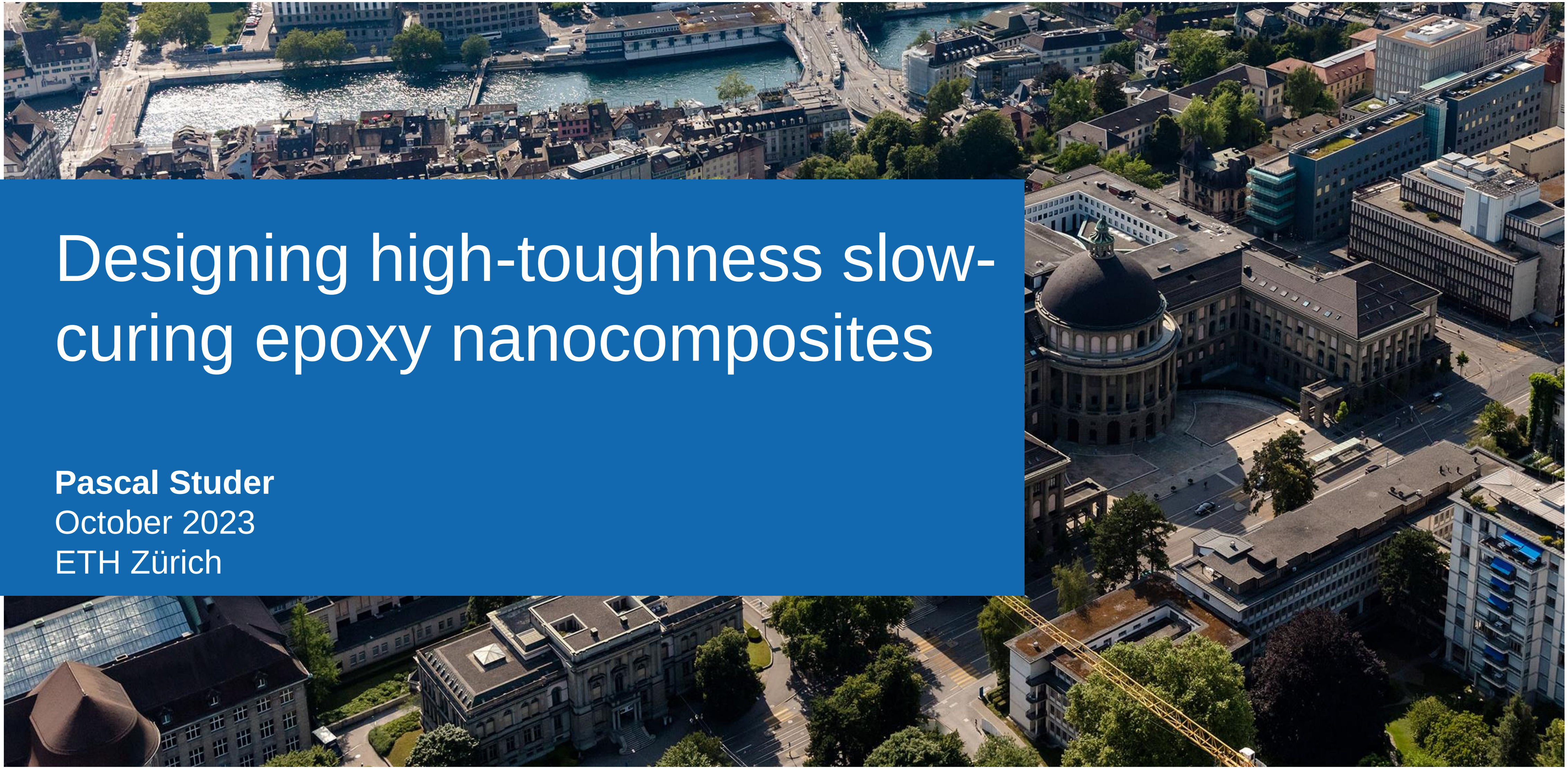


Designing high-toughness slow-curing epoxy nanocomposites

Pascal Studer
October 2023
ETH Zürich

Thanks to our collaborators

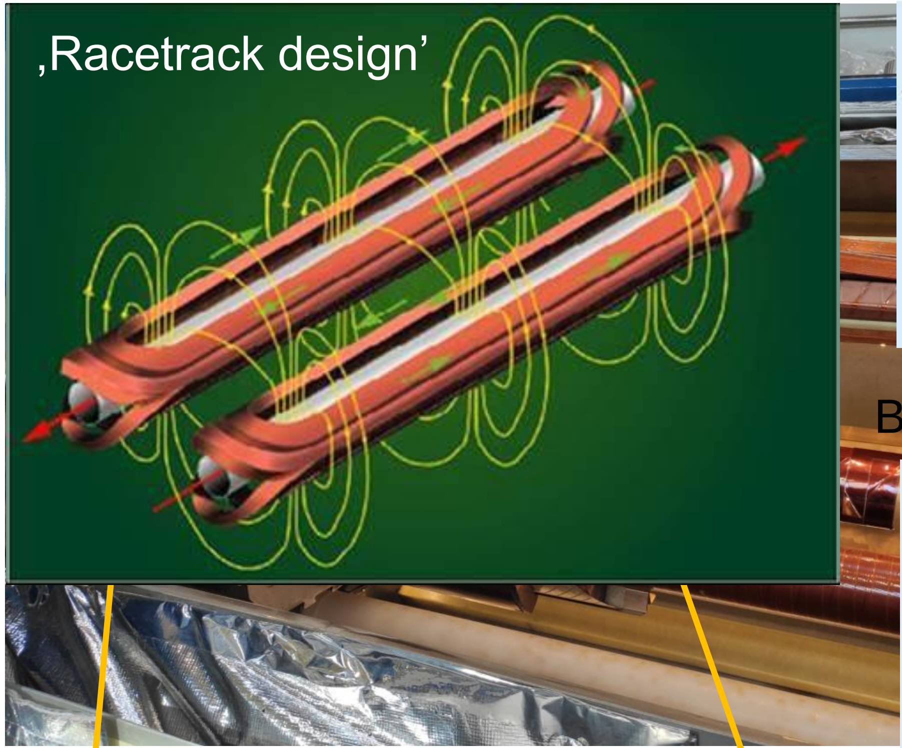
- ETH Zurich
  - Prof. Theo A. Tervoort, Prof. Jan Vermant (Head) & the Soft Matter group
  - Xiang Kong, PhD. (MagNum project)
  - Others

- PSI Villigen, CHART MagDev
  - Dr. Bernhard Auchmann, Dr. André Brém, Dr. Micheal Daly
  - And others

- CERN Meyrin, Polymer Lab
  - Dr. Roland Piccin (Head), Dr. Christian Scheuerlein, Dr. Bharti Verma, Dr. Mauro Taborelli, Dr. Stefano Sgobba, Dr. Daria Ternova, Dr. Sebastian Clément
  - And others

Introduction

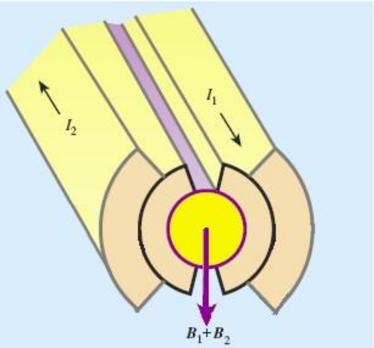
- Electromagnet at CERN (LHC dipole)



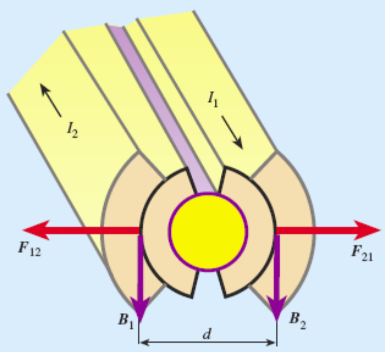
‚Racetrack design'

Cold mass

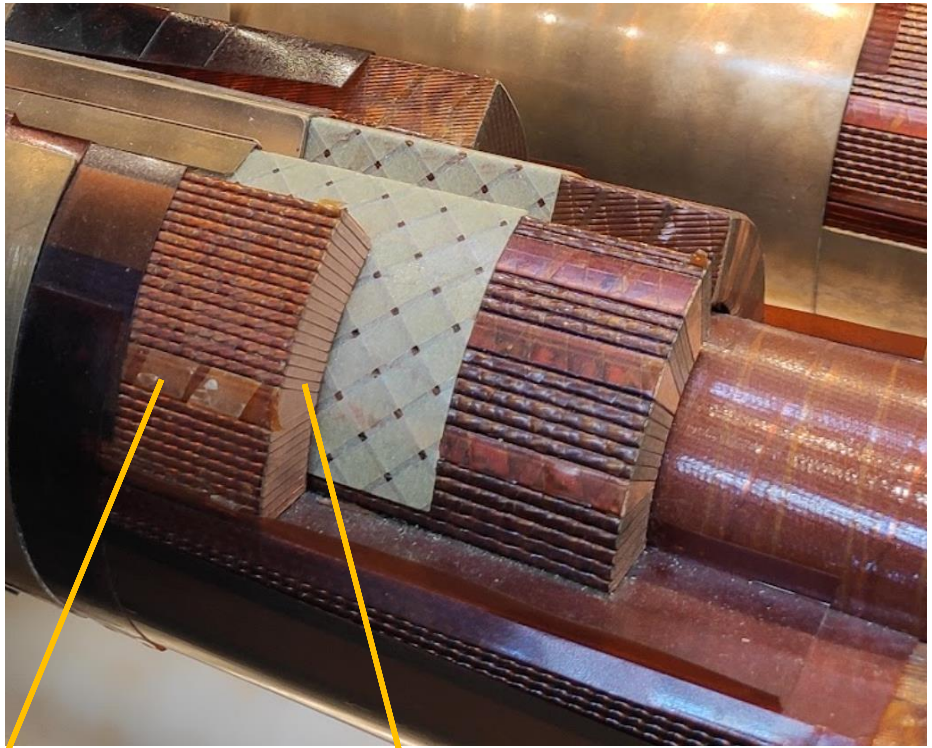
Beam pipe



B-Field in beam pipe



Forces on conductors

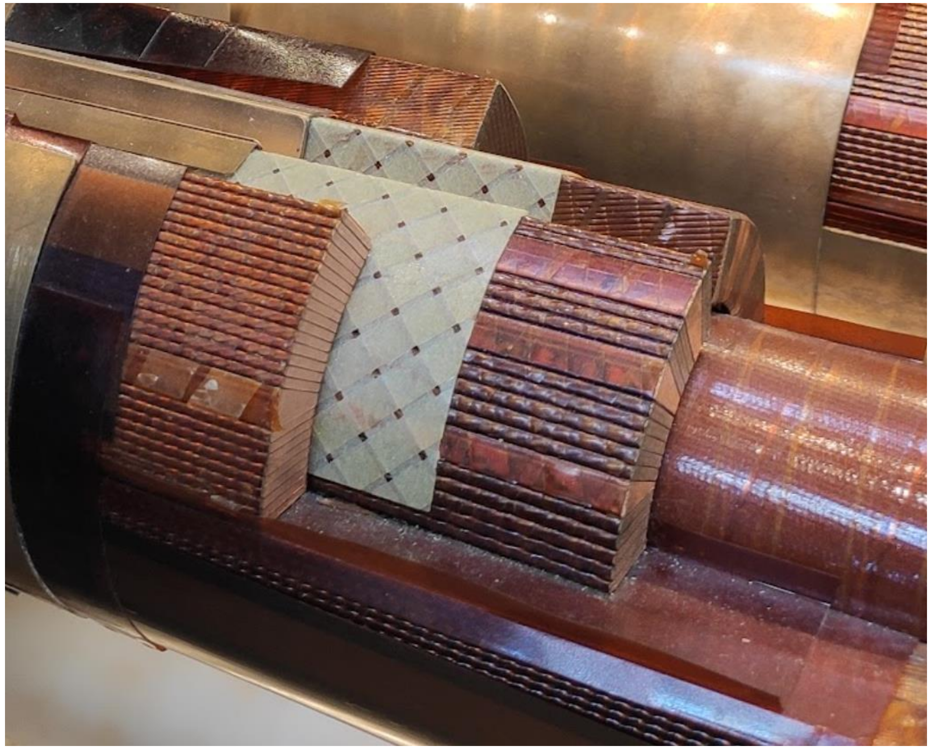


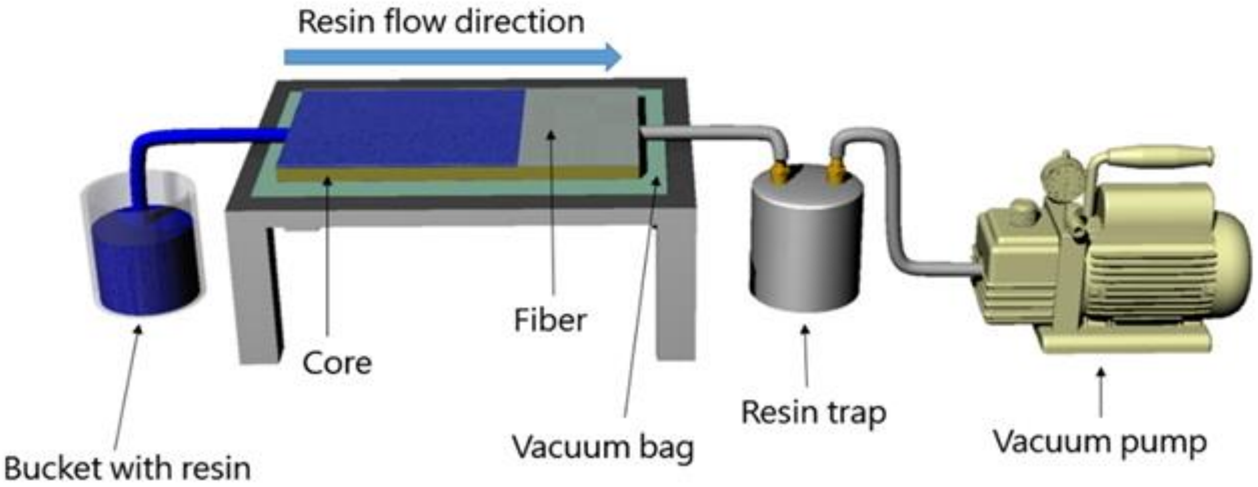
Spacer

Bundles of conductor wires covered by copper and fiberglass

Introduction

- VRT (Resin Transfer Molding) process

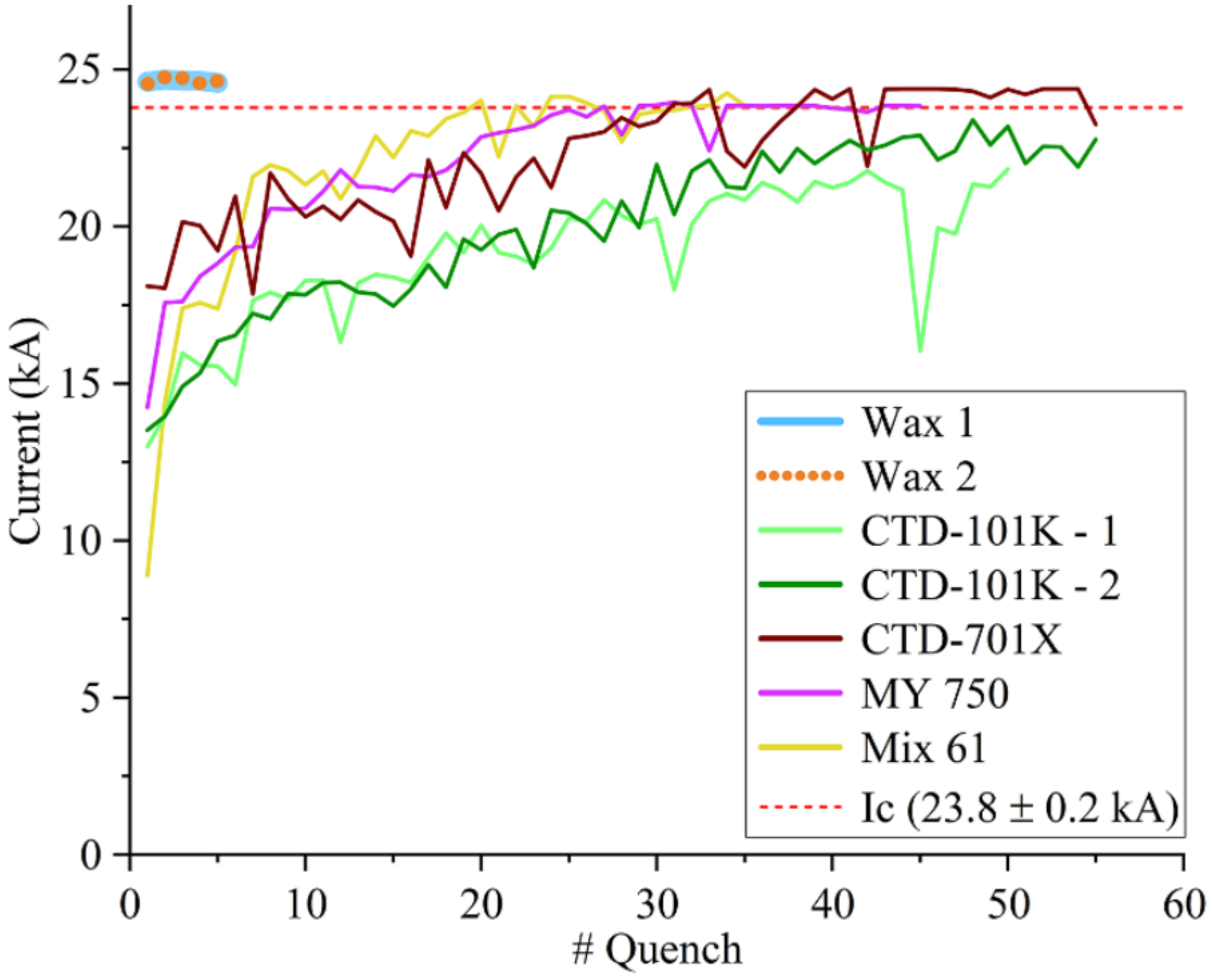




Many small spaces between conductors (and fiberglass)
How to fill them completely after the assembly of a magnet?

Introduction

- The requirements for an insulator
  - Electrical Insulation
  - Low viscosity
  - Long pot-life
  - High elastic modulus
  - Maybe: A high toughness
  - Maybe: A low curing temperature
  - Maybe: a low surface energy



Michael Daly et al 2022 Supercond. Sci. Technol. 35 055014

Introduction

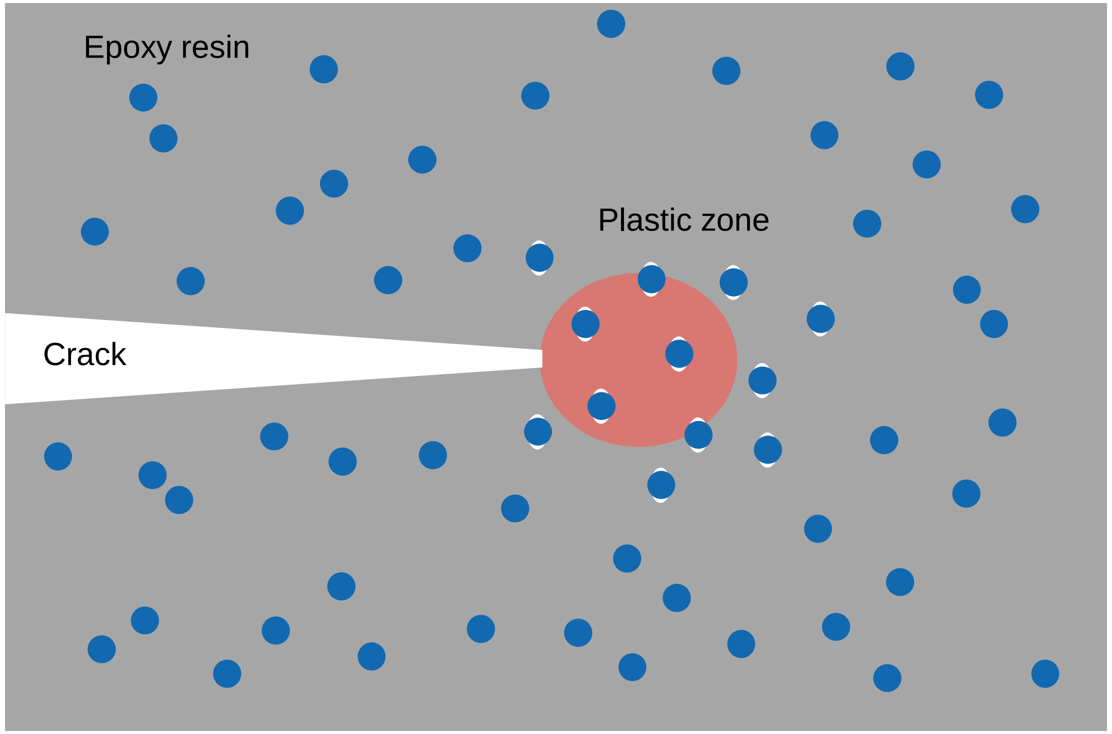
- **The toughness paradox**:

→ For non-stress managed magnets, strength & toughness are needed

→ However, high toughness means more heat dissipation at the crack tip and thus might *also promote quenching, even in the absence of macroscopic cracks*

→ Particles can improve toughness even further by localized yielding

→ Ultimate goal: Gadolinium nanoparticles with high c_p



Motivation

- Superconducting Electromagnets are operated at 4.2 K → Thermal Stresses, Lorentz forces
- Mechanical events such as cracking, delamination & yielding → Loss of superconductivity, «quenching»
- Previous work → Design of slow-curing epoxy systems combining an optimised glass-transition temperature above room temperature but below 100 °C to reduce thermal stresses, with an improved fracture toughness at cryogenic temperatures (77 K).
- Motivation for this work: **employ silica nanofillers** in these systems and try to further improve the fracture toughness of these systems, especially at cryogenic temperatures. Ultimately, use gadolinium oxide nanofillers to simultaneously improve toughness and (local) heat capacity at cryogenic temperatures.

Plain epoxy resin systems

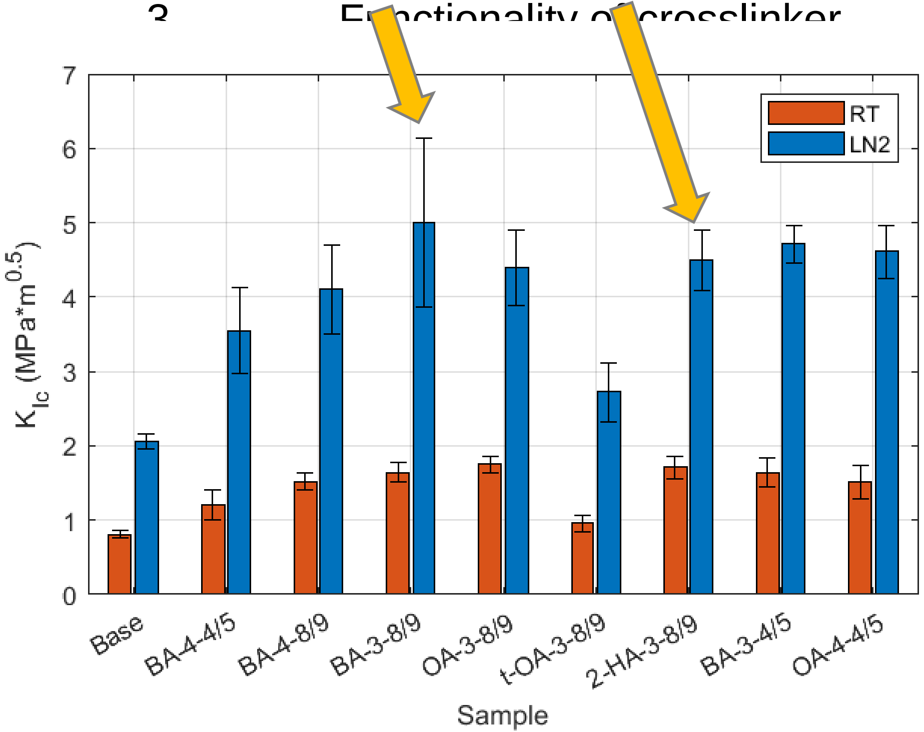
- We use our in-house developed system and compare it to a standard epoxy resin

BA-3-8/9
BA
3

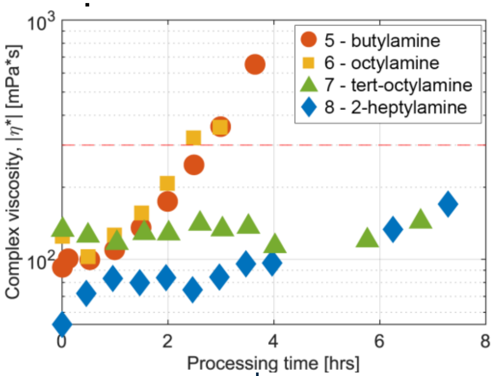
Butylamine
Functionality of crosslinker

Highest toughness:
Short pot-life

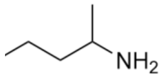
High toughness
Long pot-life



Values of the fracture toughness at RT / 77K.



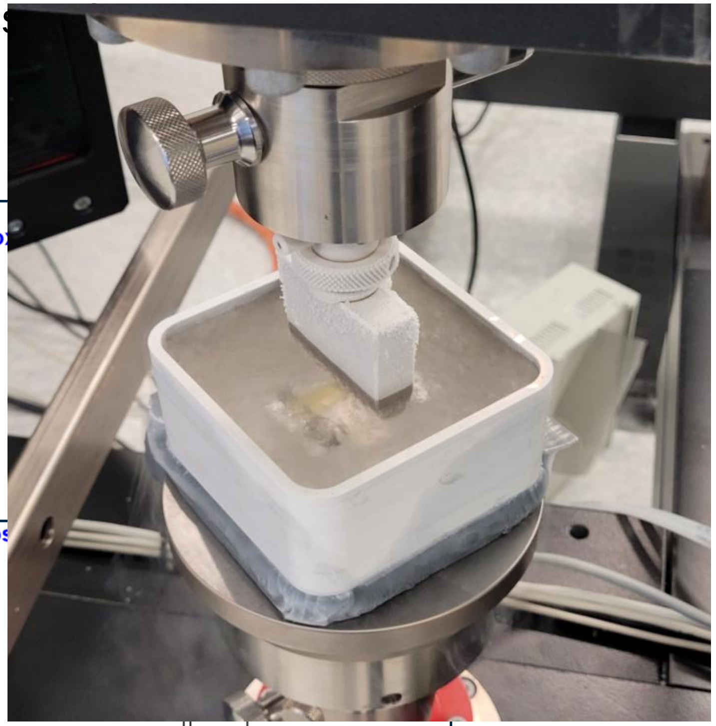
-heptylamine
2-HA



Base resin
Jus

Epo

Cros



A three-point single edge notch bending test in liquid Nitrogen (Setup by A. Brém)

Filled systems – sample preparation

SOFTMAT

- Prepared samples

Matrix \ Vol. % SiO2	**0**	**1.5**	**2.5**	**5**
DGEBA+MPD *'Base system'*	✓			✓
BA-3-8/9 *'Butylamine system'*	✓	✓	✓	✓
2HA-3-8/9 *'Heptylamine system'*	✓	✓	✓	✓
2HA-3-8/9 with 5 mol.% of 2HA replaced with BA *'Mix system'*	✓	✓	✓	✓

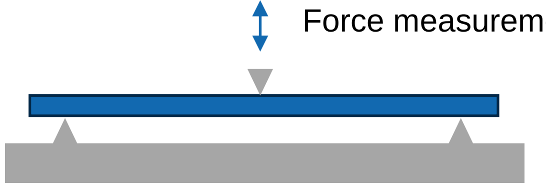
- Preparation procedure

1) DGEBA and Nanopox-F400 (DGEBA with 40 wt.% nano-SiO2) are weighed in appropriate amounts for target concentration and degassed at 75°C for 30 min.
2) MPD (the crosslinker) is added, the mixture degassed again while the MPD dissolves
3) The mixture is cooled down to ~30°C and the liquid amine chain extender added. No further degassing
4) Pour into Teflon coated mold preheated to 100C, cure 1h30min at 165°C
5) Waterjet-cutting of samples for fracture tests and thermomechanical behaviour

Results

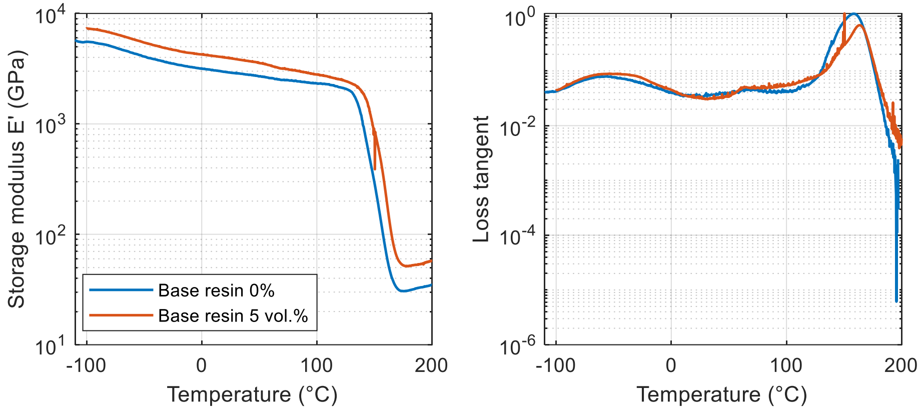
SOFTMAT

- DMTA



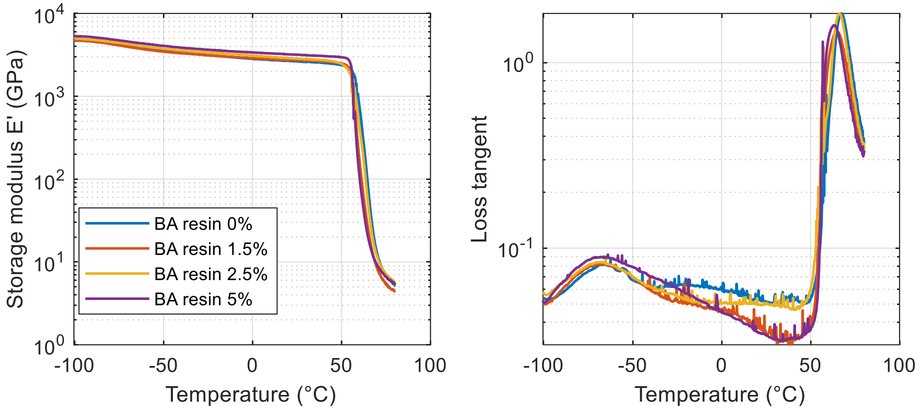
Oscillatory displacement @ 1Hz
Force measurement via FRT

Base resin



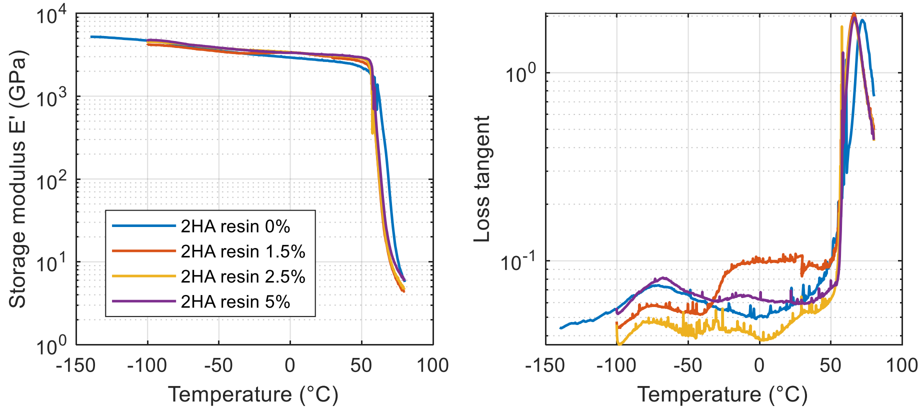
Tg values
158.6
163.6

Butylamine system



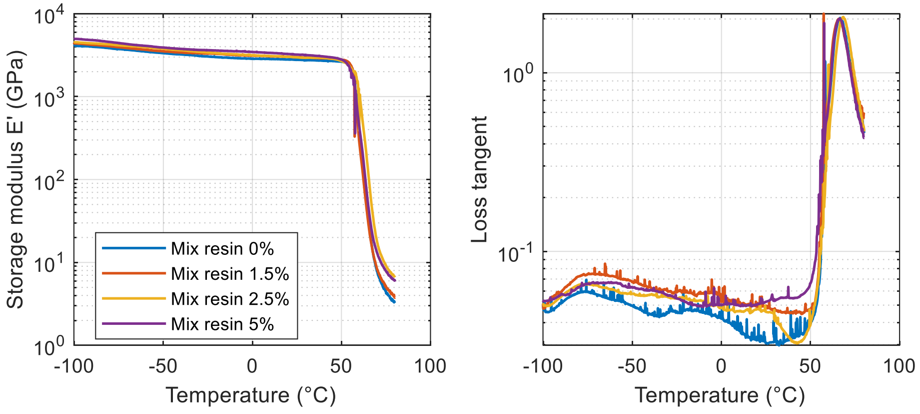
Tg values
67.4
64.7
66.0
63.3

2-Heptylamine system



Tg values
71.9
66.1
66.1
66.6

Mix system

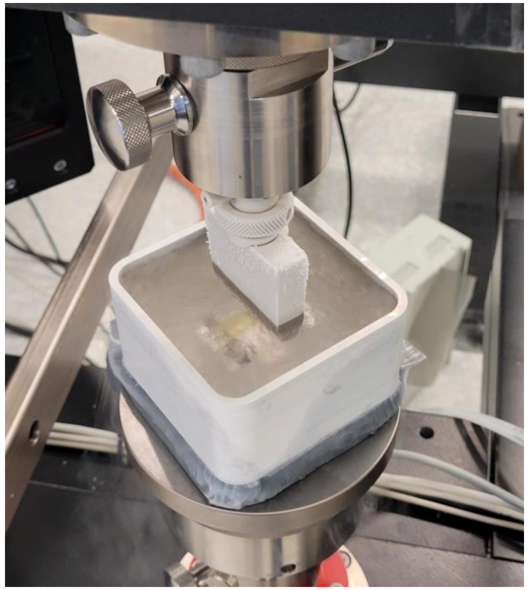


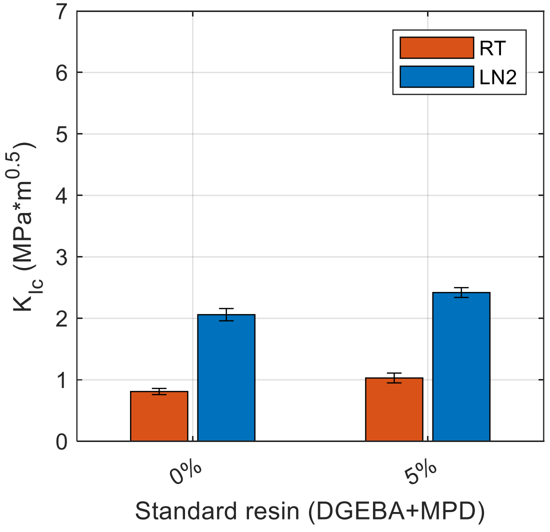
Tg values
66.6
66.0
68.5
66.4

The resins with particles are properly cured
The amount of chain-extender is optimised to obtain a Tg that is above RT but below 100 °C

Results

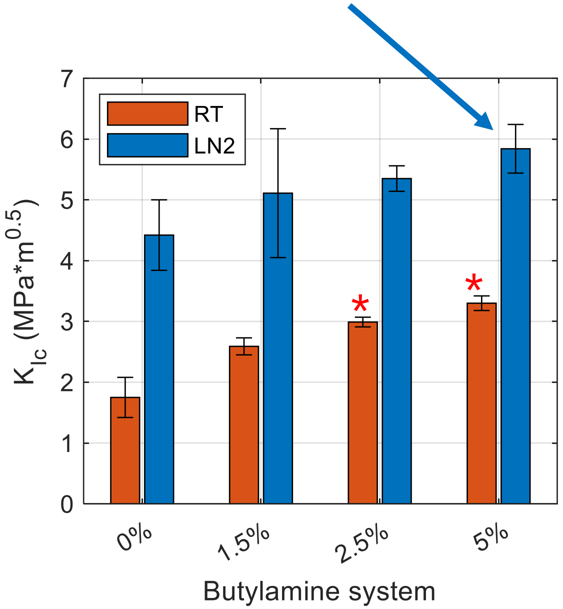
- SENB Testing



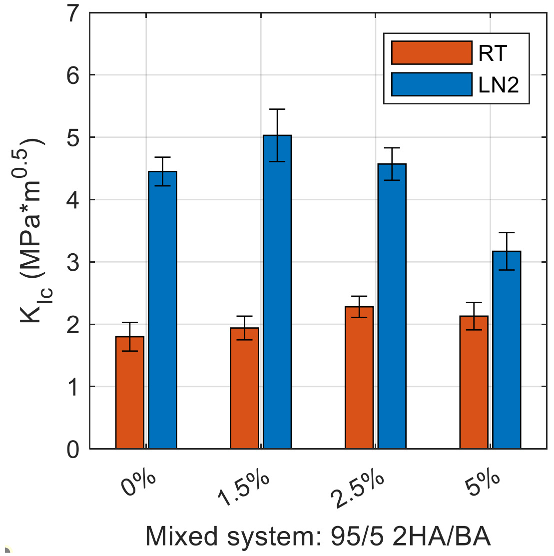


Standard resin (DGEBA+MPD)

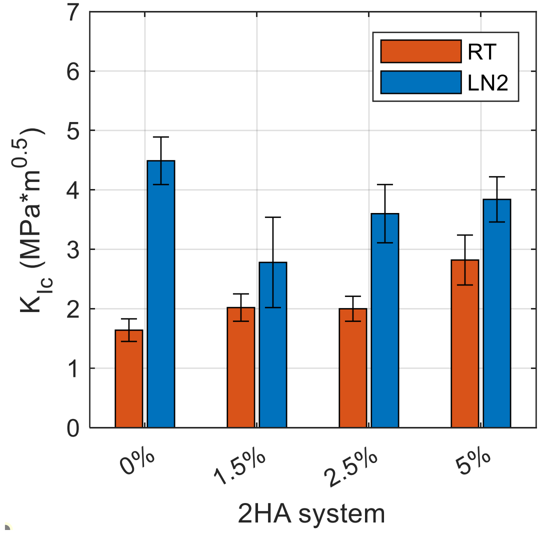
30% increase!



Butylamine system

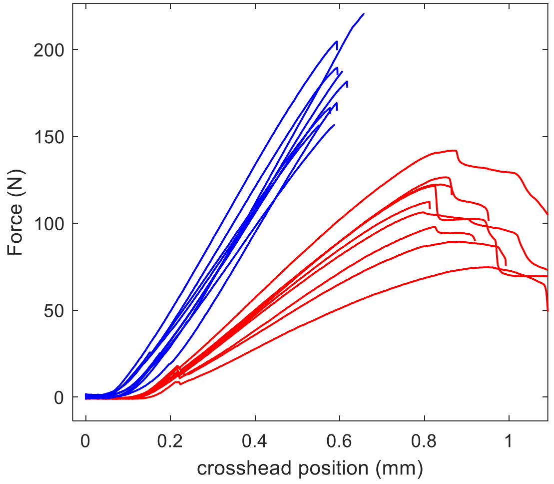


Mixed system: 95/5 2HA/BA



2HA system

Butylamine, 5% system



*: Size of plastic zone gets very large with respect to sample size.

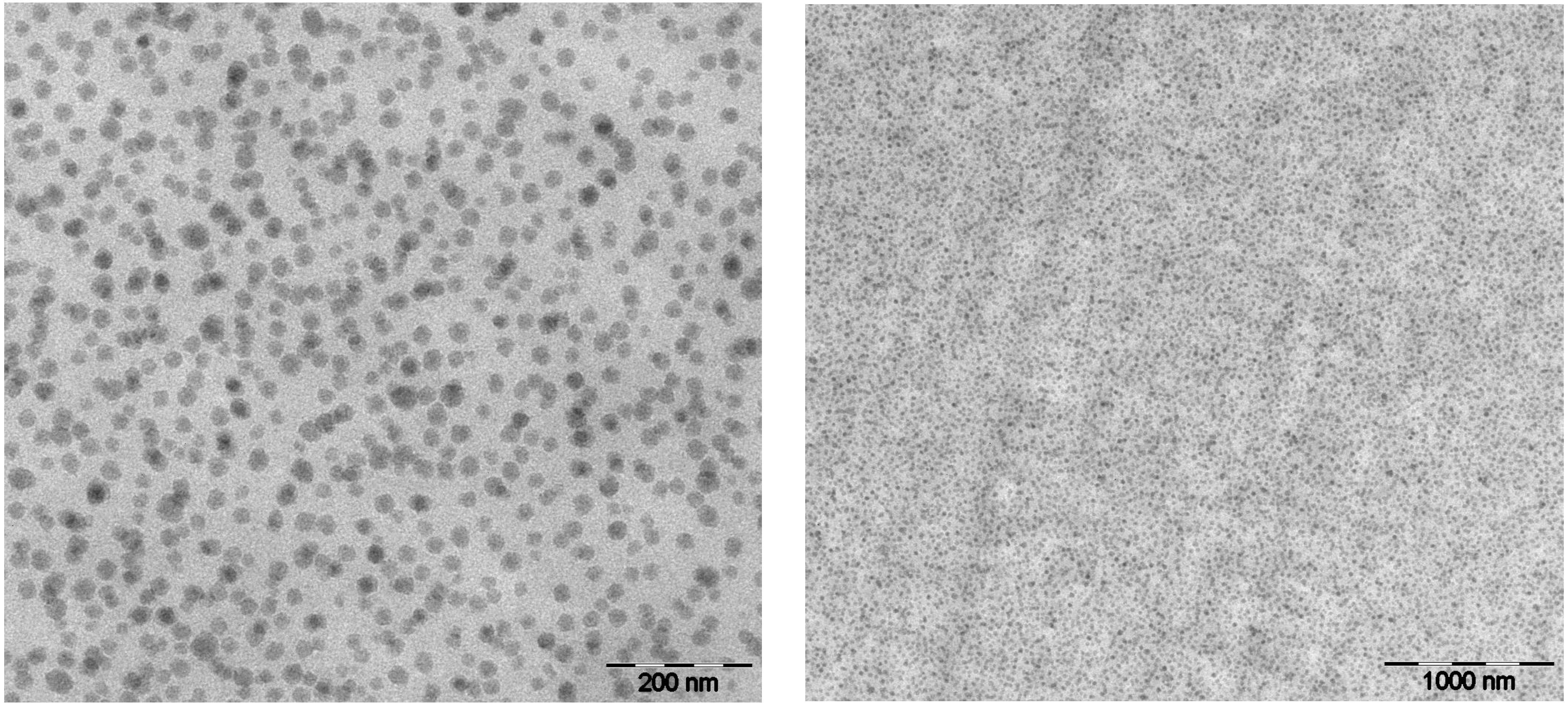
Criterion for valid K_{Ic}

$$b, a, h - a \geq 2.5 \left(\frac{K_I}{\sigma_y}\right)^2$$

Results

- Transmission electron microscopy

7.5 vol. % SiO2, Butylamine sample (excluded from study due to bubbles) 60 nm section



Particles are not agglomerated and well dispersed

Good dispersion is also observed on samples with decreased toughness

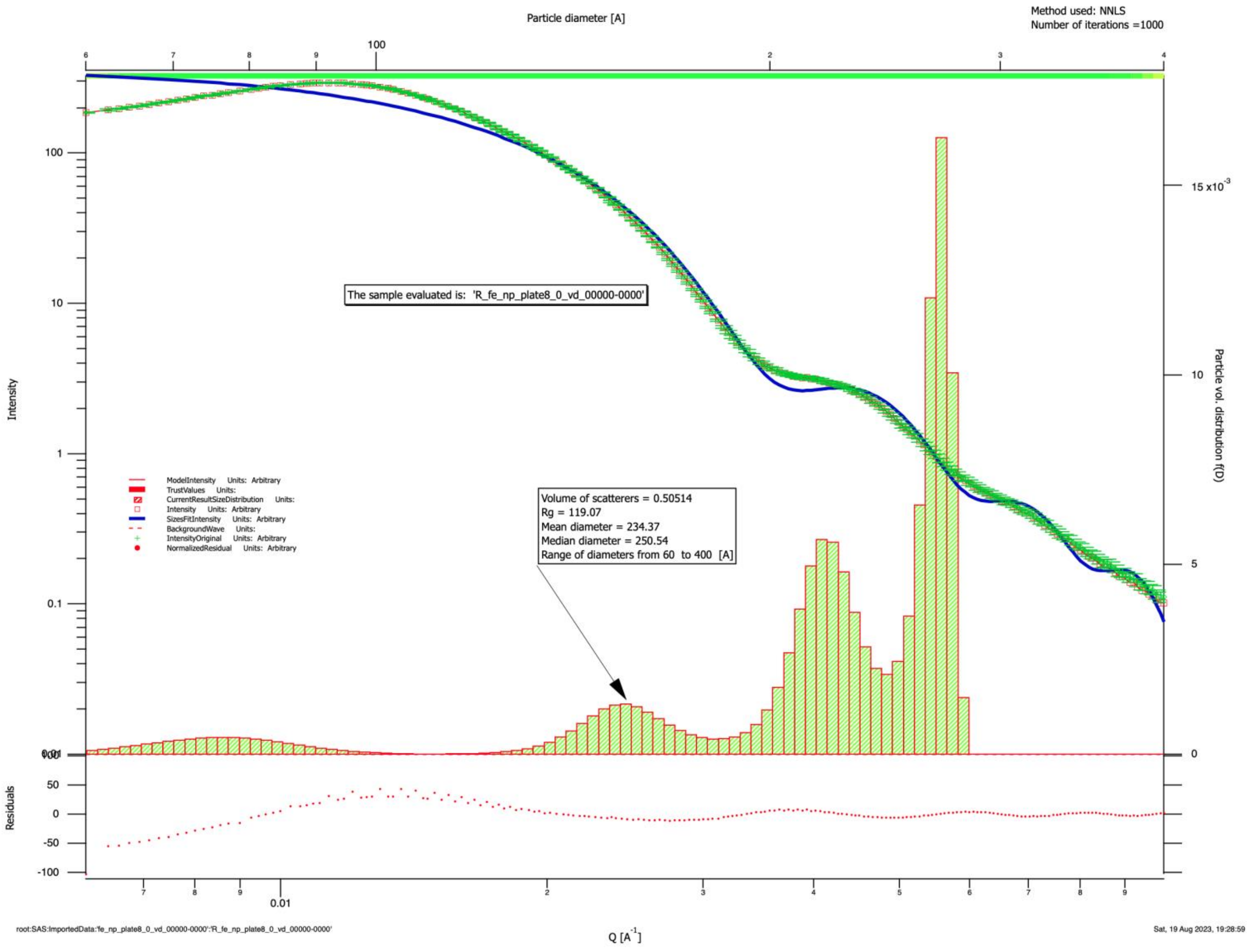
Results

- Scattering curves

- High-q peaks: Due to polymer structure
  - VdW peak
  - Epoxy network peak

- Clear scattering in mid-range from particles
  - Can be fitted to obtaine particle size distribution

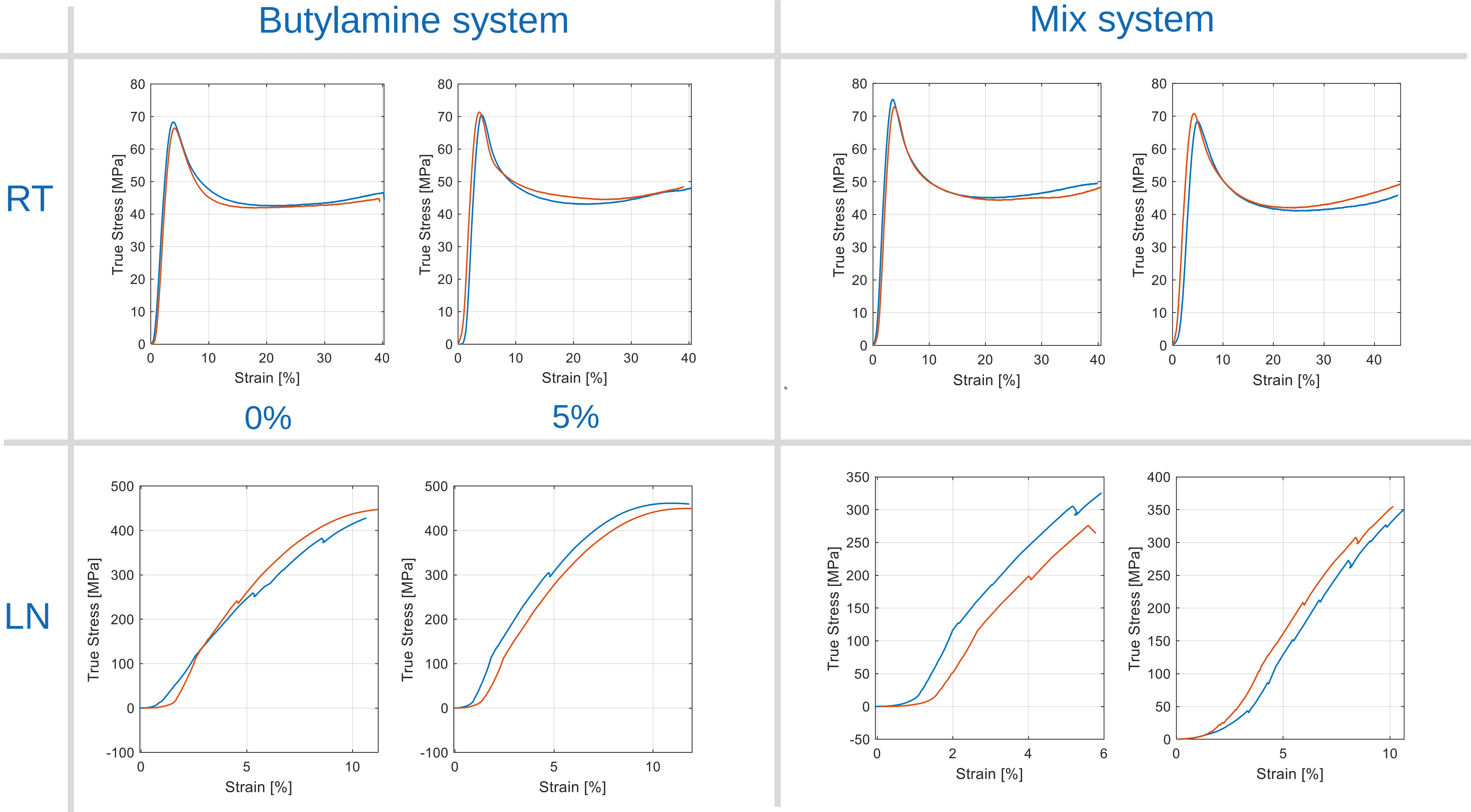
- State of agglomeration (low q-range)
  - The low-q scattering without particles is still present, see also
  - Adnan et al., J.Sol-Gel Sci. & Technology, 2020, 95, 783-794



- Scattering curves from other systems: same characteristics

Results

- Compressive Yield behaviour



Butylamine system

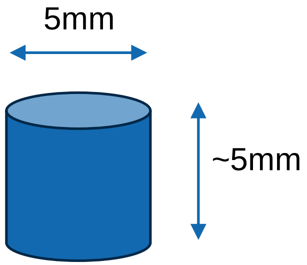
Mix system

RT

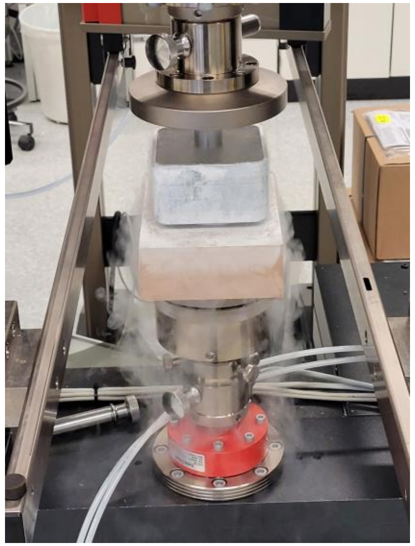
0%

5%

LN

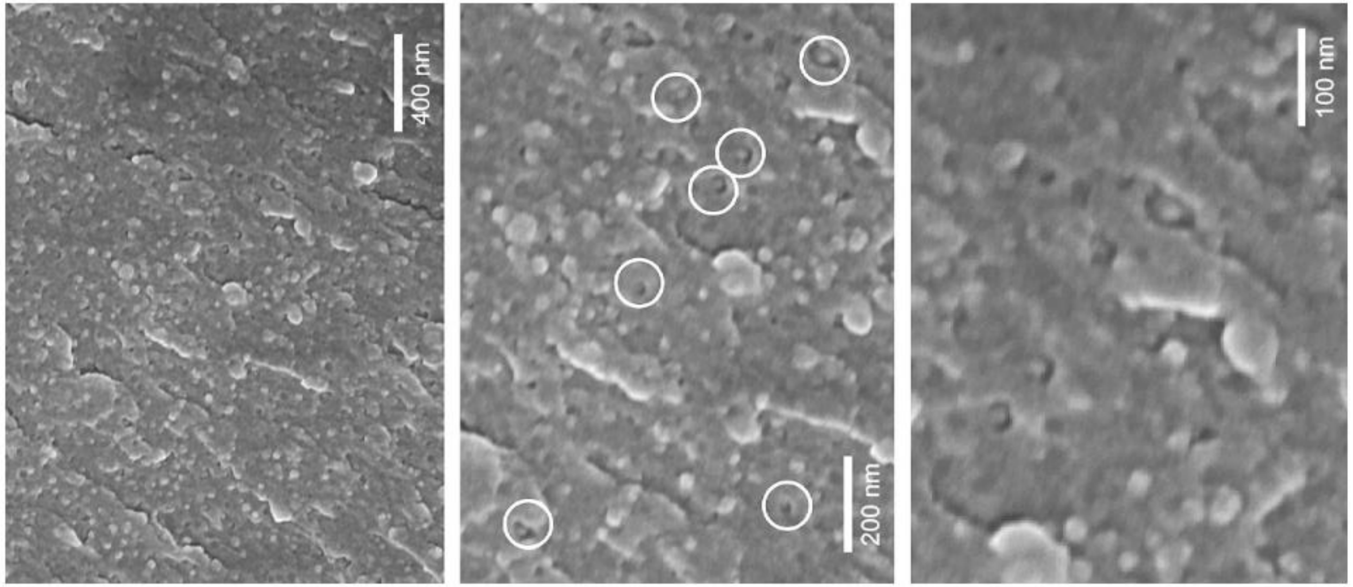


- Compliance corrected
- True stress (assuming constant volume)



Results

- Conclusion
  - We engineered epoxy systems with tuned Tg and very high toughness
  - Particles improved toughness for our systems
  - The reason for this huge improvement might be lower particle-matrix adhesion



A.J. Kinloch et al, 2006, Polymer, 48 530-541

Outlook

- Wrapping up this project
  - Surface energy measurements of cured resins
  - Rheological behaviour of selected mixes
  - SEM on crack surfaces

- Possible new research directions
  - Engineering low-surface-energy adhesives: Perfluorinated compounds
  - Employing high c_p fillers:
    - Gd_2O_3 nanoparticles
    - Gadolinium acetate tetrahydrate dispersion

- PhD 4-year mark: September 2024