Swiss Accelerator Research and Technology

CHART Scientific Report (Final Report for Phase 2)

Tough epoxy resin systems for cryogenic applications (MagRes)

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1. Introduction / Original goals of this project

Epoxy thermoset systems are the preferred materials for encapsulating superconducting coils in high and low-temperature superconductive magnets. This application demands adherence to several boundary conditions related to mechanical performance, processability, and radiation resistance.[1] The epoxy must exhibit high modulus and strength at room temperature to protect and support the superconducting coils, particularly during magnet assembly. Additionally, after mixing the reactive components, the epoxy system should have low viscosity and a slow curing reaction, or long "pot-life," to ensure thorough infiltration of the superconducting coils.

The epoxy resin encapsulating the superconducting wires is suspected to be a significant source of "quenches," which are losses of superconductivity caused by thermal events that locally increase the temperature above the superconductor's critical temperature.[2] Proposed origins of these thermal events include conductor wire movement, frictional sliding,[3] and epoxy cracking,[4] indicating a significant role of adequate fracture toughness in preventing quenching.

Consequently, the main focus of the MagRes project is on developing epoxy systems that combine low viscosity and long pot-life with high fracture toughness at both room and cryogenic (liquid nitrogen) temperatures. Achieving good mechanical properties at room temperature necessitates that the epoxy's glass transition temperature (Tg) is above room

temperature, but not excessively high, to prevent the buildup of thermal stress during cooling.[5] To achieve this goal, it is essential to employ appropriate mechanical and thermal characterization methods suitable for use at cryogenic temperatures. Developing these methods is the second objective of the MagRes research.

2. Realisation

In the initial phase of this project, the focus was on establishing and utilizing testing methods to characterize mechanical properties, including fracture toughness, elastic and yielding behaviour across a temperature range from above 100 °C down to cryogenic temperatures (liquid nitrogen temperatures, 77 K). For this purpose, a home-build setup consisting of a double walled aluminum vessel with a massive bottom plate for high mechanical stability, was developed. To provide good insulating properties, the setup is additionally covered with a 3 cm styrofoam isolation including a proper lid. The new setup fits in a regular tensile tester, allowing for both fracture toughness and compression testing (see Figure 1).

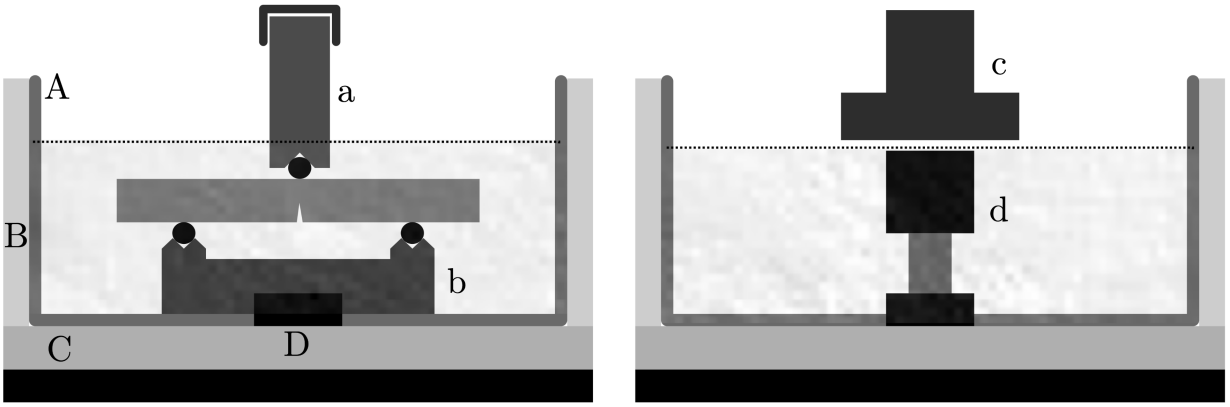

Figure 1: Schematic of the setup used for cryogenic testing; the dotted line indicates the ideal liquid nitrogen filling level. A: Rectangular aluminium bowl with a 20 mm concentric hole in the bottom plate, B: Styrofoam isolation, C: Flat sandstone plate isolation on top of compression tool bottom plate (black), D: Stainless steel cylinder of 20 mm, fitted into the concentric hole of the aluminium bowl. a: Notched PEEK slab of 20 mm diameter with a 6 mm diameter steel pin, b: Aluminium sample holder with two notches supporting 6 mm - diameter steel pins (set apart by support span), the sample holder is placed on a flat 20 mm steel cylinder (black), c: Upper compression tool plate, d: Stainless steel cylinder of 20 mm, centred on top of the sample.

The new setup was used for detailed mechanical characterisation of four currently used epoxy systems from above 100 °C down to -196 °C. In addition, standard dynamic mechanical thermal analysis (DMTA) was performed in the range of -150 °C to above 100 °C to obtain the storage modulus (E'), the loss modulus (E'') and the loss factor (tan(δ) = E''/E'). For all epoxy systems, these viscoelastic measurements feature the glass transition temperature (so-called α-transition) and a second-order transition (β-transition) at lower temperatures between -80 °C and -100 °C. Below the β-transition, the loss factor becomes small, indicative of almost pure elastic deformation. In addition, at these low temperatures, the storage moduli of all epoxy systems were found to converge to about 6-8 GPa, in agreement with Grüneissen's rule, which states that for isotropic van der Waals materials, such as amorphous polymers, at cryogenic temperatures, the bulk modulus, K_0, the shear modulus, G_0, and the Young's modulus, E_0, are solely determined by van der Waals interactions, which are similar for all epoxy systems.[5]

In addition to elastic properties, also the plastic deformation behaviour was measured using uniaxial compression testing to avoid brittle fracture. The rate dependency of the yield stress at room temperature of the epoxy systems was similar and well described by the Eyring model. At cryogenic temperatures the rate dependency disappears and the yield stress values of all four epoxy systems approach a similar athermal value. This again is to be expected, as amorphous materials have no crystalline lattice, and, therefore, no lattice defects, such as dislocations, that can lower the yield stress. As a result, at cryogenic temperatures, the yield stress of amorphous polymers approaches the theoretical limit of about $G_0/15$, which means that also the cryogenic yield stress is determined by the van der Waals interactions between the segments.[6] Importantly, it was found that the fracture toughness at cryogenic temperatures was not equal for all systems, but apparently also depends on other molecular characteristics, such as the network structure.[5]

Recently, new methods for epoxy toughening at room temperature have been developed by incorporating aliphatic dangling side chains into the epoxy network.[7] Atomic force microscopy (AFM) imaging suggests that the toughness increase is typically due to nano-scale phase separation caused by the chemical incompatibility of the aliphatic side chains with the epoxy backbone.[7]

The main objective of the MagRes project is to evaluate this relatively new concept of epoxy toughening at cryogenic temperatures by incorporating di-functional short-chain alkylamines into the epoxy network. Achieving a long "pot life" for these new epoxy systems can be realized by selecting an appropriate cure chemistry. When using an amine hardener, introducing steric hindrance to the amine group, such as with alkylamines having one or two methyl substituents in the β-position from the nitrogen atom, can result in slower reaction speeds and increased pot-life.[8] Therefore, another objective of the MagRes project is to evaluate the effect of such hindered alkylamines on reactivity and pot-life.

At cryogenic temperatures, increased toughness of epoxy systems leads to local yielding around the crack tip, causing increased heat dissipation, potentially promoting magnet quenching. At room temperature, localized yielding triggered by nanoparticles is known to further enhance toughness.[9] If this toughening mechanism also occurs at cryogenic temperatures, a new approach to improving the fracture toughness of resin systems, without inducing local heating that leads to quenching, would involve using gadolinium oxide (Gd_2O_3) nanoparticles. Gadolinium oxide is known for its anomalous high specific heat (Cp) at cryogenic temperatures. Thus, Gd_2O_3 nanoparticles could serve a dual purpose: initiating local yielding to improve cryogenic fracture toughness, and absorbing heat generated during plastic deformation, thereby preventing magnet quenching. As a preliminary step toward this goal, the final part of the MagRes study focused on evaluating the toughening effect of nanoparticles on the fracture toughness of epoxy systems at cryogenic temperatures, using silicon dioxide (SiO_2) nanoparticles.

3. Results / Conclusions / Deliverables

The building blocks of the new epoxy formulations are shown in Figure 2. The backbone of the network is formed by the diglycidyl ether of bisphenol A (DGEBA). The reactants were always chosen such that at full conversion, all epoxide groups have reacted. The average functionality, f, of the crosslinker, meta phenylene diamine (MPD), was chosen to be either 3 or 4, by using a slight excess of amine hydrogens over epoxide groups for a value of 3, since MPD has 4 active hydrogens. The difunctional diamines act as chain extenders, reducing the crosslink density (see schematic drawing in Figure 3). Therefore, the amount of diamines, given by the ratio R of the number of alkylamine molecules to the number of DGEBA molecules, can be used to adjust the Tg between 50 °C and 100 °C. The case of $f = 4$ and $R = 0$, corresponds to the so-called "base system" consisting of DGEBA fully crosslinked by MPD. The other limiting value of R, $R = 1$, would correspond to a (hypothetical) linear alternating copolymer of alkylamine and DGEBA. Throughout this report, the base system is named ``base'' and the systems with chain extender are designated as ``X-f-R'', referring to an epoxy system with chain extender ``X'', average functionality ``f'', and molar ratio of chain extender molecules to DGEBA molecules ``R''.

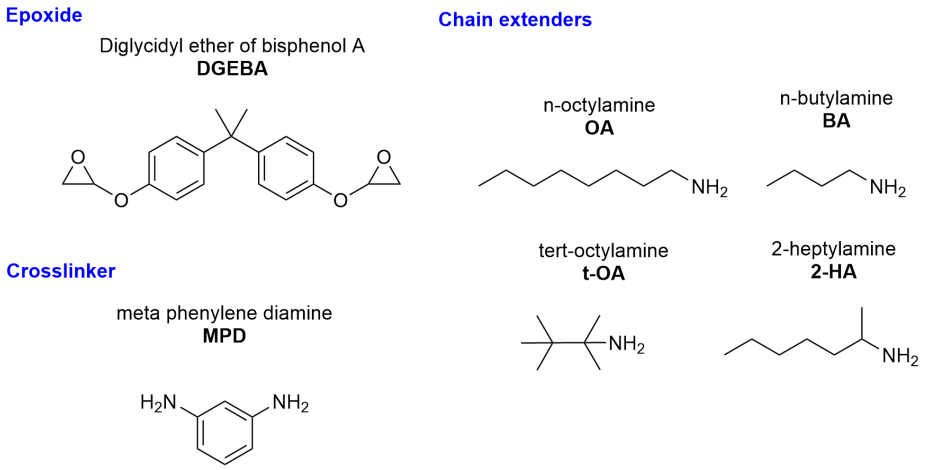

Figure 2: Structure formulas of the different precursor material used in this work to synthesize epoxy resins.

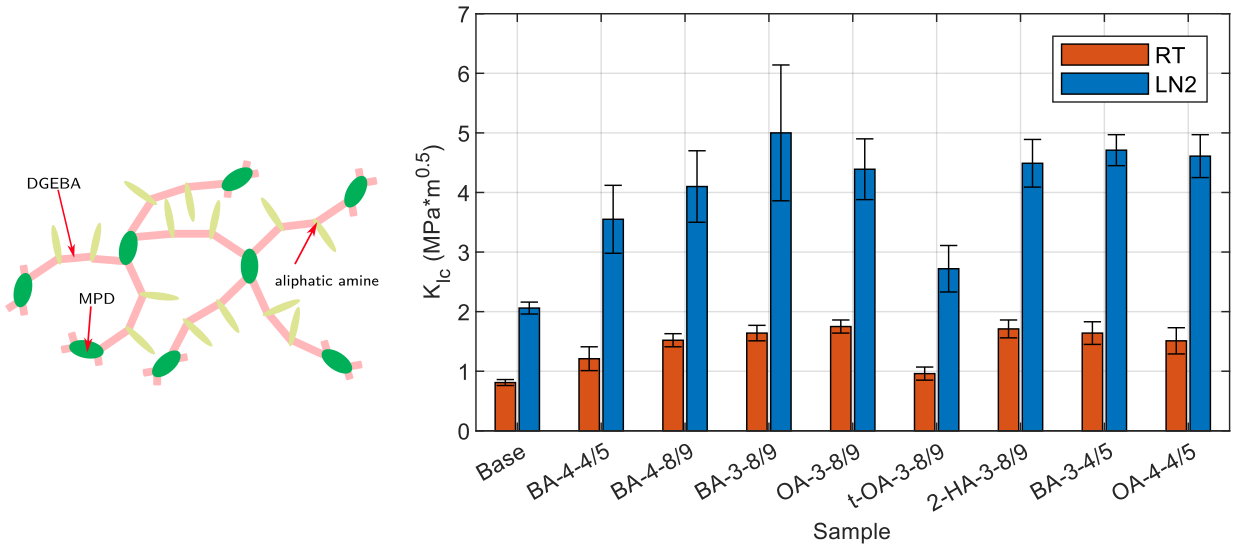

Figure 3: Left: schematic structure of the new epoxy resins. Right: room temperature and cryogenic (T=-196 °C) fracture toughness of all new epoxy resins.

The cryogenic fracture toughness values depicted in Figure 3 show that the incorporation of dangling linear aliphatic side chains also increase the cryogenic fracture toughness. Interestingly, bulky aliphatic side chains (t-OA) appear to be less effective. In addition, Figure 4 shows that using sterically hindered diamine groups, such as t-OA and 2-HA, reduces the reactivity, increasing the pot life. Especially the system 2-HA-3-8/9 combines a high cryogenic fracture toughness of $K_{Ic} = 4.7$ MPa$\sqrt{\text{m}}$ with a long pot life and good mechanical properties at room temperature (Tg = 72 °C).

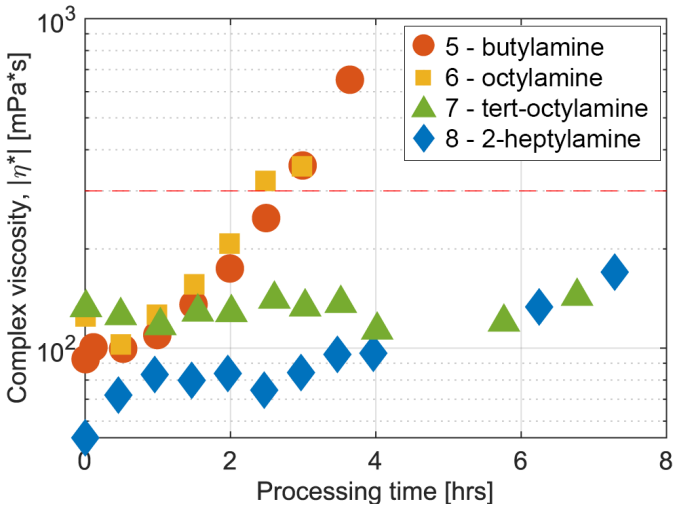

Figure 4: Time dependence of the complex viscosity of various epoxy systems with f=3 and R=9:8 and different diamines measured at 22.5 °C as a function of time. The diamines with β-hydrogens (2-HA and t-OA) have a much longer pot life.

The next objective of this study was to evaluate the toughening effect of hard nanoparticles at cryogenic temperatures. Figure 5 shows transmission electron microscopy (TEM) micrographs of a representative nanocomposite (BA-3-8/9) with 7.5 vol% SiO_2 nanoparticles, showing a homogeneous distribution of nanoparticles without agglomeration.

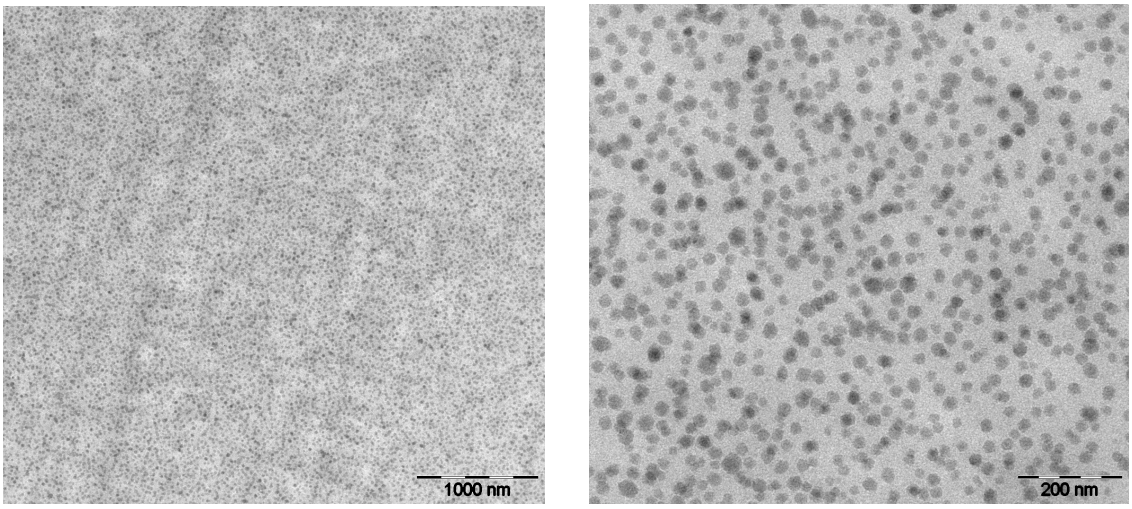

Figure 5: TEM micrographs of a representative nanocomposite (BA-3-8/9 sample with 7.5 vol% SiO_2) at two different magnifications showing a homogeneous distribution of nano-particles without agglomeration.

The effect of the SiO_2 nanoparticles on fracture toughness is depicted in Figure 6. In this figure, it shows that the well-known toughening mechanism of adding hard nanoparticles in epoxies at room temperature, also works well at cryogenic (liquid nitrogen) temperatures. Especially

the new epoxy systems with dangling aliphatic side chains show high fracture toughness values, up to almost 6 MPa√m. It is generally accepted that the toughening effect of the nano-particles is mainly due to debonding of the particles, creating free surfaces inside the material, which then promotes localised plastic deformation due to the increased von Mises stress.[9] The occurrence of this mechanism is confirmed in this study by scanning electron micrographs of the fracture surfaces containing nano-silica after fracture toughness testing at room temperature, clearly showing traces of voiding.

This could explain why the fracture toughness of the butylamine-based resins increases so strongly with the addition of nano-silica, as the low surface energy (especially the low dipole-hydrogen contribution to the surface energy) of these grades would favour easy debonding from the nano-particles.

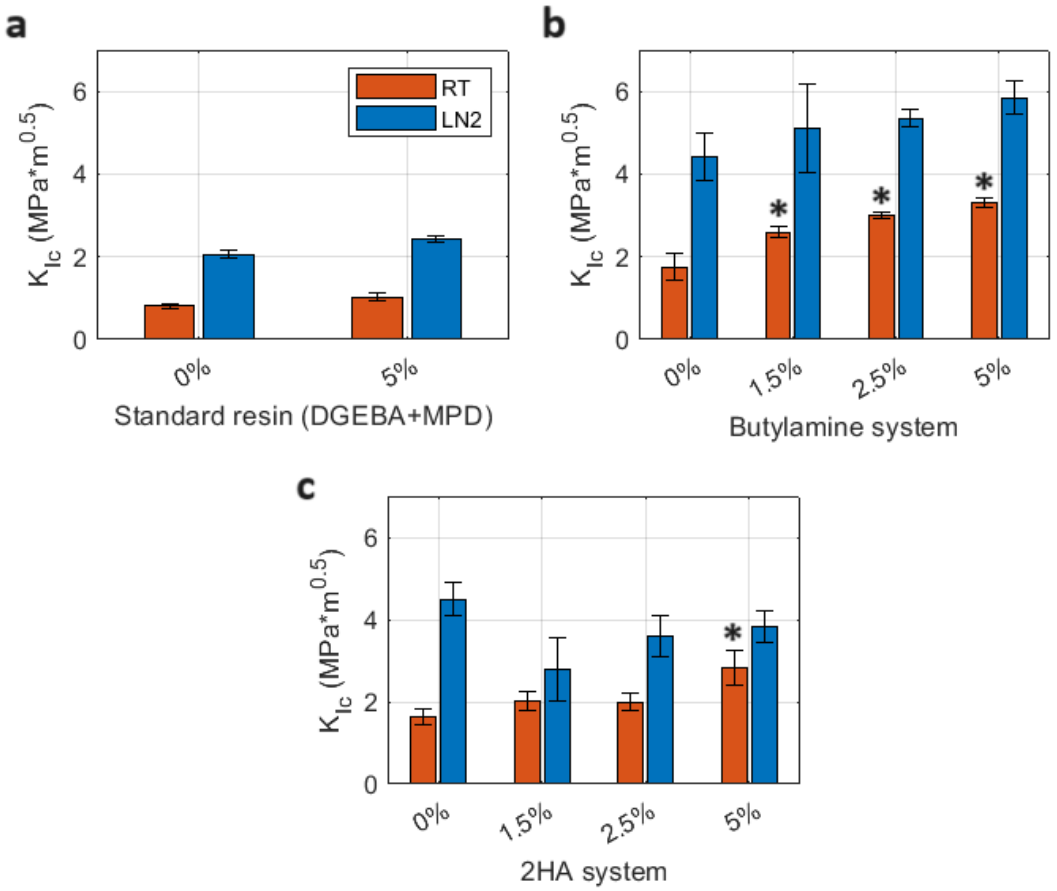

*Figure 6: Plane-strain fracture toughness values measured at room temperature (red) and at 77 K (blue) for various formulations: a: base system. b: BA-3-8/9 system and c: 2HA-3-8/9 system. The symbol * marks samples for which the criterion for plane-strain dominated fracture according to ASTM-D5045-14 were not fulfilled due to excessive yielding.*

Summarising, in the MagRes project, we succeeded to formulate new epoxy systems featuring dangling aliphatic side chains, that combine good mechanical properties at room temperature (50 °C < Tg < 100 °C) with a high fracture toughness at cryogenic temperatures (-196 °C) and a long pot life. In addition, we showed that the addition of hard SiO_2 nanoparticles further increases the cryogenic fracture toughness. The latter result opens the road to the use of Ga_2O_3 nanoparticles, which could enhance the fracture toughness, while simultaneously absorbing the heat due to plastic deformation, at 4 K.

4. Publications and Outreach

- Brem, A.; Gold, B. J.; Auchmann, B.; Tommasini, D.; Tervoort, T. A. Elasticity, Plasticity and Fracture Toughness at Ambient and Cryogenic Temperatures of Epoxy Systems Used for the Impregnation of High-Field Superconducting Magnets. *Cryogenics* **2021**, *115*, 103260. https://doi.org/10.1016/j.cryogenics.2021.103260.
- Studer, P.; Schwegler, A.; Tervoort, T.A. Tough epoxy resin systems for cryogenic applications. *Cryogenics*, **2024**, submitted.
- Studer, P., Tervoort, T.A. Tough epoxy nanocomposites for cryogenic applications, **2024**, in preparation.
- Brem, A.; Gold, B.; Auchmann, B.; Tommasini, D.; Tervoort, T; Tough Epoxy Systems for the Impregnation of (Future) High Field Superconducting Magnets, **2019**, 22th CEC/ICMC Conference, Hartford, Connecticut, USA.
- Studer, P.; Tervoort, T.A.; Tough epoxies for cryogenic applications, **2024**, 19th Conference on Deformation, Yield and Fracture of Polymers, Kerkrade, the Netherlands.

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