKK composite – heating scans of material after isotherm



Crystallisation morphology

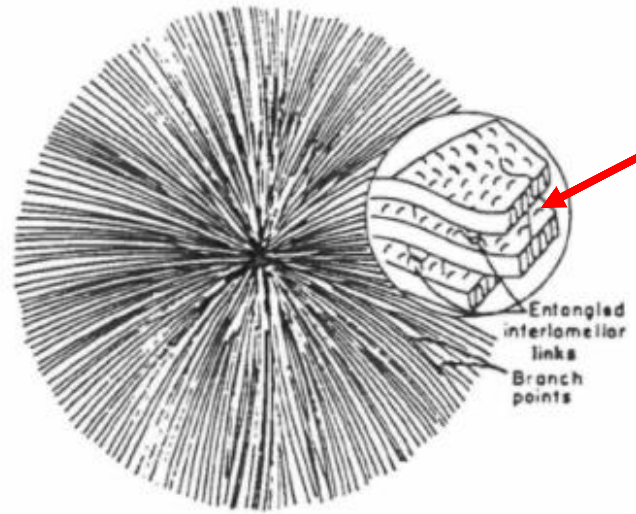
High temperature endotherm

- Primary crystallisation
- Spherulitic growth



Low temperature endotherm:

- Secondary crystallisation
- Crystallisation of amorphous material in interlamellar regions



Interlamellar regions where amorphous material crystallises

P. C. Painter and M. M. Coleman, *Fundamentals of Polymer Science: An Introductory Text, Second Edition.* Routledge, 1997.

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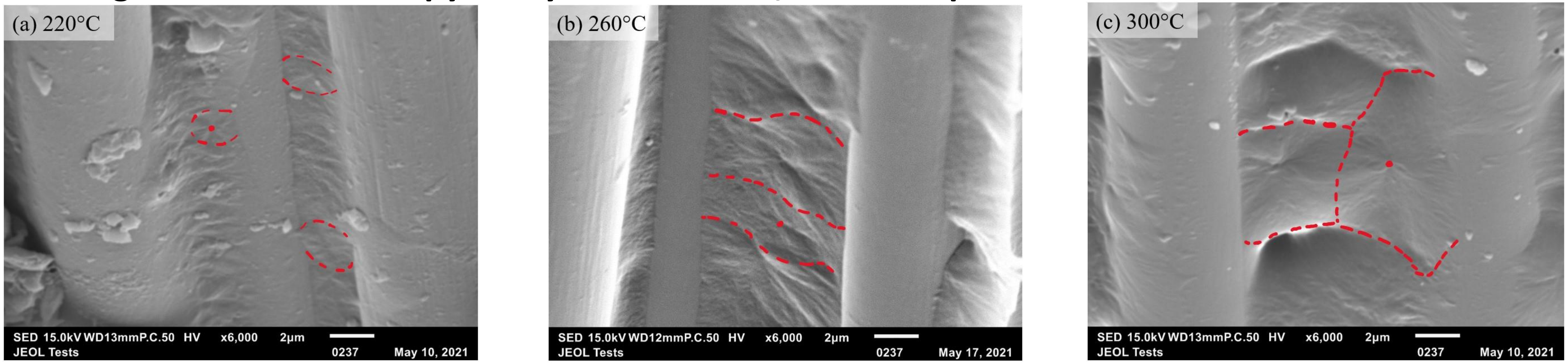
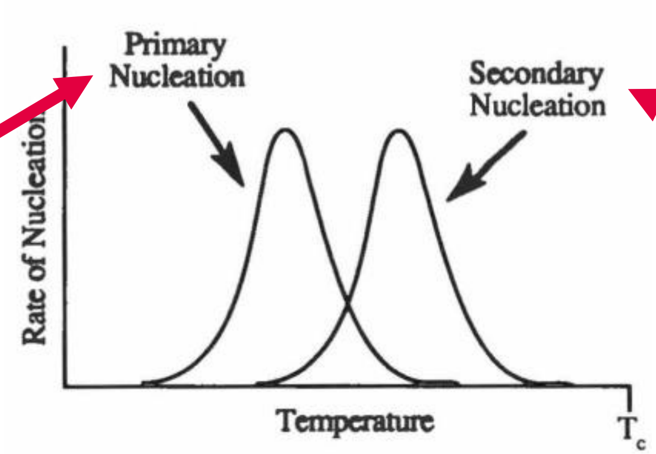
Effect of different isothermal holds on crystallinity

Scanning electron microscopy of cryofractured CF/PEKK samples



Spherulitic nucleation is incentivised
(many, small spherulites)



P. C. Painter and M. M. Coleman, *Fundamentals of Polymer Science: An Introductory Text, Second Edition*. Routledge, 1997.

Spherulitic growth is incentivised
(lower amount, large spherulites)

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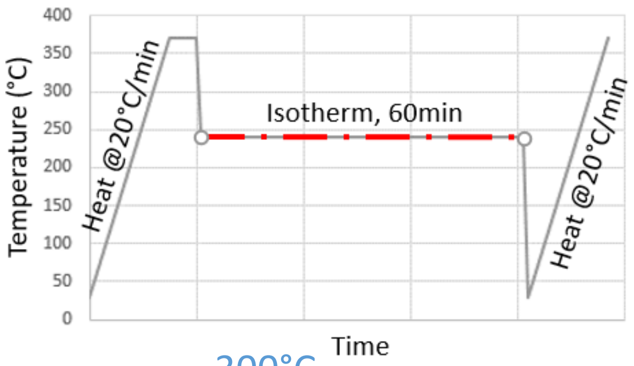
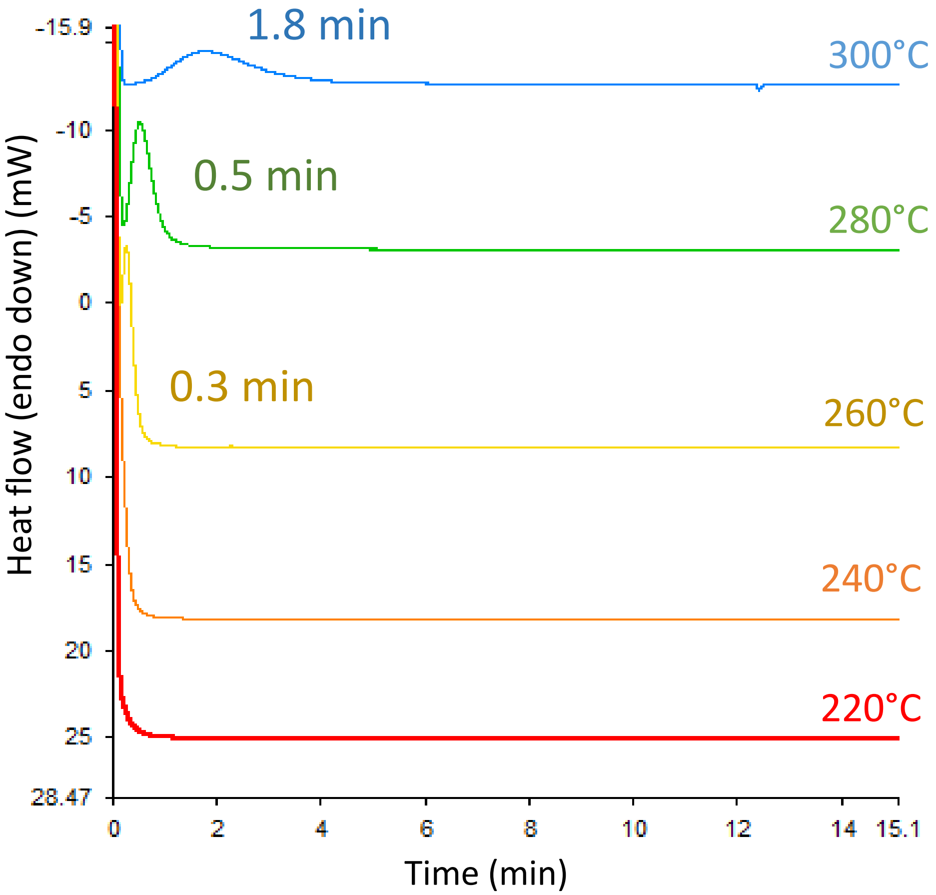
Effect of different isothermal holds on crystallisation kinetics

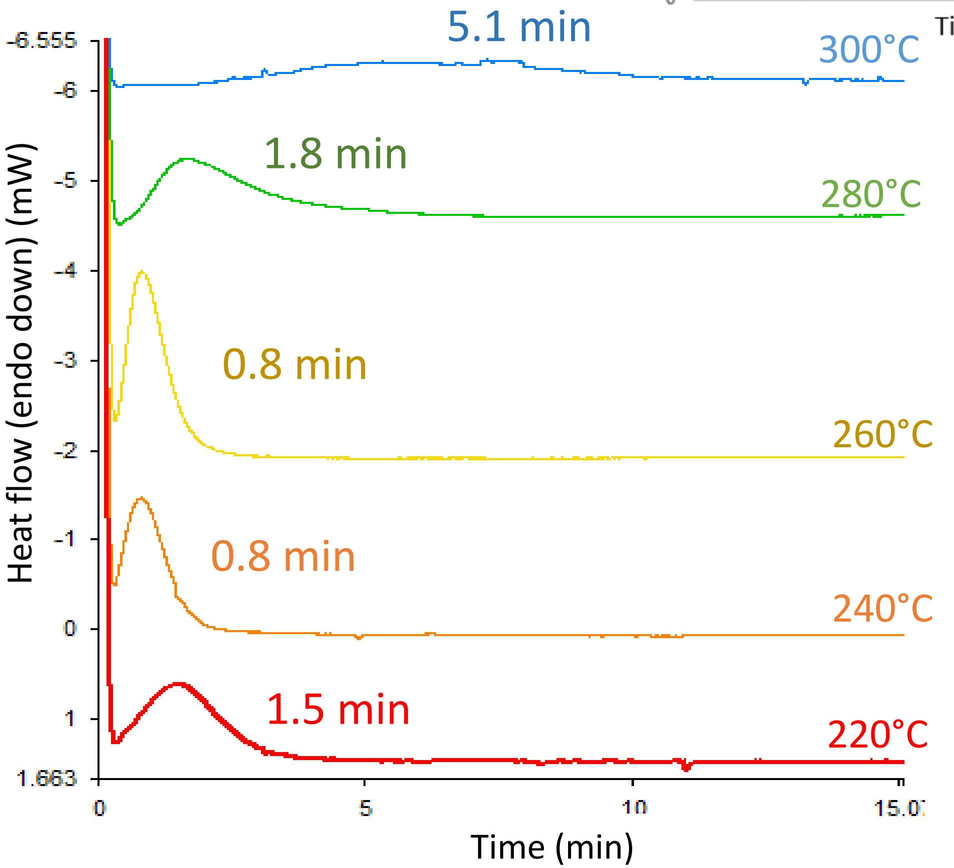
Differential Scanning Calorimetry results during isothermal holds at different temperatures



Neat PEKK



CF/PEKK composite



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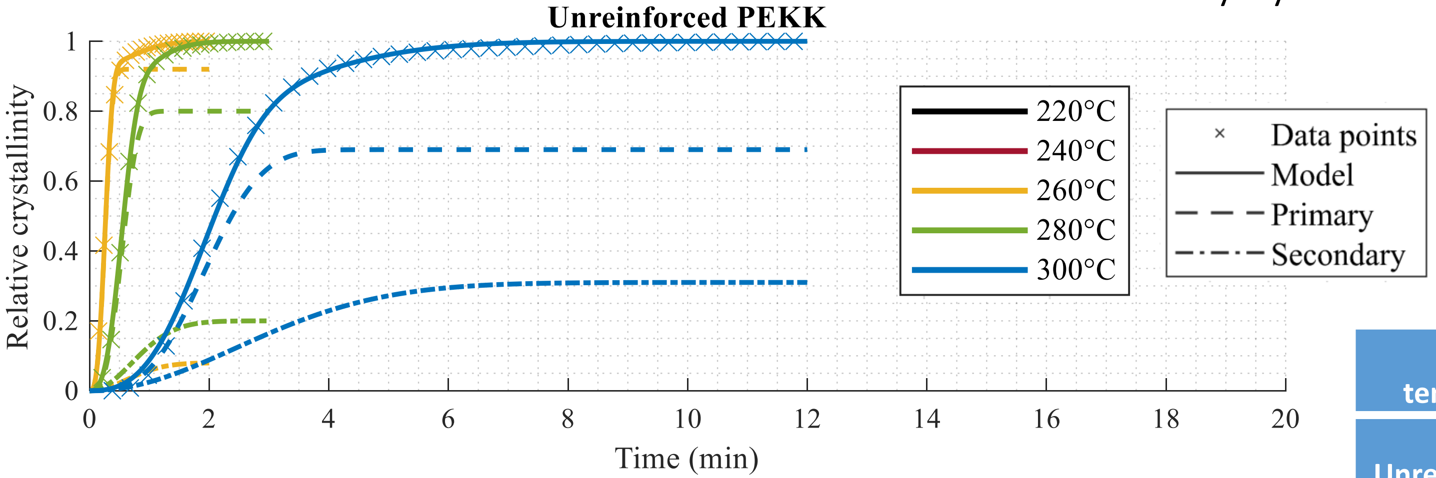
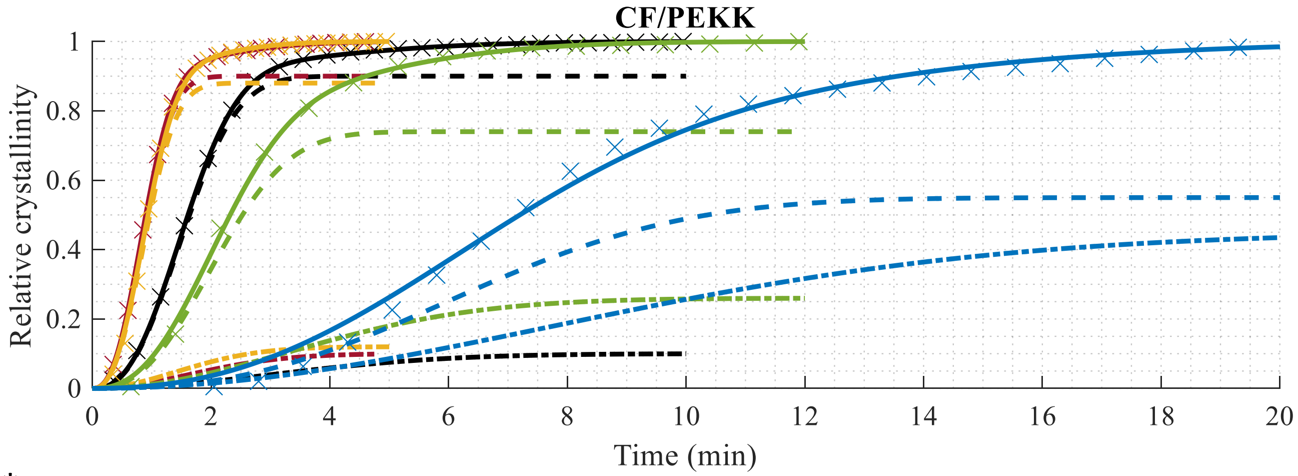
Modelling of isothermal crystallisation kinetics

Velisaris-Seferis model*: $\alpha(t) = \frac{\int_0^t Q\,dt}{\int_0^\infty Q\,dt} = \underbrace{w_1[1-\exp(-k_1 t^{n_1})]}_{\text{Primary crystallisation}} + \underbrace{(1-w_1)[1-\exp(-k_2 t^{n_2})]}_{\text{Secondary crystallisation}}$





- Crystallinity evolution vs. time for neat PEKK (n_1 = 3, n_2 = 2) and CF/PEKK (n_1 = 2.5, n_2 = 2).
- Values for w_1 follow experimental results.
- k_1 and k_2 optimised by MATLAB.

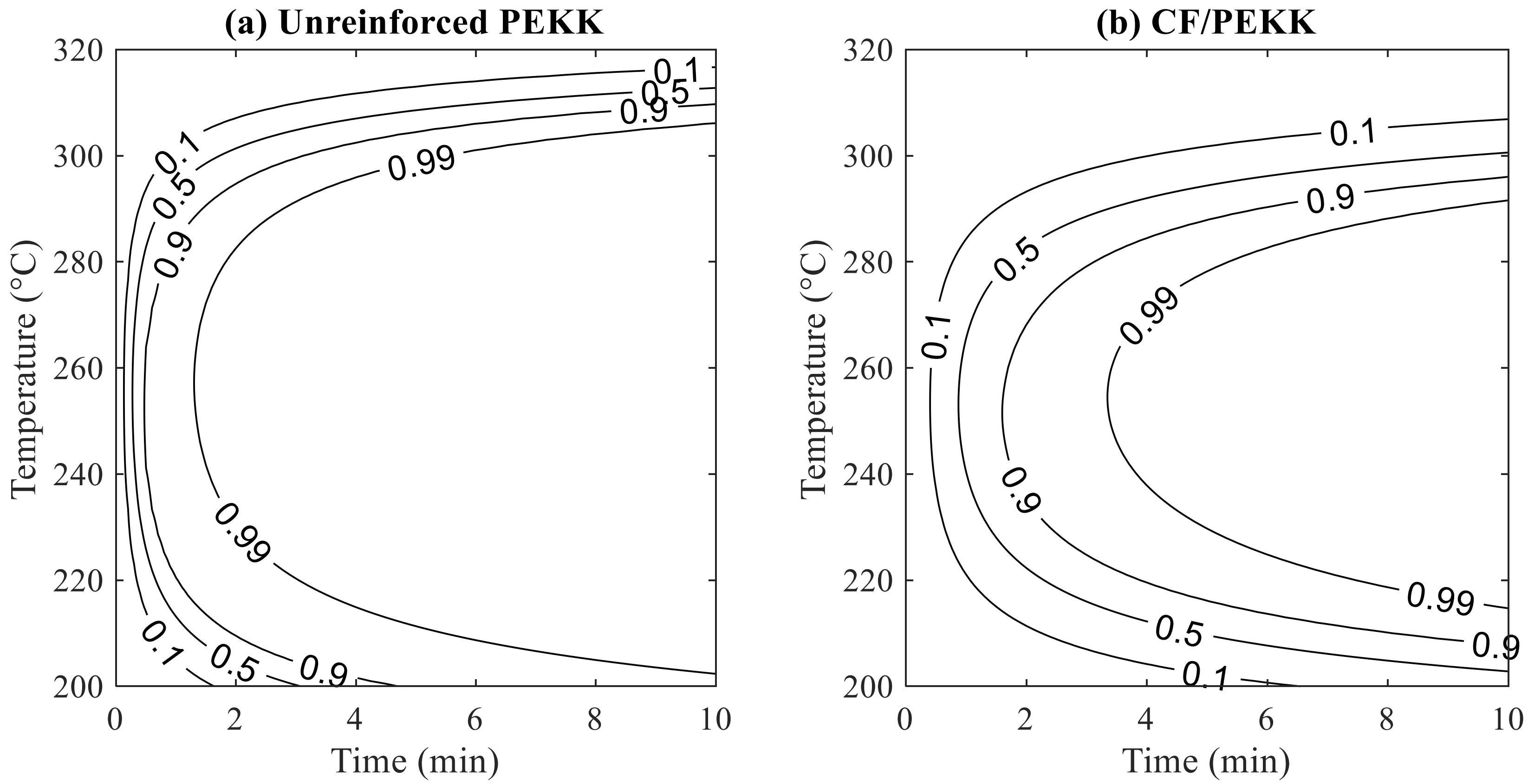
Isothermal temperature (°C)		220	240	260	280	300
Unreinforced PEKK (n1 = 3, n2 = 2)	w_1	-	-	0.92	0.8	0.69
	w_2	-	-	0.08	0.2	0.31
	k_1	-	-	38.859	4.3684	0.0961
	k_2	-	-	1.3068	1.0171	0.0838
CF/PEKK (n1 = 2.5, n2 = 2)	w_1	0.9	0.9	0.88	0.74	0.55
	w_2	0.1	0.1	0.12	0.26	0.45
	k_1	0.2363	1.0109	0.9123	0.1107	0.0069
	k_2	0.0556	0.1914	0.2539	0.0472	0.0084

*Velisaris CN, Seferis JC. Crystallization kinetics of polyetheretherketone (peek) matrices. Polymer Engineering & Science 1986;26:1574–81. https://doi.org/10.1002/pen.760262208.

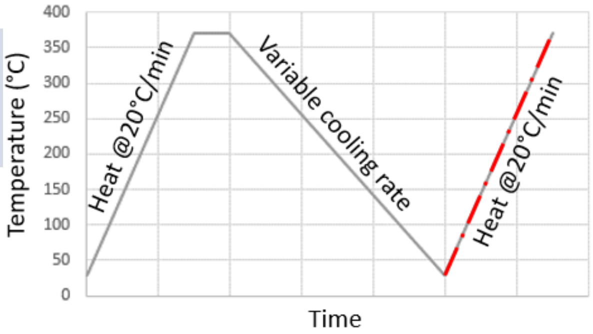
Time-Temperature-Transformation diagrams

TTT plots show crystallinity development with respect to time and temperature using contour lines.
<u>A relative crystallinity of 1 = material is fully crystallised</u>

<u>Isothermal crystallisation</u>

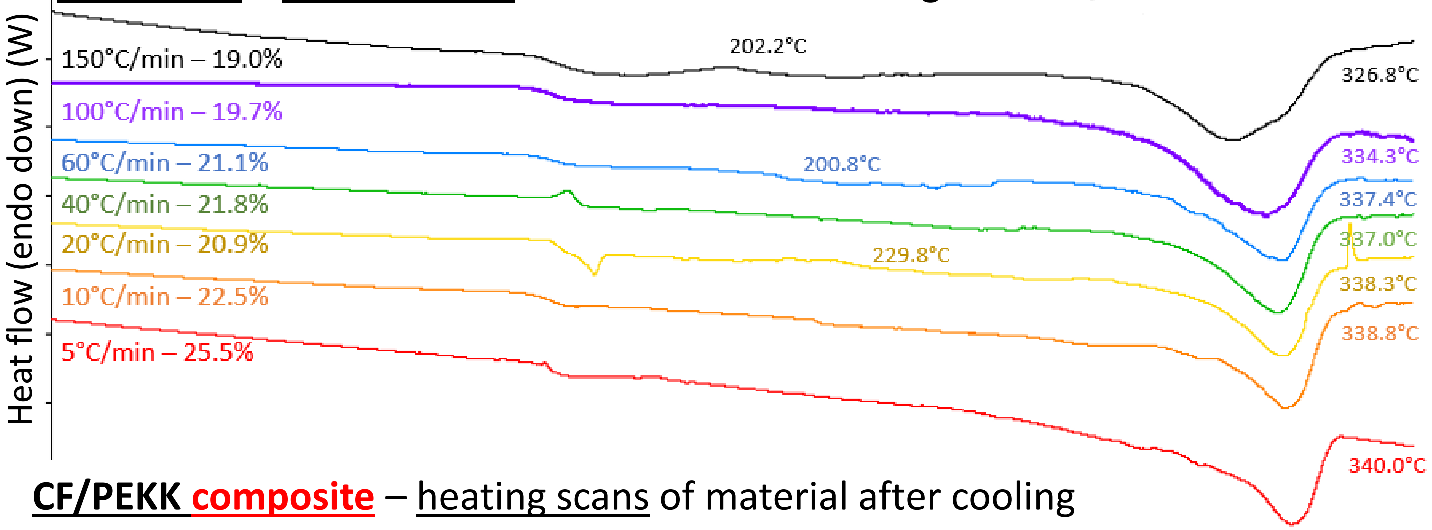


Effect of different cooling rates on crystallinity

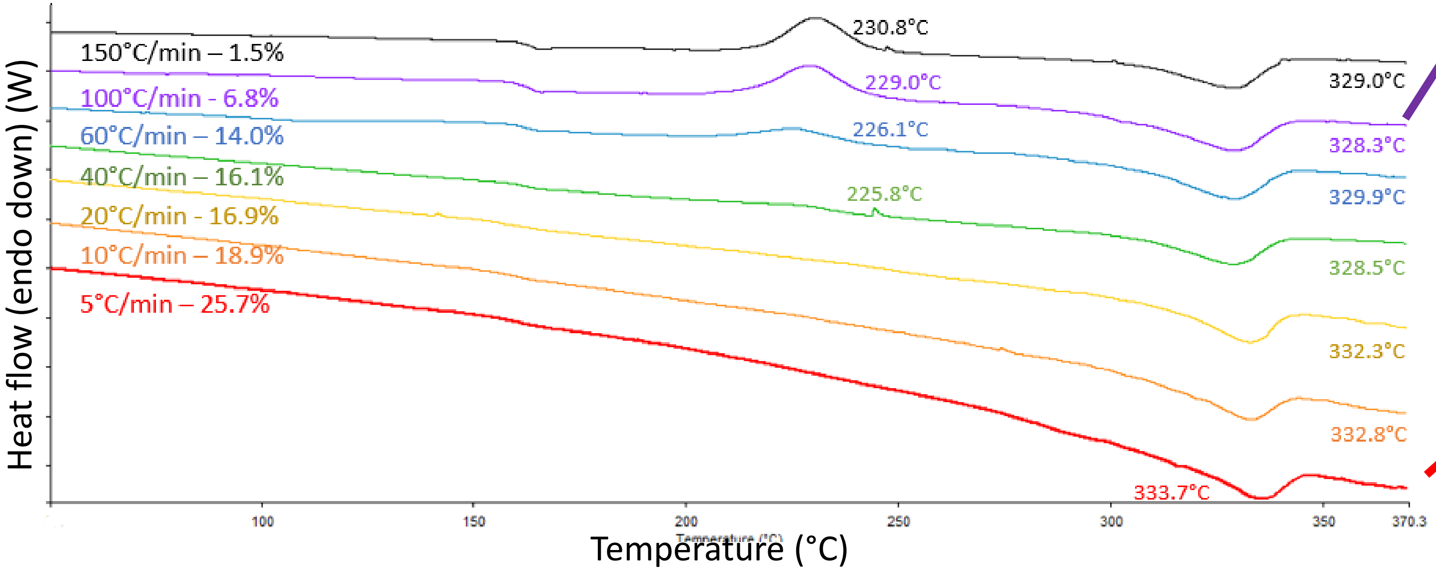


Differential Scanning Calorimetry results

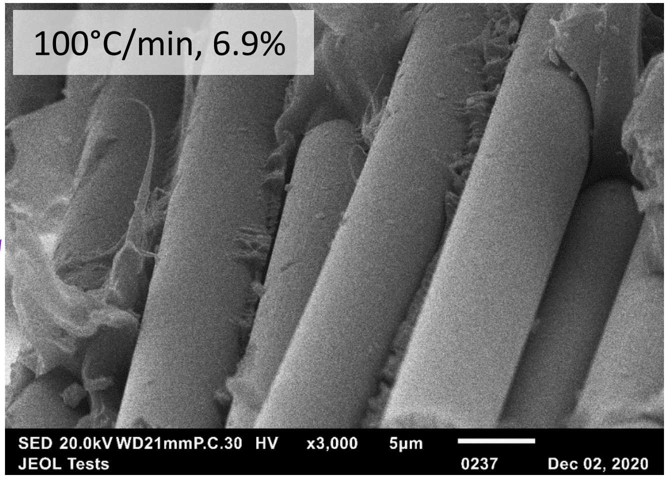
Neat PEKK – heating scans of material after cooling

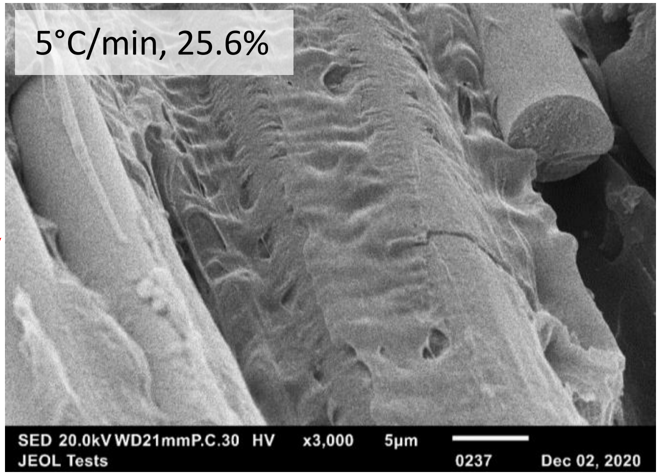


CF/PEKK composite – heating scans of material after cooling



SEM of cryofractured CF/PEKK samples





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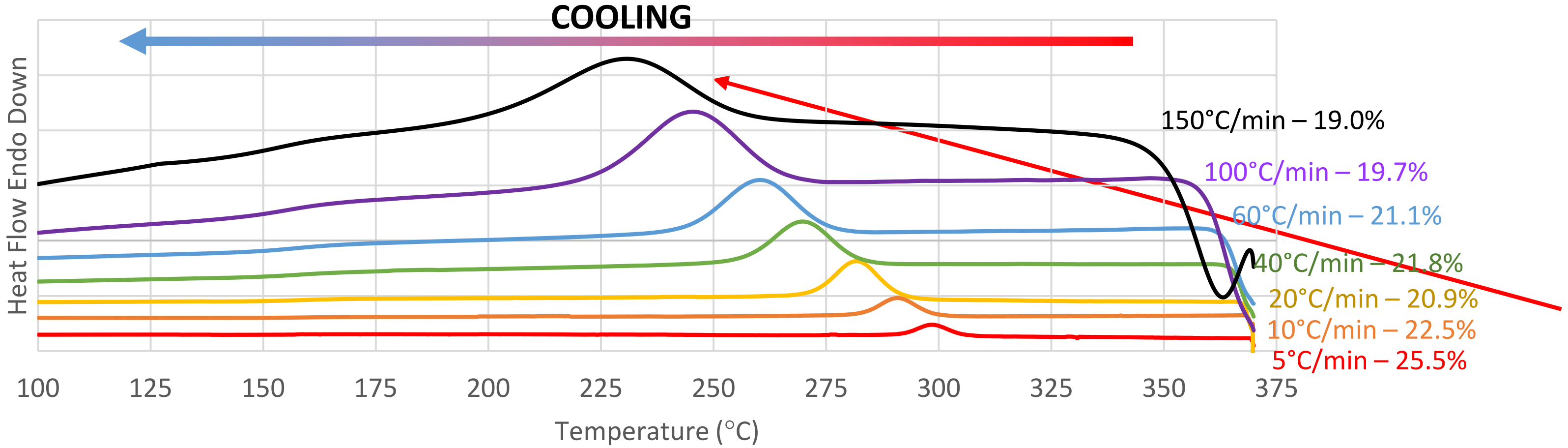
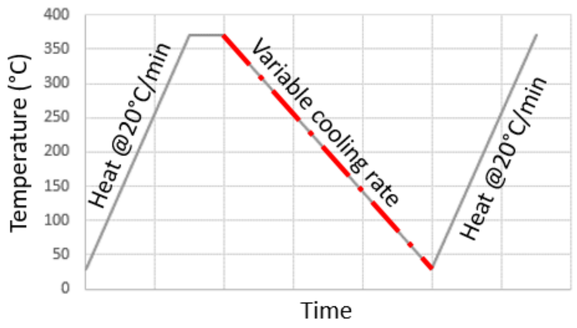
Effect of different cooling rates on crystallinity

Differential Scanning Calorimetry results

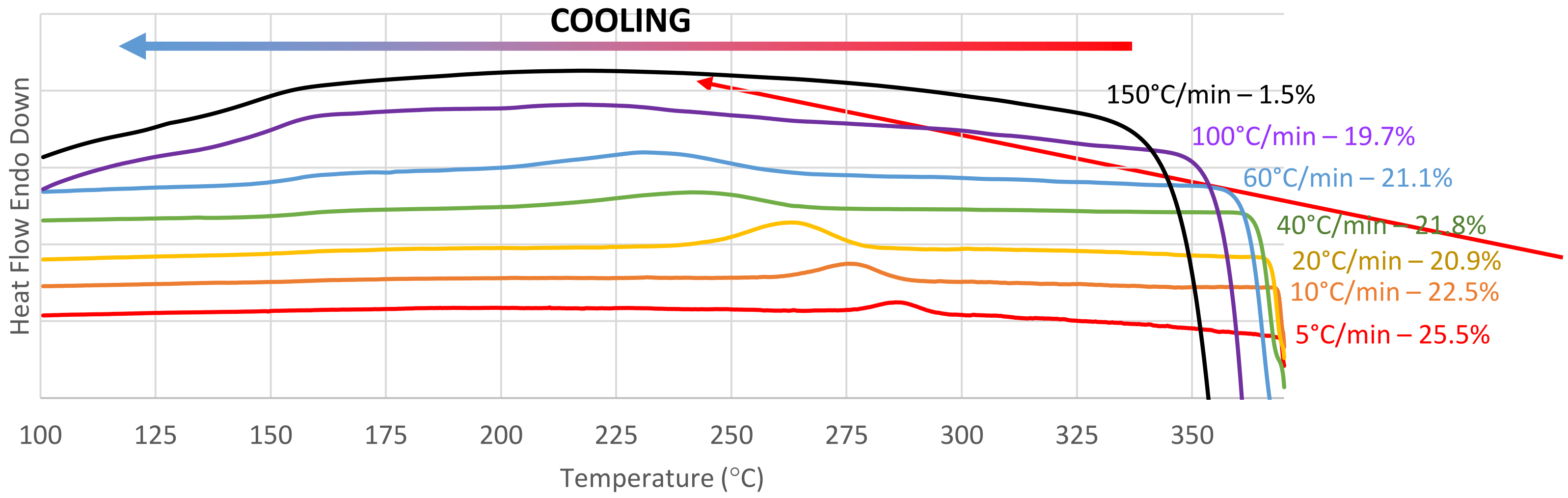
Neat PEKK – heating scans of material after cooling





Neat PEKK crystallises to some extent even at the fastest cooling rate – crystallisation exotherm during cooling step is present

CF/PEKK composite – heating scans of material after cooling



CF/PEKK does not have time to crystallise at the faster cooling rates and therefore remains amorphous – no crystallisation exotherm during cooling

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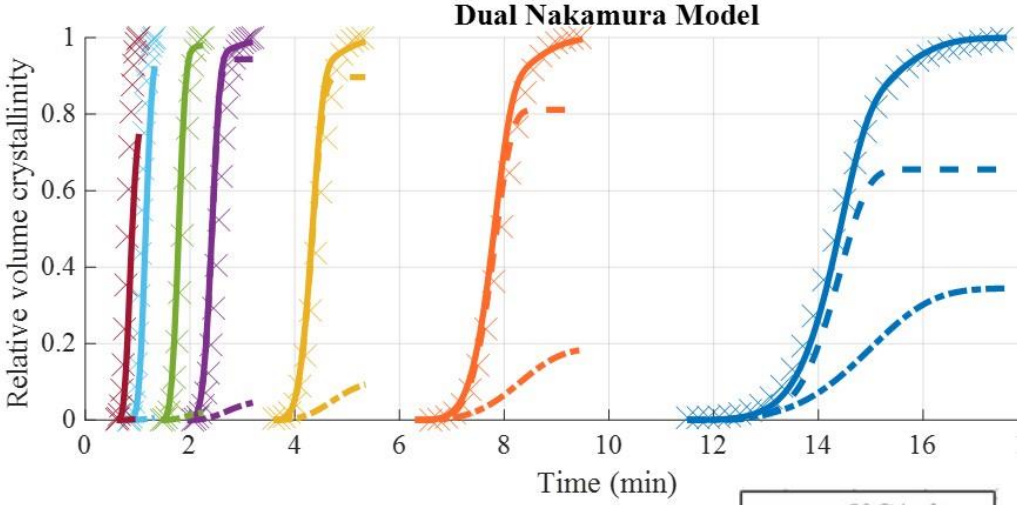
Non-isothermal crystallisation kinetics modelling

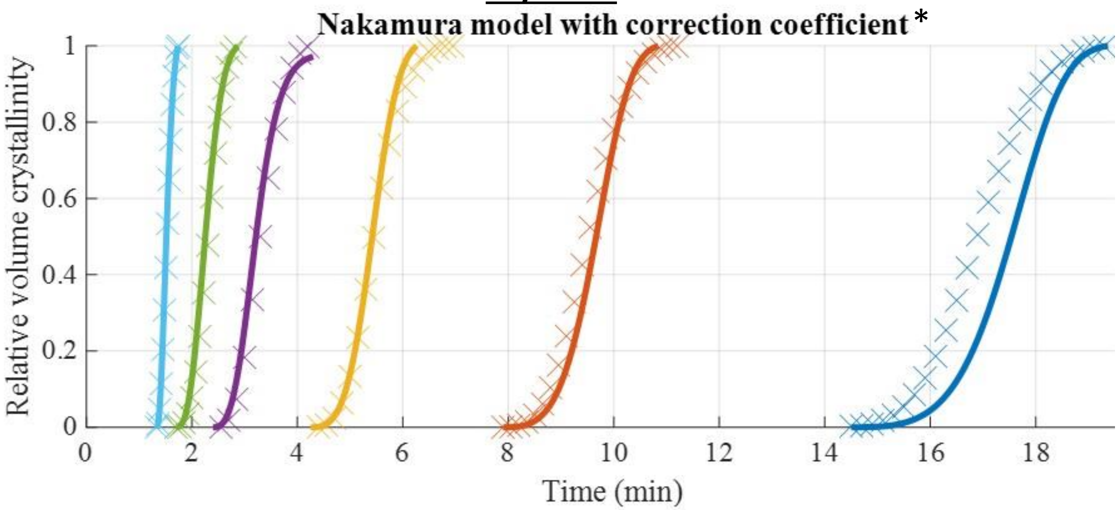
Dual Nakamura model: $\alpha = w_1\left[1-\exp\left(-\left(\int k_1{}^{1/n_1}\,dt\right)^{n_1}\right)\right] + (1-w_1)\left[1-\exp\left(-\left(\int k_2{}^{1/n_2}\,dt\right)^{n_2}\right)\right]$

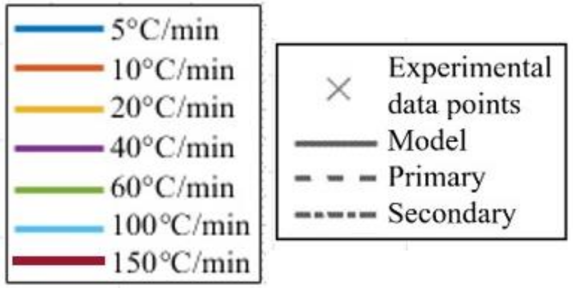
Relative crystallinity evolution vs. time for neat PEKK (n1 = 3, n2 = 2) and CF/PEKK (n1 = 2.5, n2 = 2). k1 and k2 obtained form isothermal modelling. w1 optimised by MATLAB, as there is no obvious primary to secondary crystallisation ratio in non-isothermal crystallisation.

Unreinforced PEKK



CF/PEKK





Rel. volume crystallinity = 1 in each case equates to the crystallinity achieved for each cooling rate individually, e.g. for neat PEKK:

- 5°C/min = 25.5% crystallinity
- 50°C/min = 19.0% crystallinity

*Note on correction coefficient: Nakamura model on its own underestimates crystallinity development at the faster cooling rates. Using a coefficient to correct this will allow for better modelling of crystallinity development of a laminate experiencing different temperature gradients and distributions.

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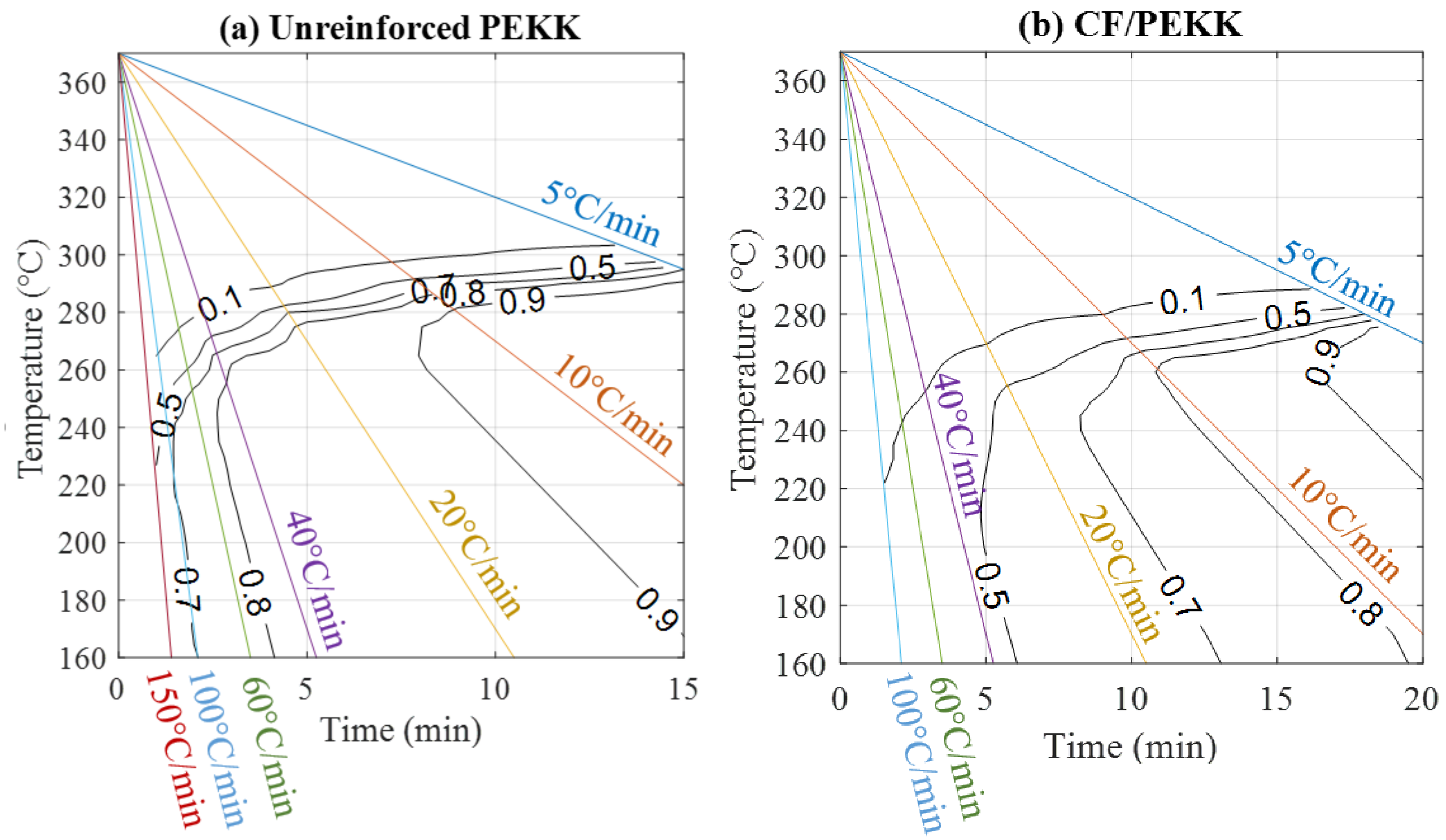
Time-Temperature-Transformation diagrams

TTT plots show crystallinity development with respect to time and temperature using contour lines.
A relative crystallinity of 1 = crystallinity obtained when cooling at 5°C/min.

Non-isothermal crystallisation



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Concluding remarks

- Tuneability of PEKK makes it a very interesting material (impacting Tg, Tm, crystallinity, viscosity).
- PEKK undergoes a dual crystallisation mechanism.

PEKK 7002PT (T/I ratio 70/30)

- PEKK has the capability to crystallise up to approximately 25%.
- Higher crystallinity results in a better fibre-matrix adhesion.
- Crystallisation kinetics of PEKK in composite form with a high CF content (~68% weight) are inhibited and therefore slower than in unreinforced form, likely due to the fibres impeding macromolecular chain movement and rearrangement.
- The fastest kinetics of CF/PEKK when being processed under isothermal conditions are between 240-260°C.
- Crystallisation kinetics were successfully modelled and broken down into primary and secondary crystallisation, and time-temperature transformation diagrams were generated which can be helpful as guides within manufacturing contexts.

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References

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Other published work:

- Pérez-Martín H, Mackenzie P, Baidak A, Ó Brádaigh CM, Ray D. Crystallinity studies of PEKK and carbon fibre/PEKK composites: A review. Composites Part B: Engineering 2021;223:109127. https://doi.org/10.1016/j.compositesb.2021.109127.
- Pérez-Martín H, Buchalik-Bopp S, Guettler BE, Mackenzie P, Baidak A, Ó Brádaigh CM, et al. Effect of crystallinity and morphology on the mechanical properties of CF/PEKK composites manufactured under compression moulding and Automated Tape Placement. Materials Today Communications 2023;36. https://doi.org/10.1016/j.mtcomm.2023.106442.

References for work on crystallisation kinetics modelling:

- Velisaris CN, Seferis JC. Crystallization kinetics of polyetheretherketone (peek) matrices. Polymer Engineering & Science 1986;26:1574–81. https://doi.org/10.1002/pen.760262208
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Thank you!

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