Epoxy composites for application in superconducting magnets

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Structure of the presentation

1. Motivation
2. Engineering approaches
3. Examples / research
4. Experimental tools for preparing SENB samples
5. Conclusion & Outlook

Superconducting electromagnets

- Particles guided by magnetic fields
  - Electromagnets, Lorentz force
  - Operated in the superconducting state at very low temperatures
  - Superconductor: $NbTi$ / Nb_3Sn

- CHART
  - CH-Accelerator Research & Technology
  - Collaboration CERN, ETH, EPFL

resulting B-field direction

Particle trajectory

ETHzürich
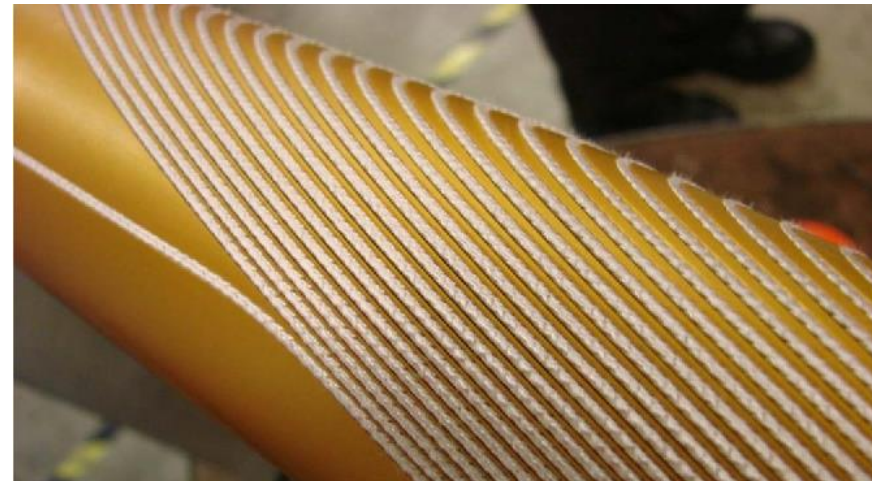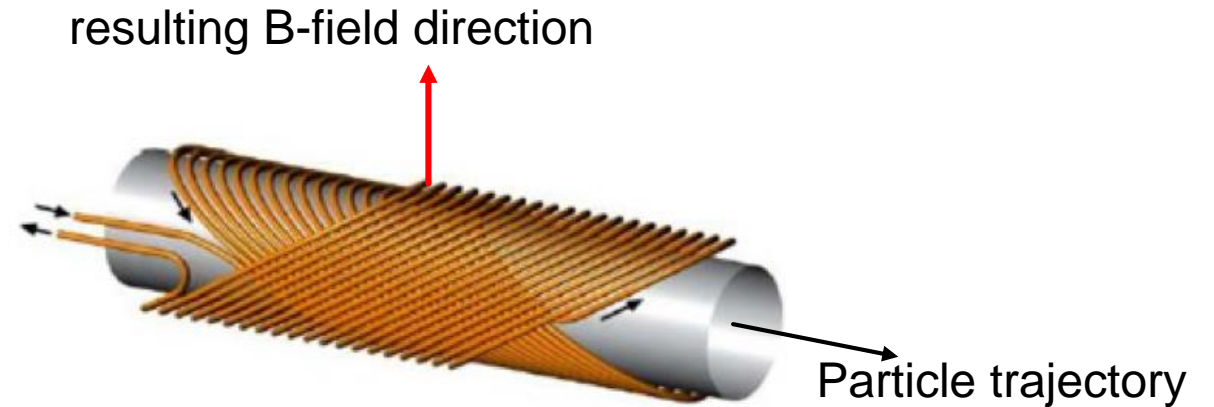
Requirements for epoxy application in superconducting magnets

- Function of the epoxy:
  - Keeping the superconductors in place → high modulus, **high fracture toughness**
  - Electrical insulation → Electrical insulator

- Processing requirements
  - No outgassing → Cross-linking without emission of volatiles & low volume change
  - Long pot-life → Low initial viscosity, slow reaction

- Other requirements
  - Radiation stability
  - Operation at cryogenic temp. (~4 K) → matching of thermal expansion coefficients

Aluminum bronze

Epoxy (or other)
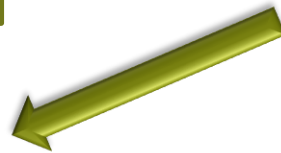
Superconductor

T = 4.2 Kelvin
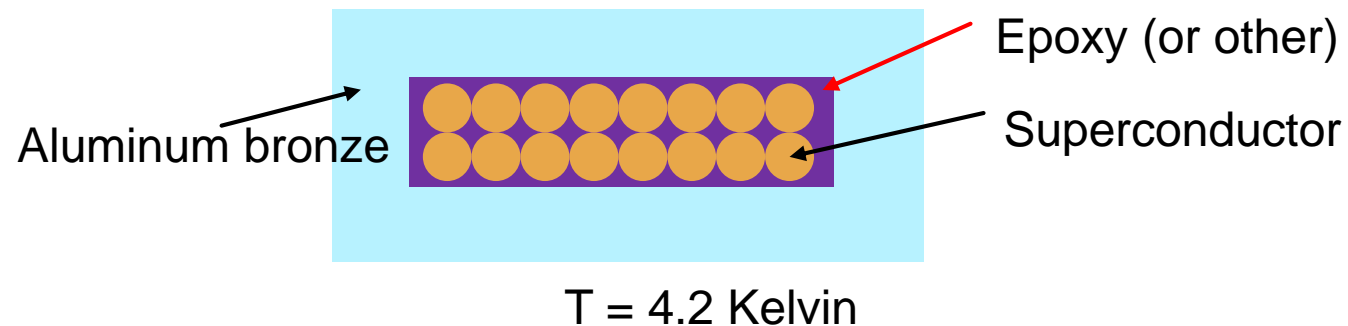
The causal chain of why research is needed

- **Cooling to cryogenic temperature** leads to thermal stresses
- *Strong magnetic fields* exert forces on conductors

- **Above a critical stress,** the material releases elastic energy by **cracking or localized yielding**
- The released energy is dissipated as heat

- Approaching 0 K, heat capacity of almost all materials vanishses
- Thus, cracks and yielding result in **significant local temperature increases at 4 K**

- **Superconductor becomes resistive** above a critical temperature and given current density
- Shutdown of the magnet
- Significant cost factor

Possible approaches to solve the problem

- **Prevent thermal stresses**
- → matching of thermal expansion coefficient to superconductor and metal (outside)

- **Increase K_{Ic}**
- → prevention of cracking
- **Control yielding behaviour**

- **Increase heat capacity**
- → prevent temperature increase to above critical temperature

- **Increase thermal conductivity**
- → reduce the peak temperature

- **Finding new superconductors with higher critical temperature**
- → not part of my work

Definition of fracture thoughness

- Many engineering materials fail well below their theoretical strength.

- **Irwin** found an approximation for the solution near the crack tip:

$$\sigma_{yy} = \frac{\sigma_\infty \sqrt{\pi a}}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 + \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right)$$
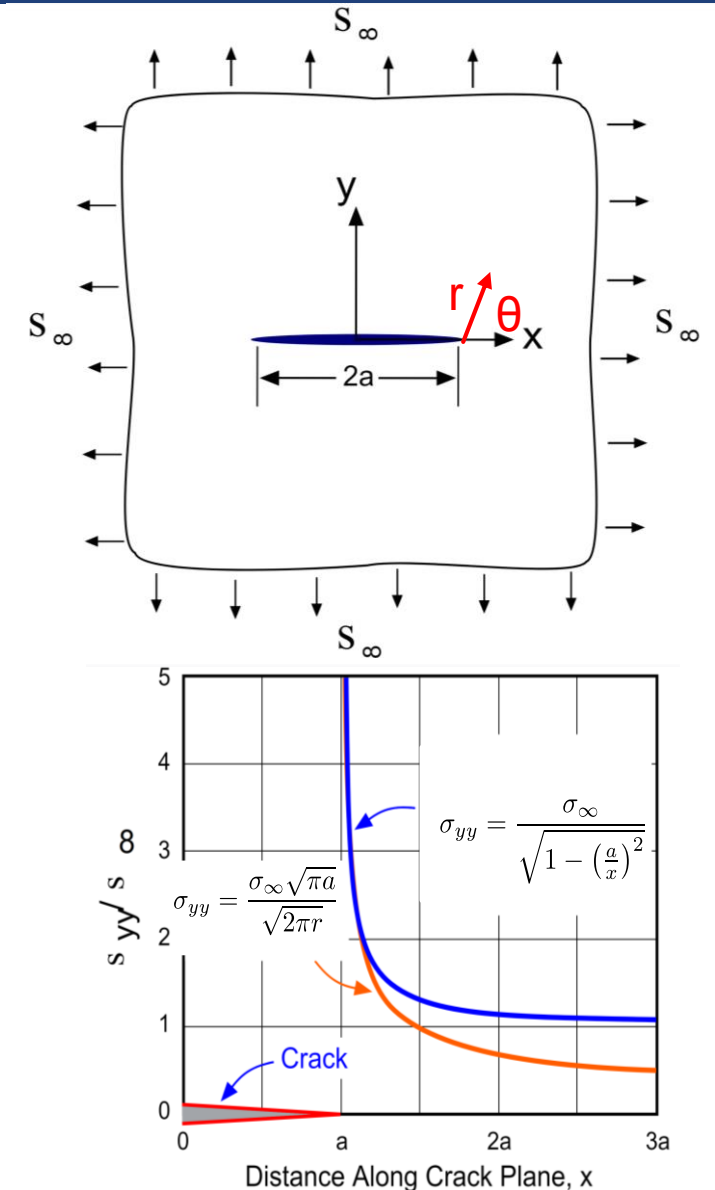
- Thus, the stresses at a specific location near the crack tip defined by θ and r depend on the factor defined as the stress intensity K_I:

$$K_I := \sigma_\infty \sqrt{\pi a}$$
$$K_I = \sigma_\infty \sqrt{\pi a} \cdot Y$$

Mode I

- The singularity at r=0 suggests that all materials fail for a > 0 and σ☐ > 0. However, every material some plasticity or microcracking at the crack tip.

theoretical elastic stress

redistributed stress
(elastic-plastic)

crack

plastic zone (realistic)
theoretical plastic zone

- The critical value of **K_I** at which failure occurs is an intrinsic material property, the so-called „fracture thoughness" **K_{IC}**.
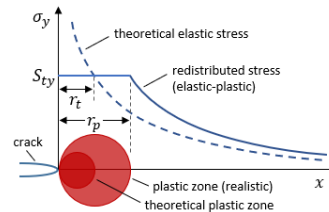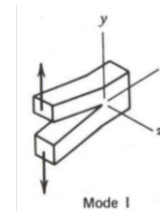
$$c = \frac{\pi^2 \sigma_\infty^2 a}{8\sigma_Y^2} = \frac{\pi}{8}\left(\frac{K_I(\sigma_\infty, a)}{\sigma_Y}\right)^2$$

Plastic zone size, dugdale model
CTD-101K (LN2): 3.07 microns

S_∞

S_∞ S_∞

S_∞

$$\sigma_{yy} = \frac{\sigma_\infty}{\sqrt{1 - \left(\frac{a}{x}\right)^2}}$$

$$\sigma_{yy} = \frac{\sigma_\infty \sqrt{\pi a}}{\sqrt{2\pi r}}$$

Crack

Distance Along Crack Plane, x

Different ideas of epoxy composites for increasing K1c

Particle toughening

- Incorporate hard particles (micro/nano)
  - **Yielding** of epoxy around particles
  - Crack deflection → increase in crack surface area
- Possible sedimentation (microfillers)
- Possible aggregation (nanofillers/particles)

Plane stress – tensile → yielding

Ceramic
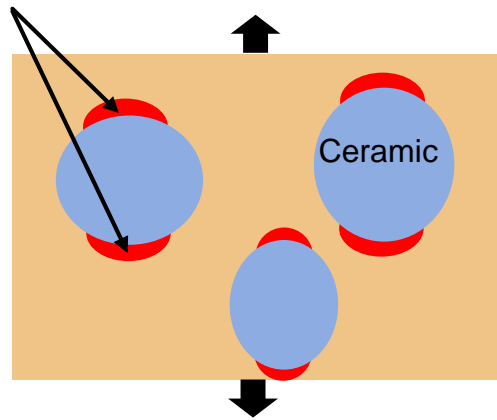
Rubber toughening

- Incorporate soft but tough particles in epoxy matrix
- Different mechanisms
  - **Matrix crazing** (Formation of many small crazes increases energy-release rate, adhesion dependent, low modulus required to prevent debonding particle/matrix)
  - **Shear yielding**: Interaction between stress fields around particles leads to shear bands, acting as an energy-dissipative mechanism, facilitated by cavitation of the rubber (increasing von Mises stress)
- Not applicable! Below Tg, rubber is not soft anymore
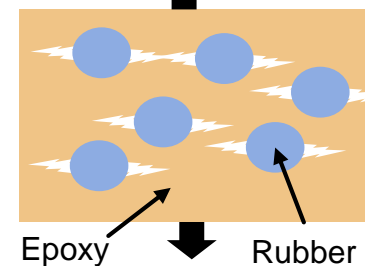
Matrix crazing　　　　　　　　　Shear yielding

Epoxy　　　Rubber
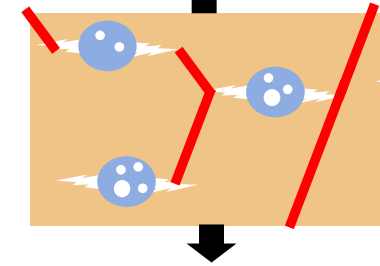
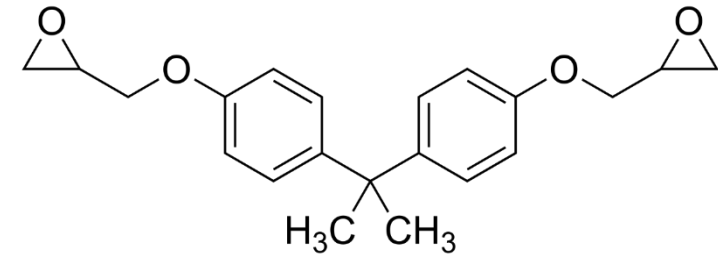# Epoxy with TiO$_2$ nanoparticles

Preparation procedure

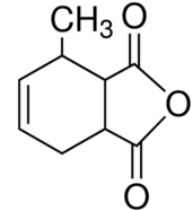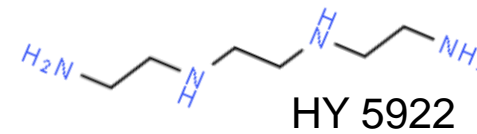1. Nanoparticle suspension

Oleylamine
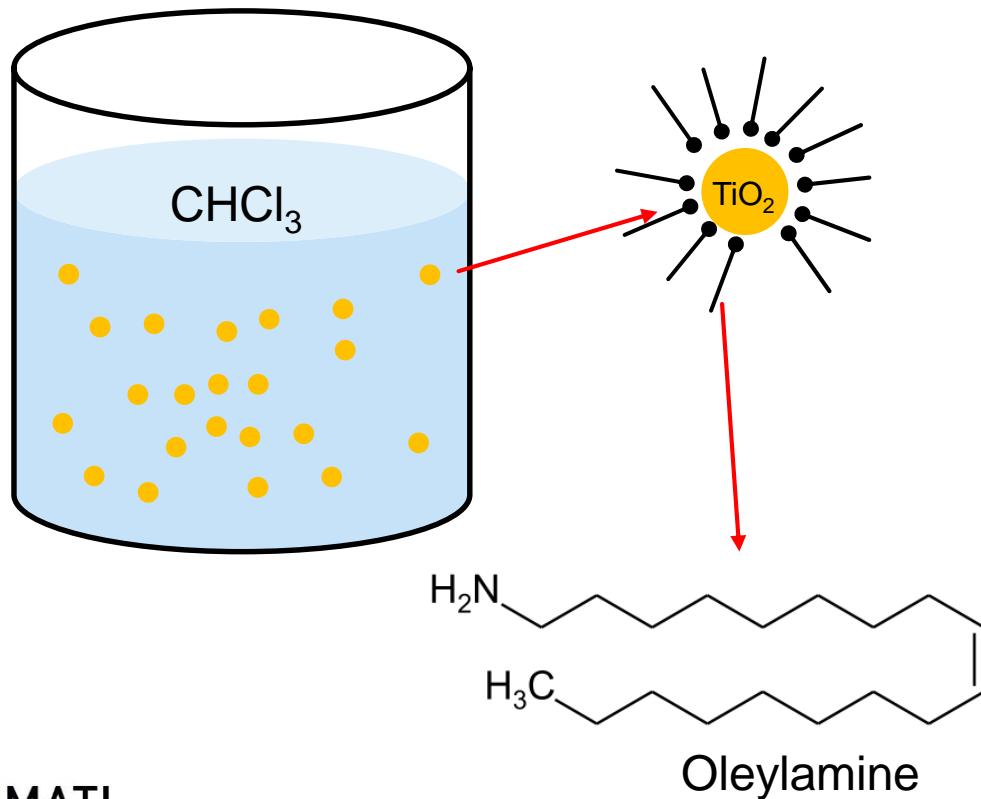
2. Mix particle suspension with hardener or resin

Epoxy resin:

Some hardeners:

HY 5922

CTD-101K Part B

3. Remove CHCl$_3$ with roto-evap

4. Mix hardener & resin → curing

Epoxy with TiO$_2$ nanoparticles (MY750 resin)
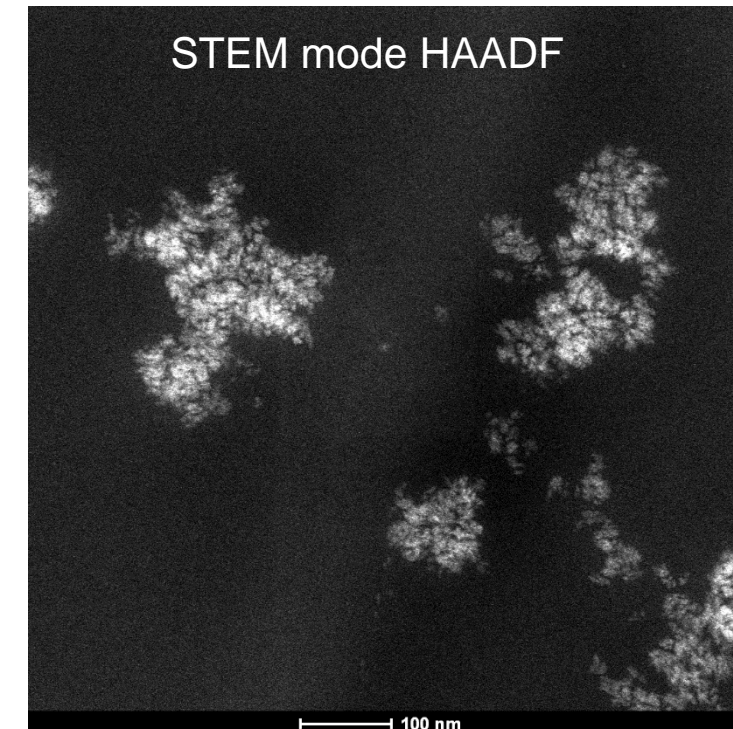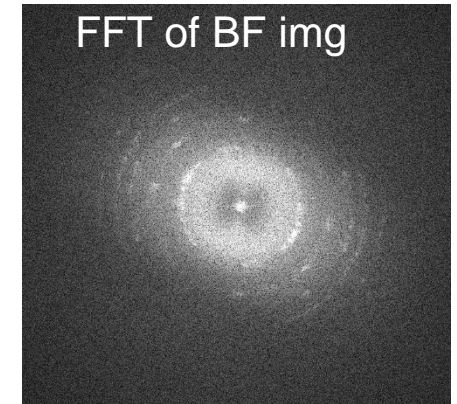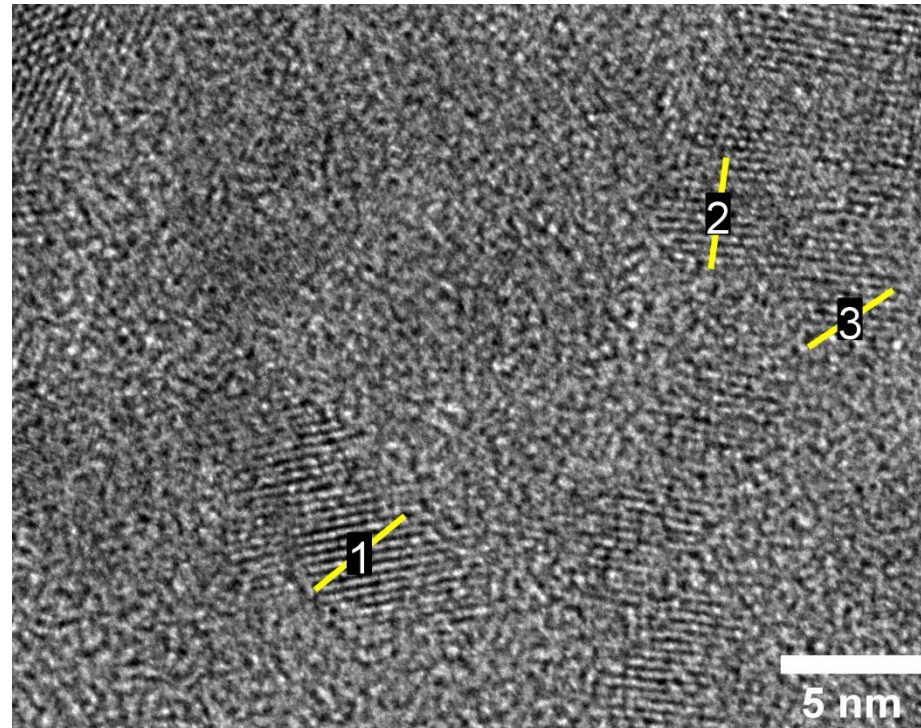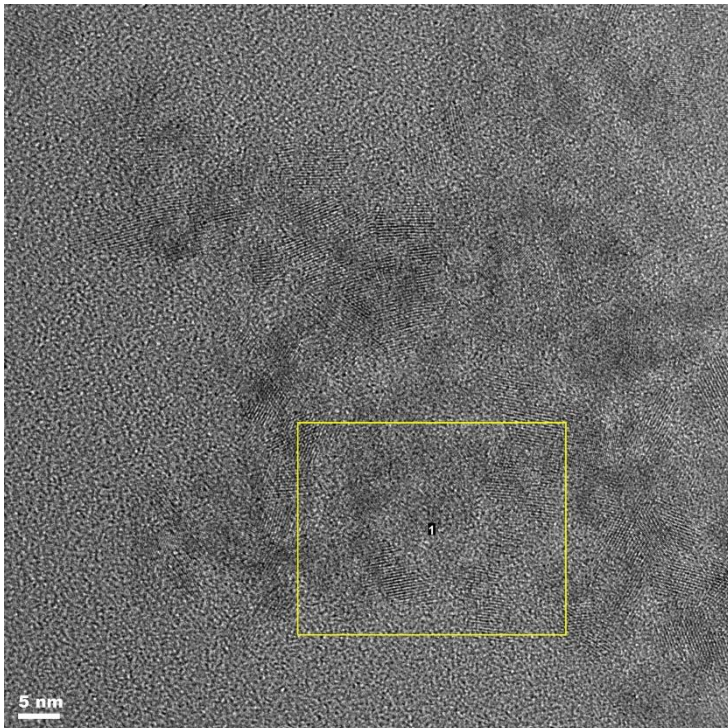
STEM images: Tecnai F30, FEG, 300 kV (ScopeM)
TEM samples prepared by ultramicrotomy
→ Agglomeration

FFT of BF img

Bright Field   Bright Field, zoom in   3.9, 3.7, 3.4 nm

STEM mode HAADF

Thanks to Fabian Gramm (ScopeM, ETHZ)

DMATL.
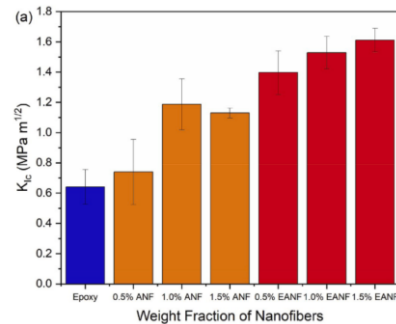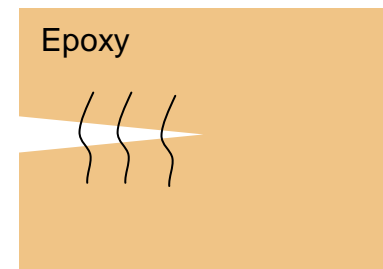
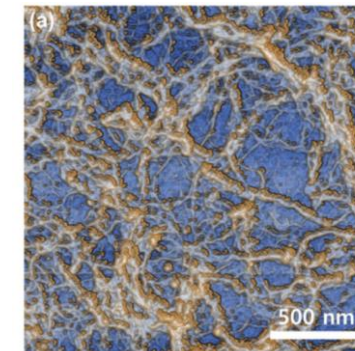# Different ideas of epoxy composites for increasing K1c

Crack bridging

- Epoxy-aramide nanofiber composite
- Toughening by fiber bridging over crac
- Process:
  - 1. Dissolution of aramide in DMSO/KOH/(H2O)→ polyanion solution
  - 2. Precipitation by adding proton donor (H2O
  - 3. Filtration / Drying / Characterization
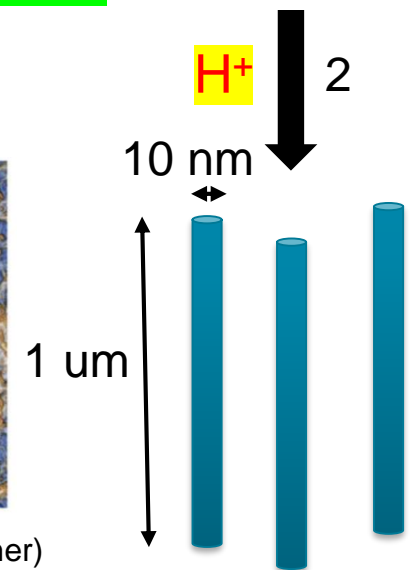 - 4. Incorporation into epoxy

Epoxy

Jung et al., 2020 (Polymer)

OH⁻

OH⁻

OH⁻

H⁺   2

Interactions:
Electrostatic
Van der Waals
Aromatic

10 nm

1 um
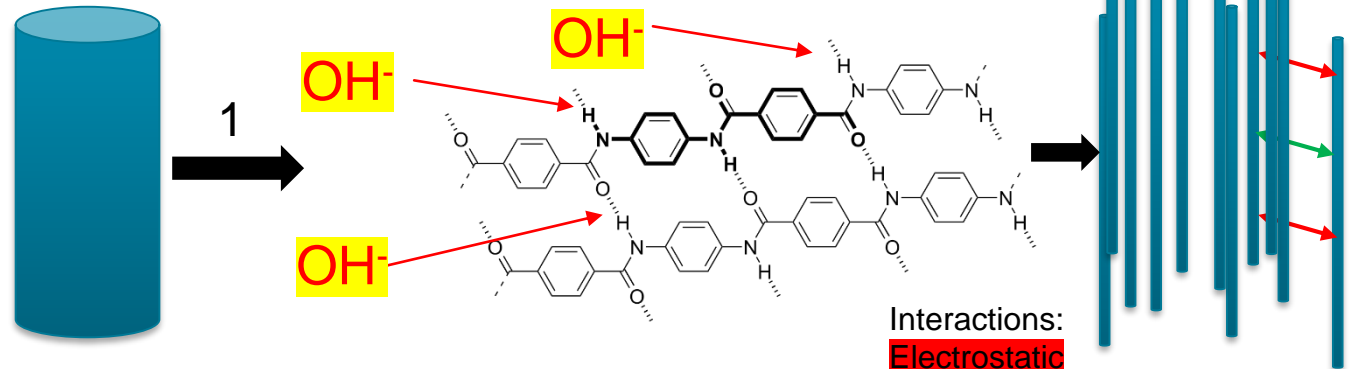
Aramide fiber / DMSO / KOH solution
After stirring for 5 days

Jung et al., 2020 (Polymer)

# Results on preparing aramide nanofiber colloidal solutions

0.2% solution

- 0.2% aramide in DMSO/KOH
- KOH pellets
- Stirred 7 days
- Precipitated with proton donor H2O (added 0.5 mL/mg of aramide)
- Formation of a colloidal gel

2% solution

- 2.3% aramide in DMSO/H2O (1:25)
- KOH pellets crushed
- Stirred 9 hours
- Precipitated with proton donor H2O (added 0.5 mL/mg of aramide)
- Forms clumps
- Problem: Not fully dissolved (next slide) & concentration
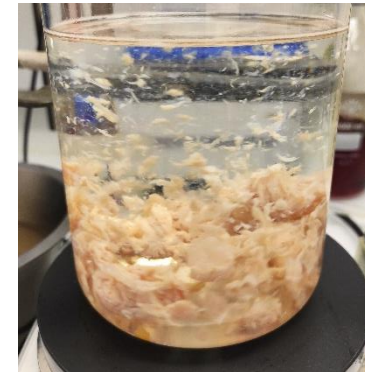
Preparation times for aramide polyanion solutions

Composition (1:25 H2O/DMSO), KOH	Preparation method (RT)	6h	24h	
1 % aramide sol.	Stirred, 400 rpm			
1 % aramide sol.	Tumbler, ~80 rpm			
2 % aramide sol.	Tumbler, ~50 rpm			

Aramide nanofibers, open questions

- Preparation of dried nanofibers for application from higher concentrated solutions (1%, 2%, 4%,…)
 - What happens when the concentration of proton donor is slowly increased instead of instantaneous mixing?
  - Dilution necessary before precipitation? Influence on microstructure?
  - What would be an appropriate diluent? (aprotic, polar, basic)
    - Acetone, EtOH+KOH, H2O+KOH, ?
- What is the influence of temperature on both aramide dissolution and precipitation?
- Effect of nanofibers in epoxy on pot-life viscosity?
- How do the fibers align during infusion of dense structures?

Different ideas of epoxy composites for increasing K_{Ic}

## Pre-stressing (internal pressure)

- Idea: incorporate nascent UHMWPE (highly crystalline) particles into epoxy

- After curing, melt the UHMWPE → lower crystallinity → specific volume goes up → pre-stress closes cracks

- Chain explosion → improved adhesion?

UHMWPE
Epoxy

↓ Melting

Pre-stressed material
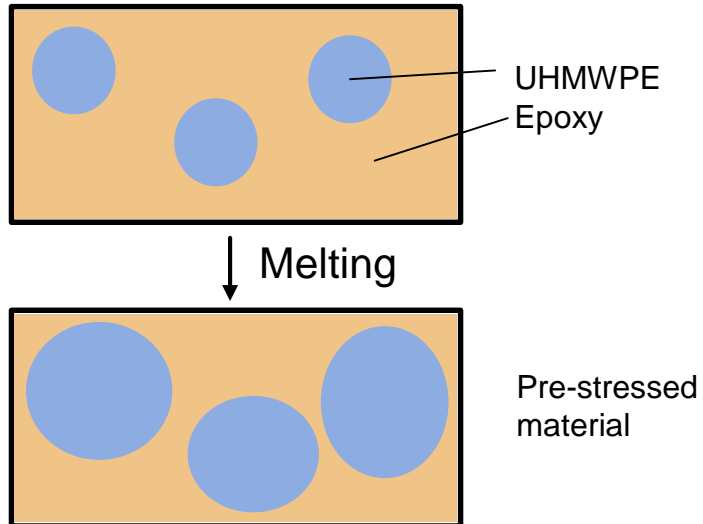
UHMWPE in Epoxy (CTD-101K)

- **First trial**
  - Simply mixing GUR 4120 (commercial UHMWPE grade) with epoxy, degassing according to standard protocol & curing
    - White layer on top
    - Probably due to trapped air

- **Second trial**
  - Mixing GUR with liquid hardener (part B)
  - Degassed 10 mBar, 60 °C, 30 min → bubbling
  - Mixed with other components, degassed, cured, ultrasonic bath 2 min
  - Similar result
  - Air is entrapped since top level sank

- **Third trial**
  - Suspending GUR in ether (lower density → sediments)
  - Centrifugated, tip sonicated & centrifugated again
  - Now cured
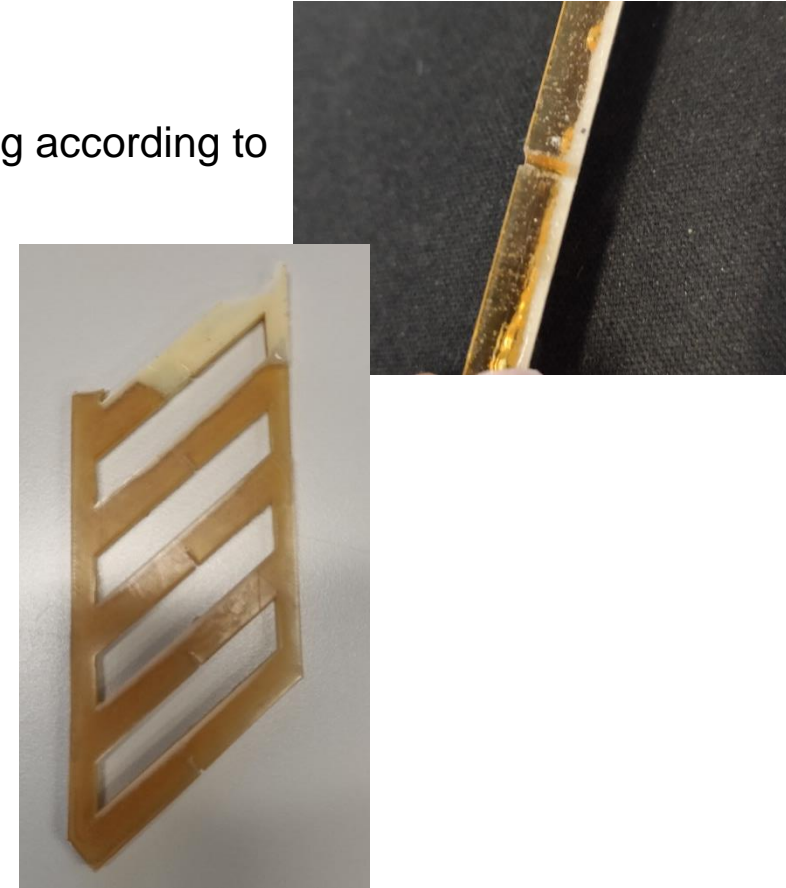
Possible approaches to solve the problem

- ▪ **Prevent thermal stresses**
- ▪ → matching of thermal expansion coefficient to superconductor and metal (outside)

- ▪ **Increase K1c**
- ▪ → prevention of cracking

- ▪ **Increase heat capacity**
- ▪ → prevent temperature increase to above critical temperature

- ▪ **Increase thermal conductivity**
- ▪ → reduce the peak temperature

- ▪ **Finding new superconductors with higher critical temperature**
- ▪ → not part of my work

Combined approach: heat capacity & thermal expansion match.

Zirconium tungstate (ZrW$_2$O$_8$)

- *negative* coefficient of thermal expansion ($\alpha = -7.2 * 10^{-6}$ K^{-1}) of ZRW$_2$O$_8$

- → overall reduction in thermal expansion coefficient

- → thermal stresses are distributed throughout epoxy rather than on interface superconductor/epoxy/metal
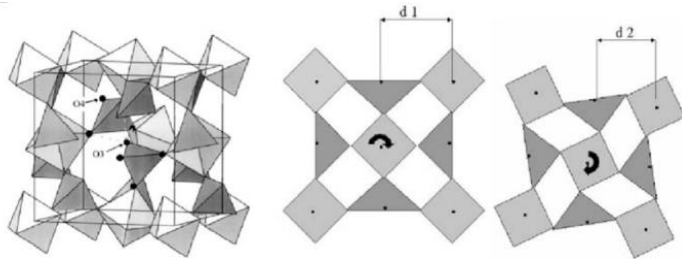
Schematics of Zirconium Tungstate and the RUM mechanism
10.1007/s10853-009-3692-4

## + Gadolinium Oxide (Gd$_2$O$_3$) composite

- Gadolinium oxide has anomaly in heat capacity at ~3K → where the magnet is operated

- Cracking and yielding would result in lower local temperature rise
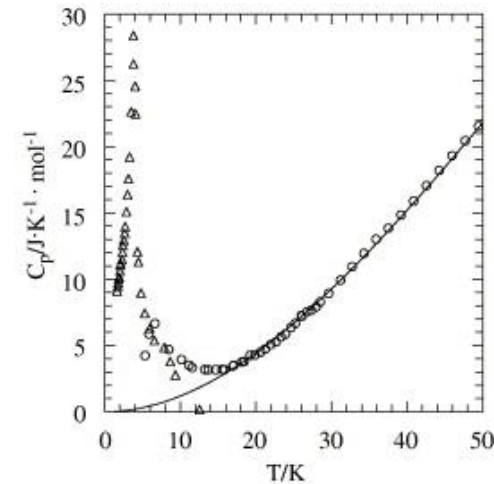
Heat capacity of GD$_2$O$_3$
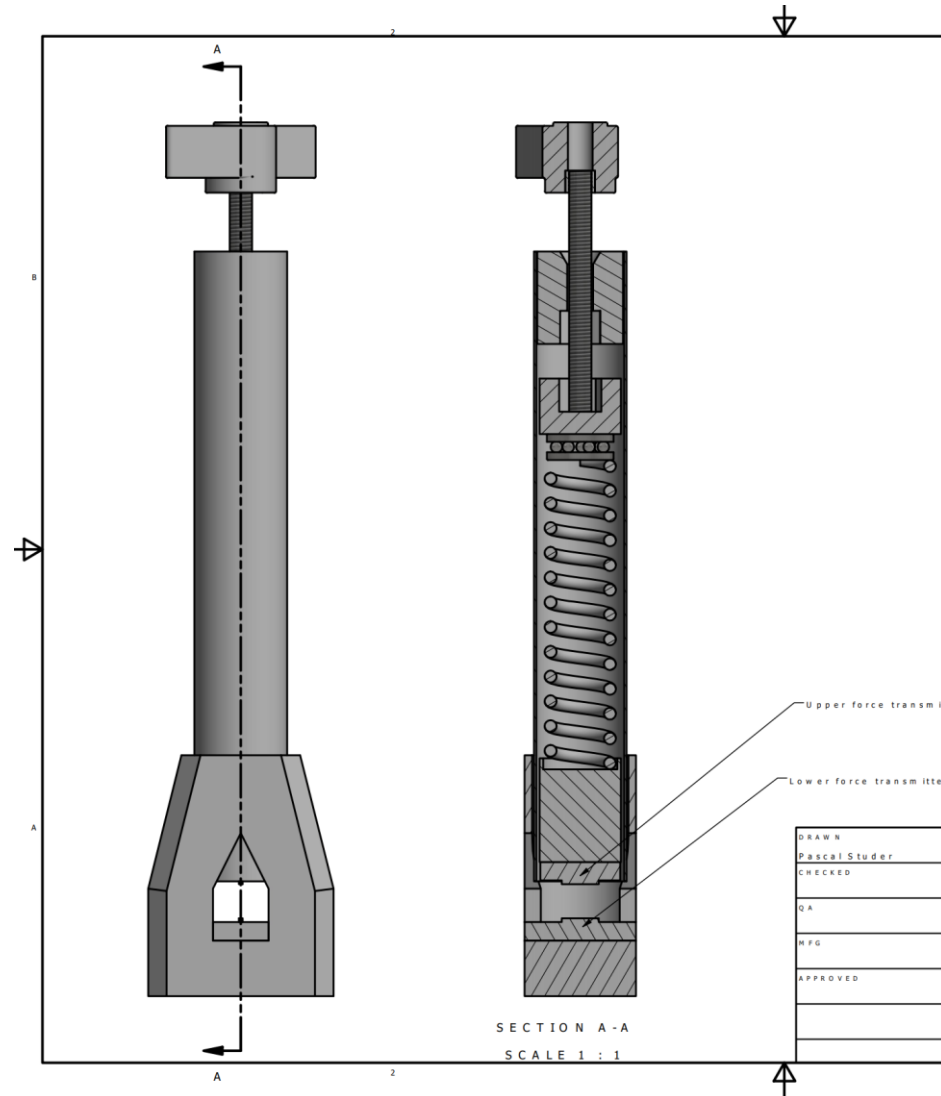*10.1016/j.jct.2005.02.014*

Measuring K_{Ic} for filled epoxy composites

- Single-etch notch bend samples (SENB) → difficult preparation

The test setup

Sample preparation

Stopping the crack
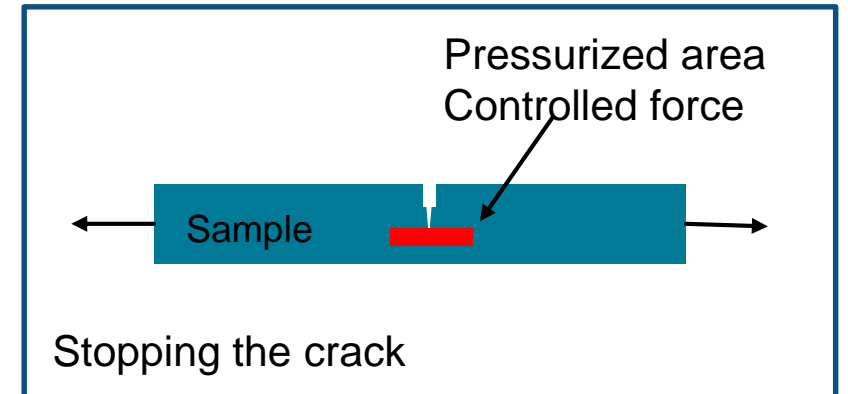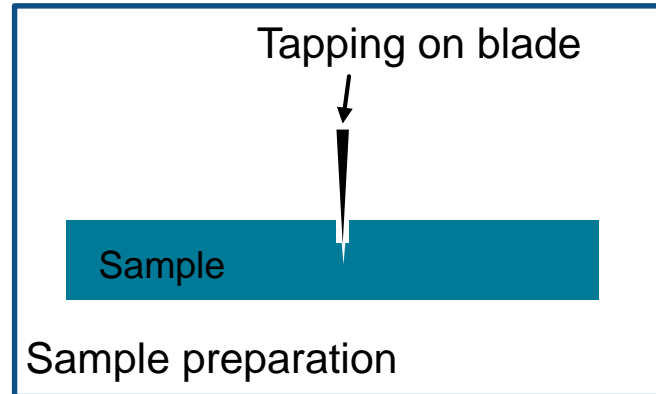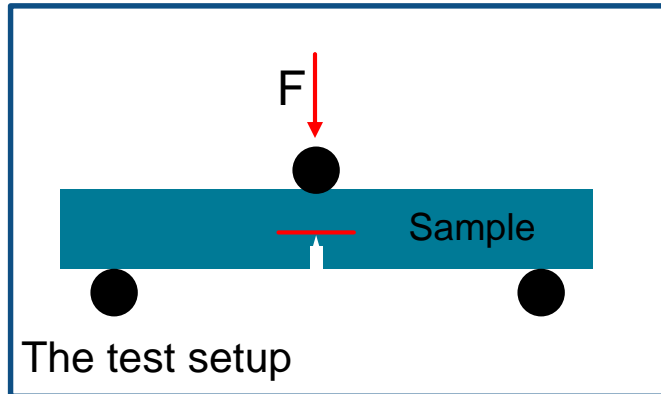
Measuring K_{Ic} for filled epoxy composites

- Device design
  - Controlled force
  - Most parts 3D printed
  - Except force transmitter (CNC)
- In progress…

SECTION A-A
SCALE 1 : 1

Conclusion & Outlook, questions

- Further research
  - Explore toughening of epoxy composite with nascent UHMWPE **and PTFE**
  - Fabricate aramide nanofiber epoxy composite
  - Finish the sample notching device, obtain reliable K_{Ic} values

- Thanks
  - André Brem, Bernhard Auchmann and Theo Tervoort for their support
  - Fabian Gramm (ScopeM) for support with TEM imaging
  - Chris for helping with the design of the improved sample notcher