

Tough epoxies for cryogenic applications

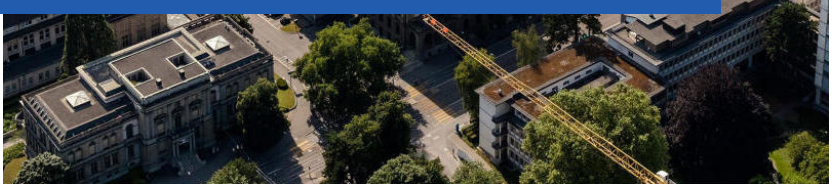
Pascal Studer and Theo Tervoort



Acknowledgements

Bernhard Auchmann, André Brem (PSI), Roland Piccin (CERN), Alain Schwegler and Kirill Feldman (ETH Zurich)

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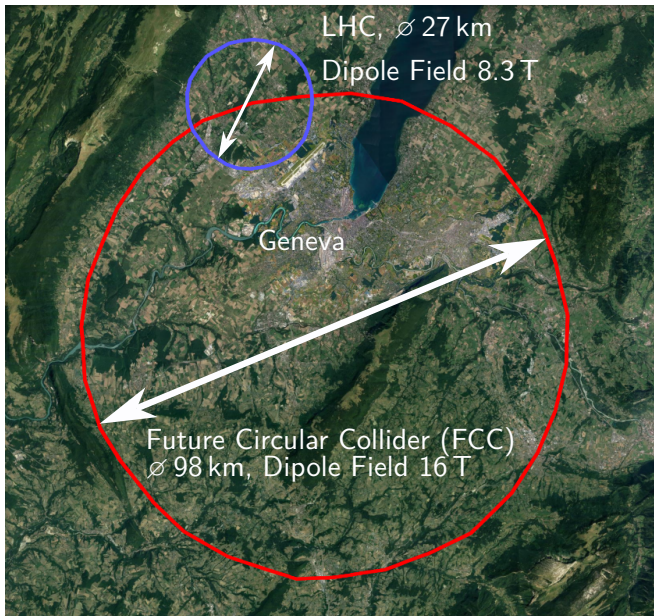
Introduction

High Toughness Epoxy Systems

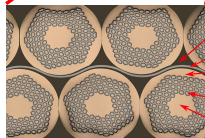
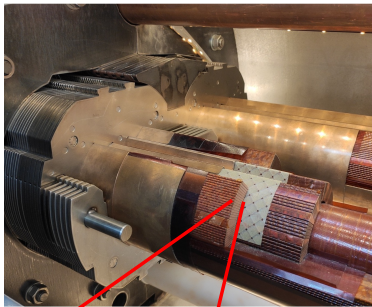
Nanocomposites

Low-Surface-Energy Epoxy Systems

Conclusions



- To change from 8 T to 16 T new coil concepts are needed
- The cables, made by Nb_3Sn superconducting strands are insulated with S2-glass and wound around titanium or stainless steel poles
- Heat treatment is necessary to create superconducting phase (e.g. 180 h @ 660 °C)
- To ensure solidity and insulation of coil windings, coils are impregnated with epoxy resin after “baking process”
- Operating temperature of the magnets: liquid helium @ 1.9 K
- Different materials with different thermal expansion coefficients result in thermal stresses
- High Lorentz forces additional to the thermal stresses lead to “micro-cracking” of the epoxy matrix



epoxy

glass mat

copper

Nb₃Sn superconductive filament

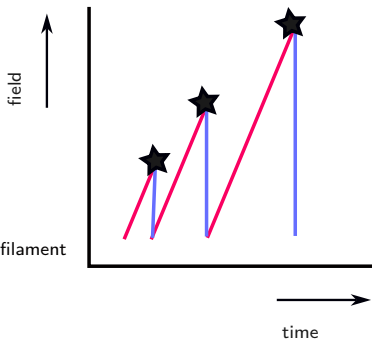
copper core

Berkeley Laboratories

Stresses in epoxy insulation

- Thermal stresses
- Lorentz forces

Heat that develops during cracking and/or delamination and/or yielding leads to *quenching*, which necessitates *training* of the magnets:

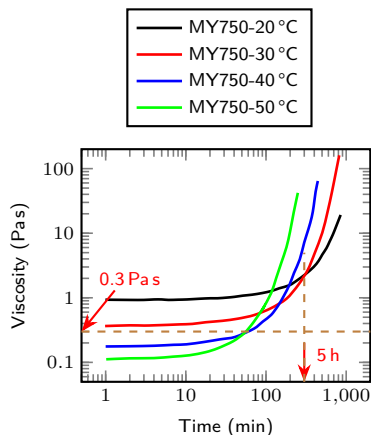
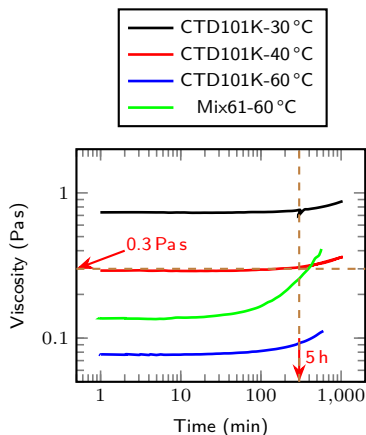


Comparison of 3 commercially available epoxy systems

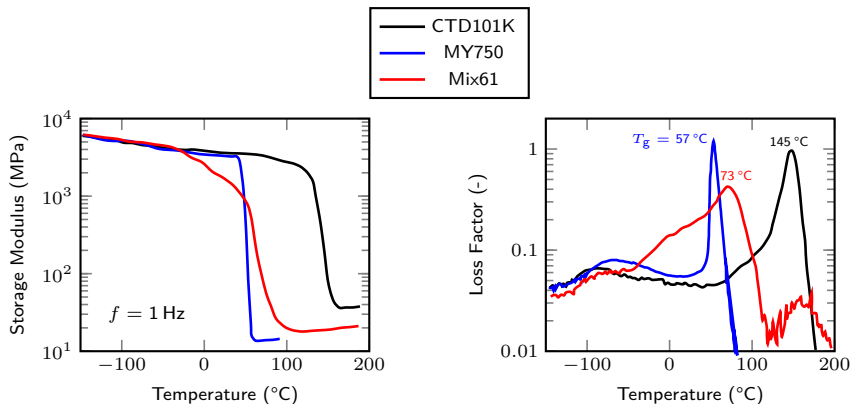
- **CTD-101K** (Composite Technology Development, Inc., Colorado, USA): Aromatic glycidyl amine resin based on diglicidyl ether of bisphenol-A (DGEBA) with an anhydride curing agent.
- **NHMFL 61 "Mix 61"** (National High Magnetic Field Laboratory, Tallahassee, Florida, USA) includes a high molecular weight additive secondary curing agent
- **MY 750 + HY 5922**: (Huntsman Advanced Materials GmbH, Basel, Switzerland): Aromatic glycidyl amine resin based on diglicidyl ether of bisphenol-A (DGEBA) with a liquid, aliphatic polyamine hardener

Potlife requirements

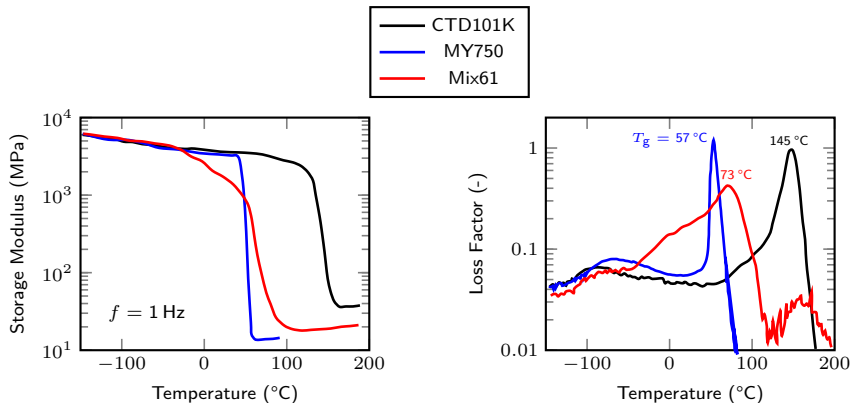
Processing conditions for impregnation of superconducting coils: a viscosity of $\eta = 0.3$ Pa s should be guaranteed for at least 5 h at a given impregnation temperature (dashed brown lines).



Dynamic Mechanical Analysis



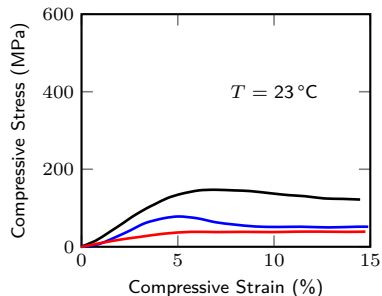
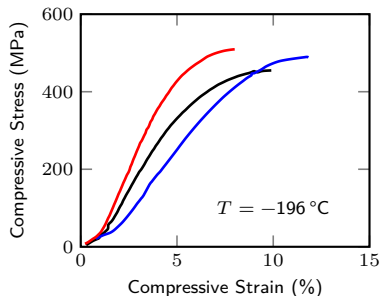
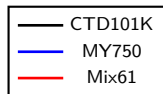
Dynamic Mechanical Analysis



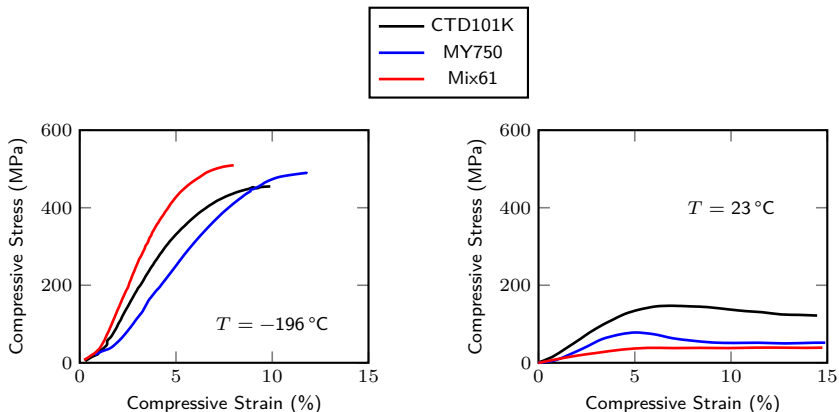
At cryogenic temperatures, the Young's modulus is dominated by van der Waals forces

For all epoxies: $E \approx 6$ GPa to 8 GPa

Uniaxial Compression Testing



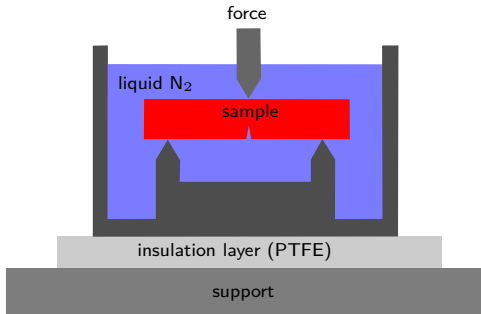
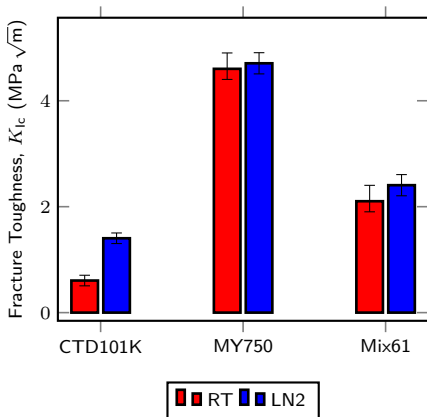
Uniaxial Compression Testing



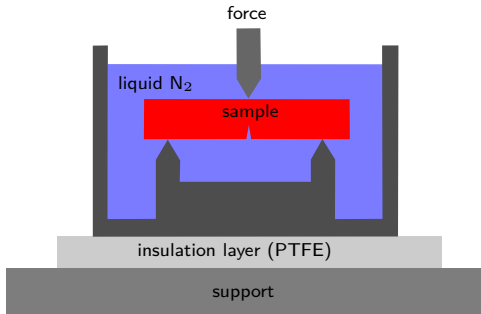
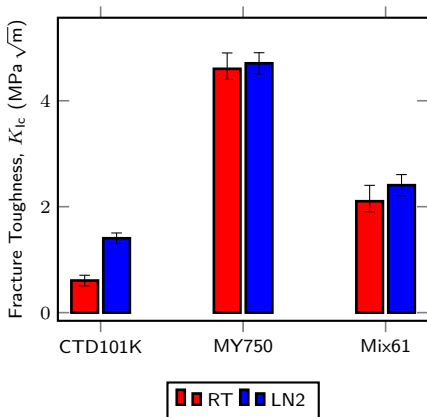
At cryogenic temperatures, the yield stress, $\sigma_y \propto E$, is also dominated by van der Waals forces

For all epoxies: $\sigma_y \approx 450$ to 550 MPa

Fracture Toughness Testing



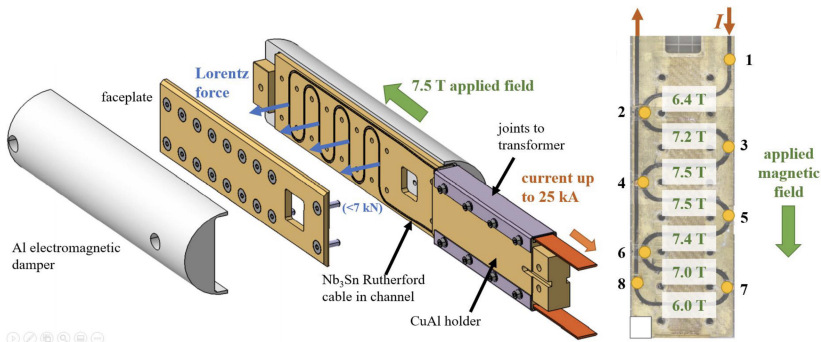
Fracture Toughness Testing

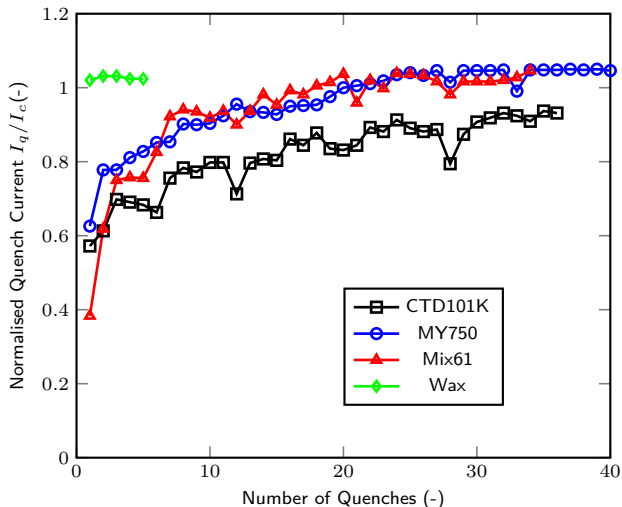


At cryogenic temperatures, K_{Ic} can be very different

Interestingly, $K_{Ic}^{RT} < K_{Ic}^{LN2}$

BOX Facility to Measure Training Curves of Nb₃Sn Rutherford Cables



Training Curves of Nb₃Sn Rutherford Cables with Various Insulator Materials using the BOX Facility

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Nanocomposites

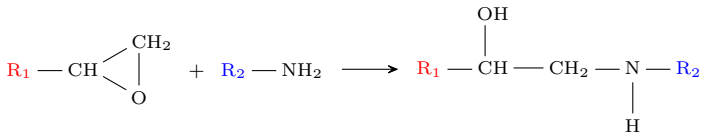
Low-Surface-Energy Epoxy Systems

Conclusions

Monomers used for synthesising the epoxy resins

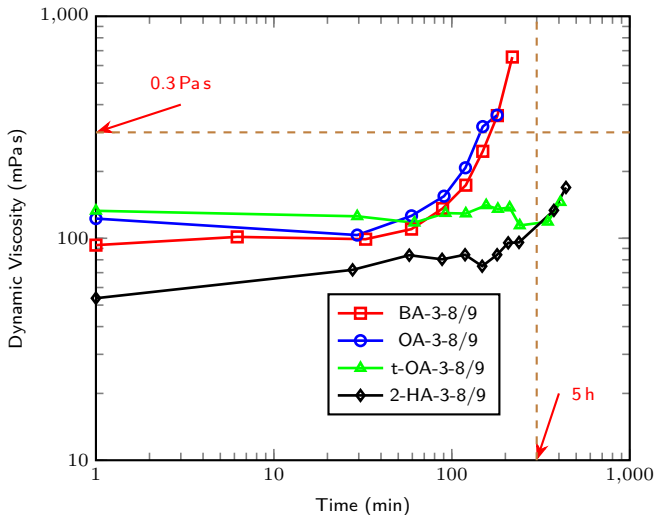
f denotes the functionality. EEW/AEW denotes the epoxy or the amine hydrogen equivalent weight.

Name	Abbreviation	Chemical Formula	f	EEW/AEW (g/mol)
diglycidyl ether of bisphenol A	DGEBA		2	172
m-phenylenediamine	MPD		4	27.0
n-octylamine	OA		2	64.6
n-butylamine	BA		2	36.6
tert-octylamine	t-OA		2	64.6
2-heptylamine	2-HA		2	57.6



Reaction of an epoxy group with an amino group.

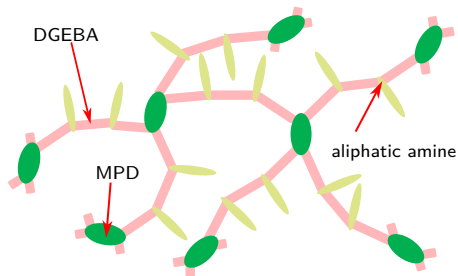
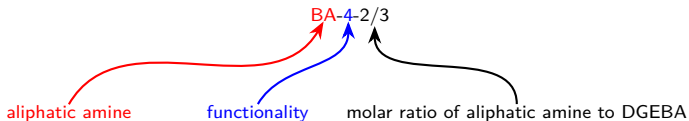
Influence Chemical Structure on Potlife



Steric hinderance of the methyl group in β -position significantly increases the potlife.

Network Design Parameters

R is the molar ratio of chain extender molecules to DGEBA molecules. The variable f is the average functionality of the tetrafunctional hardener, based on the excess of hardener used. If no excess of hardener is used, $f = 4$.

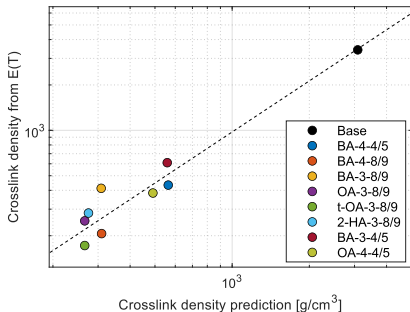
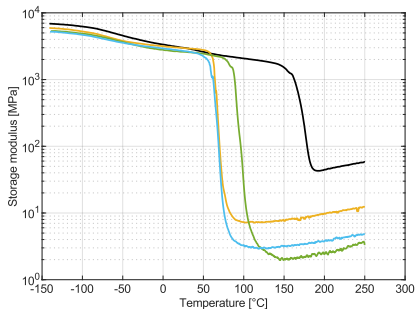


schematic network: functionality $f = 4$; ratio $R = 2/3$

Assuming a perfectly cured network, each tri- or tetrafunctional MPD molecule contributes $3/2$ or $4/2$ of elastically active chains, respectively. The molar volumetric crosslink density can then be estimated using the equation:

$$n_{\text{pred}} = \frac{\rho}{M_{\text{MPD}}} \cdot \frac{m_{\text{MPD}}}{m_{\text{tot}}} \cdot \frac{\bar{f}}{2}$$

Dynamic Mechanical Analysis



Estimation of the crosslink density n :

$$n = \frac{G(T)}{RT} = \frac{E(T)}{3RT} \quad T > T_g$$

Influence of the Ratio R of Alkylamine to DGEBA Linkages

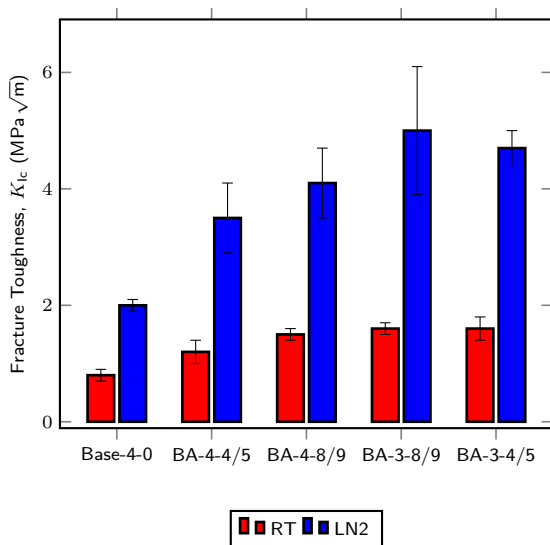
Sample	f	R	T_g °C	ρ g/m ³	n_{pred} mol/m ³	n_{meas} mol/m ³
Base-4-0	4	0	179	1.217	3088	3415
BA-4-4/5	4	4/5	76	1.153	563.2	433.3
BA-4-8/9	4	8/9	68	1.145	309.6	206.5
BA-3-8/9	3	8/9	73	1.147	308.5	412.4
OA-3-8/9	3	8/9	54	1.109	266.1	250.8
t-OA-3-8/9	3	8/9	100	1.108	266.1	172.1
2-HA-3-8/9	3	8/9	72	1.115	275.2	282.7
BA-3-4/5	3	4/5	79	1.153	558.3	609.7
OA-4-4/5	4	4/5	61	1.115	490.8	383.9

Increasing the ratio R of alkylamine to DGEBA molecules, the length of the linear chains between crosslinks is increased, thus reducing the crosslink density n and, thereby, the density ρ and T_g .

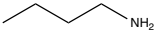
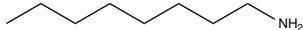
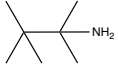
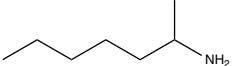
Influence of the Average Functionality f of the MPD Hardener

Sample	f	R	T_g °C	ρ g/m ³	n_{pred} mol/m ³	n_{meas} mol/m ³
Base-4-0	4	0	179	1.217	3088	3415
BA-4-4/5	4	4/5	76	1.153	563.2	433.3
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The average functionality f can also be tuned to modify the distance between crosslinking molecules. However, since the mass fraction of hardener is quite small, the predicted crosslink density does not change much when f is changed from 4 to 3

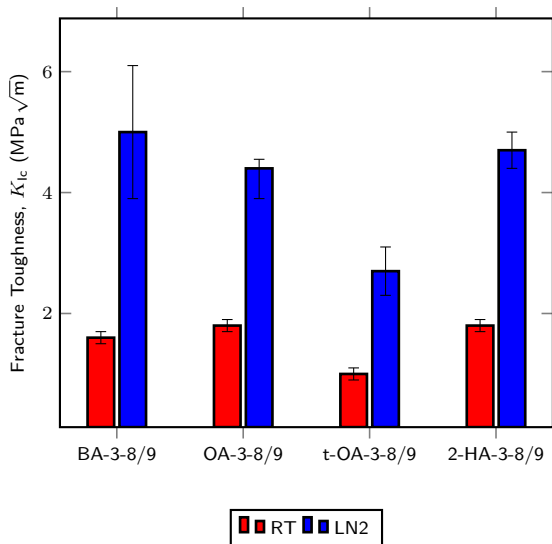
Influence of f and R on RT and LN2 Fracture Toughness

Effect of chemical composition

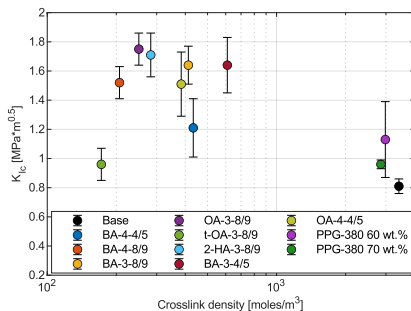
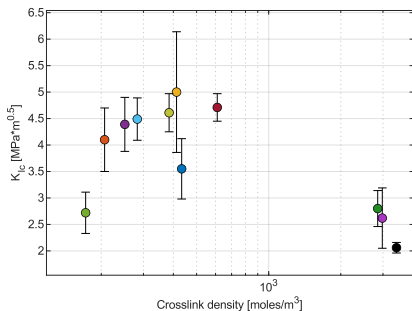
Sample	Chemical Structure	T_g °C	ρ g/m ³	n_{pred} mol/m ³	n_{meas} mol/m ³
Base-4-1		179	1.217	3088	3415
BA-4-4/5		76	1.153	563.2	433.3
BA-4-8/9		68	1.145	309.6	206.5
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Comparison of using dangling side chains of different chemical composition and molar weight, while the other network parameters such as f and R , are held constant.

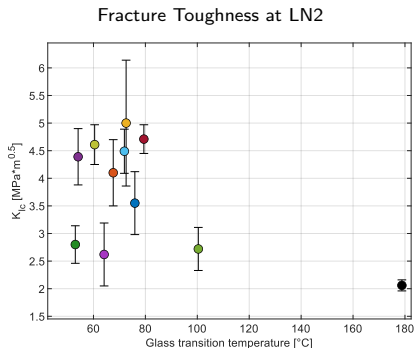
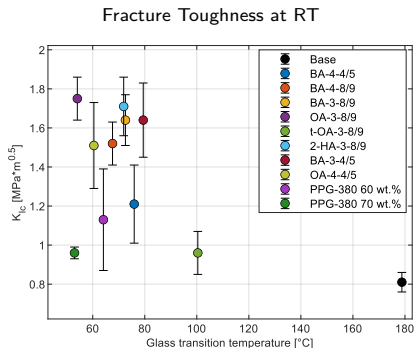
Influence of Chemical Composition on Fracture Toughness



Fracture Toughness as a Function of Crosslink Density

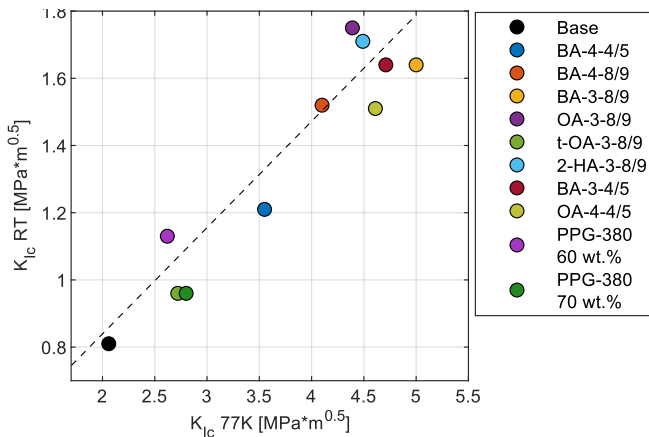


Fracture Toughness as a Function of T_g

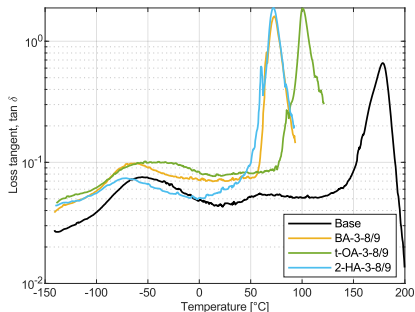
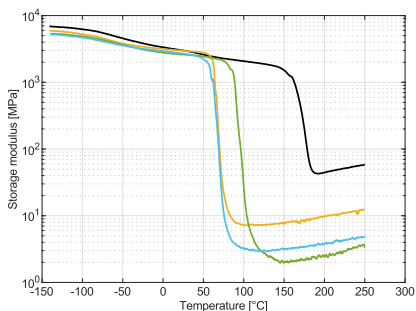


PPG-DGE 380 x wt %: x wt % poly(propylene glycol) diglycidyl ether of molecular weight 380 mixed with (100-x) wt % DGEBA

Correlation between Fracture Toughness at RT and LN2

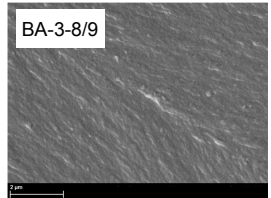
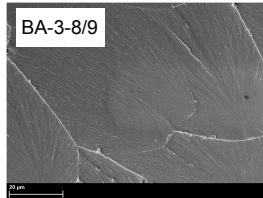
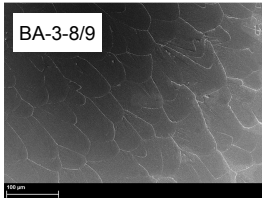
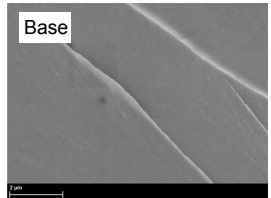
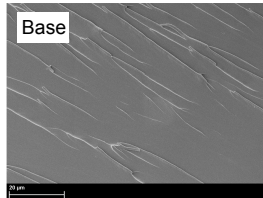
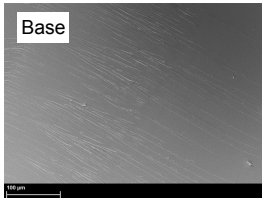


Dynamic Mechanical Thermal Analysis (DMTA)



No apparent correlation with increased fracture toughness at cryogenic temperatures: sample t-OA-3-8/9 with reduced fracture toughness has similar dynamic mechanical behaviour as samples BA-3-8/9 and 2-HA-3-8/9 which have high fracture toughness.

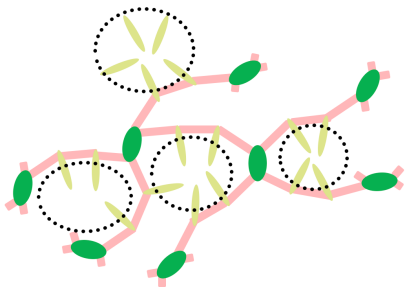
Scanning Electron Microscopy (SEM)



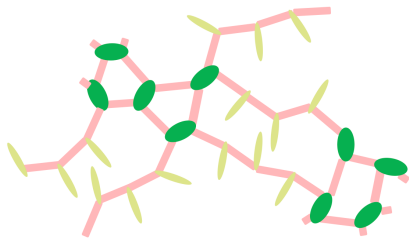
SEM pictures after cryogenic fracture toughness testing

Alternative Explanations for Increased Cryogenic Fracture Toughness

Nanophase Separation

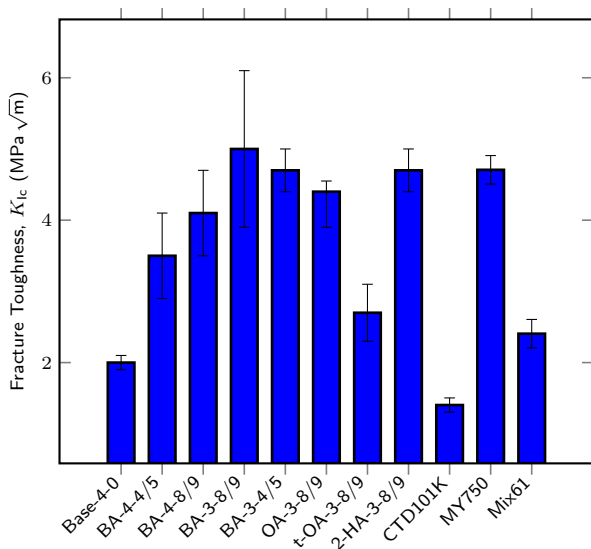


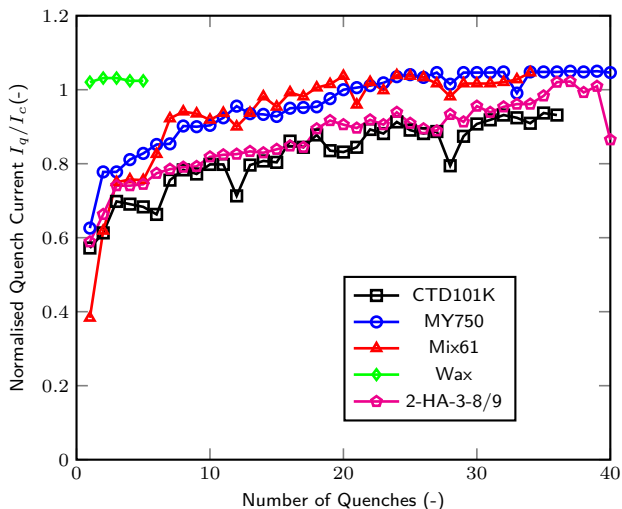
Inhomogeneous Networks



- No differences in wide-angle and small-angle X-ray scattering
- No difference in DMTA

Cryogenic Fracture Toughness of All Systems



Training Curves of Nb₃Sn Rutherford Cables with Various Insulator Materials using the BOX Facility

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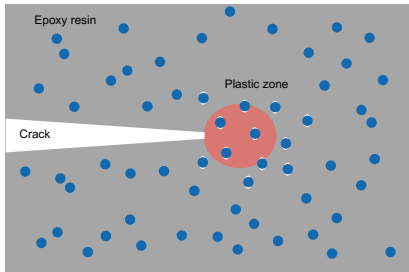
High Toughness Epoxy Systems

Nanocomposites

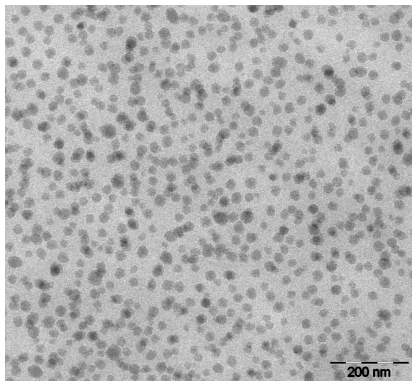
Low-Surface-Energy Epoxy Systems

Conclusions

Why nanocomposites?



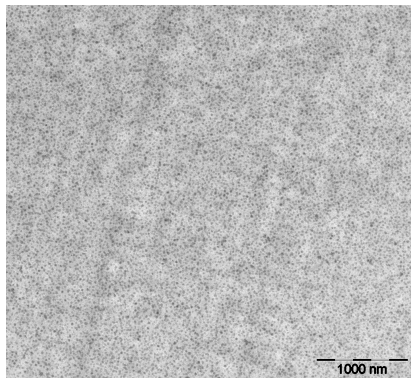
- For non-stress managed magnets, strength & toughness are needed
- However, high toughness means more heat dissipation at the crack tip and thus might also promote quenching, even in the absence of macroscopic cracks
- Particles can improve toughness even further by localized yielding
- **Ultimate goal: use of gadolinium nanoparticles with high c_p at cryogenic temperatures**



BA-3-8/9 sample with 7.5 vol % SiO₂

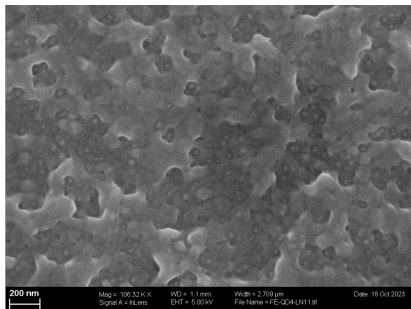
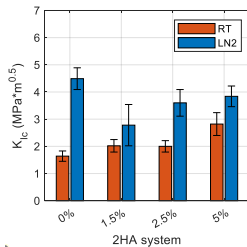
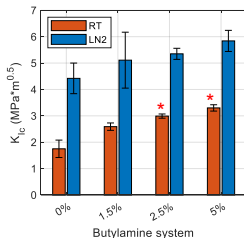
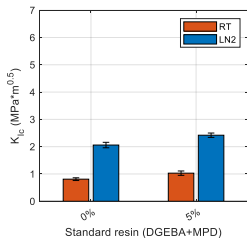
Procedure:

- 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.
- MPD (the crosslinker) is added, the mixture degassed again while the MPD dissolves.
- The mixture is cooled down to about 30 °C and the liquid amine chain extender added. No further degassing.
- Pour into Teflon-coated mould preheated to 100 °C, cure 1 h 30 min at 165 °C.
- Waterjet-cutting of samples for fracture tests and thermomechanical behaviour

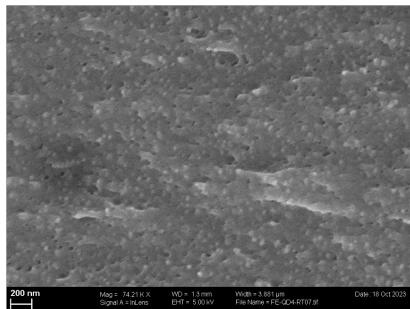


BA-3-8/9 sample with 7.5 vol% SiO₂

- No agglomeration.
- The resins with particles are properly cured.
- T_g is optimised around 60 °C



BA with 5 wt % @ RT



BA with 5 wt % @ LN2

Surface Free Energy

By measuring the static contact angle with respect to water, ethylene glycol and iodomethane, we can estimate the dispersive and polar contributions to the surface free energy.

Base system	BA-3-8/9 system	2-HA-3-8/9 system
Dispersive 35.5 J m^{-2}	Dispersive 36.3 J m^{-2}	Dispersive 34.3 J m^{-2}
Polar 10.1 J m^{-2}	Polar 2.9 J m^{-2}	Polar 5.3 J m^{-2}
Total 45.6 J m^{-2}	Total 39.2 J m^{-2}	Total 39.6 J m^{-2}

Reduced surface energy of the butyl amine and heptyl amine systems possibly promotes detachment of the nanoparticles from the matrix, which then initiates plastic deformation, thus increasing the fracture toughness.

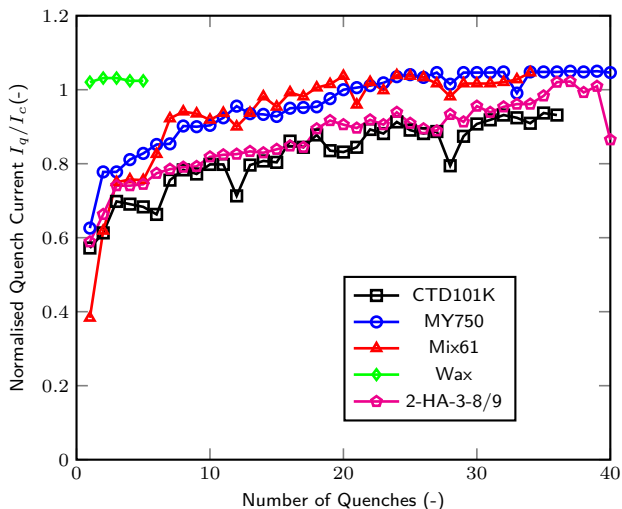
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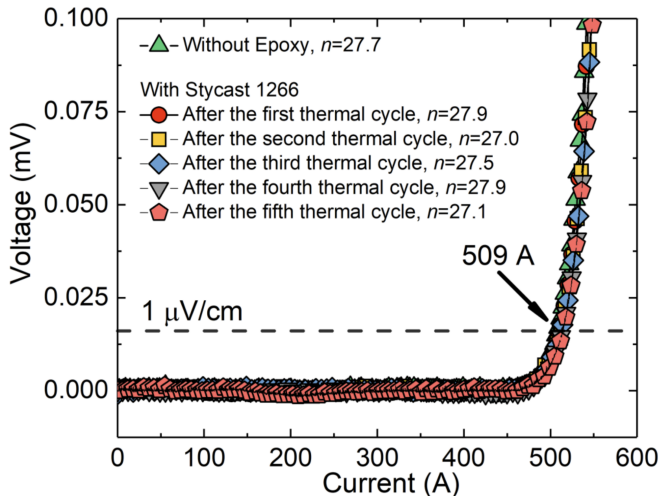
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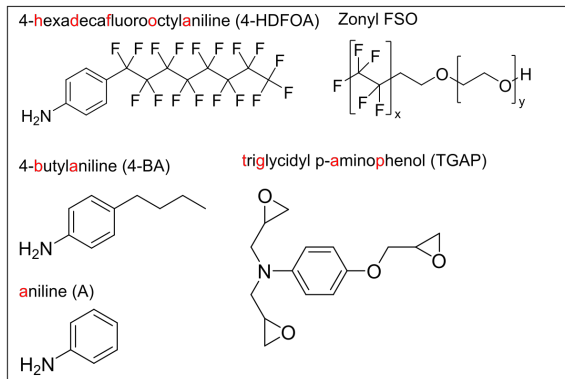
Low-Surface-Energy Epoxy Systems

Conclusions

Training Curves of Nb₃Sn Rutherford Cables with Various Insulator Materials using the BOX Facility



V-I characteristics of the REBCO sample painted with mould release ZYVAX at 77 K. The sample was tested without epoxy and then tested with the epoxy Stycast 1266 after thermal cycles.



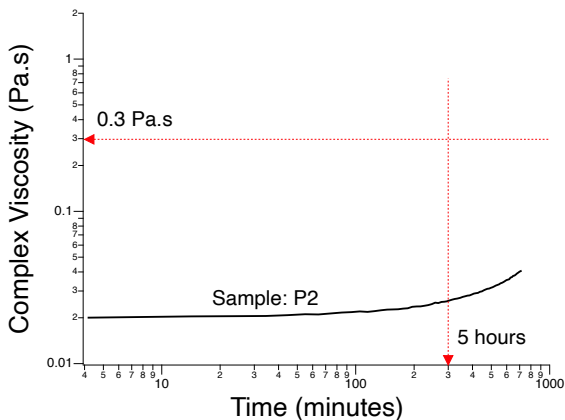
Chemical structure of the building blocks used for synthesis of the epoxy resins. The epoxide molecule (TGAP) has three monofunctional epoxy groups. The corresponding reactants are phenylamines substituted with various moieties at the 4-position. The amine functional group can react with two epoxide groups.

$$\frac{m_{\text{TGAP}}}{M_{\text{TGAP}}} \cdot f_{\text{TGAP}} = \frac{m_{\text{A}}}{M_{\text{A}}} \cdot 2 + \frac{m_{\text{BA}}}{M_{\text{BA}}} \cdot 2 + \frac{m_{\text{HDFOA}}}{M_{\text{HDFOA}}} \cdot 2$$

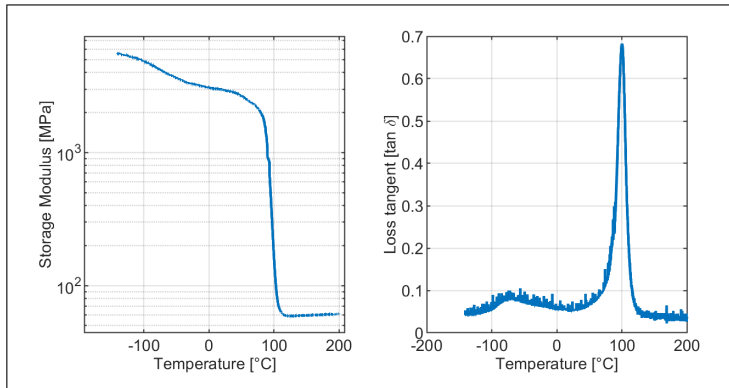
Comparison of surface energy γ of low-surface-energy epoxy resins P1-P4 to wax and the base system

Resin	\angle H ₂ O	\angle (CH ₂ OH) ₂	\angle CH ₃ I	γ_d (mN m ⁻¹)	γ_p (mN m ⁻¹)	γ (mN m ⁻¹)
Base	65 ± 1	35 ± 2	35 ± 2	35.5	10.1	45.6
Wax	90 ± 2	87 ± 2	27 ± 2	7.4	12.7	20.1
P1	88 ± 3	56 ± 2	14 ± 1	17.9	6.1	24.0
P2	88 ± 4	68 ± 1	20 ± 3	15.6	6.3	21.9
P3	91 ± 4	67 ± 1	30 ± 2	14.3	6.5	20.8
P4	88 ± 4	68 ± 1	25 ± 3	14.6	5.8	20.4

Potlife of sample P2 (5% 4-HDFOA)

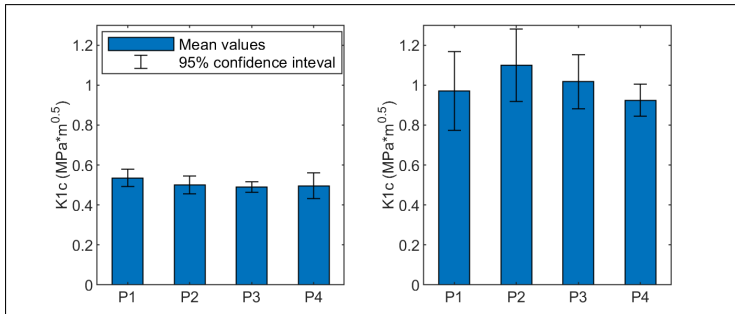


DMTA of sample P2 (5% 4-HDFOA), other samples are similar



All samples have a T_g of about 100 °C

Fracture toughness of all samples at room temperature and at 77 K



The low-surface-energy epoxy systems have a fracture toughness comparable to CTD101K.

Introduction

High Toughness Epoxy Systems

Nanocomposites

Low-Surface-Energy Epoxy Systems

Conclusions

Conclusions

- Incorporating various short-chain alkylamines, acting as chain extenders, into the epoxide backbone of the covalent network, allowed for epoxy resins with carefully tuned T_g 's.
- Significant increases in the cryogenic and room-temperature fracture toughness were observed with the use of flexible-chain alkylamines such as butylamine, octylamine and 2-heptylamine, however not with bulky alkylamines such as tert-octylamine.
- The use of sterically hindered amines such as 2-heptylamine, decelerated the curing reaction, thereby extending the processing window by several hours.
- The well-known toughening effect of nano-silica also works at cryogenic temperatures.
- Epoxy resins consisting of 4-butylaniline mixed with a perfluorinated aniline and crosslinked with a tertiary epoxy (TGAP) reduces the surface energy of these resins to the level of polyolefin waxes.

Thank you for your attention!

$\tan(\delta)$ of all samples: all samples have a T_g of about 100 °C

