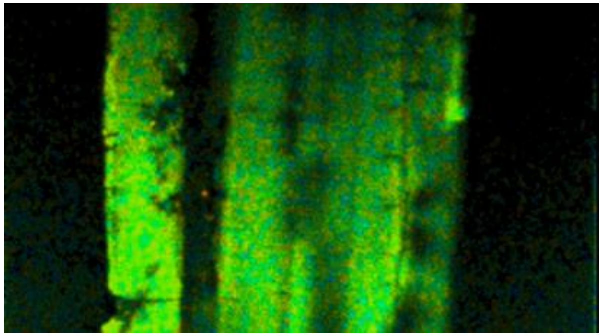
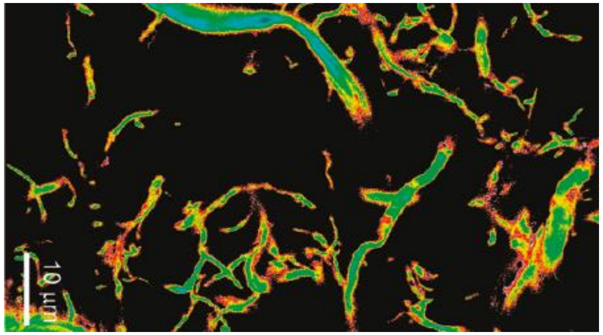
Fall 11-9-2015

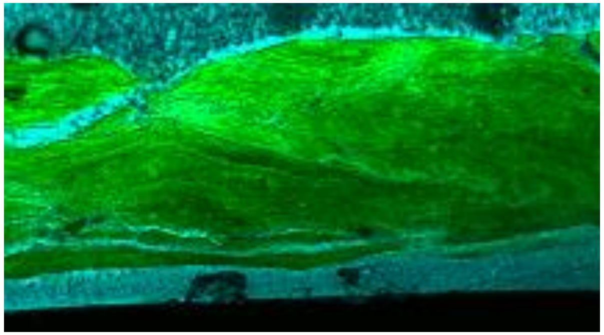
Imaging the interphase in polymer composites

Jeffrey Gilman
NIST

Visualizing Polymer Composite Interfacial Deformation







Chelsea Davis

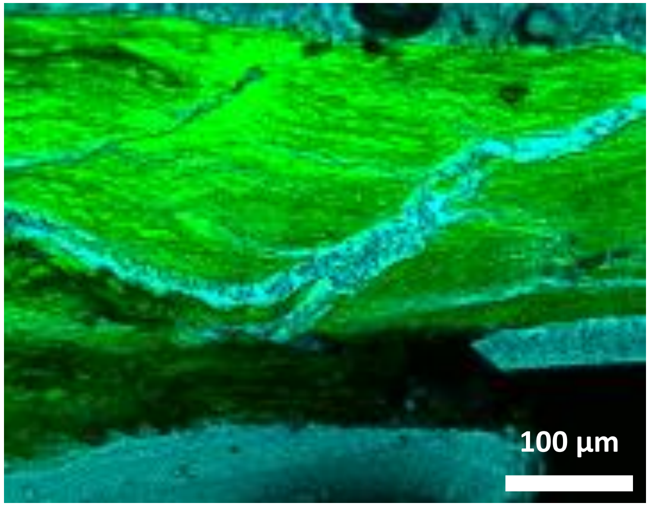
Jeremiah Woodcock, Ryan Beams

Stephen Stranick, Jeffrey Gilman

Material Measurement Laboratory

National Institute Standards and Technology

Interfacial Visualization Project Overview

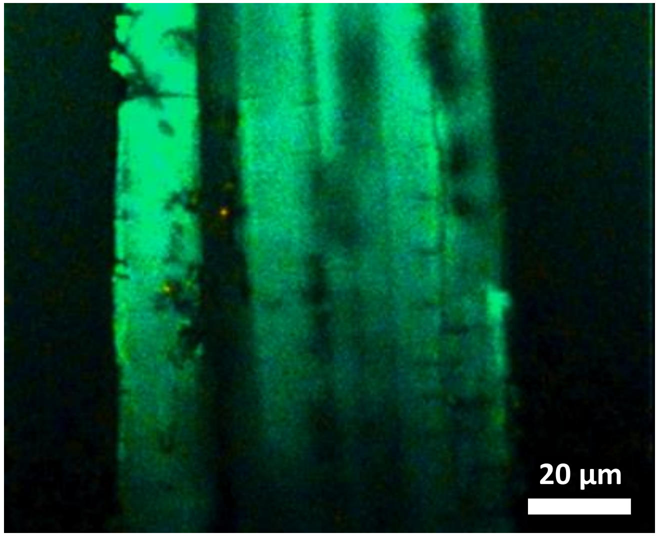


Debonding of interface via Förster Resonance Energy Transfer (FRET)

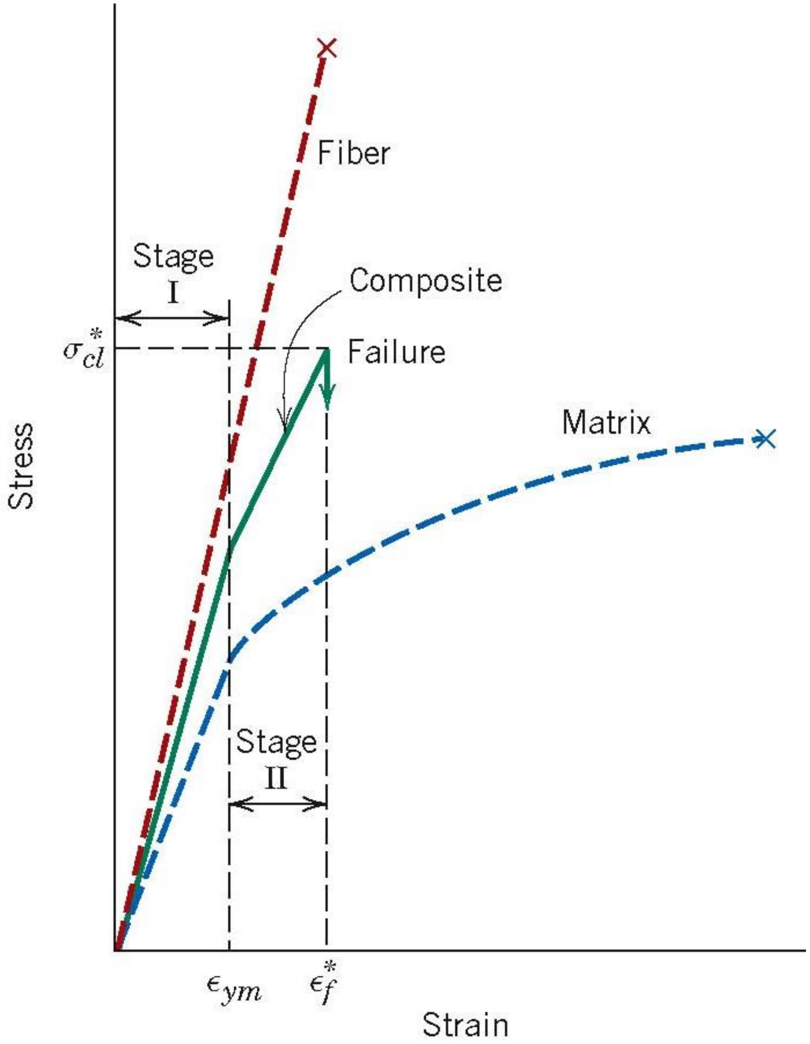
- Cellulose nanofibrils in epoxy
- Qualitative observation of interfacial separation in macroscopic composite

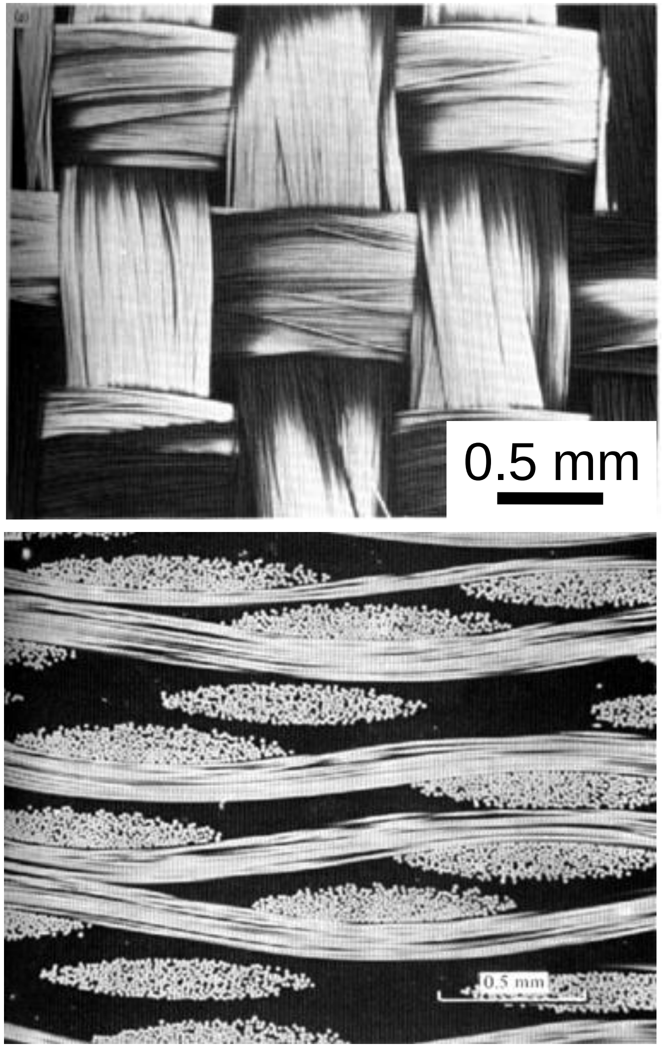
Fiber-reinforced composite interfacial damage sensing with mechanophores

- Silk fibers in epoxy
- Semi-quantitative measurement of stress transfer across interface in single fiber tensile experiments



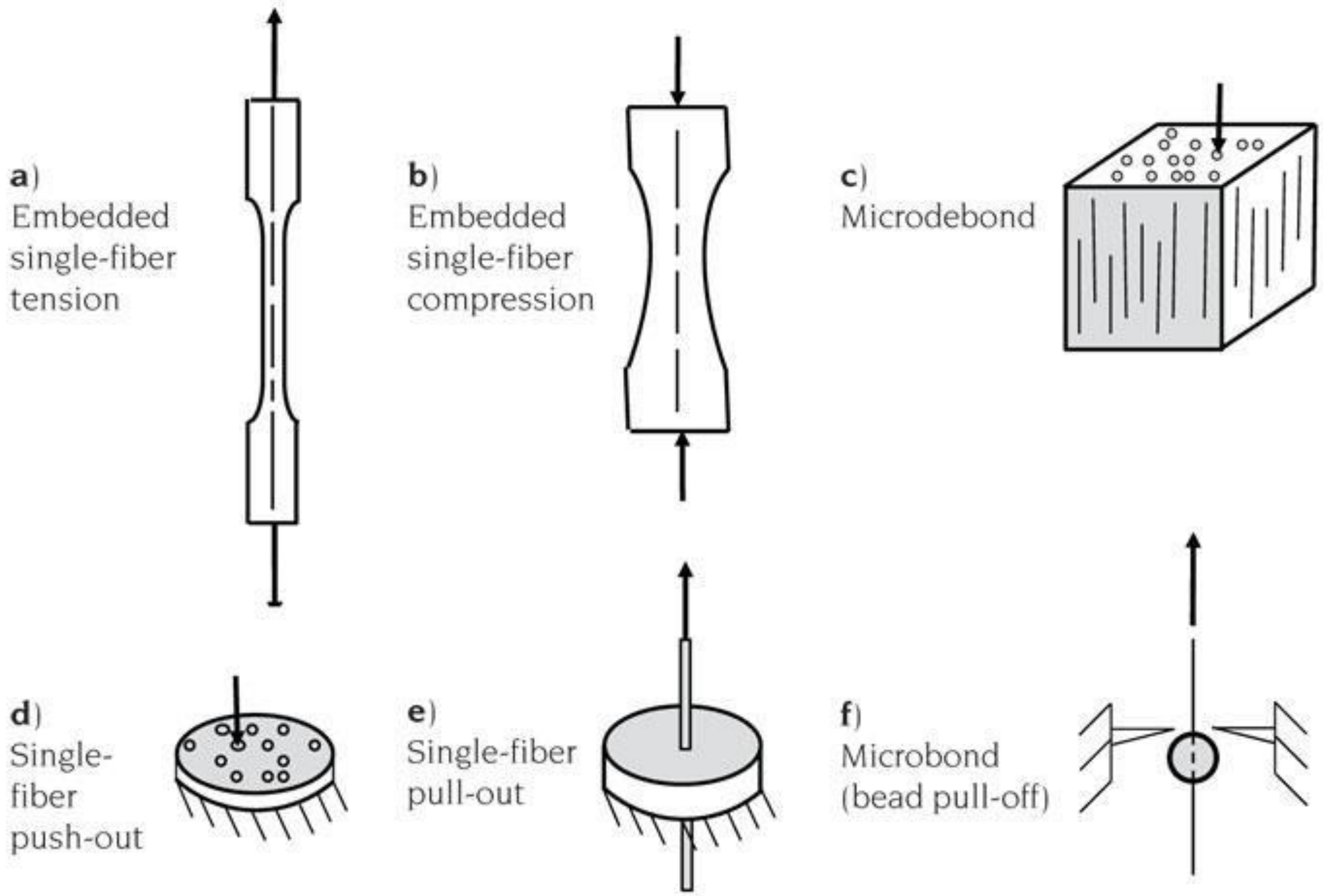
Why FRPCs?





D. Hull and T.W. Clyne, *Introduction to Composite Materials*, 2nd ed., 1996.

Composite Interfacial Strength Characterization



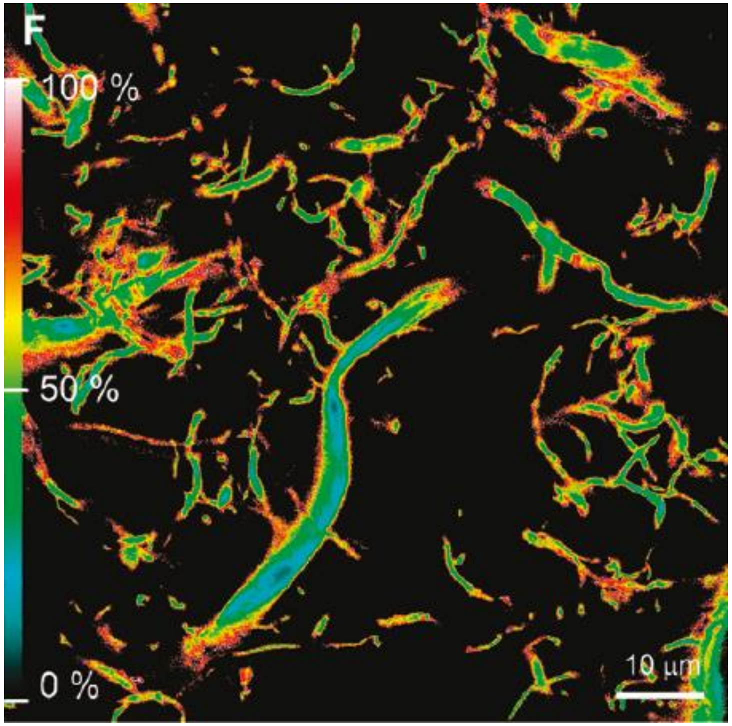
Current techniques allow quantification of macroscale composites; what about nanoscopic reinforcement?

Adams, CompositeWorld, 2011.

Visualizing Interfacial Debonding

Goal

- Develop and validate method to characterize interfacial debonding in a cellulose/epoxy nanocomposite

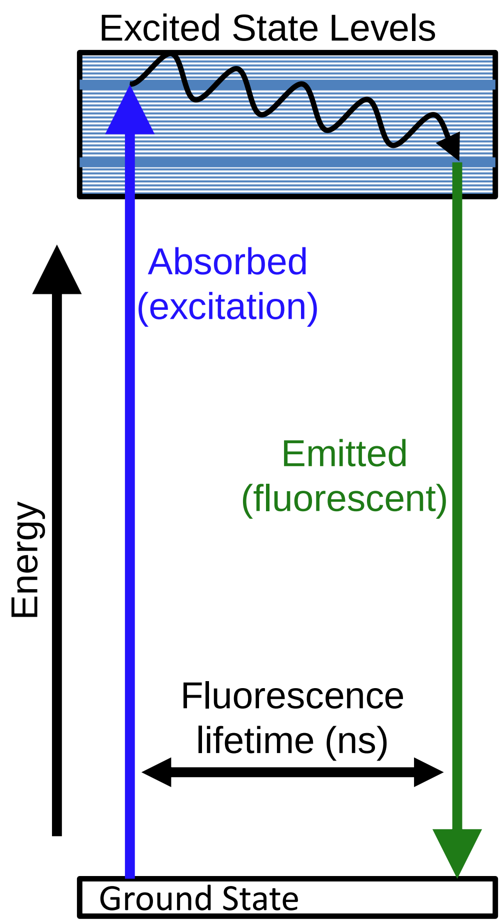


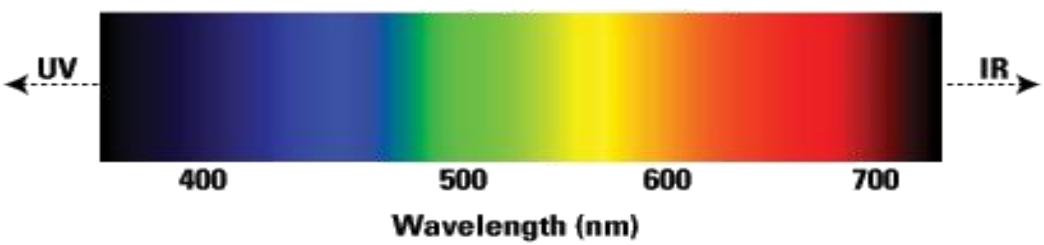
Approach

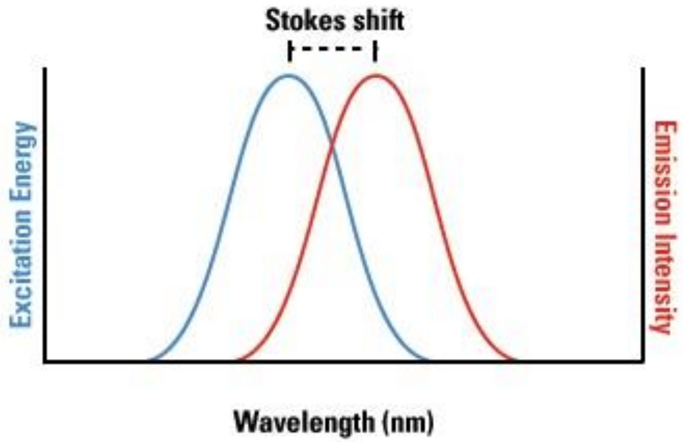
- Functionalize reinforcement and matrix phases with interacting FRET dye pair
- Prepare well defined interface (bilayer sample)
- Apply thermal treatment to damage interface

Zammarano M. et al., ACS Nano. 2011.

Förster Resonance Energy Transfer (FRET)

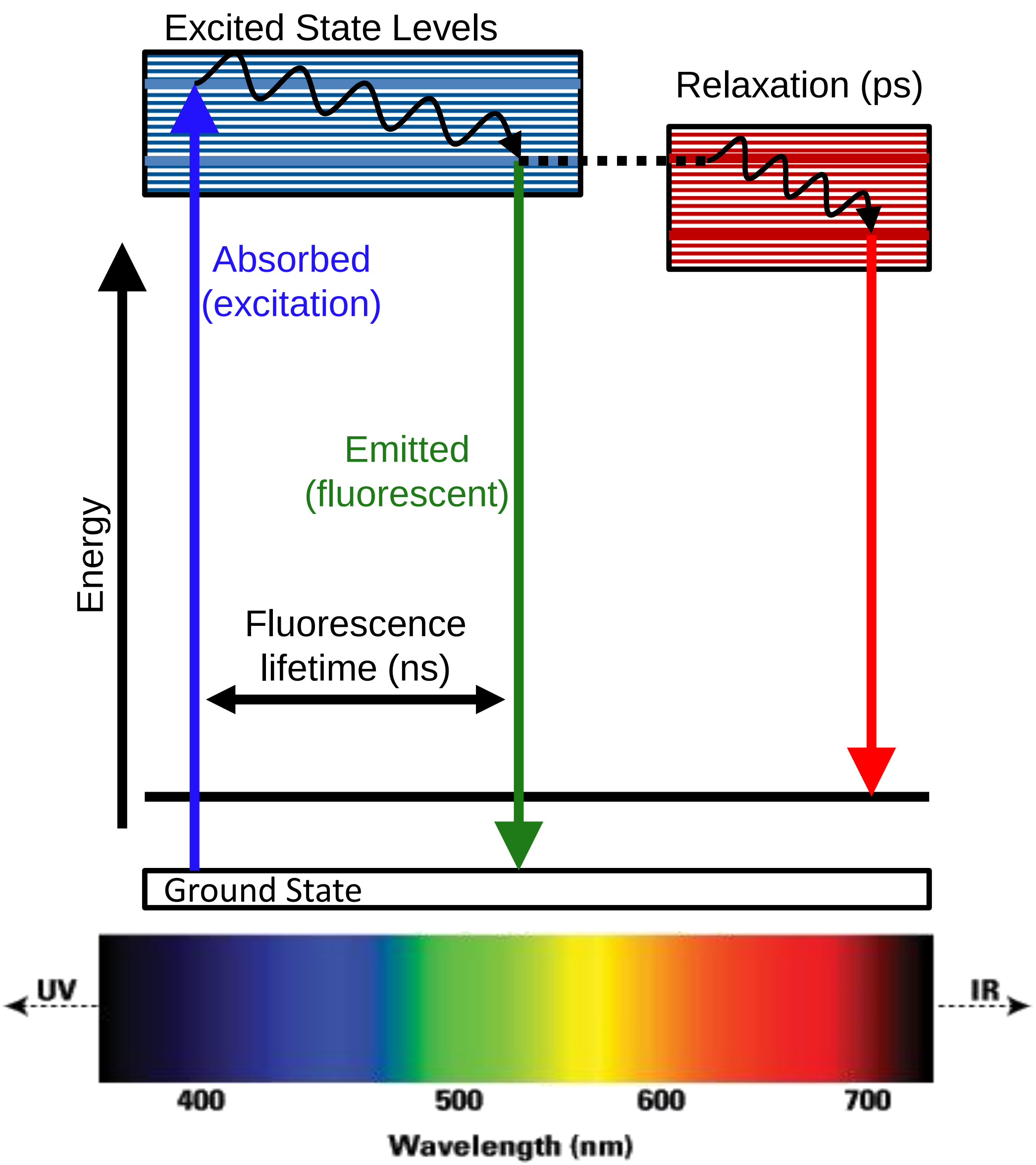


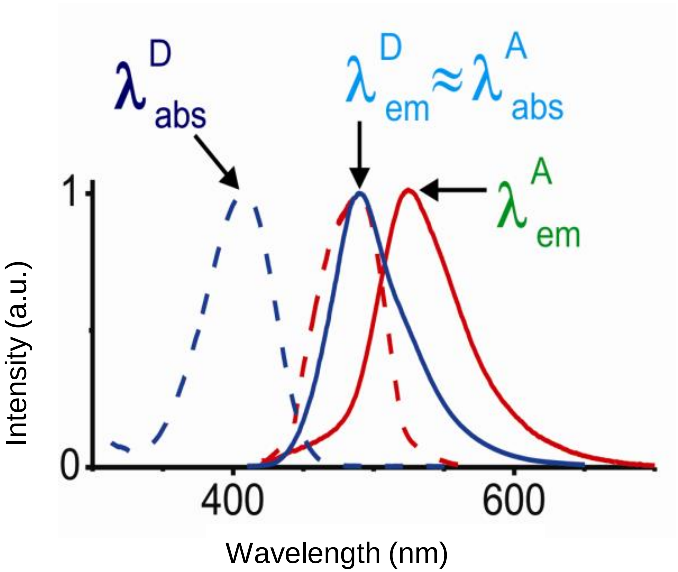




Förster, Annalen der Physik, 1948.
Clegg, Methods in Enzymology 1992.

Förster Resonance Energy Transfer (FRET)



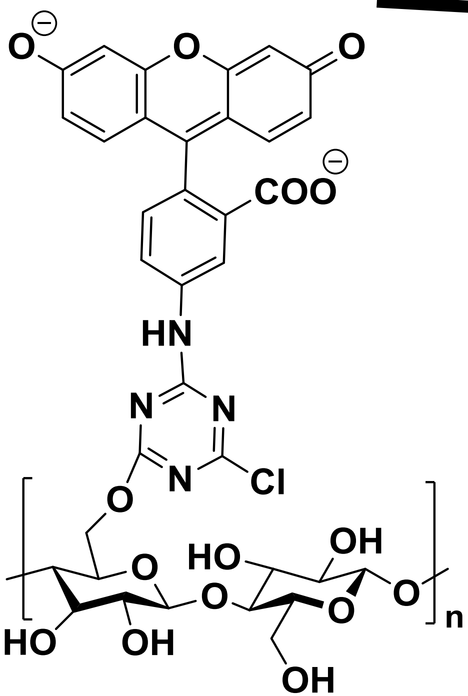


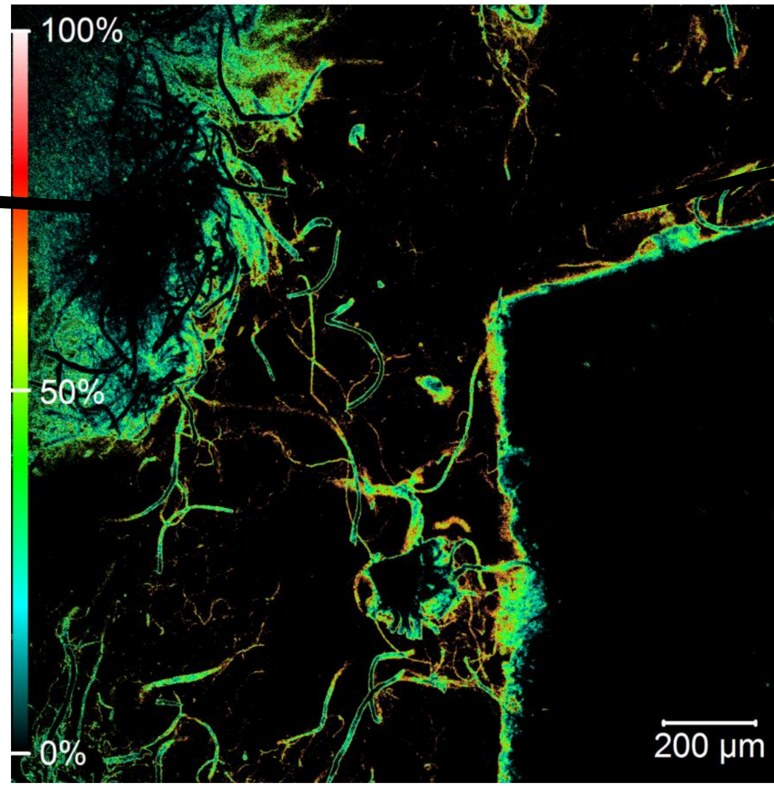
Förster, Annalen der Physik, 1948.
Clegg, Methods in Enzymology 1992.

FRET at a Composite Interface

Acceptor

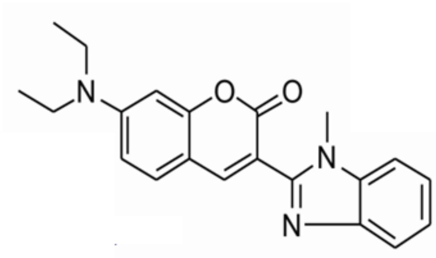
Cellulose
(DTAF)

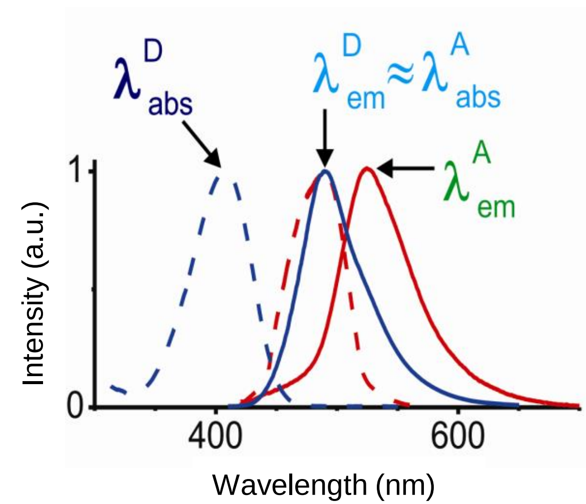




Donor

Polyethylene
(Coumarin)

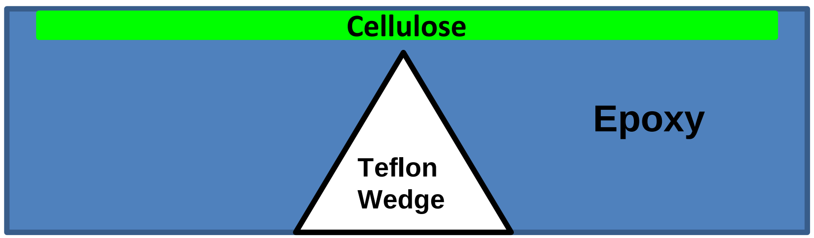




Zammarano M. et al., ACS Nano. 2011.

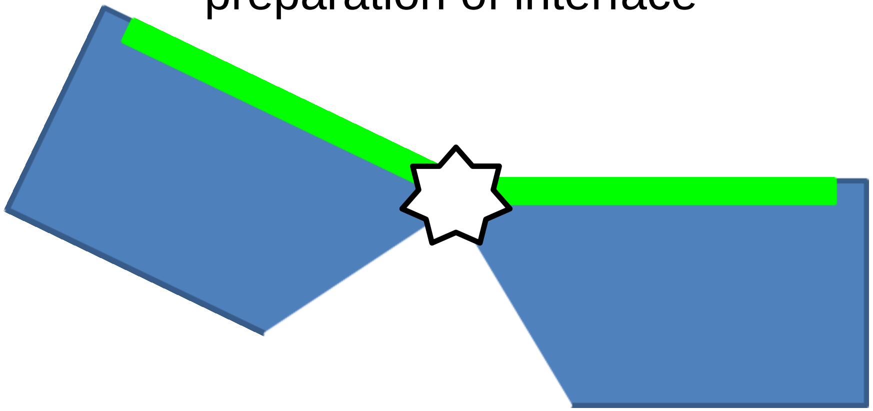
Bilayer Composite Interface Preparation

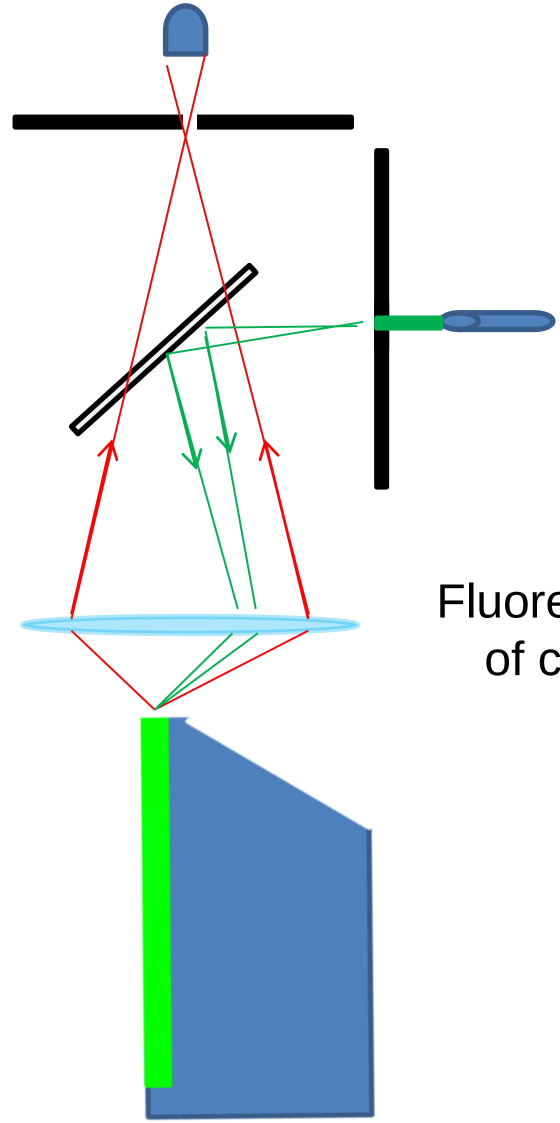
Molding of nanofibrillated cellulose onto partially-cured epoxy



Epoxy (DGEBA/Jeffamine D230)
with 0.1 mass% Coumarin
Pressed DTAF-modified cellulose

Freeze-fracture and surface preparation of interface

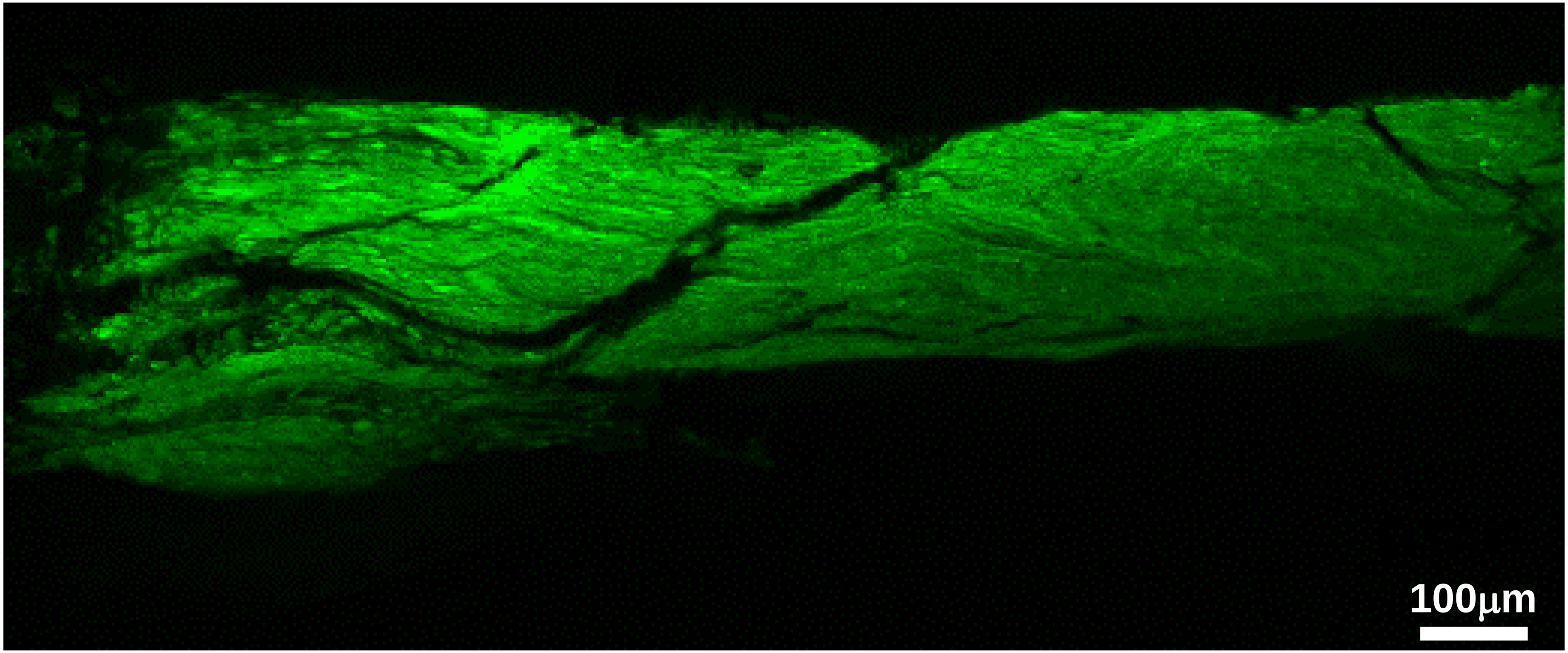


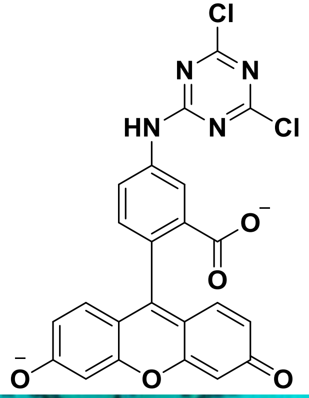


Fluorescent imaging of cross-section

J. Woodcock et al., In Preparation.

Cellulose (DTAF channel)

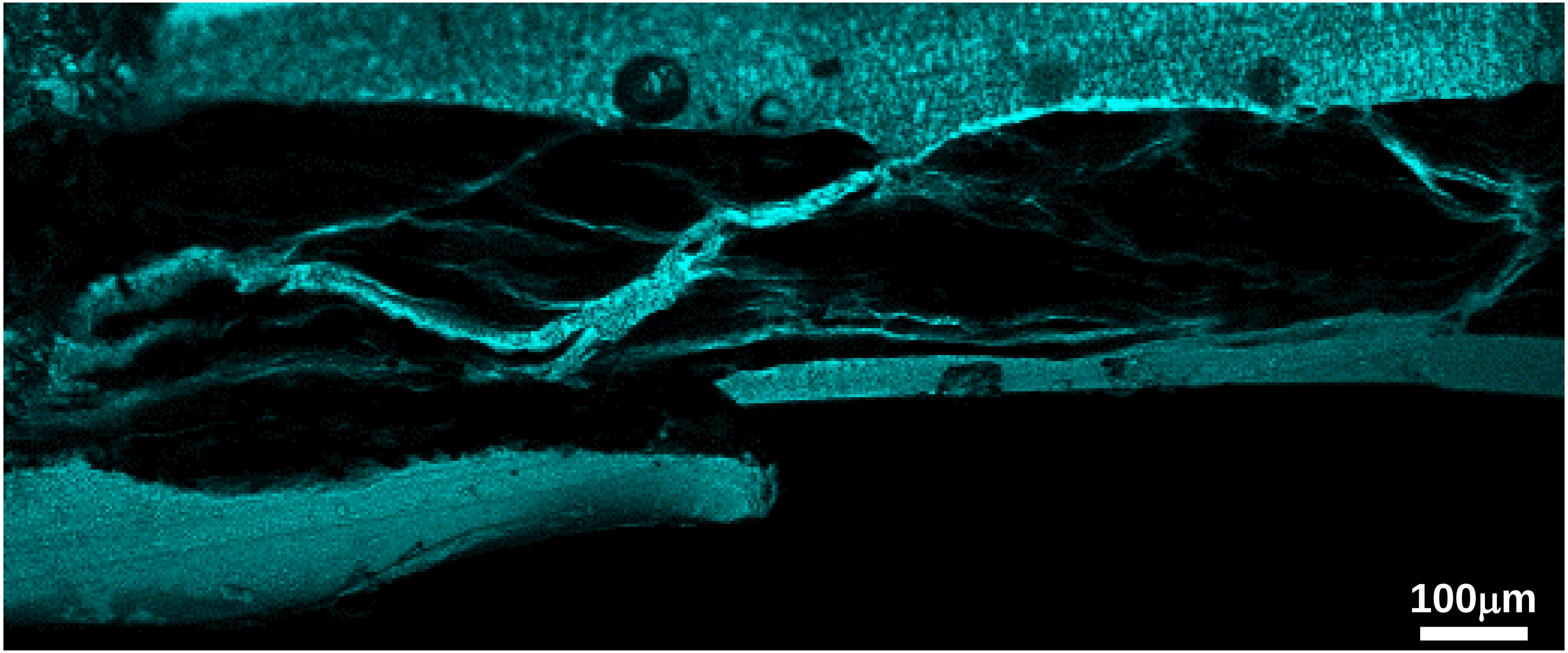


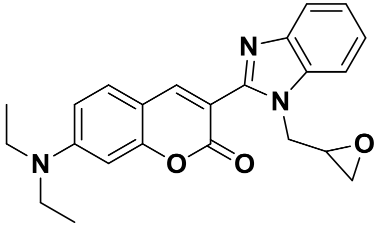


(Dichlorotriazinyl) Aminofluorescein (DTAF)

J. Woodcock et al., In Preparation.

Epoxy (Coumarin channel)

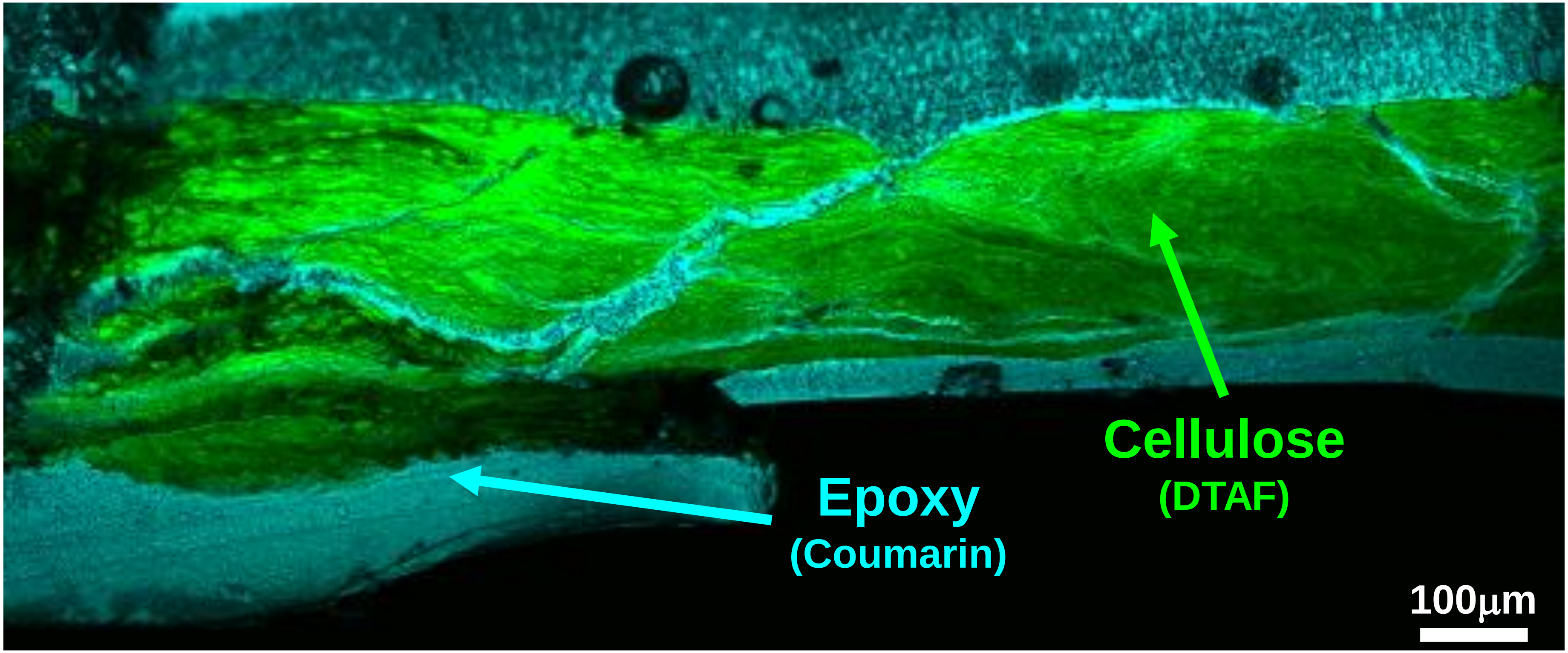




Epoxide-functionalized Coumarin

J. Woodcock et al., In Preparation.

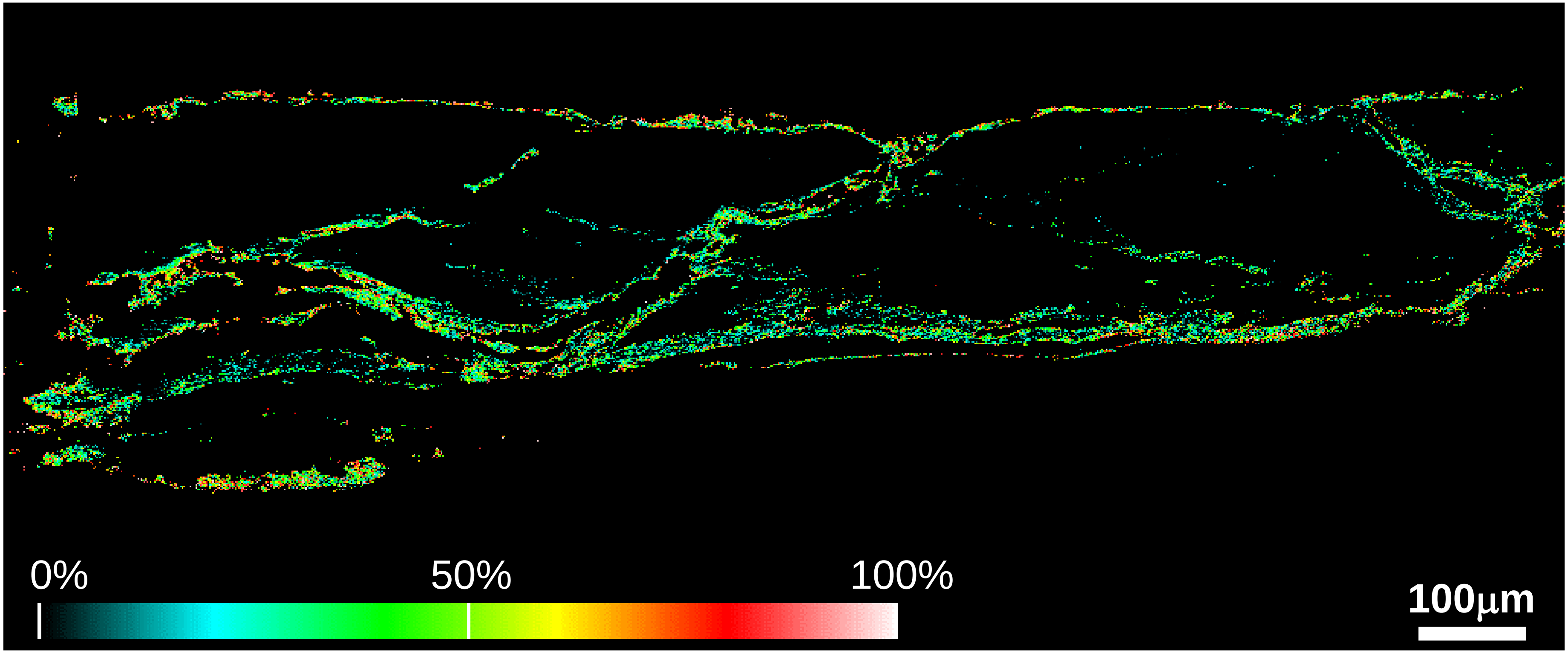
Dual Channel Image of Interface



2 channel composite image of Coumarin (λ=475 nm) and DTAF (λ=515 nm) emission

J. Woodcock et al., In Preparation.

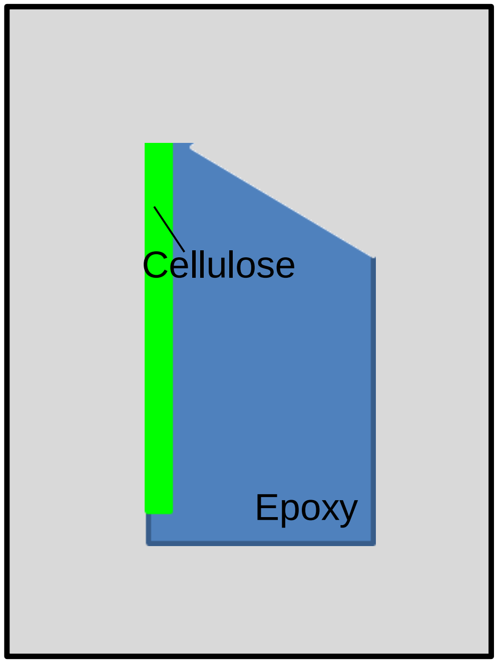
FRET Efficiency Map



J. Woodcock et al., In Preparation.

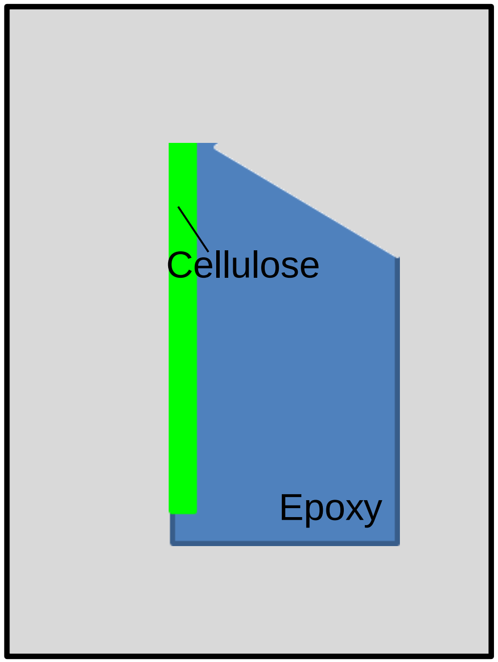
Interfacial Debonding Approach

Thermal Conditioning Cycle



Bilayer composite sample conditioned (T=40°C and controlled humidity)

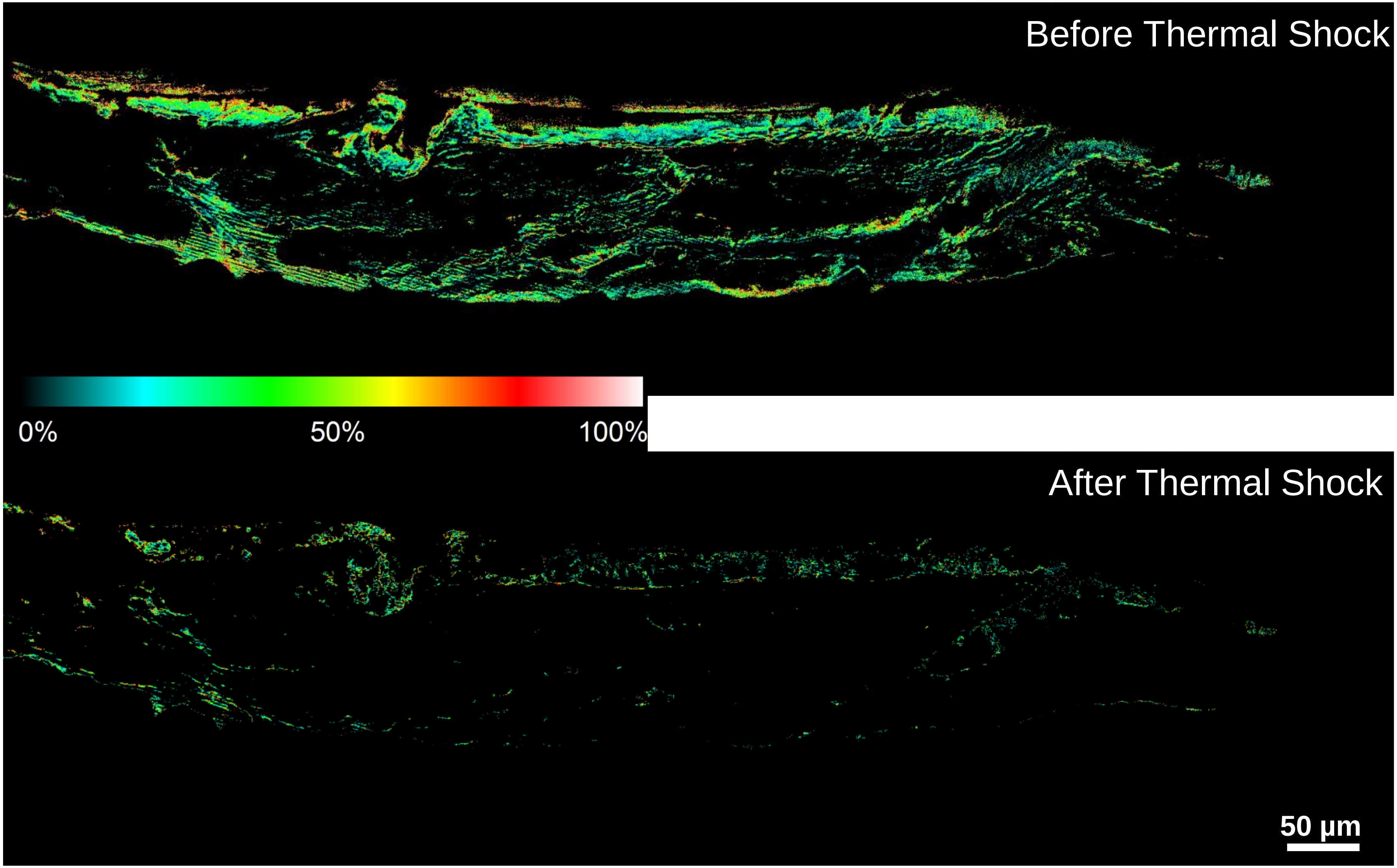
Sample submerged in liquid nitrogen for 5 min



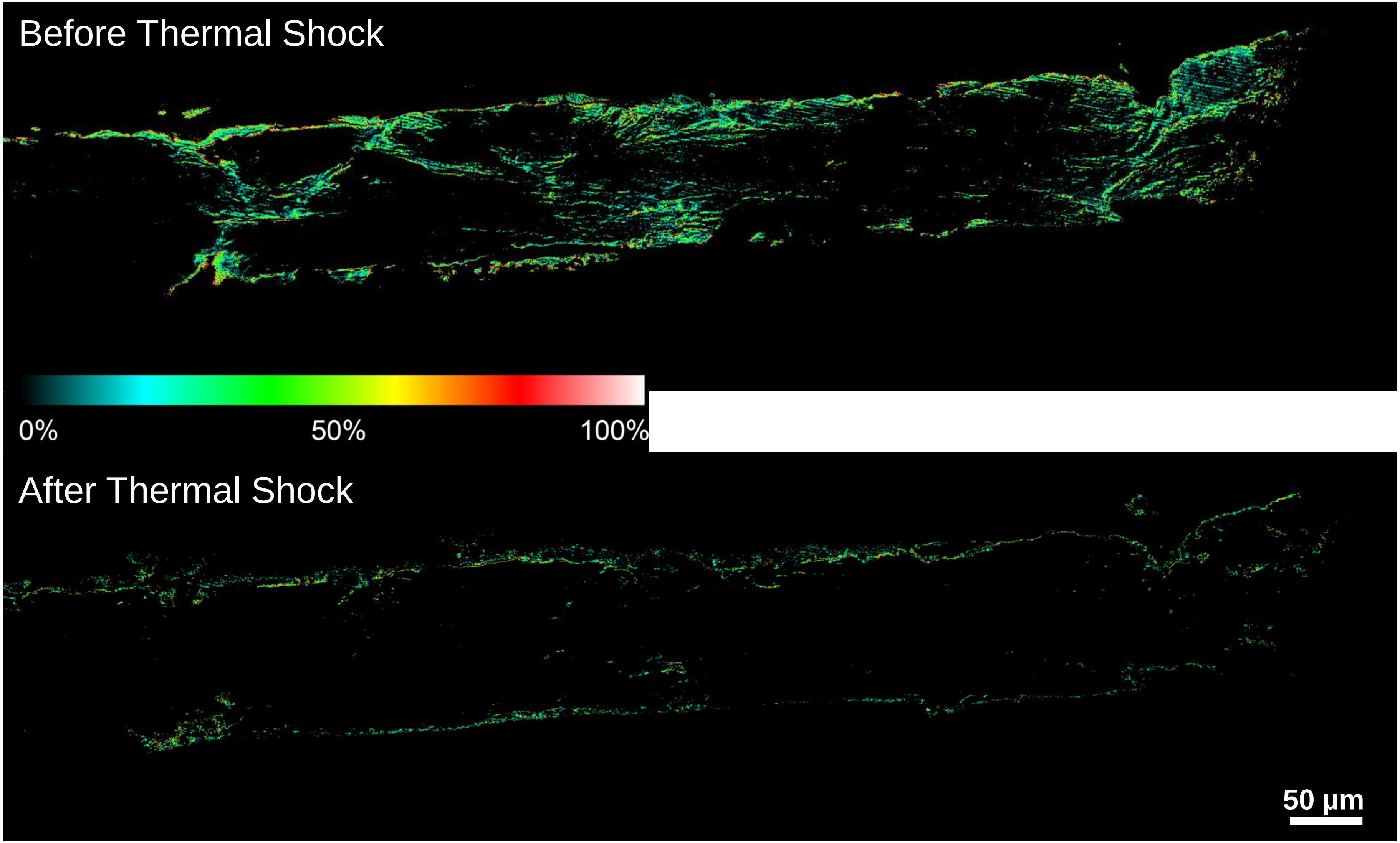
Sample replaced in conditioning chamber for 12 h (same conditions)

J. Woodcock et al., In Preparation.

Monitoring Debonding using FRET: Humidified



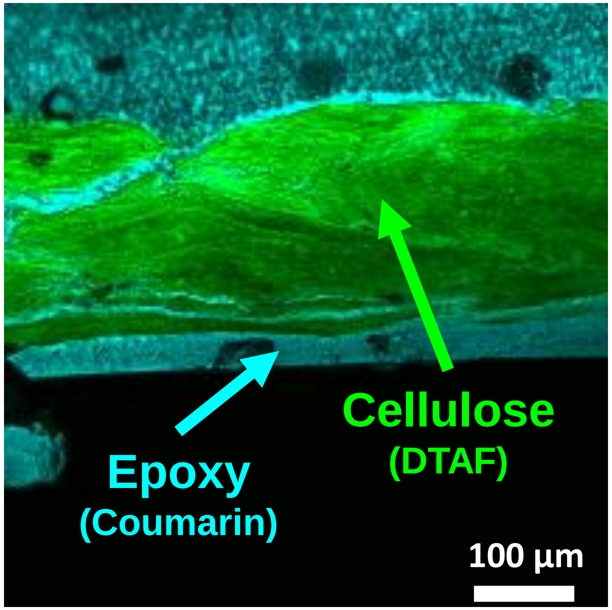
Monitoring Debonding using FRET: Dried

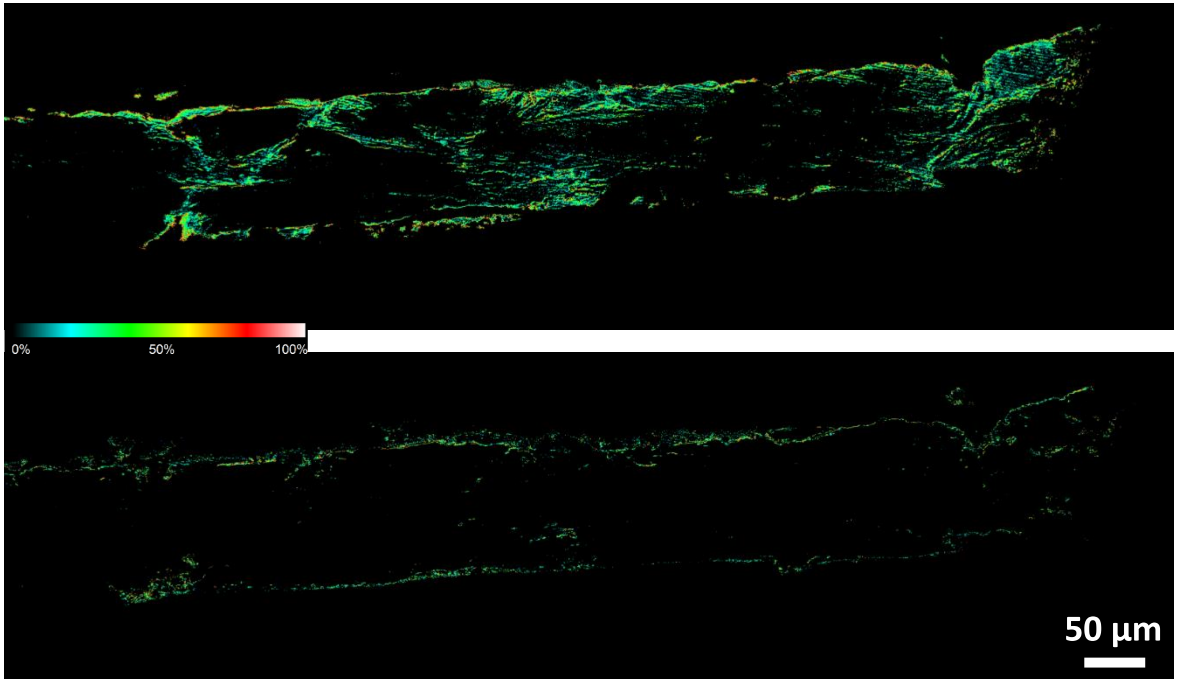


Cellulose Debonding Summary

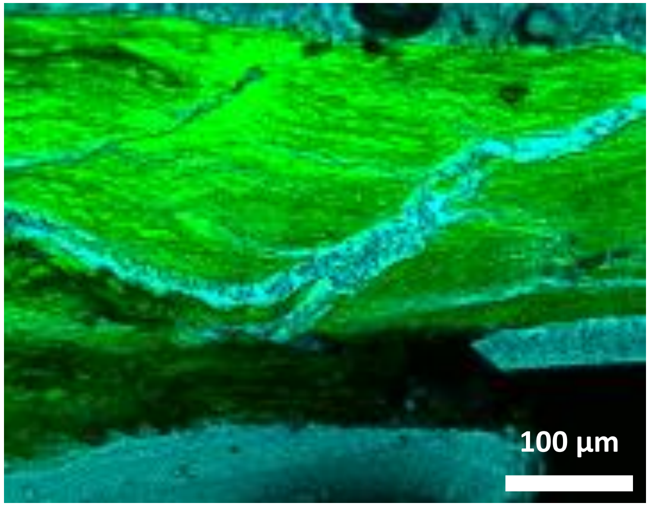
- Developed materials system to monitor interface in cellulose/epoxy composite system utilizing fluorescence microscopy

- Presented first results demonstrating optical imaging of sub-micron interfacial debonding





Interfacial Visualization Project Overview



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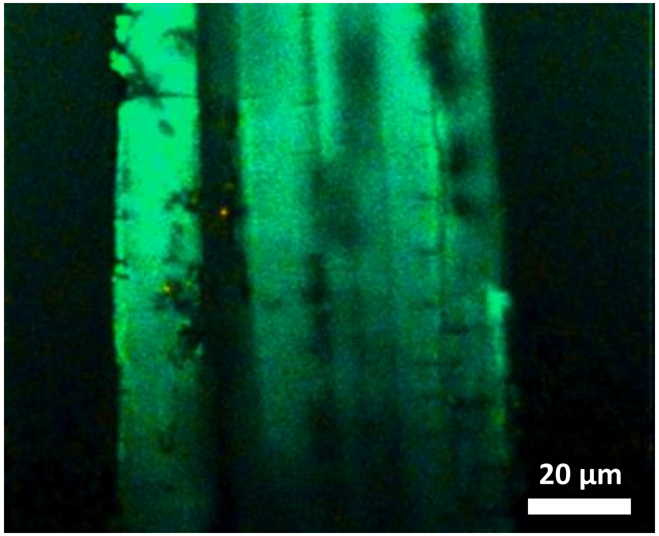
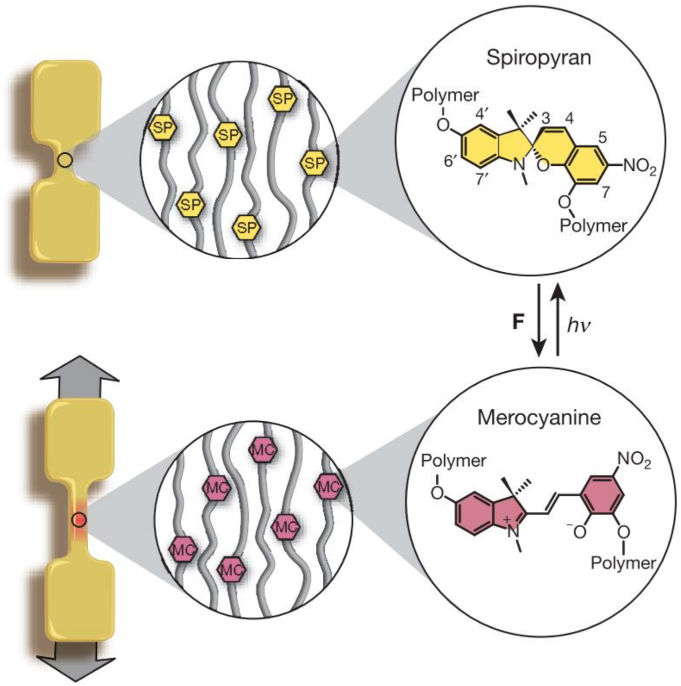
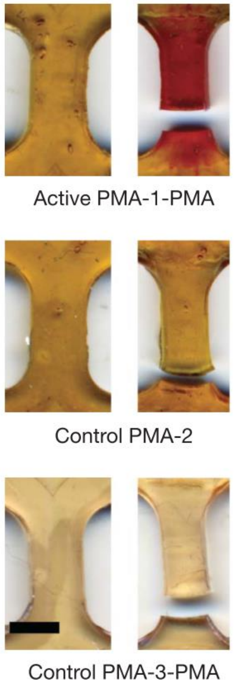
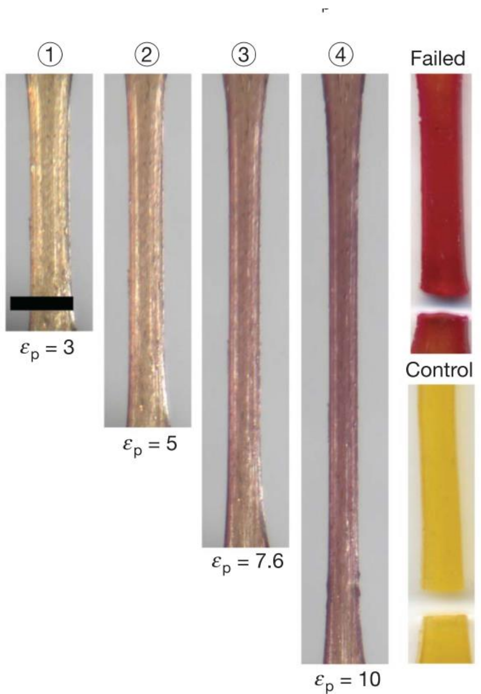


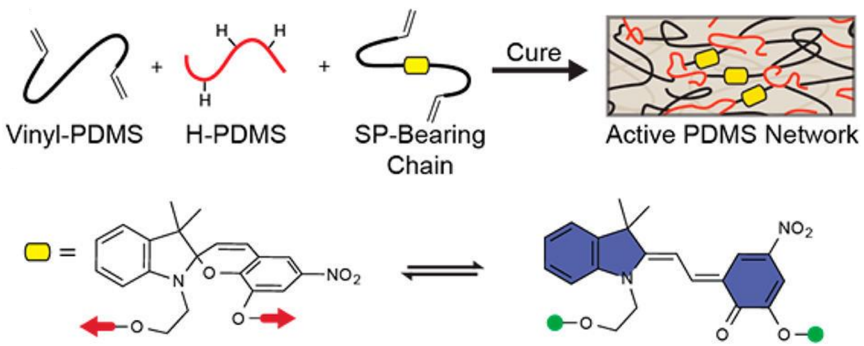
Previous Mechanophore Work







Potisek, et al., JACS 2007.
D. Davis, et al., Nature 2009.



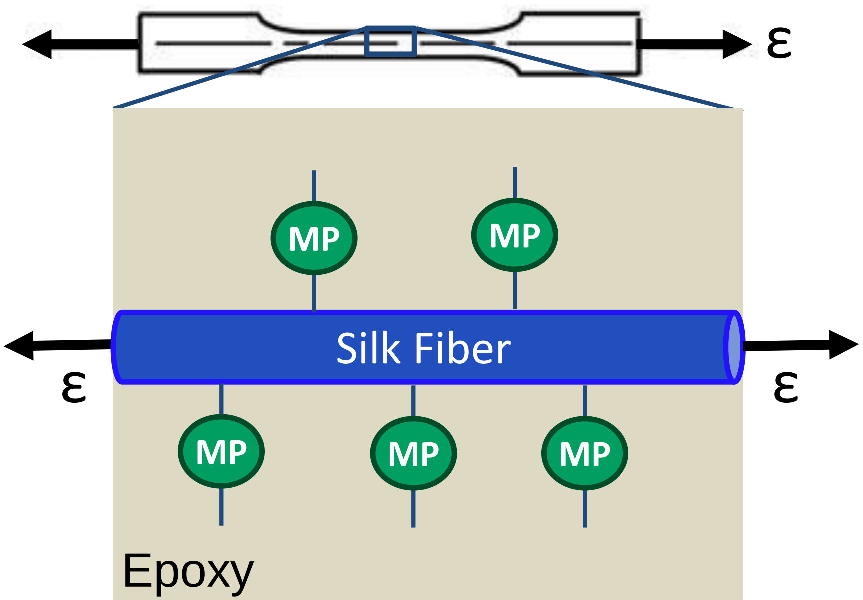
Gossweiler, et al., ACS Mac. Let. 2014.

Interfacial Mechanophore in Silk Fiber System

Goal

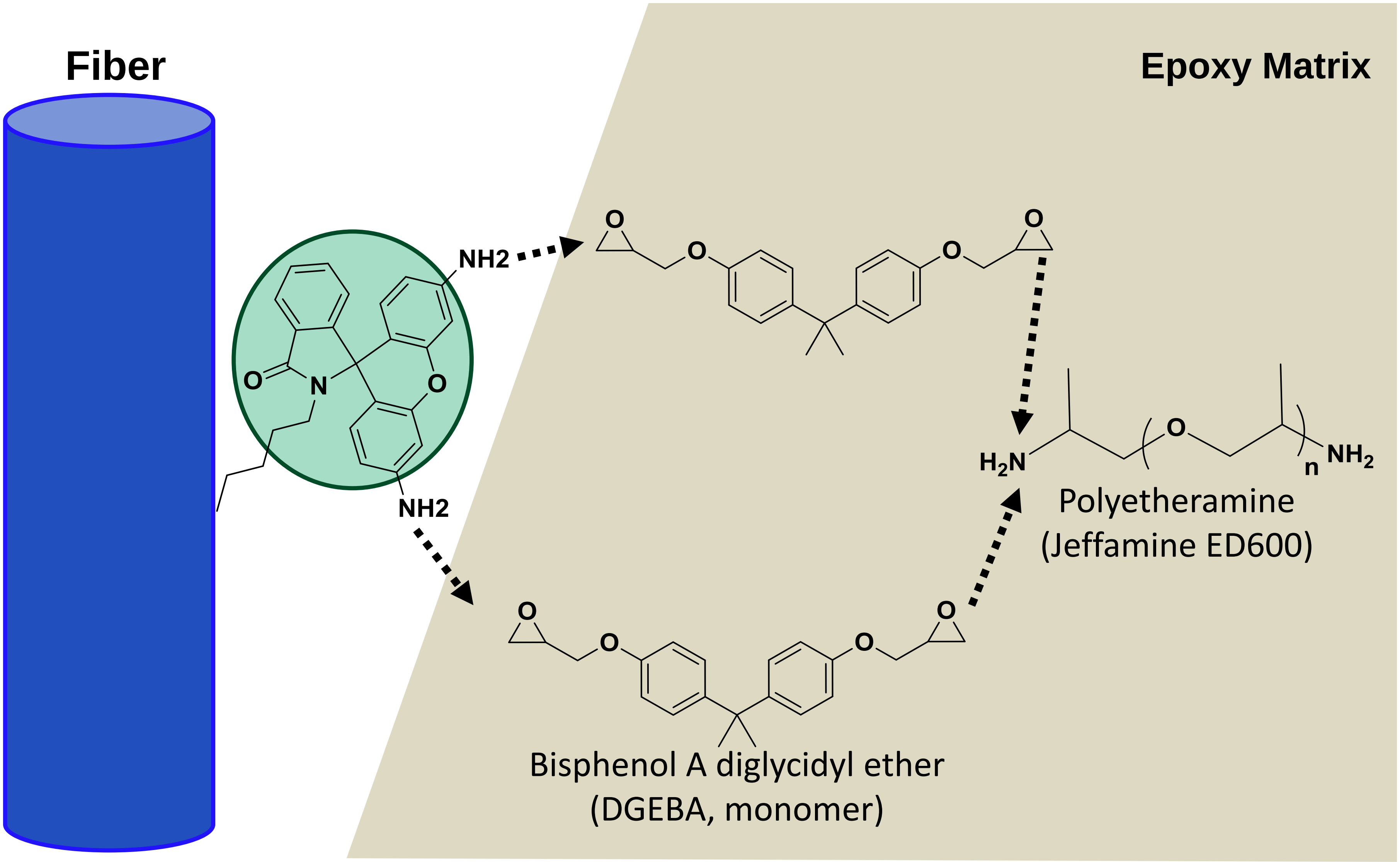
- Detect interfacial separation in a fiber-reinforced composite using fluorescent activation

Approach



Collaborators:
Silk provided by F. Volrath (Oxford Silk Group)
Silk functionalization by J. Woodcock (MML)
FLIM imaging with R. Beams (MML) and S. Stranick (MML)

Mechanophore Attachment

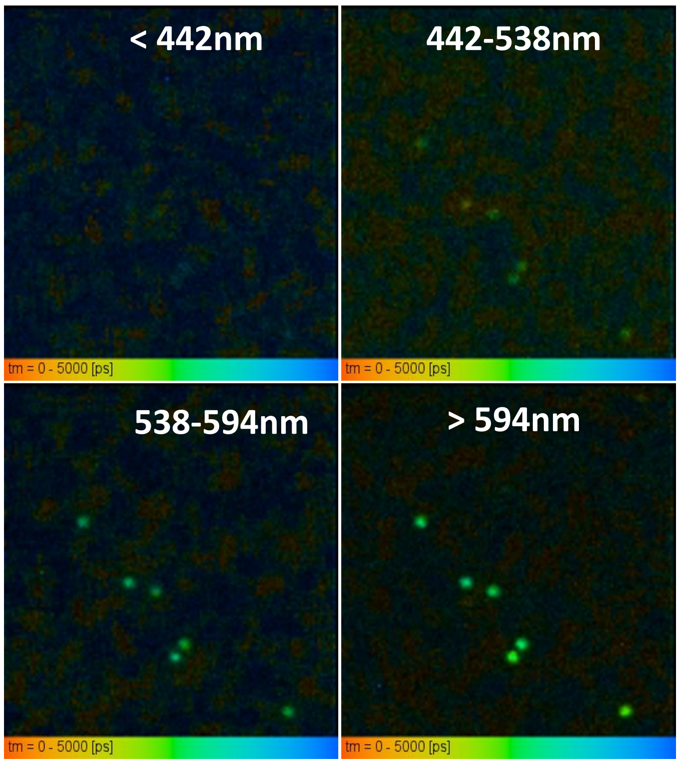


Woodcock, Davis, Beams, et al., In Preparation.

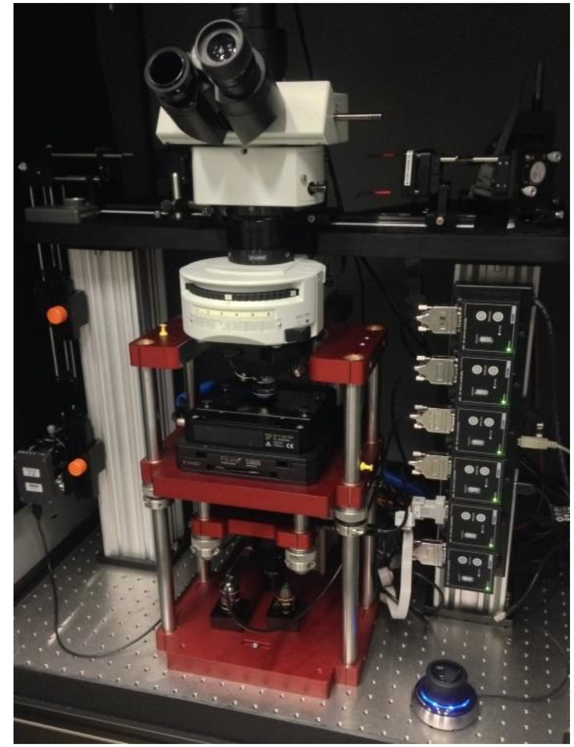
Fluorescence Lifetime Imaging Microscopy (FLIM)

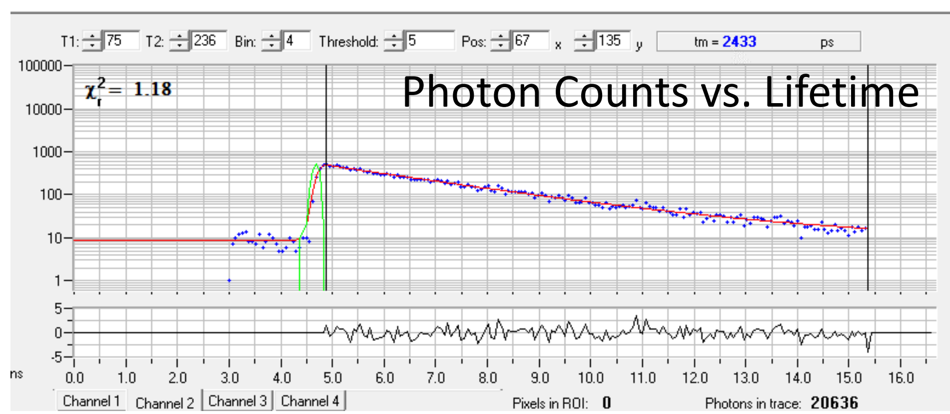
NIST FLIM System

Excitation: Pulsed, two photon IR laser
Detector: Four channel, time correlated single photon counting (TCSPC)



FLIM image of fluorescent Si particles (D=200nm)

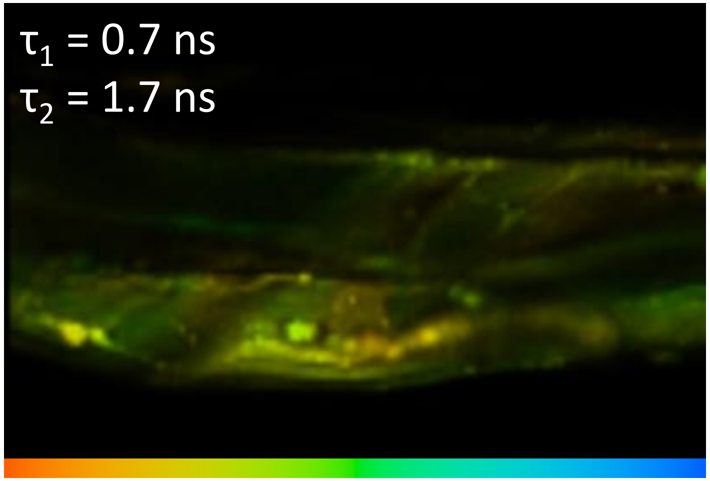




Beams, Stranick, et al., In Preparation.

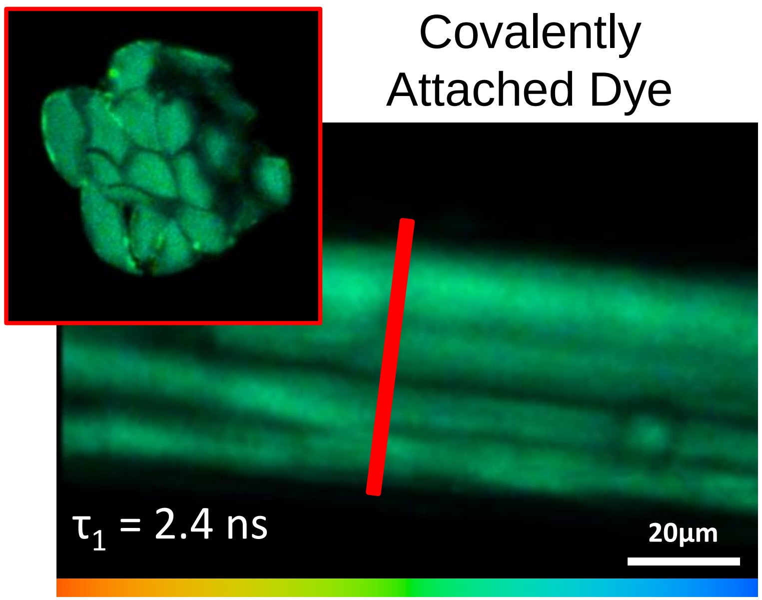
Attachment of Dye to Silk Fiber (Bombyx Mori)

Physically Adsorbed Dye

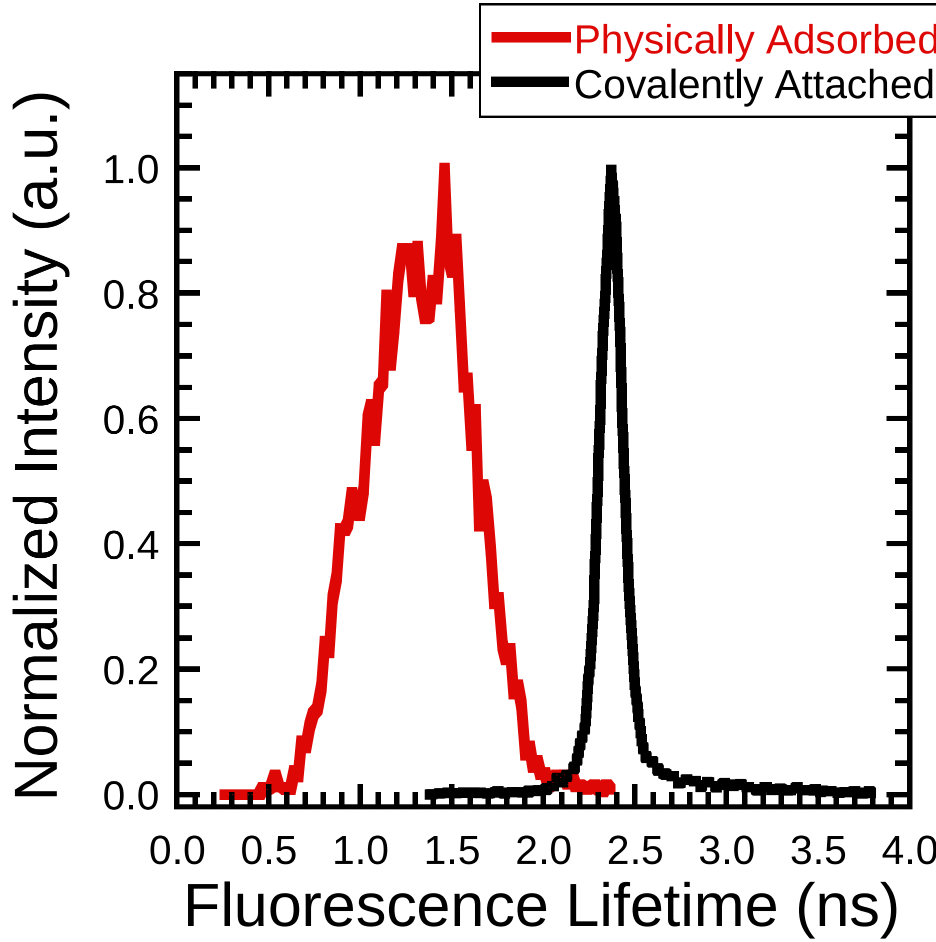


0-4000 ps

Covalently Attached Dye



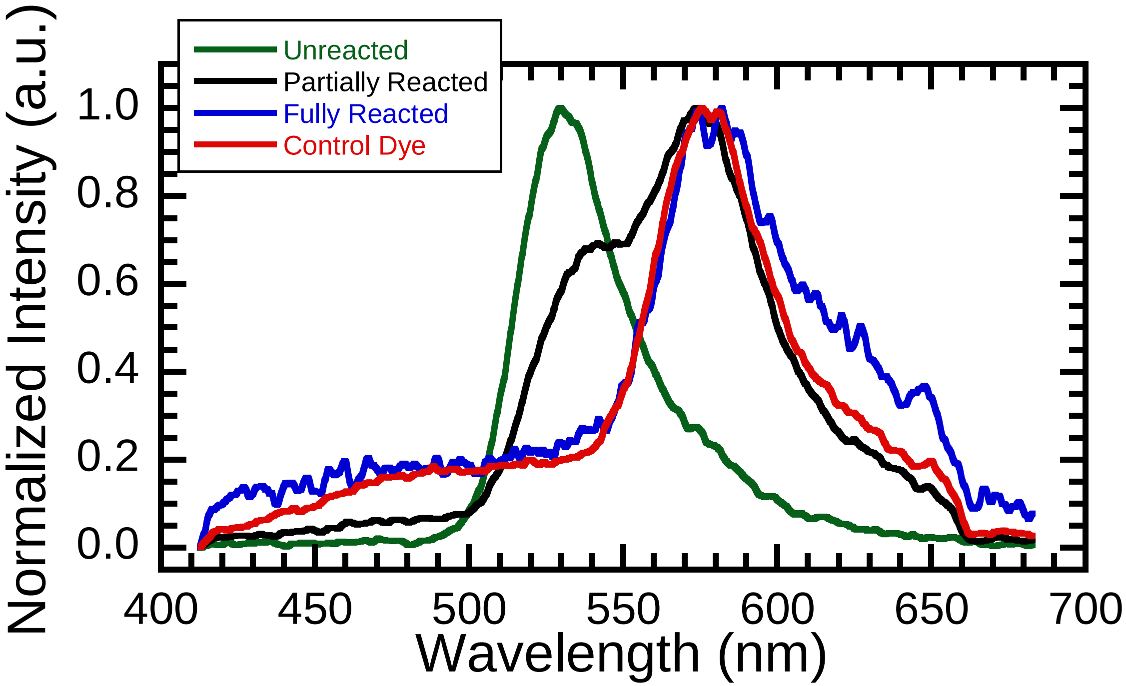
0-4000 ps

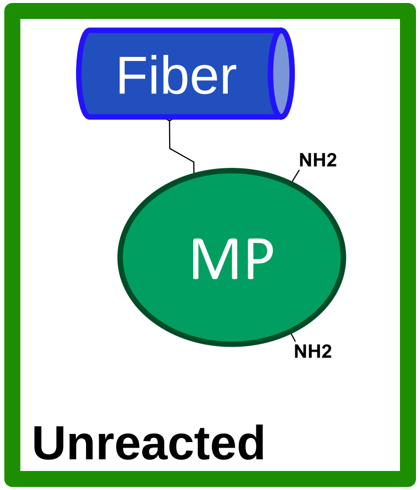


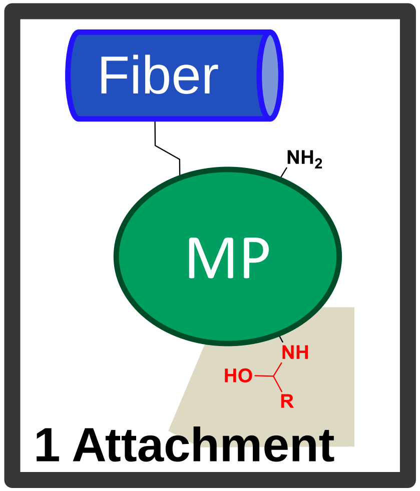
Woodcock, Davis, Beams, et al., In Preparation.

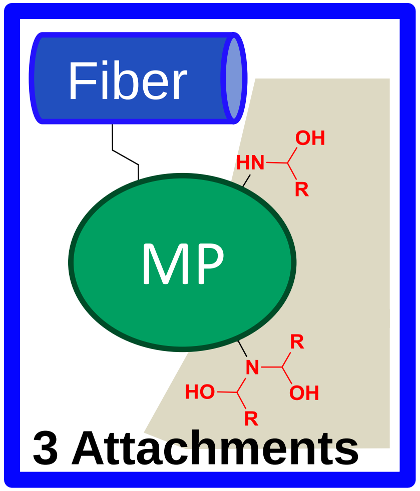
Matrix Attachment: Spectral Effects of Curing

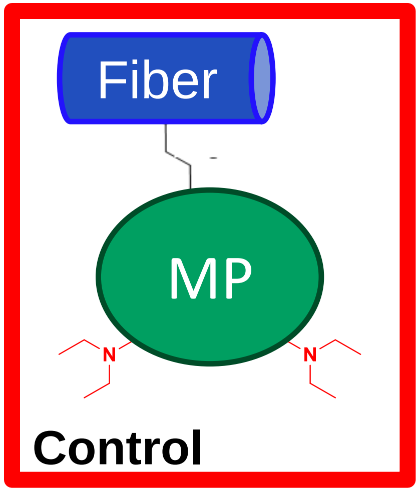
As mechanophore is reacted more strongly with epoxy matrix, emission wavelength shifts towards that of control (monofunctional) dye.



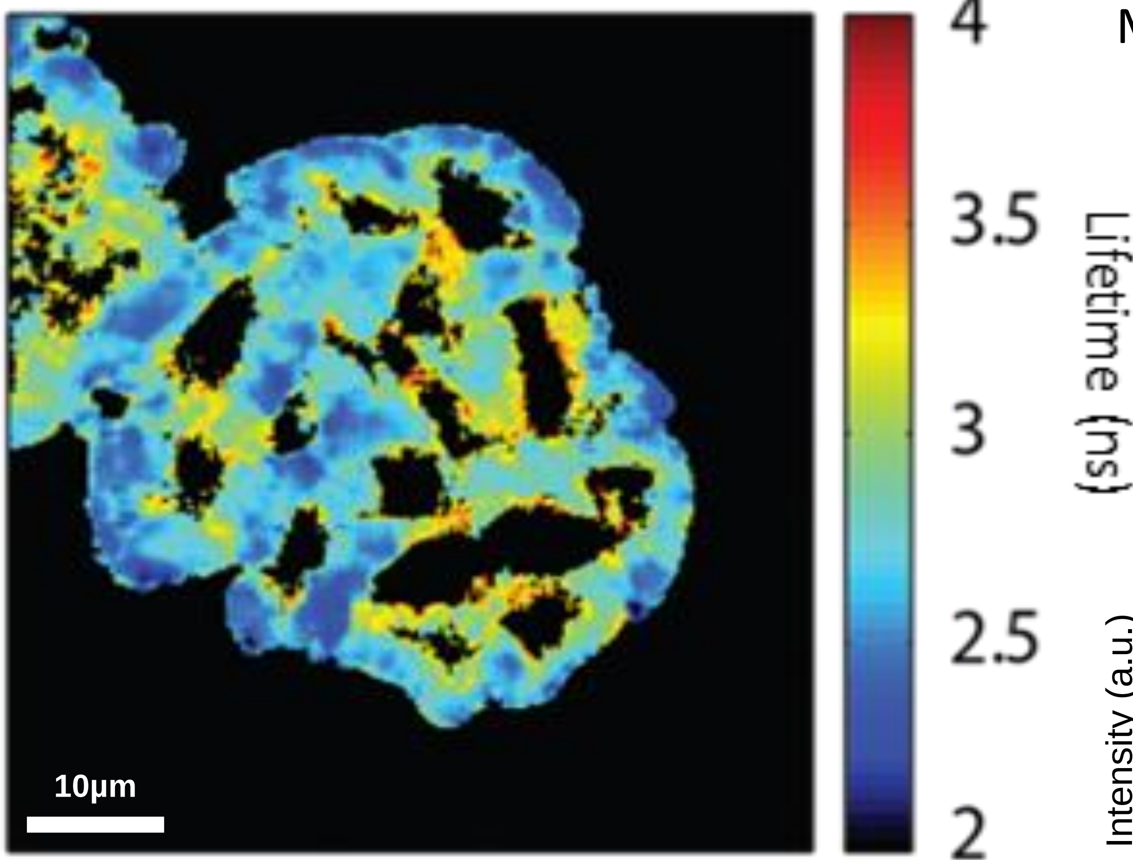






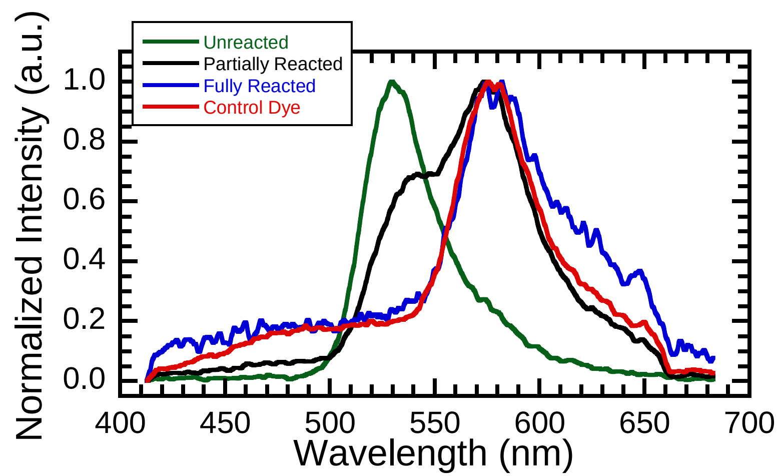


Hyperspectral Imaging to Monitor Reaction

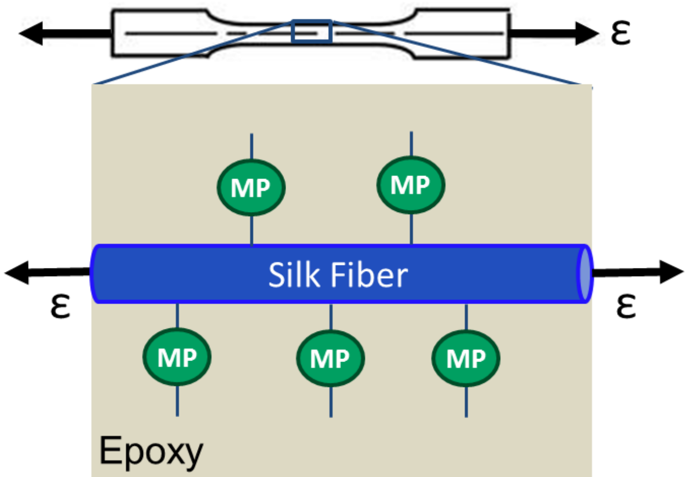


Silk Fiber Cross-Section
Mechanophore (T = 80 °C cure)
Partially reacted with matrix

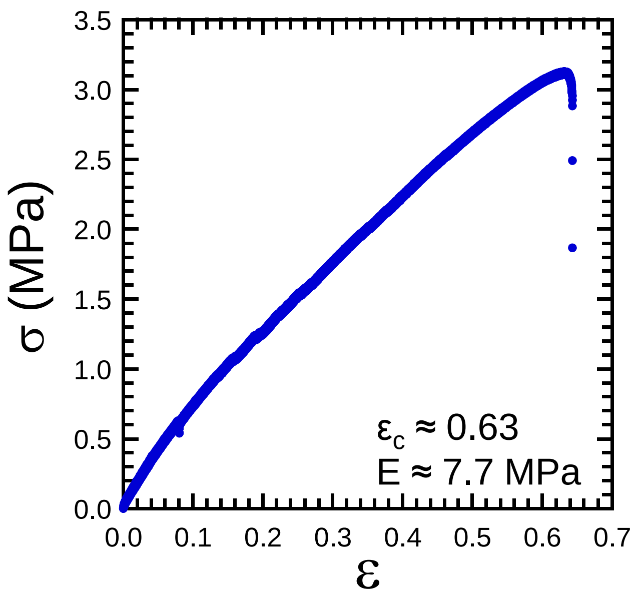
Lifetime and wavelength varies by location, highlighting areas where mechanophore is fully reacted across composite interface.

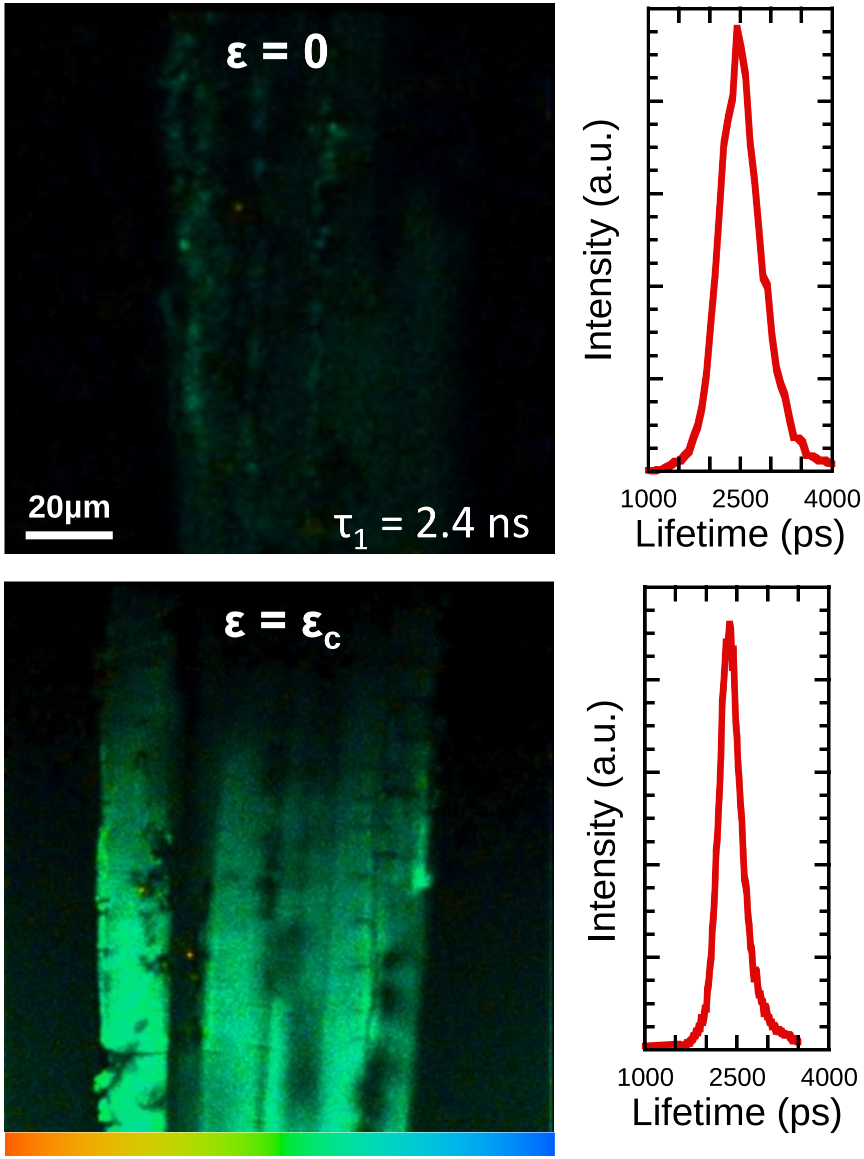


Mechanophore at Interface of Silk/Epoxy Composite



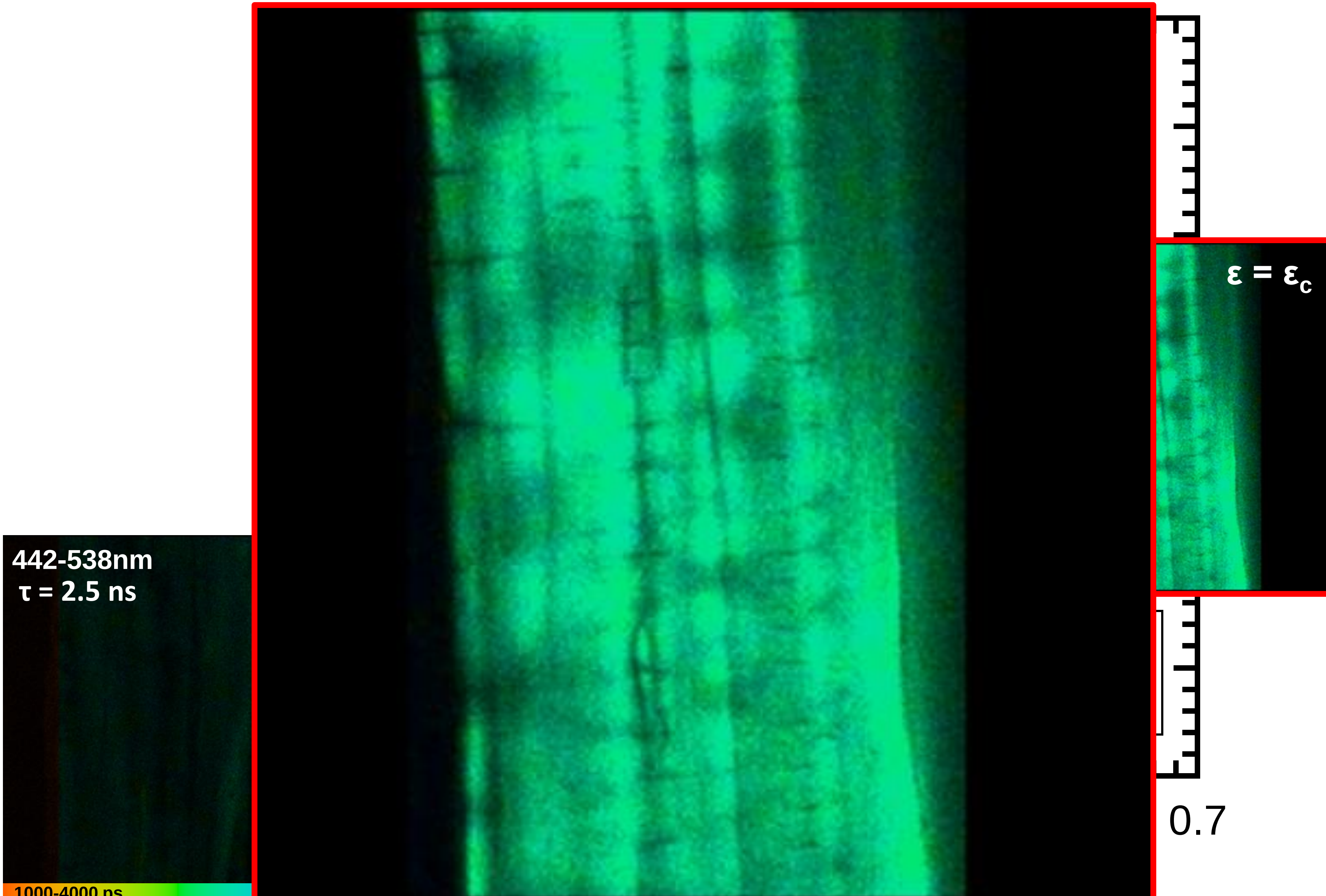
Ex situ tensile strain of single silk fiber in rubbery matrix by fluorescence lifetime imaging (FLIM)





Davis, Woodcock, Beams, et al., In Preparation.

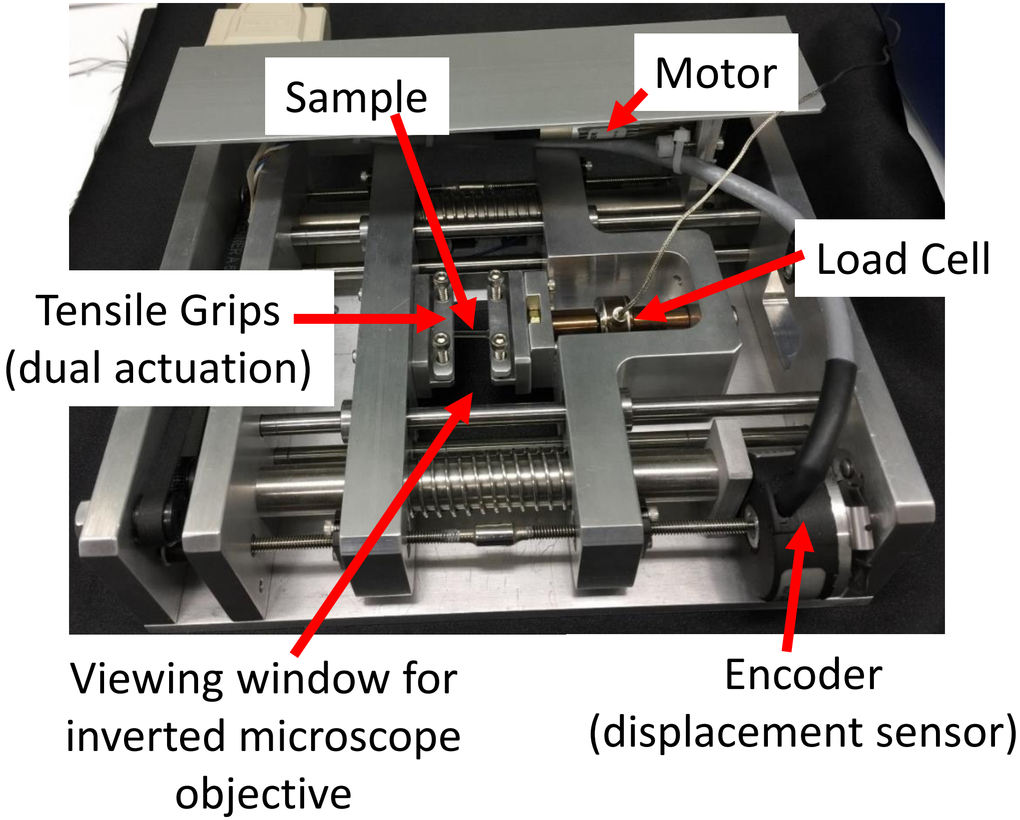
Mechanophore Intensity Response

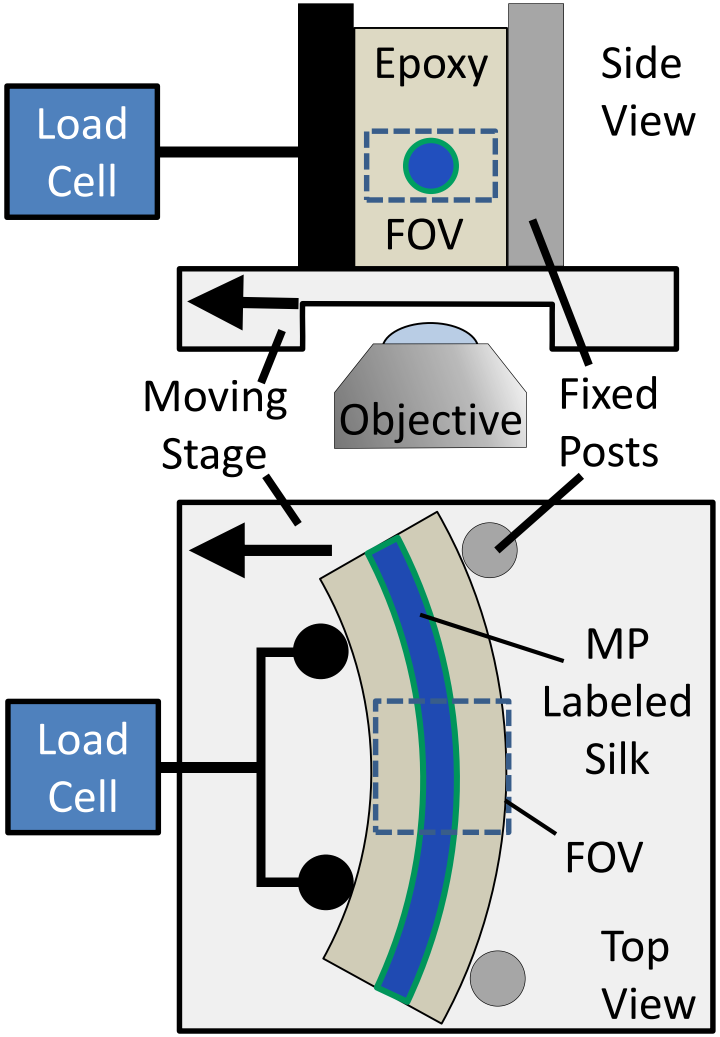


Discussion and Future Work

In situ Strain Stage

Dual motion crossheads keep region of interest centered over the microscope objective.





Acknowledgements

- Team
  - Aaron Forster, NIST
  - Ning Chen, NIST
  - Jae Hyun Kim, NIST
  - Fritz Volrath, Oxford Silk Group
  - Darshil Shah, Oxford Silk Group
- Funding
  - National Research Council Postdoctoral Fellowship
  - NIST Nano EH&S Initiative
  - Air Force Office of Scientific Research, Hugh DeLong
  - Army Research Office, Robert Mantz

Postdoctoral positions open immediately