Advancing Crystallization Modeling in Thermoplastic Composites: Incorporating Fiber Effects and Real-World Processing Conditions

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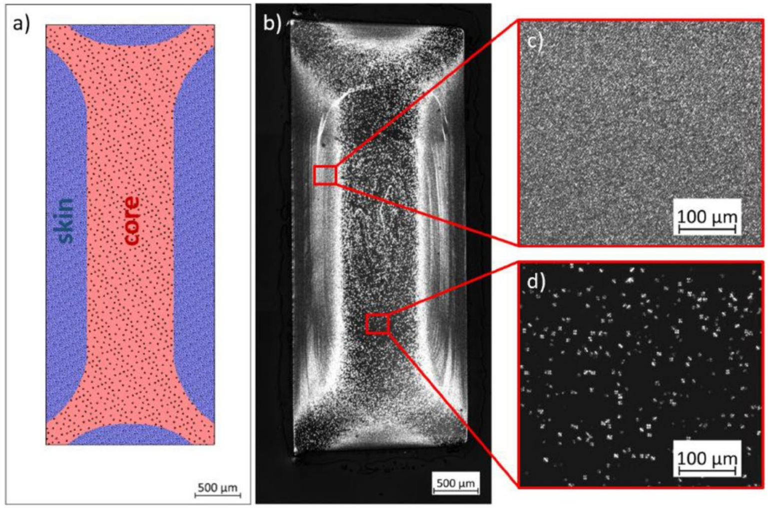
Research Overview

- Our manufacturing lab is one of the largest undergraduate plastics manufacturing labs in the U.S.
- We have traditionally been recognized for our capabilities in injection molding.
- Over the past decade, we have also developed substantial expertise in material characterization related to real-world processing.

Crystallization analysis in Moldflow

AUTODESK Moldflow Insight 2024

- What do we primarily study about crystallization?
  - Flow-induced crystallization
  - Morphological changes
- By improving crystallization models or using high-quality crystallization data, we can enhance the prediction accuracy of:
  - Cavity pressure decay
  - Mechanical properties
  - Shrinkage and warpage prediction
- The crystallization of material influences the flow analysis
  - Modeling of the viscosity
  - pvT
  - Solidification
  - Latent heat in the energy equation
  - Orientation effect on shrinkage



Polymers *2023, 15(3), 721*

Crystallization modeling

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Theoretical basis for crystallization analysis

The option to perform a crystallization analysis when using a thermoplastic, semi-crystalline material with appropriate crystallization morphology properties data has been implemented.

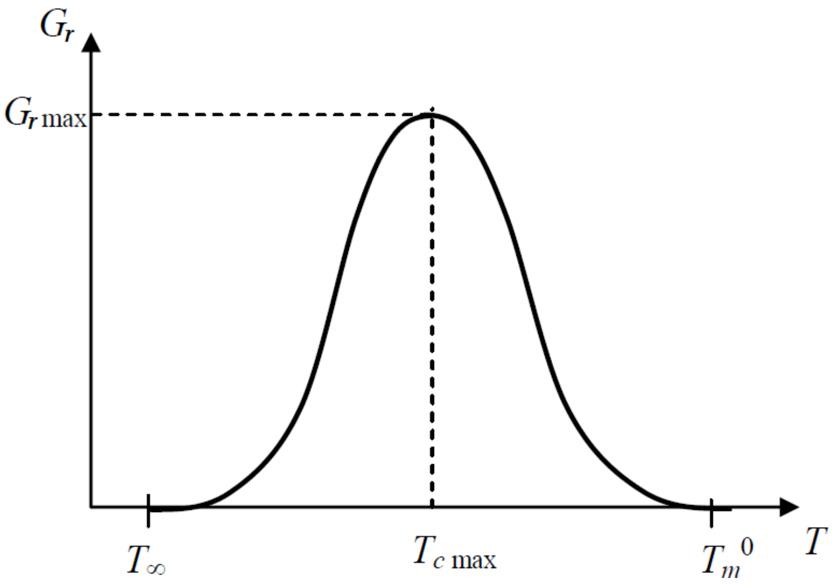
Crystallization kinetics modeling

The modeling of the crystallization kinetics, including flow enhanced crystallization, and the flow-induced morphological changes of semi-crystalline materials during and after shearing flow have been implemented in the thermoplastic flow solvers.

The crystal growth rate was not seen to be strongly influenced by material flow. Therefore, it is assumed that the growth rate depends only on temperature and follows the Hoffman-Lauritzen theory[1]:

$$G(T) = G_0 \boxed{exp\left[-\frac{U^*}{R_g(T-T_\infty)}\right]} \boxed{exp\left[-\frac{f\,K_g}{T(T_m^0-T)}\right]}$$

where $T_\infty = T_g - 30$, and $f = \frac{(T+T_m^0)}{2T}$. G_0 and K_g are material grade-specific constants which can be determined under quiescent conditions, U^* is the activation energy of motion, R_g is the gas constant, T_g is the glass transition temperature, and T_m^0 is the material grade-specific equilibrium melting temperature which is assumed to depend on pressure only. A linear function is chosen to describe the pressure dependence[2]:



Chain movement

Tendency to form nuclei

- The polymer crystallization rate (1/t) typically follows a parabolic dependence on temperature.
- The <u>Hoffman-Lauritzen theory</u> is the primary model used to describe crystallization kinetics in Moldflow and other simulation software.

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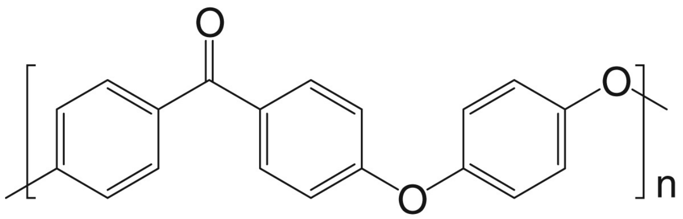
PEEK is a high-performance plastic

Poly(ether ether ketone)



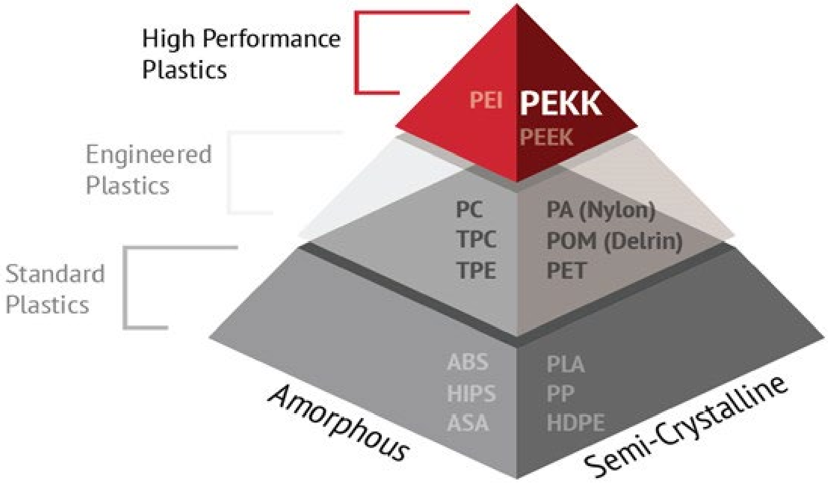


Image from HITOP Industrial

- PEEK is a high-performance polymer characterized by a high glass transition temperature (T_g), melting temperature (T_m), and decomposition temperature (T_d).
- Due to its excellent long-term reliability, PEEK is commonly used in demanding applications such as shoulder/hip replacements and bearings.

Image from Medprin Biotech GmbH

Image from SKF

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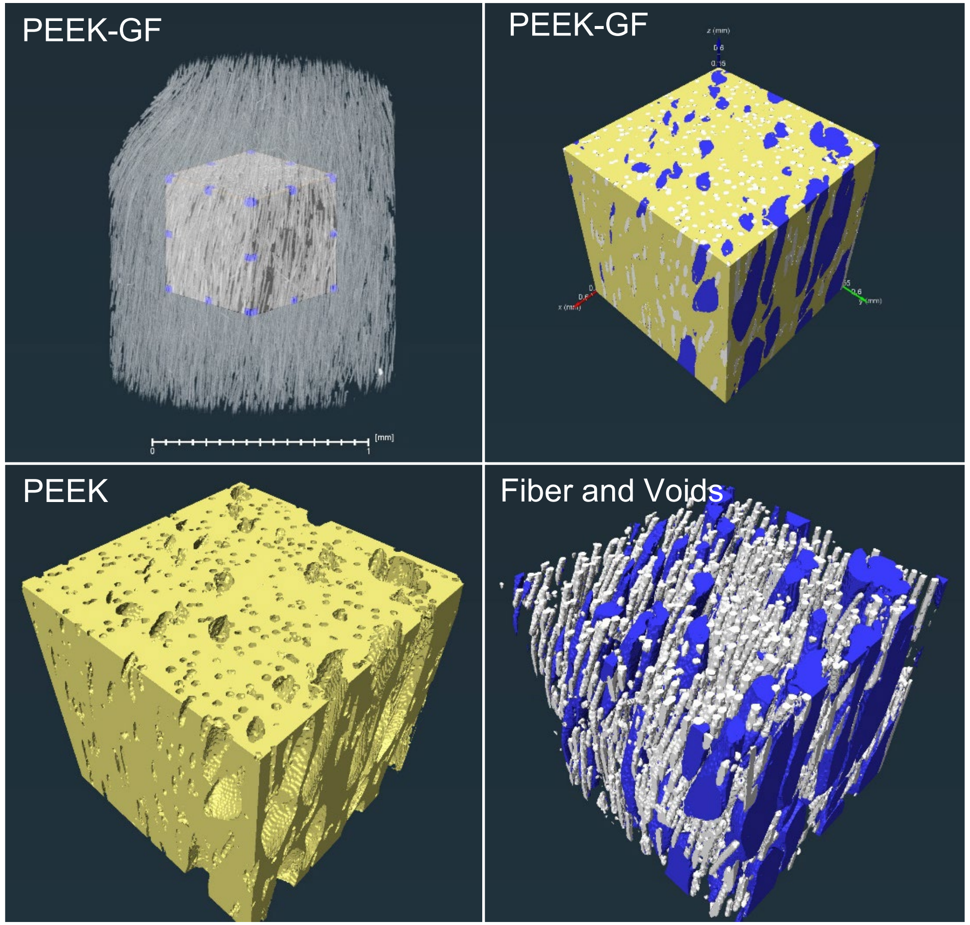
PEEK Fiber-Reinforced Composites

- PEEK fiber-reinforced composites are important materials due to their enhanced stiffness.
- The addition of fibers introduces additional factors to consider, particularly their influence on crystallization and rheological behavior.
- Fiber impacts include:
  - Surface Nucleation
  - Slowdown Effect
  - Viscosity
  - Polymer Relaxation

  …



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Processing of PEEK

Extrusion

Injection Molding

- Wide Range of Processing Temperatures
- Flow Impact

We need to take these two factors into consideration!

Image from HITOP Industrial

High shear, and **rapid cooling conditions.**

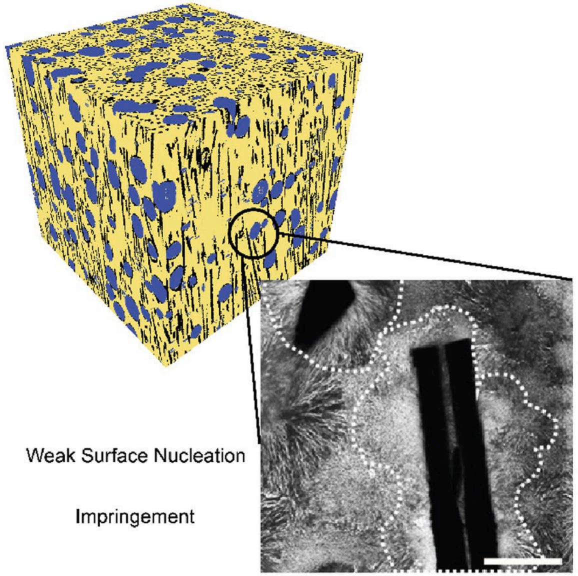
Image from Stratasys

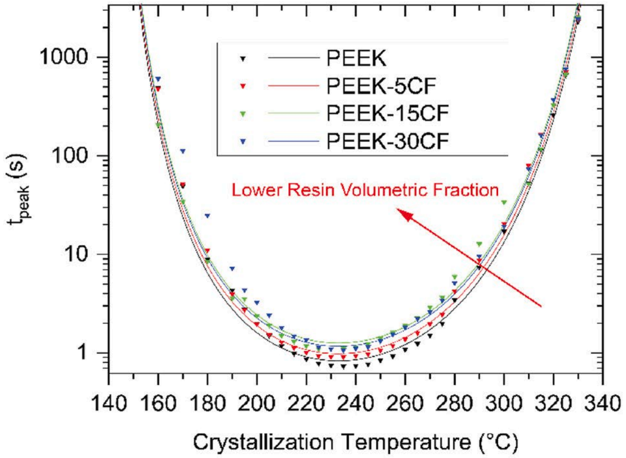
Low shear, and **moderate cooling conditions.**

Quiescent Crystallization kinetics of PEEK composites

Zhang, Alexander, Seo, Gohn, Behary, Schaake, Colby, Rhoades, ***Thermochimica Acta***, 2023. 721, 179442

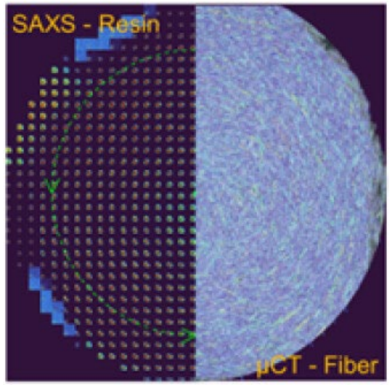
Zhang, Flanigan, de Kort, Colby, Rhoades, **Composites Part B: Engineering**, 2025, 112386

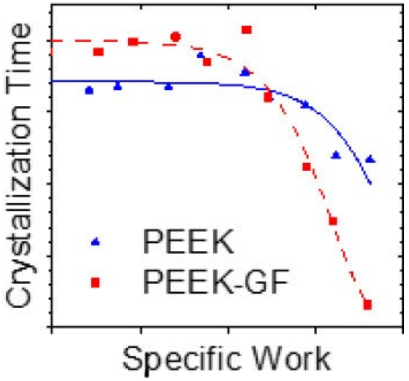




Flow-induced Crystallization of PEEK composites

Zhang, Alexander, Seo, Jacob, Kort, Schaake, Weigand, Rhoades, Colby, Macromolecules, 2024, 57(16), 8012-8024

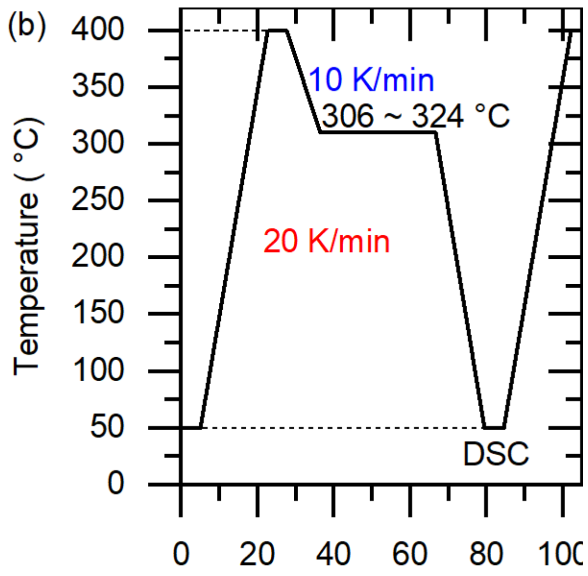


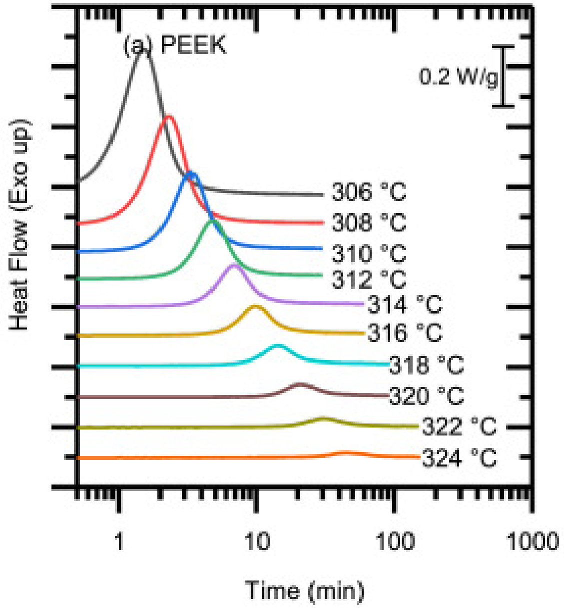


Isothermal Crystallization in DSC

- Differential Scanning Calorimetry (DSC) is a key instrument for studying polymer crystallization.
- In isothermal crystallization mode, the exothermic heat flow is monitored during crystallization at a constant temperature, allowing extraction of temperature-dependent crystallization times for modeling.
- Isothermal crystallization is the key step for capturing crystallization kinetics used in simulation models.

Mettler Toledo DSC3





Thermochimica Acta, 2023. 721, 179442

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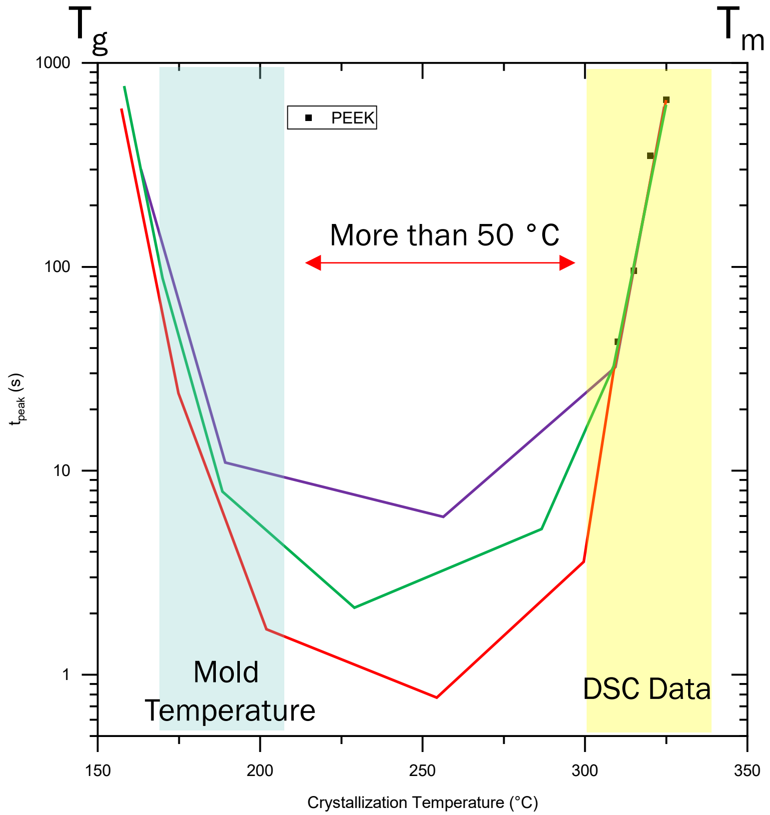
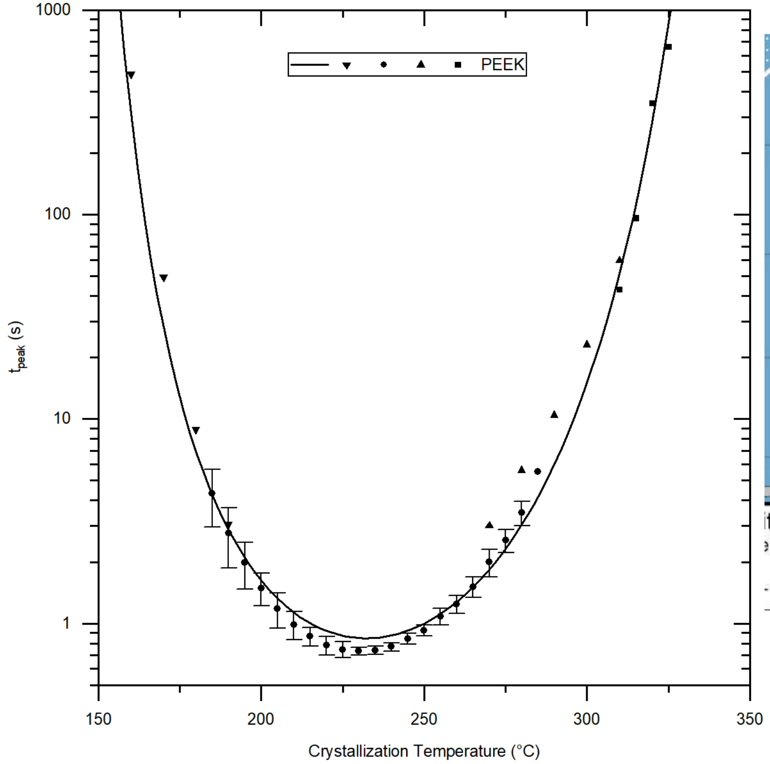
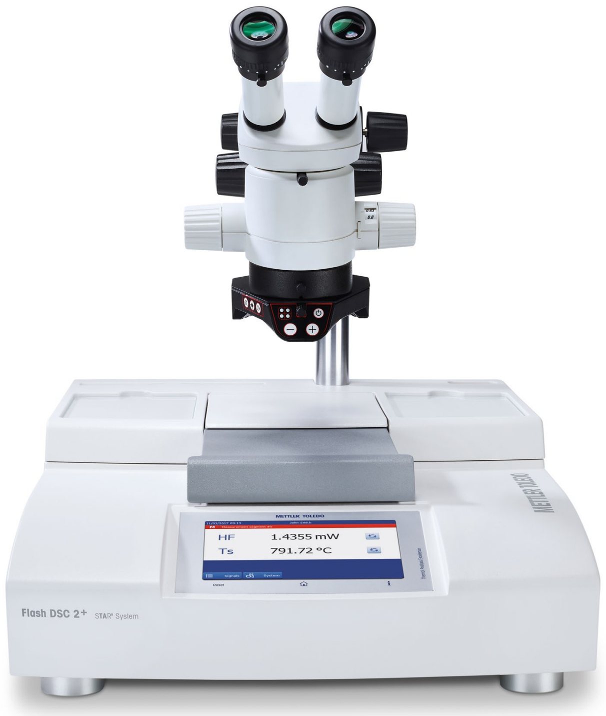
Isothermal Crystallization in DSC (Cont’D)

- The cooling rate used in DSC is not fast enough to reach the crystallization temperature below 300 °C in PEEK.
- As a result, relying solely on DSC data to establish the Hoffman–Lauritzen model leads to inaccurate predictions.
- Moreover, the temperature range accessible by DSC is typically at least 50 °C higher than the actual processing temperatures for most polymers.

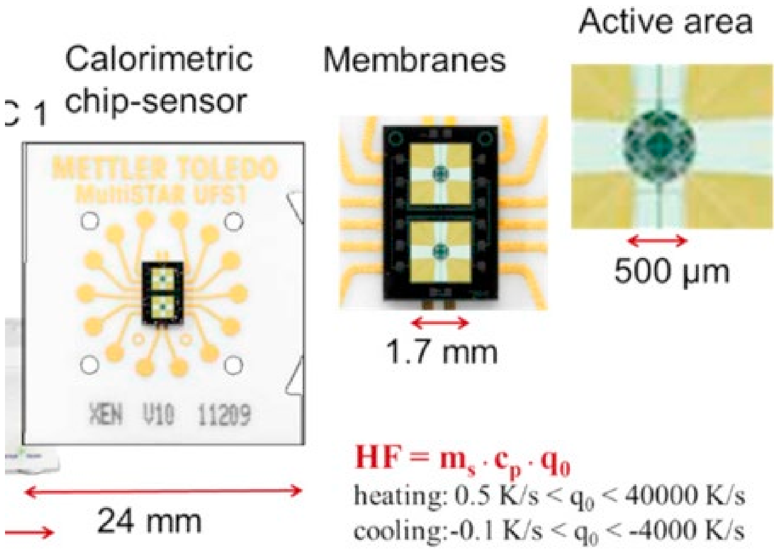




Nanocalorimetry



Mettler Toledo Flash DSC



$\mathbf{HF = m_s \cdot c_p \cdot q_0}$

heating: 0.5 K/s < q_0 < 40000 K/s

cooling: -0.1 K/s < q_0 < -4000 K/s

Macromolecules, *54 (16), 7512-7528*

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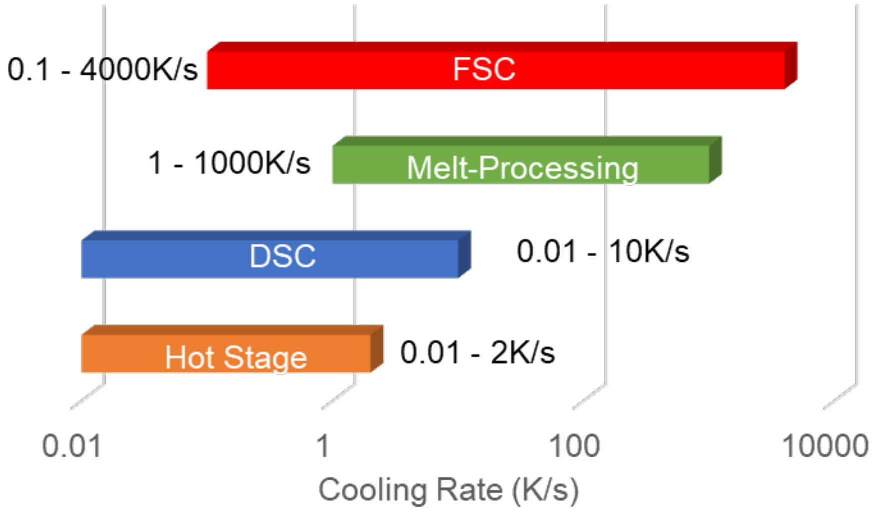
Compass to Understand Crystallization Pathway

- FSC can effectively simulate real-life processing techniques, such as injection molding, fiber spinning, and selective laser sintering, among others.



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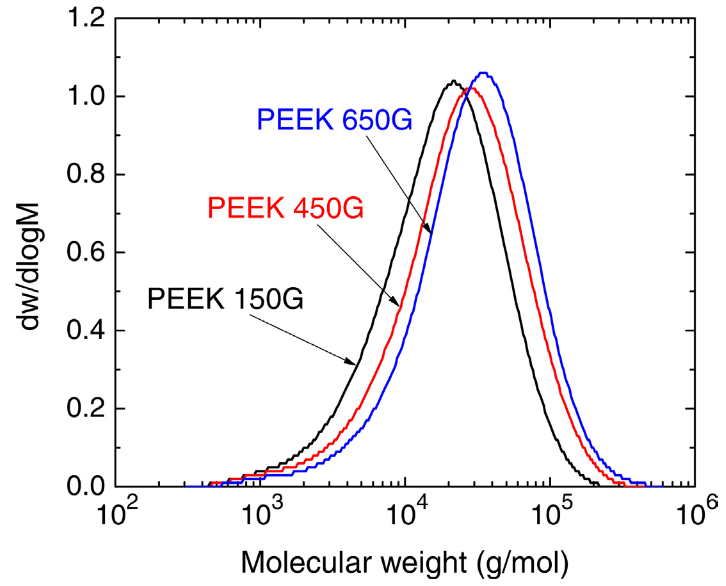
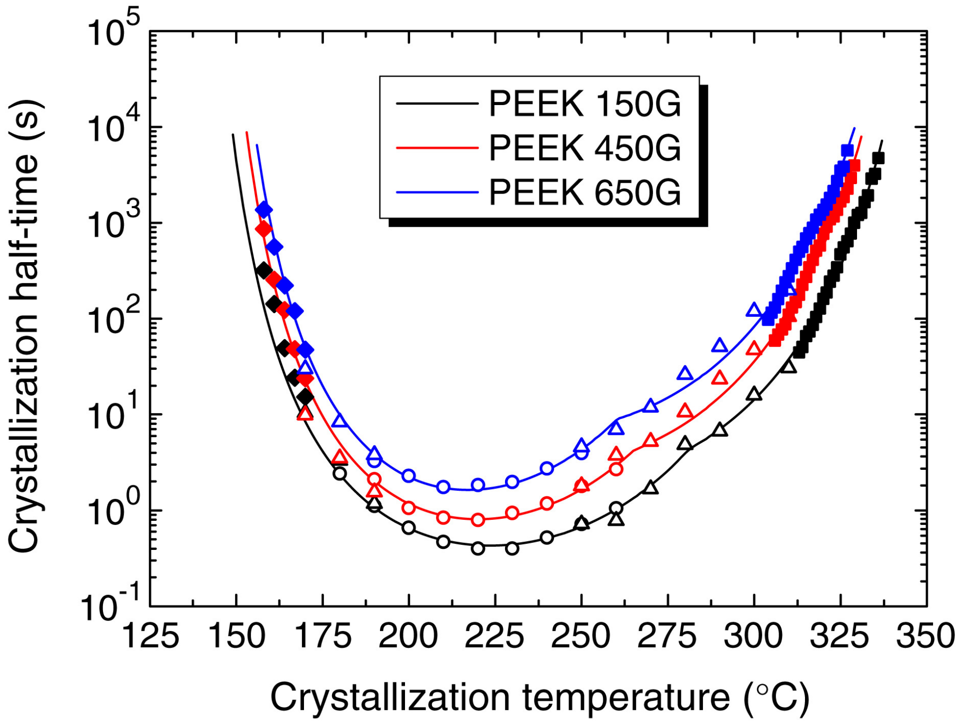
Crystallization Kinetics of PEEK

- PEEK crystallization exhibit unimodal crystallization kinetics.
- Low Mw PEEK 150G exhibits the fastest crystallization kinetics.
- This information was hard to capture by DSC.

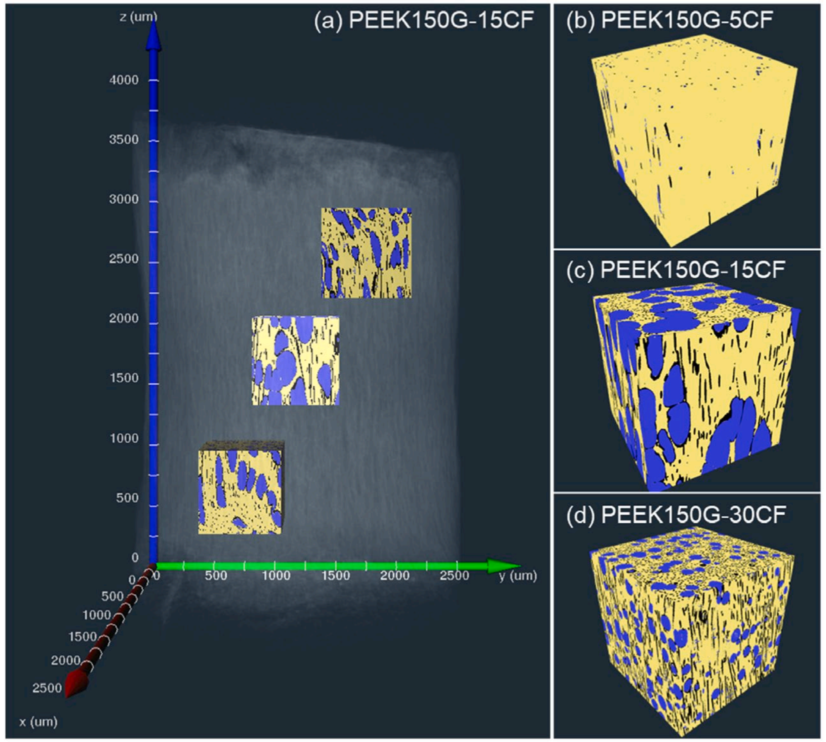


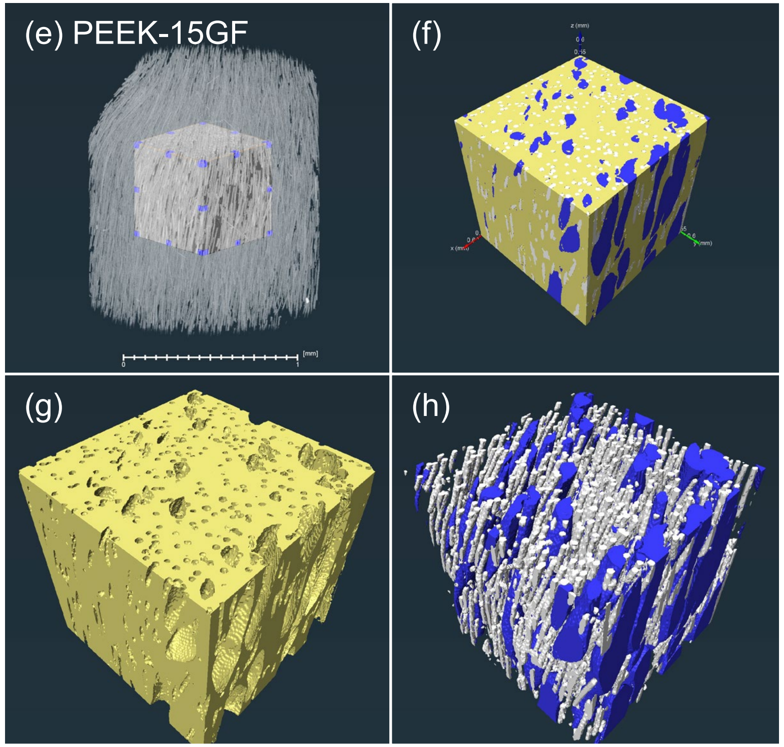


Polymer Crystallization, 2019, 2, e10055.

X-ray CT of PEEK fiber-reinforced composites

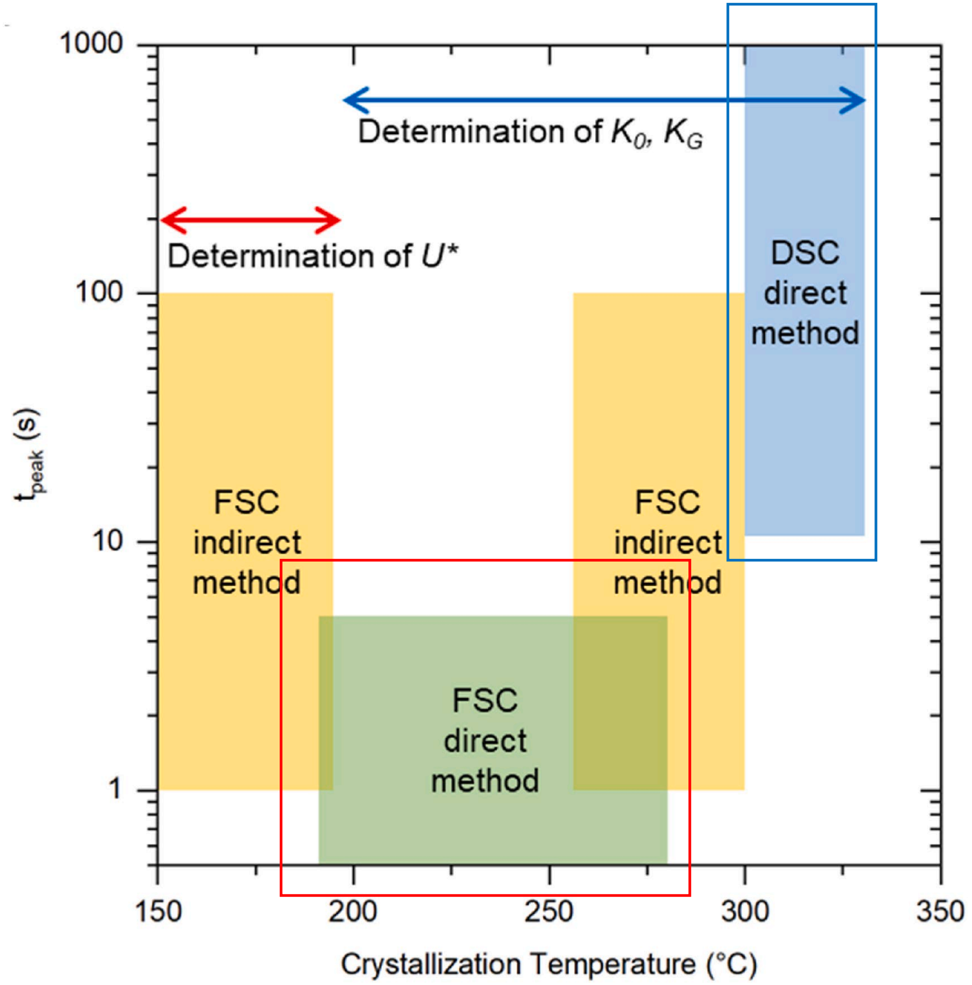
- Typical size of FSC sample is 30 to 1000 ng. Special attention needs to make on composites samples.
- X-ray Computed Tomography (XCT) with high resolution provides very details of PEEK composites.
  - Volume and weight fraction of resin, fiber, and voids
  - Fiber diameter, length, orientation

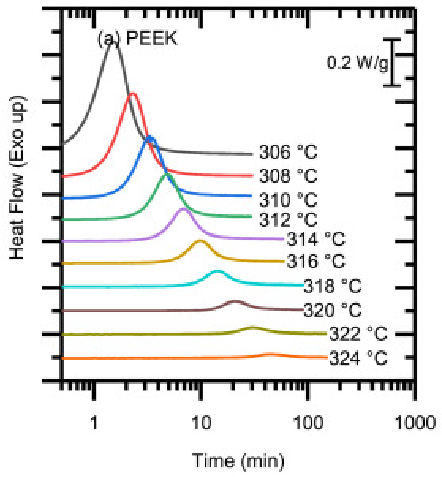


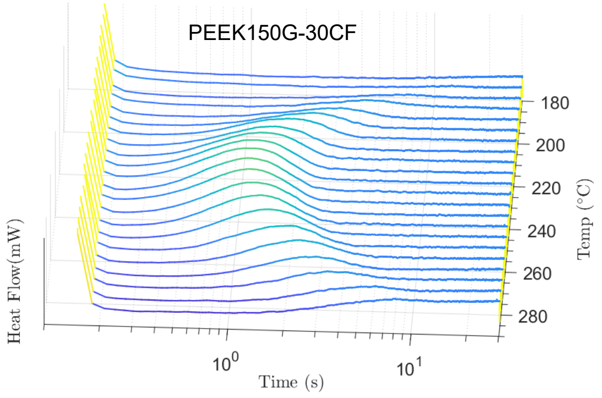


PEEK isothermal crystallization – FSC

- PEEK isothermal crystallization is followed in a wide range from near T_g to near T_m.
    - FSC isothermal crystallization – direct method







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PEEK isothermal crystallization – FSC

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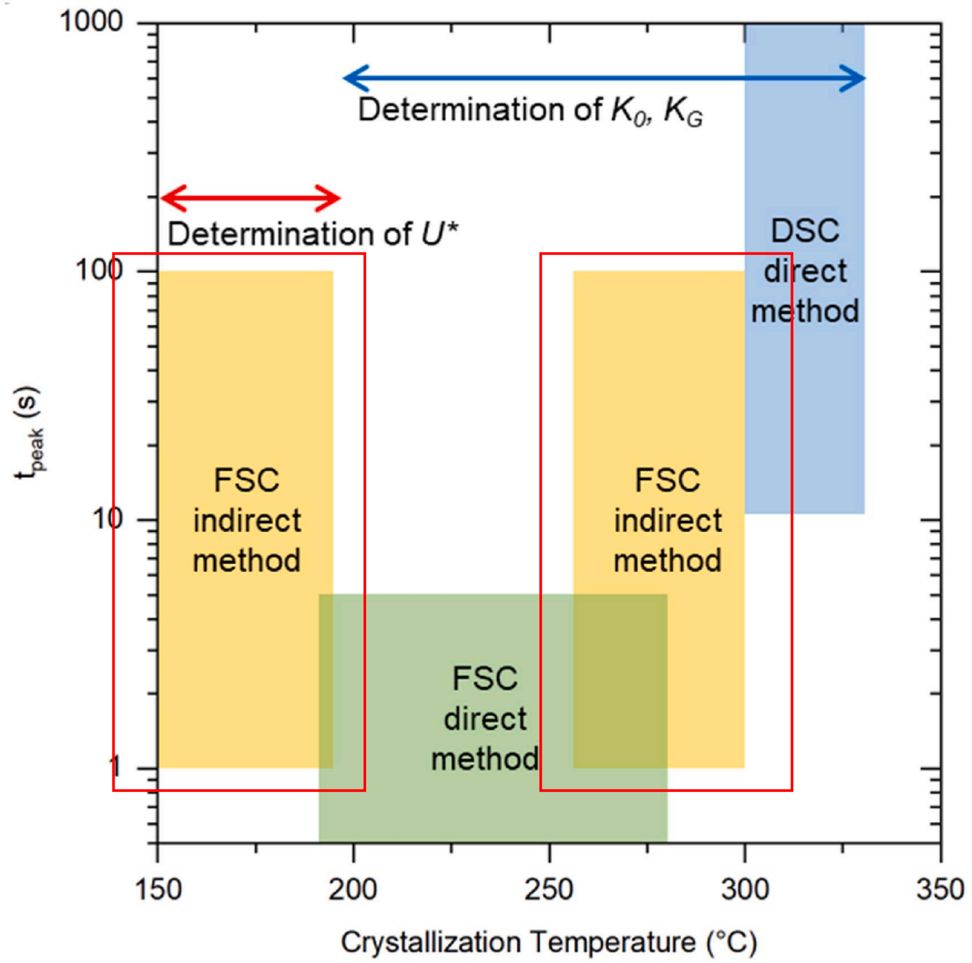
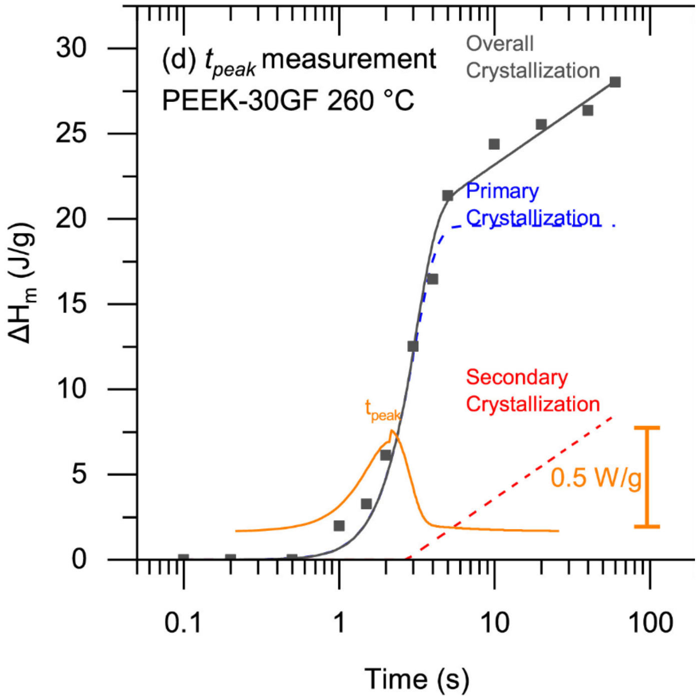


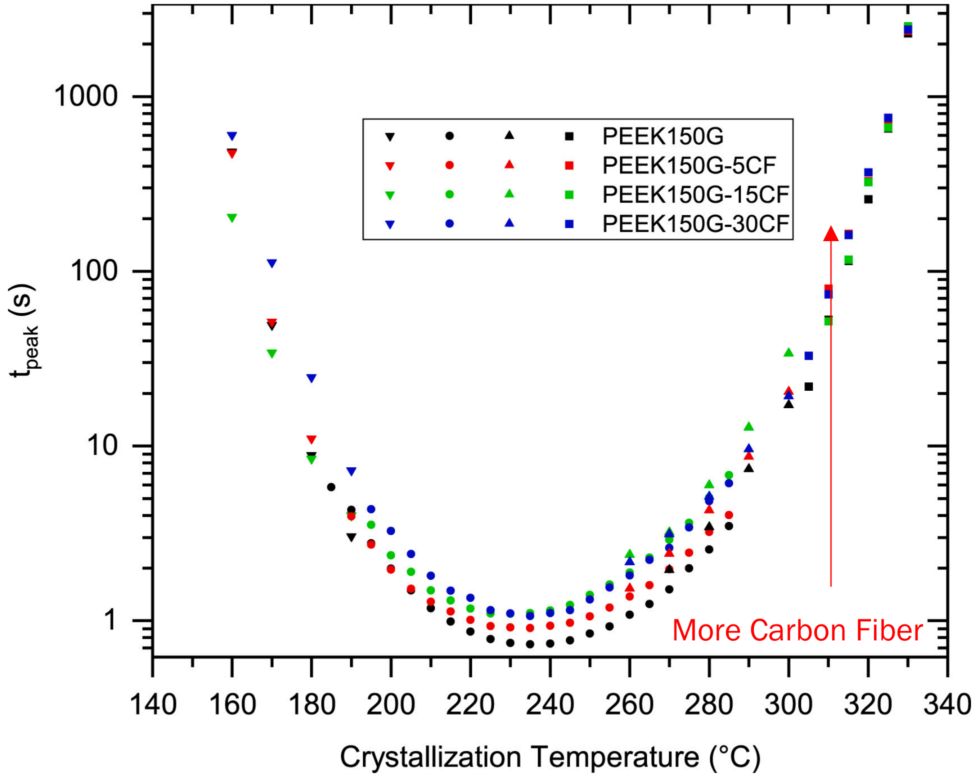
$$\Delta H_m = \Delta H_{m,max}\left\{1-\exp\left[-[\frac{\tau}{\tau_{0.5}}(ln2)^{\frac{1}{n}}]^n\right]\right\}+A_2[\ln(\tau)-\ln(\tau_{0.5})]\left[0.5\left(\frac{|\tau-\tau_{0.5}|}{\tau-\tau_{0.5}}+1\right)\right]$$

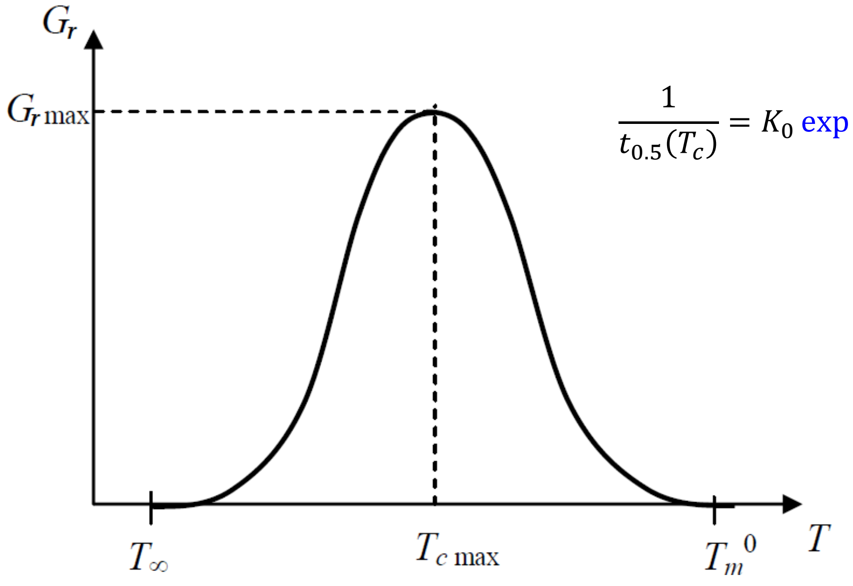
- τ crystallization time
- ΔH_m heat of fusion
- $\Delta H_{m,max}$ heat of fusion at the end of primary crystallization
- n Avrami parameters
- A_2 secondary crystallization parameter



Crystallization Kinetics of PEEK Composites

- PEEK and its carbon fiber composites show a parabolic relationship between crystallization time and temperature.
  - The ideal processing temperature is typically in the range of 220 - 240 °C.
  - The addition of carbon fiber slows down the overall crystallization.
- Addition of carbon fiber does not affect the terms related to chain movement and tendency to form nuclei.





$$\frac{1}{t_{0.5}(T_c)} = K_0 \exp\left[\frac{-U^{\cdot}}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_G\left(T_c + T_m^{\circ}\right)}{2T_c^2 \Delta T}\right]$$

Chain movement

Tendency to form nuclei

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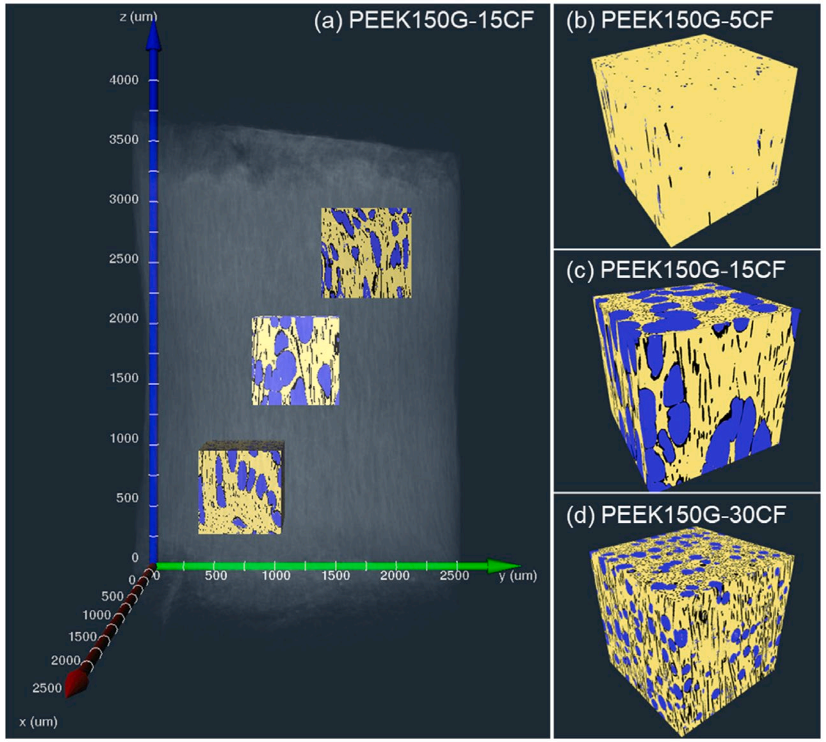
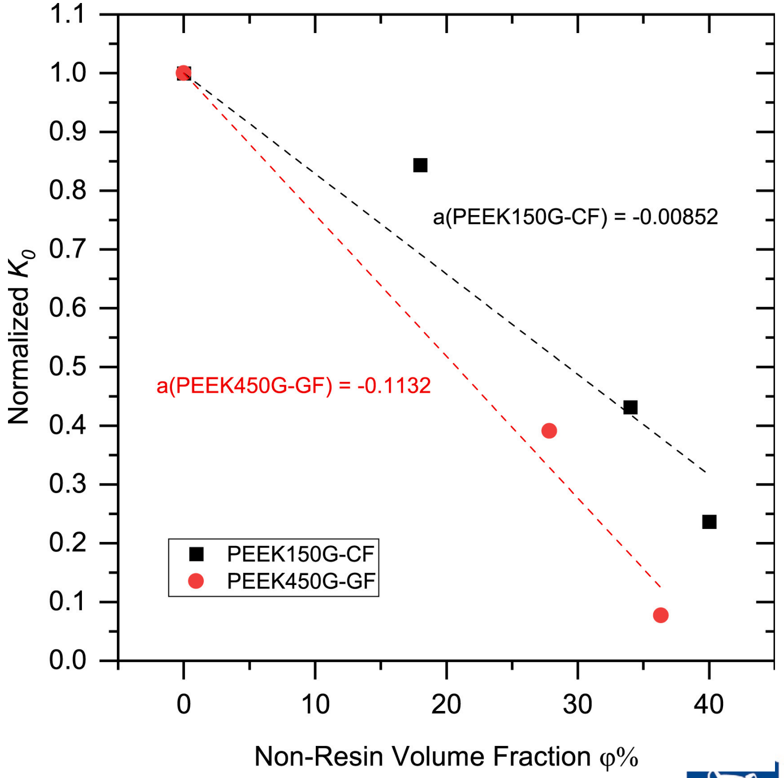
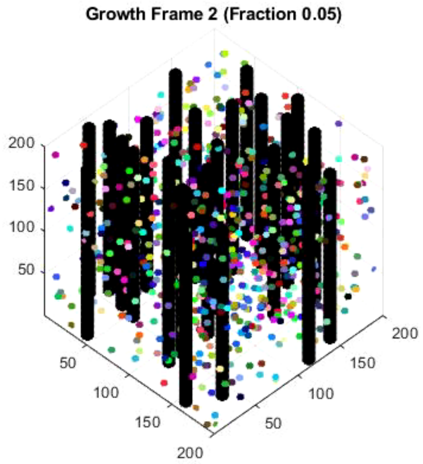
Effect of fibers on HL constant (K0)

$$\frac{1}{t_{0.5}(T_c)} = \boldsymbol{K_0} \exp\left[\frac{-U^{\cdot}}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_G(T_c + T_m^\circ)}{2T_c^2 \Delta T}\right]$$

- X-ray CT was used to measure the volumetric fractions of voids and fibers.
- In the five PEEK composites studied, the Hoffman–Lauritzen model constant decreased with increasing non-resin volumetric fraction.
- The slowdown effect caused by fibers and voids is attributed to the early impingement of crystal growth.

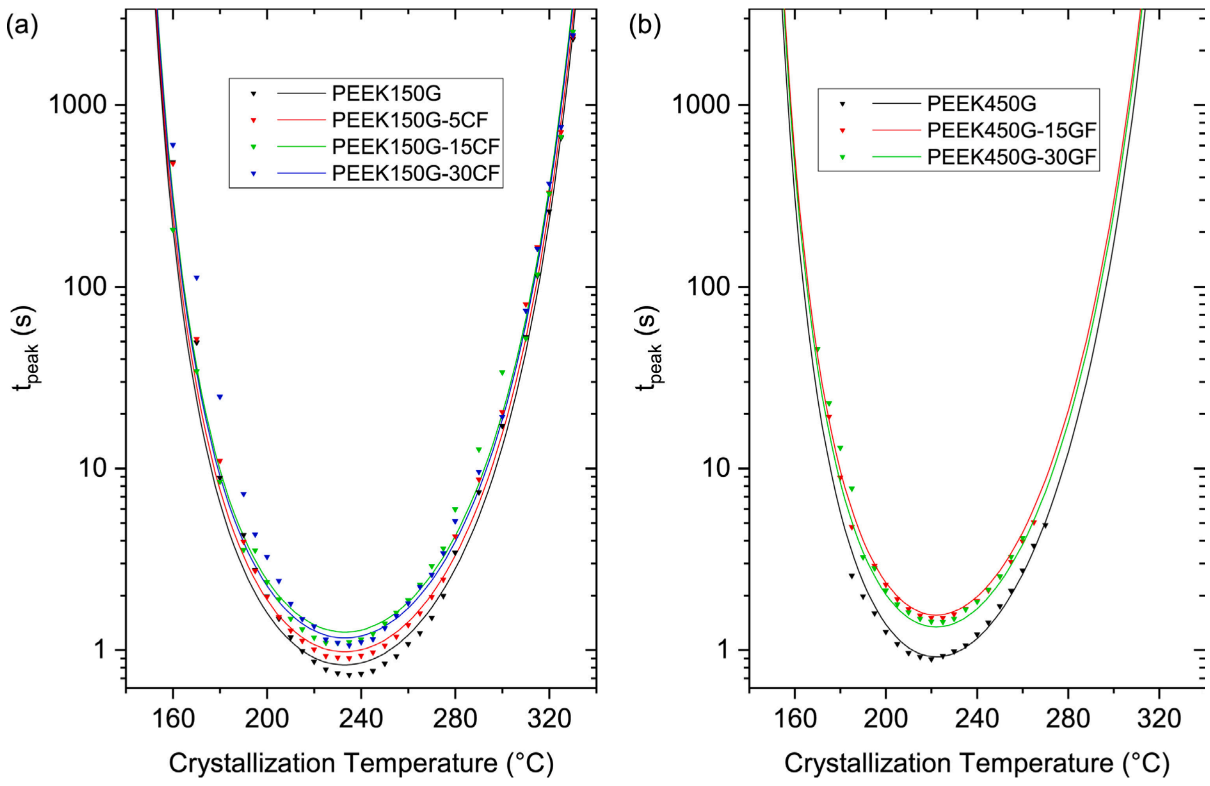






New model for quiescent crystallization kinetics

- Our proposed new model can accurately describe the overall crystallization kinetics in PEEK fiber-reinforced composites.
  Only one additional parameter, *a*, is required, since the volumetric fraction of resin is relatively easy to estimate.



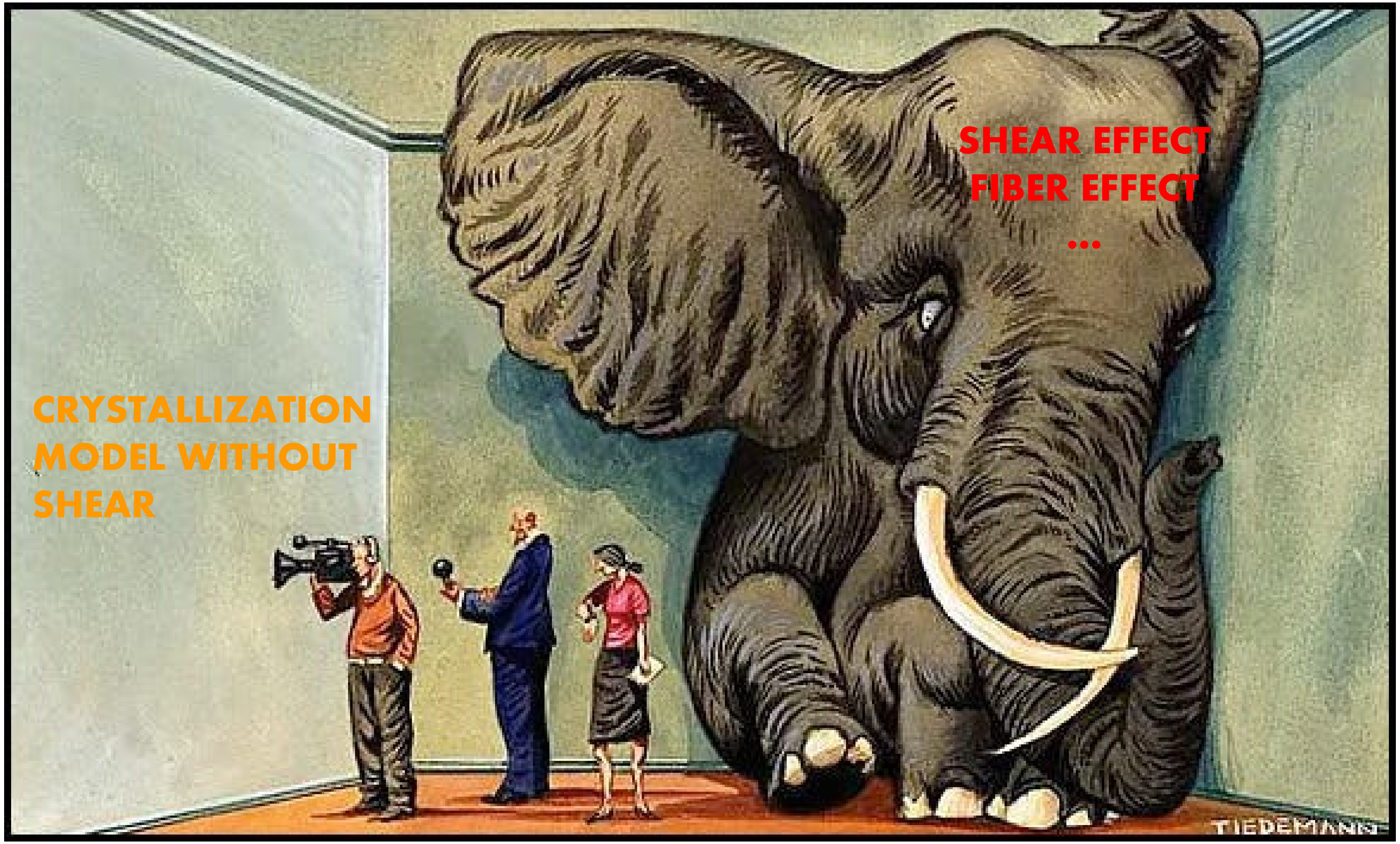
$$\frac{1}{t_{0.5}(T_c)} = \boldsymbol{K_0} \exp\left[\frac{-U^{\cdot}}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_G\left(T_c + T_m^{\circ}\right)}{2T_c^2 \Delta T}\right]$$

$$\downarrow$$

$$\frac{1}{t_{0.5}(T_c)} = [\boldsymbol{1} + \boldsymbol{a}(\boldsymbol{1} - \varphi_{\text{resin}})]\boldsymbol{K_0} \exp\left[\frac{-U^{\cdot}}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_G\left(T_c + T_m^{\circ}\right)}{2T_c^2 \Delta T}\right]$$

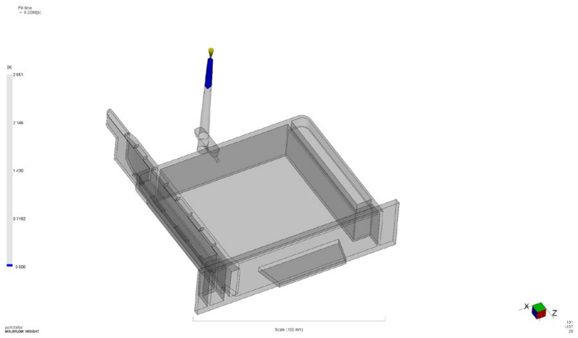
(a=0 for neat resin, a<0 for composites)

ELEPHANT IN THE ROOM!



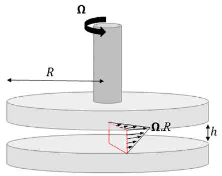
Cartoon by Gaurav Jain

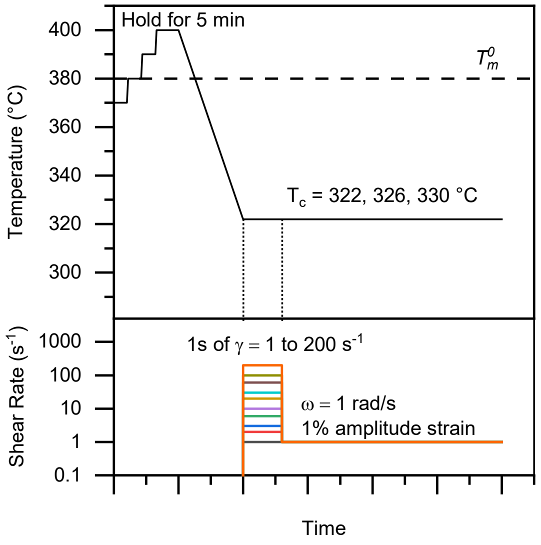
- Majority of the injection molding processes involve high shear conditions.
- It is often assumed that the presence of fibers does not alter crystallization under shear – but is this assumption valid?
- Most shear-induced crystallization models do not account for the effect of fibers.



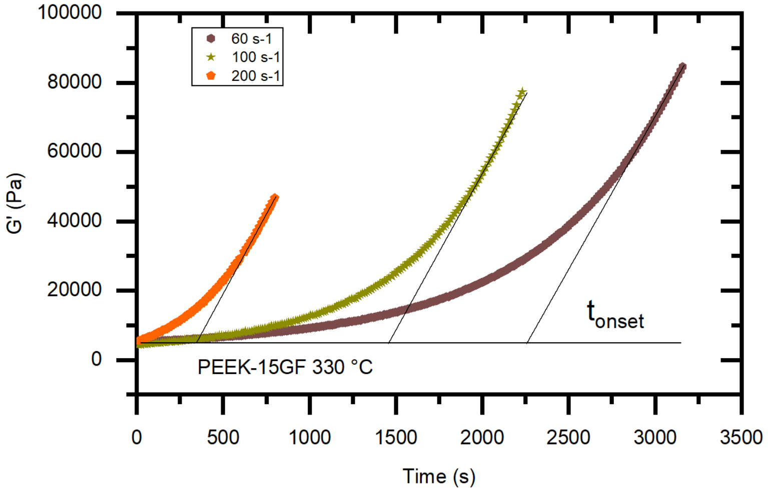
Flow-induced crystallization

- Experiments were carried out utilizing the ARES-G2 with a parallel plate.
- Different shear rates were applied to introduce varying levels of specific work.
- At higher shear rates, the nucleation time of the polymer decreases.





$$W = \eta \dot{\gamma}^2 t_s$$



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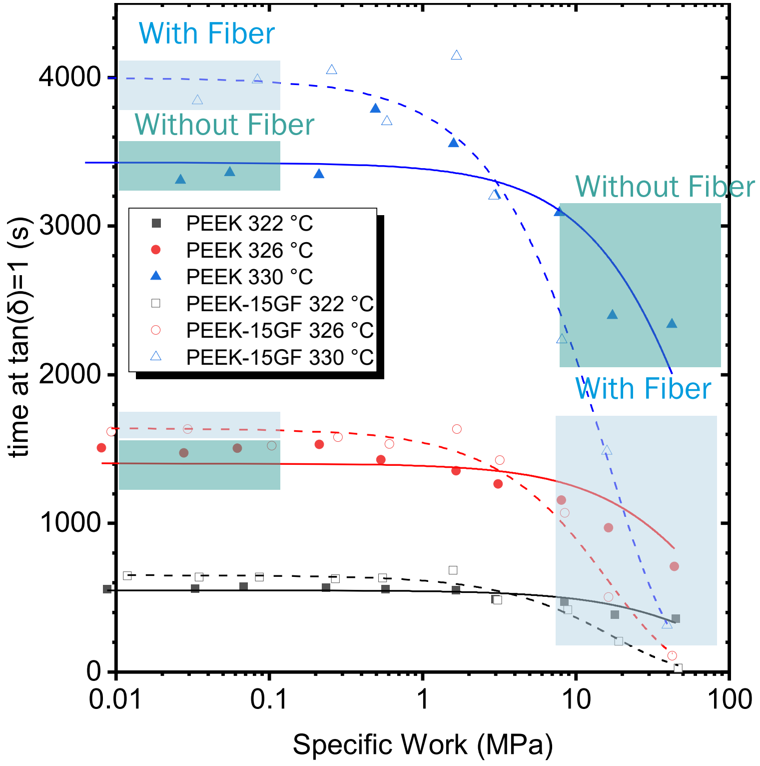
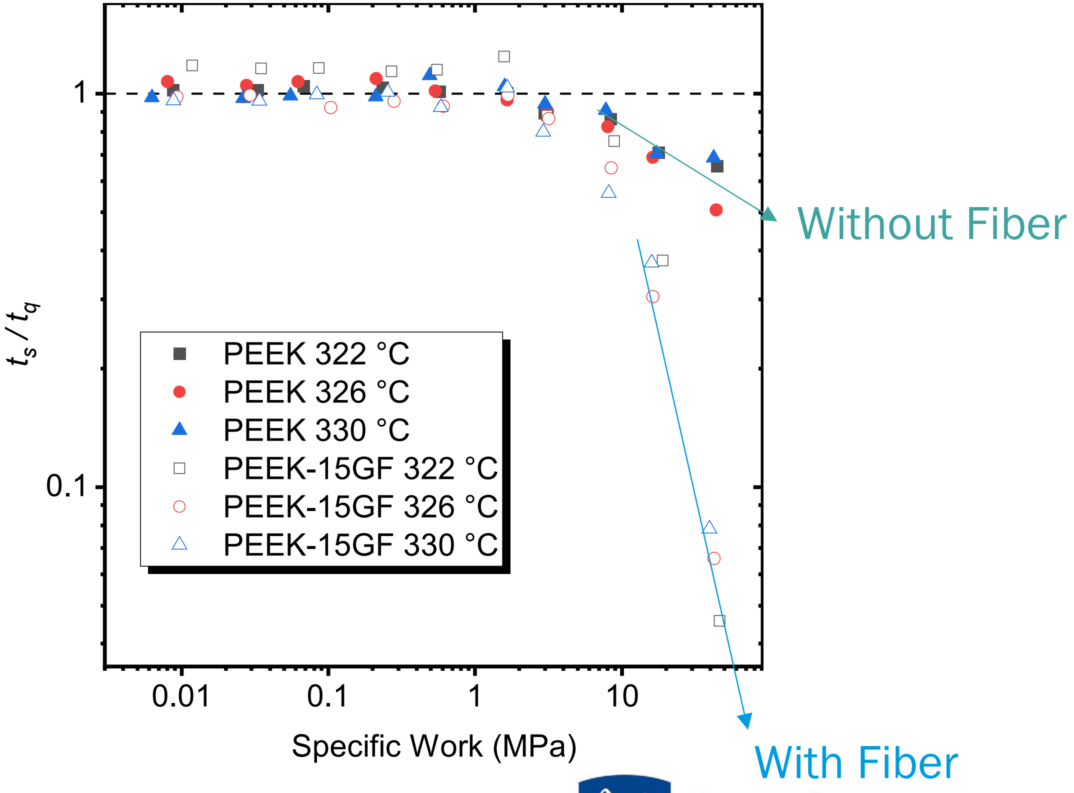
Flow-induced Crystallization Acceleration

- Under near-quiescent conditions, the addition of fiber slows down the crystallization of PEEK.
- PEEK glass fiber composites show a notably stronger responsive to flow-induced acceleration.
- Normalization using the ratio of crystallization time after shear to quiescent crystallization time shows universal trends.





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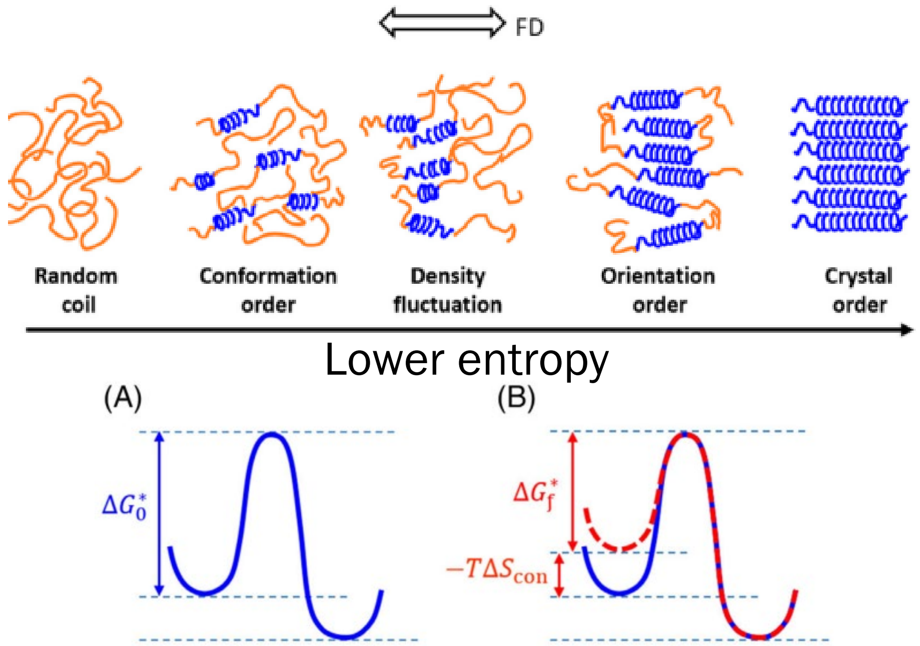
Flory Entropy Reduction Model

- Polymer flow helps stretch random coils into more oriented chains.
- This process reduces the degree of disorder (entropy or S), thereby increasing the value of $-T\Delta S$.
- As a result, the free energy barrier for nucleation decreases, making it easier to form nuclei.
- In our model, the applied specific work partially contributes to coil stretching and entropy reduction. This effect can be represented by the following equation:



Amount of specific work

Change in free energy barrier: $-T\Delta S = -V^*(T_c)WE$

Energy conversation rate

Change in Overall crystallization Kinetics:

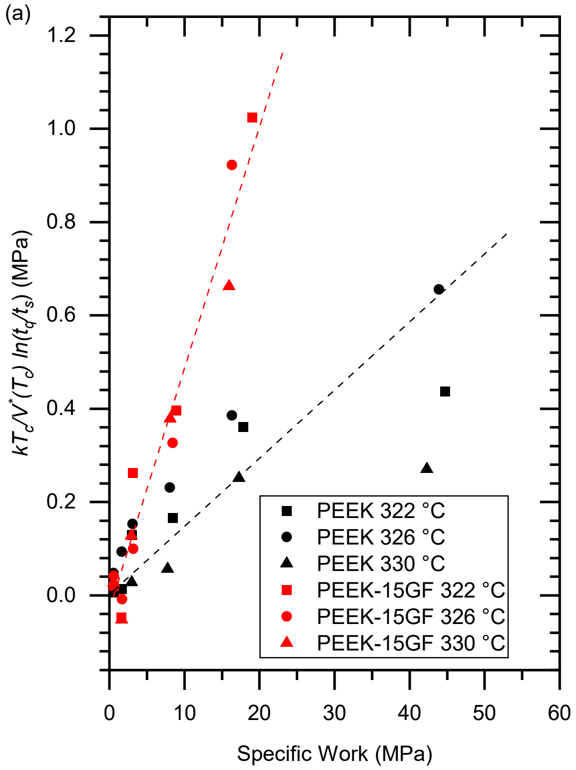
$$t_s = \frac{t_q}{\exp\left(\frac{V^*(T_c)WE}{kT_c}\right)}$$

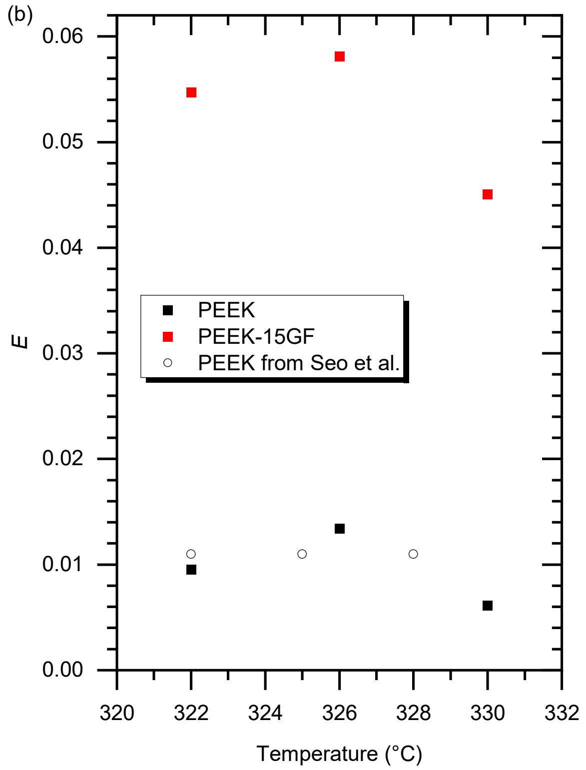
With Shear Condition (W > 0 for shear)

J. Polymer Sci., 2022, 60(23), 3149 - 3175

New model for flow-induced crystallization of PEEK Composites

- By combining Flory's entropy reduction model with the Hoffman–Lauritzen heterogeneous nucleation model, we can extract the energy conversion factor, *E*.
- In neat resin, approximately 1% of the applied shear energy contributes to chain alignment. In composites, this value is about five times higher.
- Based on these findings, we propose a new model for flow-induced crystallization in PEEK composites.





$$\frac{1}{t_S(T_c)} = \left[1 + a(1 - \varphi_{resin})\right] K_0 \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_G(T_c + T_m^0)}{2T_c^2 \Delta T}\right] \exp\left[\frac{-V^*(T_c) W E}{kT_c}\right]$$

Composites Effect: a=0 for neat resin, a<0 for composites

Shear Effect: W = 0 for no shear, W > 0 for shear

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Conclusions

AUTODESK Moldflow Insight 2026?

For those interested in methodology

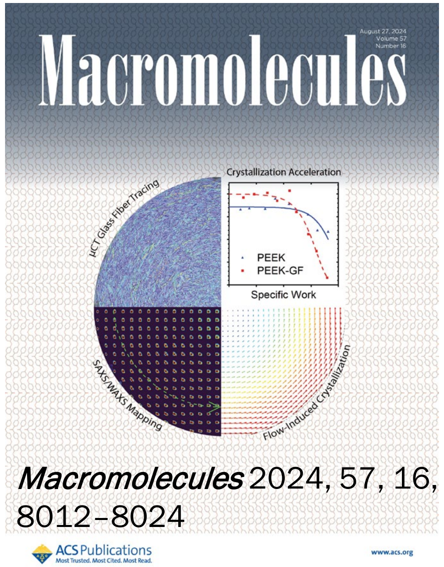
- We have the capability to characterize composites under both high undercooling near quiescent and high shear conditions.

- Our team has developed methodologies to monitor the kinetic responses.

For those interested in flow simulation

- The inclusion of fibers may hinder crystallization in near quiescent conditions, yet significantly expedite it under shear forces.

- The acceleration of flow-induced crystallization, along with the alignment of the resin and the dynamics of the fibers, are crucial factors that should not be overlooked in simulations.



Macromolecules 2024, 57, 16, 8012–8024

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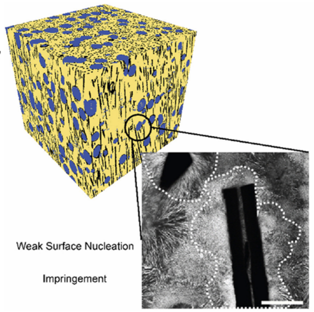
Alex McHale (Penn State Behrend; Honda)

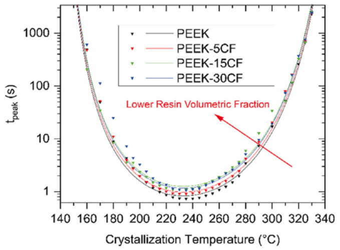
Evan Quinn (Penn State Behrend; Port Erie Plastics)

Quiescent Crystallization kinetics of PEEK composites

Zhang, Alexander, Seo, Gohn, Behary, Schaake, Colby, Rhoades, ***Thermochimica Acta***, 2023. 721, 179442

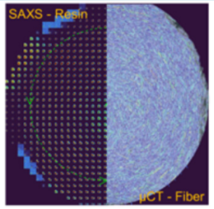
Zhang, Flanigan, de Kort, Colby, Rhoades, **Composites Part B: Engineering**, 2025, 112386

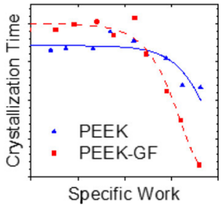




Flow-induced Crystallization of PEEK composites

Zhang, Alexander, Seo, Jacob, Kort, Schaake, Weigand, Rhoades, Colby, ***Macromolecules***, 2024. 57(16), 8012-8024





Thank you

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