Tech report I

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Tech Report Development of optimized resins systems for superconductive magnet coil applications (MagRes)

by

Pascal Studer

Theo Tervoort

Abstract: This tech report presents the development of new epoxy resin formulations suited for the application as insulation materials in superconducting electromagnets.

Keywords: Epoxy resin, superconducting electromagnets, toughness

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1 Introduction

1.1 Motivation

Thermal events inside epoxy resins, such as cracking and yielding, are thought to contribute to quenching of superconducting electromagnets, which is is a large cost and time factor in the operation of these magnets. Traditional epoxy resins are inherently brittle and thus prone to cracking, and are thus thought to be a major cause of quenching in superconducting electromagnets. The properties of epoxy resins needed for the application as insulation material in superconducting electromagnets can be divided into properties during the infiltration and after the curing of the epoxy resin. During the infiltration of large electromagnets, a long pot-life and low viscosity are needed in order to infiltrate the whole structure before the viscosity increases too much due to the crosslinking reaction and thereby stops the infiltration process. This is a major advantage that epoxy resins (among other thermoset resins) can provide over thermoplastic polymer, unless the polymer is synthesized in situ. After the crosslinking reaction, the epoxy resin should provide mechanical support to the magnetic coils and electrical insulation. It should have a good resistance to cracking, which can result in quenching. Furthermore, the resins should have a good resistance against gamma radiation, which occurs in large amounts during the operation of particle accelerators.

In figure 1, the plane-strain fracture toughness is plotted against the tensile strength for various material classes among with prominent examples from each material class. It can be seen that the epoxy materials exhibit a fracture toughness between $0.4 \text{ MPa}\sqrt{\text{m}}$ and $5 \text{ MPa}\sqrt{\text{m}}$, while providing a good strength. Among the polymeric materials, thermoplastics such as polyamides, polycarbonates or polypropylenes can provide even better values. However, these exhibit high viscosities in the molten state at decent molecular weights, so they cannot be applied as insulation materials in superconducting electromagnets. For the application of thermoplastics, they would have to be synthesized in situ. Metals are not suited because of their conductivity, while ceramics also pose a problem due to their high viscosities and high processing temperatures.

In the past, it proofed to be difficult to find commercial formulations satisfying these special requirements, while giving all the other desirable properties that epoxy resins can provide. In previous work, specific systems targeted for this application were characterized mechanically by Brém et al. under cryogenic conditions $(-196 \,^{\circ}\text{C})$ by immersion in liquid nitrogen [3]. Of these resins, the commercial system MY750 exhibited a fracture toughness at $T = -196 \,^{\circ}\text{C}$ of $4.7 \,\text{MPa}\sqrt{\text{m}}$, which is a high value for a thermoset resin under these conditions. However, this resin



Figure 1: Ashby map showing the plane strain fracture toughness plotted against the tensile yield strength of all known material classes. Adapted from [1].

had the major drawback of having a relatively short pot life, with the viscosity exceeding the critical limit of 300 mPas after approximately 60 min at processing temperatures of $30 \,^{\circ}\text{C}$ or $50 \,^{\circ}\text{C}$. The other resins, while providing a better pot-life, did not show the desired high value of fracture toughness. Thus, one of the main objectives of the research showed in this report was to find new epoxy formulations which can overcome these challenges.

1.2 Scope and aim of this work

In order to advance the development of new epoxy resins specialized for the application in superconducting electromagnets, it is necessary to understand the structure-property relationships that ultimately determine the properties of the cured product by a large amount. Furthermore, the processing properties are also very important. They are determined by the monomers that are used in the formulation of the resin. Thus, another goal of this work is to understand the underlying chemistry and to learn how to select monomers which lead to appropriate processing-windows, gel-times and viscosities.

The first question is the influence of the crosslink density on the resulting toughness at cryogenic temperatures. This question was addressed for resins at room temperature [4], and an increase in fracture toughness with increasing molecular weight between crosslinks, was found. It was concluded that the reduction of the crosslink density increased the toughness by allowing more blunting of the crack tip, thus reducing the stress concentrations at the crack tip. Other reported results indicate that the toughness is related to the distance to the glass transition temperature since reduction of crosslink density typically lowers the glass transition temperature [2]. One of the objectives of this research is to establish if this behaviour can be replicated and if the crosslink density is also related to toughness at cryogenic temperatures. Another important question that needs to be addressed is that of the influence of the distribution of the contour lengths of the different crosslinks in the resin, and whether a network consisting of crosslinks of equal lengths or a network consisting of unequal lengths is beneficial for the resulting properties. Research done by Gong et al. shows that in soft hydrogels, the presence of a double network consisting of two networks with different crosslink contour lengths can increase the toughness of the hydrogels considerably [7]. Also the fracture toughness of rubbers is increased for polydisperse networks [9]. The reason for these effects is not fully clear, but might be related with preliminary sacrificial breaking of the more dense component of the network [6]. Many other works demonstrate that mechanical properties can be altered significantly by control of network topology [11], [12]. Lastly, we want to gain an understanding of the influence of the chemical nature of the crosslinks on the resulting properties.

2 Materials and methods

2.1 Materials

The hardeners that were used for all experiments can be found with their corresponding abbreviations in table 1. They comprise different aromatic and aliphatic amines. The aromatic amines such as MPD, DDM and DDS typically have much longer curing times compared to the aliphatic amines due to the electronwithdrawing and electron-delocalizing effect of the phenyl rings, to which the reactive amine groups are attached. In contrast, the aliphatic amines such as ED or PA cure much faster. Each functional amine group in these molecules can react with two epoxide groups during the cross-linking reaction. Thus, the functionality of the presented hardeners is 2N, where N is the number of amine functionalities.

Abbreviation	Name CAS-number Supplier, Product No. (Details)	Chemical structure
		NH ₂
MPD	meta phenylenediamine 108-45-2 Sigma Aldrich, P23954	NH ₂
DDM	diaminodiphenylmethane 101-77-9 Sigma Aldrich, 32950	H ₂ N NH ₂
DDS	diaminodiphenylsulfone 80-08-0 Sigma Aldrich, A74807	H ₂ N NH ₂
ANI	aniline 62-53-3 Sigma Aldrich, 132934	
ED	ethylenediamine 107-15-3 Sigma Aldrich, E26266	H ₂ N NH ₂
РА	propylamine 107-10-8 Sigma Aldrich, 240958	NH ₂

Table 1: List of hardeners used in this work

The epoxy resins that were used in this work are described in table 2. The threemembered rings containing an oxygen atom are called epoxy groups. Each of these epoxy groups can react with a primary or secondary amine from a suitable hardener, as the hardeners listed in table 1.

Abbreviation	Name CAS-number Supplier, Product No. (Details)	Chemical structure
PPG-DGE	poly(propylene glycol) diglycidyl ether 26142-30-3 Sigma Aldrich, 406732 Mn 380/640	° ° ° ° ° ° ° ° ° ° ° ° ° °
PEG-DGE	poly(ethylene glycol) diglycidyl ether 26142-30-3 Sigma Aldrich, 475696 Mn 200/400/500	° C C C C C C C C C C C C C C C C C C C
NG-DGE	neopentyl glycol diglycidyl ether 17557-23-2 Sigma Aldrich, 338026	°ooo
DGEBA	bisphenol A diglycidyl ether 1675-54-3 Sigma Aldrich, D3415	
TGAP	triglycidyl p-aminophenol 5026-74-4 Sigma Aldrich, 412813	

Table 2: List of epoxy monomers used in this work

Table 2: (continued)

Abbreviation	Name CAS-number Supplier, Product No. (Details)	Chemical structure
TGDDM	tetraglycidyl diaminodiphenylmethane 28768-32-3 Sigma Aldrich, 412805	
Poly(DGEBA)	Poly(Bisphenol A -co-epichlorohydrin) glycidyl end-capped 25036-25-3 Sigma Aldrich, 405450	

2.2 Methods

2.2.1 From synthesis to samples

Various sample shapes such as bars, cylinders and SENB samples were prepared from the starting materials in the following way. First, the mold was assembled. The mold mainly consists of two quadratic 250 mm aluminium plates, each of which is covered with PTFE-foil on the inner side, in order to facilitate the demolding of the epoxy plate. The aluminium plates are separated by a 6 mm thick hightemperature silicone frame which defines the shape of the plate to be produced. The mold is held together by metal clamps, and the plate thickness of 5 mm is defined by aluminium spacers which are placed between the plates and outside of the silicone frame before tightening the metal clamps. After the formulation of an epoxy resin, the epoxy components of the formulation were weighed into a 250 mL round-bottom flask, which was subsequently heated to the desired mixing temperature in an oil bath under constant stirring. At the same time, the mold was heated in the oven to the same temperature, in order to facilitate the later transfer of the liquid mixed resin into the mold. After the mixing temperature was reached, the hardener was added to the mixture and dissolved. Then, the mixture was typically degassed at 10 mbar until bubbles evolved infrequently. After the degassing,

the mixture was poured into the preheated mold. The temperature of the mold in the oven was traced by fixing an external thermocouple on the aluminium surface of the mold, since it was noticed that the mold needed approximately 30 min to reach the set temperature of the oven. The timer for the curing was started after the temperature of the mold was sufficiently close to target temperature. After curing, the assembly was cooled down slowly at ambient temperature in order to prevent cracking before demolding. The finished plates were then typically sent to an external company for water-jet cutting of the samples.

2.2.2 Fracture toughness

The test setup for fracture toughness testing can be seen in figure 2. With this setup, the sample can be submerged in liquid nitrogen, allowing to measure the fracture toughness at T = -196 °C. The tests were conducted according to the standard defined in ASTM D5045-15. The applied force F on the sample was measured with a Zwick tensile tester at a displacement speed of 2 mm s^{-1} . The support span was 38 mm, the sample width W = 9.5 mm and the sample thickness B approximately 5 mm. The test value K_Q for the fracture toughness was thus calculated with the formula

$$K_Q = \left(\frac{F_Q}{BW^{0.5}}\right) \left(6x^{0.5} \frac{1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)}{(1+2x)(1-x)^{1.5}}\right)$$
(1)

where x = a/W is the initial crack length divided by the width of the sample, F_Q the force at break and B the sample thickness. The calculated value K_Q can then be considered as the plane-strain fracture toughness K_{Ic} if certain conditions are fulfilled, ensuring a plane-strain situation in the sample:

$$B, a, (w-a) \ge 2.5 \left(\frac{K_Q}{\sigma_Y}\right)^2 \tag{2}$$

2.2.3 Dynamic mechanical thermo-analysis (DMTA)

The setup for performing DMTA measurements is shown in figure 3. The measurements were performed on an ARES-G2 rheometer (Anton Paar, Austria) equipped with a forced convection oven with the ability to cool the sample with liquid nitrogen. The tests were performed on beam shaped samples in a three point bending geometry with a support span of 40 mm. The rotating lower axis was only used for sample alignment. A force rebalance transducer (FRT) is located on the upper axis,



Figure 2: Schematical drawing of the test setup for performing single edge notch bending tests (SENB).

allowing for very precise measurements of torque and axial force. In the DMTA measurements, small oscillatory strains are imposed on the sample, the maximum strain amplitude being about 0.05 %. The sample response is measured and important viscoelastic constants such as the storage modulus and the loss modulus are calculated. The accessible temperature range with this cooling system spans from -175 °C upto 600 °C, well above the thermal degradation temperature of common epoxy resins, which starts around 200 °C.



Figure 3: Schematical drawing of the test setup for performing dynamic mechanical thermo analysis (DMTA).

2.2.4 Nuclear magnetic resonance (H-NMR)

NMR measurements were performed in a 300 MHz spectrometer (Bruker, Germany). Usually H-NMR experiments were performed. H-NMR was used for the quality analysis of the monomers used for epoxy synthesis, as well as for the quantification of the epoxide equivalent weight (EEW), which is defined as the mass of substance for 1 mol of epoxide groups. Deuterated chloroform was used as NMR solvent. As an internal standard, a known amount m_B of 1,1,2,2-tetrachloroethane (TCE) was added to the NMR tube. The amount of analyte, m_A , was also measured. The EEW could then be calculated by using the formula:[5]

$$\text{EEW} = \frac{m_A}{m_b} \frac{S_B}{S_A} \frac{f_A}{f_B} M_B,\tag{3}$$

where the subscript A refers to the analyte, and B to the reference. The two most outer hydrogen atoms of each epoxide group give a doublet of a multiplet peak, which can often be distinguished from the rest of the spectrum and integrated. The integral of this signal is S_A , while the integral of the single peak of TCE is S_B . The masses of the analyte and the reference are denoted by m_A and m_B , the number of hydrogen atoms giving rise to the integrated peak f_A and f_B , and the molar mass of the reference as M_B . The EEW is an important and useful quantity to know for the formulation of epoxy systems.

2.2.5 Differential scanning calorimetry

Differential scanning calorimetry was conducted on a TA-Instruments DSC-2500 differential calorimeter. The technique was used for various purposes, such as quantification of the reaction rate at different temperatures or determination of the glass transition temperature of cured resins. DSC measurements were conducted with approximately 2 mg of sample in hermetically sealed aluminium pans.

2.2.6 Estimation of the crosslink density

In order to estimate the crosslink density under the assumption of full conversion, the formula 4 shown below provided by Hill was used [8]. In this formula, C_n represents the volume density of *n*-functional crosslink points which have fully reacted. Following the logic that to each crosslink point of functionality n, n/2 are attached, the crosslink density can thus be estimated using this formula. For this purpose, the density of each sample was measured by a scale to obtain the density of the different crosslinks.

$$v_e = \frac{3}{2}C_3 + \frac{4}{2}C_4 + \frac{5}{2}C_5 + \dots = \sum_{f=3}^{\infty} \frac{f}{2}C_f \tag{4}$$

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3 Results

3.1 Towards tough epoxy compositions

H-NMR studies were performed on epoxy components of commercially available resins using a 300 MHz NMR-spectrometer (Bruker, Germany). Samples were dissolved in deuterated chloroform (CDCl3) and an internal standard, 1,1,2,2-tetrachloroethane, was added in order to quantify the content of different functional groups present in the sample. These studies have revealed that often monomers containing a backbone consisting of aliphatic polyglycol are employed in the formulation in these systems. This observation shaped our hypothesis that the addition of such aliphatic polyglycols increases, in some yet unknown way, the toughness of these resins at cryogenic temperatures. We hypothesized that these flexibilizers can increase the toughness by making the network more extensible. The analysis of such an H-NMR can be seen in figure 4



Figure 4: H-NMR spectrogram showing peak assignments to the suspected structure from the hardener of a tough epoxy resin.

3.2 Systematic study to find formulations suitable for application in superconducting electromagnets

One important requirement for the general application of epoxy resins in superconducting electromagnets, is that they have to provide mechanical stability to the conductor wires, especially for magnets that are not pre-stressed. In order to provide this mechanical stability to the conductor wires, the epoxy resin should not be in the rubbery state at room temperature, since this could lead to displacements of the conductors during cooldown of the magnet. In section 3.3, it is shown that the addition of flexibilizers to the epoxy network can increase the toughness of epoxy resins. However, the disadvantage of using flexibilizers is that they decrease the glass transition of the resulting resin. In order to quantify this reduction of glass transition of the resin for flexibilizers of different molecular weights and to select suitable compositions for magnet infiltration, a systematic study was conducted.

3.2.1 Effect of flexibilizers on the glass transition temperature

The effect of the addition of flexibilizers was investigated using a combination of three components:

- A, Epoxy 1: PPG-DGE 380, PPG-DGE 640, PEG-DGE 200, PEG-DGE 400 or NGDGE as flexibilizers.
- B, Epoxy 2: DGEBA, TGAP or TGDDM, which are either 2-, 3- or 4functional epoxy monomers with an aromatic backbone, thus promoting a high glass transition.
- C, Hardener: MPD, a slow curing aromatic amine hardener, promoting a low viscosity of the resin

Resins were prepared in small amounts in glass vials and subsequently cured in the oven, after which samples of approximately 2 mg by weight were analyzed by a DSC temperature ramp at $2 \,^{\circ}\text{C}\,\text{min}^{-1}$. The glass transition temperature was determined as the inflection point of the DSC curve. In figure 5, three figures are plotted. Each figure is for a fixed component B. It can be seen that the addition of flexibilizer reduces the glass transition very strongly, with longer chain flexibilizers having a more pronounced effect at the same mass fraction.



Figure 5: In this figure, each plot shows the decrease of Tg with the addition of more flexibilizer when the component B of the resin composition is fixed.

In figure 6, the results of the toughness are plotted for some selected resins. The resins were selected by linear interpolation of the glass transition data shown before, to achieve a glass transition temperature slightly above room temperature. It can be seen from this analysis that no large variations in the toughness arise when a larger amount of PPG-DGE 380 is replaced by a smaller amount of PPG-DGE 640 in a resin formulation. Furthermore, it became apparent that increasing the functionality of component B did not facilitate achieving a higher toughness. In figure 7, the results from dynamic mechanical analysis are shown for the same resins. It shows that the optimization of the glass transition aroung 50 °C. It is noticeable that for resins with a more polydisperse distribution of crosslink contour lengths, such as the one composed of PPG-DGE 640, TGDDM and MPD (yellow curve), the transition from the glassy to the rubbery state is smeared out over a larger temperature range.



Figure 6: Plots of the toughness at room temperature and in liquid nitrogen for some selected resins. With the exception of the leftmost resin, all the shown resins have an optimized glass transition temperature slightly above room temperature.



Figure 7: Plots of the temperature dependent mechanical properties determined by DMTA for some selected resins. With the exception of resin PPGDGE380 25 % + DGEBA, all the shown resins have an optimized glass transition temperature slightly above room temperature. Tests were conducted at a temperature ramp of $3 \,^{\circ}C/min$.

3.3 Investigation of the effect of network properties on the toughness

3.3.1 Effect of flexibilizers on the toughness

The effect of the addition of flexibilizers on the toughness at cryogenic temperatures was investigated comparing a series of samples with increasing amount of flexibilizer (aliphatic polyglycol), which is shown in figure 8. All of the three resins have very similar crosslink densities. The systems contained MPD, DGEBA and PPG-DGE 380, with PPG-DGE 380 being the flexibilizer due to its effect of lowering the Tg of the resulting epoxy resin. The data shows that the addition of flexibilizer can increase the toughness up to a certain extent, but for the system considered the effect levels off above 68 % by weight. The increase of the toughness can not be explained by the crosslink density or the polydispersity of the distribution of crosslinks, since the two remain almost constant.



Figure 8: Comparison of three resins with similar crosslink densities tested in liquid nitrogen, but with variations in the chemical nature of the crosslinks.

3.3.2 Effect of the crosslink density on the toughness

To investigate the effect of the crosslink density on the toughness at both room temperature and in liquid nitrogen, all the data from the formulations was collected and is presented in figures 9 (liquid nitrogen) and 10 (room temperature). The data is organized in different groups. At the temperature of liquid nitrogen, a general trend of increasing fracture toughness is visible. When trends inside the different groups are investigated, where the crosslink density was usually lowered by increasing the amount of aliphatic polyglycols (*,hexagon), the trend is not statistically significant. In the case of systems containing DGEBA and aliphatic polyglycols (o), the crosslink density did not vary much due to similar chain lengths of DGEBA and PPG-DGE 380. The occurrence of this general trend reinforces our hypothesis that by lowering the crosslink density, the crosslink molecules can gradually be regarded as statistically arranged polymer chains as described by Kuhn et al. instead of short straight linkages, and thus the extensibility is described by their characteristic ratio, C_{∞} .



Figure 9: Results of the toughness from SENB testing in liquid nitrogen plotted against the predicted crosslink densities for the various resins. Marker shapes correspond to different classes of compositions, members of each class are plotted in different colors. Almost all the systems were cured with MPD, exceptions are stated in parentheses.

The results from testing at room temperature can be seen in figure 10. There does

not seem to be any correlation between the measured toughness and predicted crosslink density at room temperature.



Figure 10: Results of the toughness from SENB testing at room temperature plotted against the predicted crosslink densities for the various resins. Marker shapes correspond to different classes of compositions, members of each class are plotted in different colors. Almost all the systems were cured with MPD, exceptions are stated in parentheses.

3.3.3 Effect of the polydispersity of chain lenghts on the toughness

For the investigation on polydisperse networks, two simple systems were prepared and tested in liquid nitrogen, the results can be compared in figure 11. In addition to the hardener, MPD, one system contained only PPG-DGE 380 while the other system contained both PPG-DGE 380 and 640. Both systems were cured for 75 min in the oven at 165 °C. Both systems darkened considerably during the curing reaction. The predicted crosslink density of the mixed system is 2.66×10^{-6} mol/mm³, while the one of the other system is 2.84×10^{-6} mol/mm³. Both systems showed similar fracture surfaces. To the authors surprise, the system with a smaller polydispersity of crosslink contour lengths resulted in a toughness twice as high than the other system at -196 °C. This finding suggests that the findings from done on hydrogels by Gong et al. [7] cannot be directly transferred to epoxy resins at cryogenic temperatures. It is evident that there are significant differences by the systems tested in the work of Gong et al. and the systems tested here. Notably, the systems tested by Gong et al. were double networks (DNs), which consisted of two interpenetrated networks of different crosslink densities, but not connected to each other by covalent bonds. In that work, it is hypothesized that the presence of a double network could increase the toughness by sliding of chains of one network past the chains of the other network. This effect would not be possible in a single network as shown here. To investigate this, epoxy double networks would have to be created, which could be a topic of future work.



Figure 11: Comparison of two resins designed to have two different chain length distributions. The first resin is composed of MPD and PPG-DGE 380, while the second resin contains the additional component PPG-DGE 640.

The second comparison of chain length distributions can be seen in figure 12. Both systems were hardened with MPD according to standard curing conditions. The first system consisted of a mixture of DGEBA and PPG-DGE 380, both of which have approximately the same chain contour length, and thus represent a system with a more monodisperse distribution of chain lengths than the second system. In the second system, the DGEBA is replaced by poly(DGEBA) 1075. The predicted crosslink densities of the two systems are $2.99 \times 10^{-6} \text{ mol/mm}^3$ and $2.42 \times 10^{-6} \text{ mol/mm}^3$, respectively. An increase in fracture toughness is observed at both room temperature and -196 °C when the polydispersity of the systems are increase in polydispersity resulted in a decrease in toughness.

It should be noted that the poly(DGEBA) 1075 system combines a superior fracture toughness at cryogenic conditions, that matches the high value of the commercial system MY750 of Huntsman. In addition, in contrast to the MY750, this poly(DGEBA) 1075 system also has a good pot life, and as such presents an attractive alternative formulation for use in superconducting magnets.



Figure 12: Comparison of two resins designed to have two different chain length distributions. The first resin is contains the epoxy components DGEBA and PPG-DGE 380, while the second resin contains the epoxy components poly(DGEBA) 1075 and PPG-DGE 380.

The last comparison in this section is shown in figure 13. In this comparison, the polydispersity of the chain length distribution in the network is increased by adding poly(DGEBA) of number average molecular weight 1075 to the resin containing only PPG-DGE 380, along with MPD as the hardener. While the predicted crosslink density for the pure PPG-DGE 380 resin (left) is $2.84 \times 10^{-6} \text{ mol/mm}^3$, the predicted amount for the resin containing the highest amount of poly(DGEBA) is $1.78 \times 10^{-6} \text{ mol/mm}^3$. However, it was shown in the study of the crosslink density that the effect of reducing crosslink density without the order of magnitudes has little effect on the toughness. Furthermore, it was shown with figure 11 that increasing polydispersity by adding more PPG-DGE 640 as long chains in the system even has a detrimental effect on the toughness. We thus conclude that in order to increase the toughness of the resin by increasing polydispersity, the chemical structure of the constituents are very important. In fact, the chemical structure of a polymer determines its characteristic ratio C_{∞} . The higher this parameter is, the stiffer the chain. First research on characteristic ratios seems to indicate

that the characteristic ratio of bisphenol A copolymers is actually smaller than PEG, which is considered to be comparable to PPG[10]. However, more literature study in this direction is required. These findings suggest that we probably have to reject our hypothesis that aliphatic polyglycols increase toughness due to their extensibility, since they would be less extensible when having a larger characteristic ratio than the bisphenol A copolymers. Instead, they probably increase the toughness by another effect which has yet to be found.



Figure 13: Comparison of the toughness at -196 °C three resin systems with increasing polydispersity of chain lengths from left to right. In this case, poly(DGEBA) with Mn 1075 is applied as the long chain in the network.

3.4 Systems provided by CERN

3.4.1 SikaBiresin[®] RE 700-04 Polyol / SikaBiresin[®] RE 106 Isocyanate

This commercial room-temperature curing two-component system is composed of a polyol and an isocyanate component, which can react together resulting in a polyurethane. It has a glass transition below room temperature. The gel time at room temperature is 30 min, making it rather unsuitable for infusion processes. Due to the flexibility of the resin at room temperature, it was only measured in liquid nitrogen. A plane-strain fracture toughness of 6.39 ± 0.72 MPa \sqrt{m} , which is quite a good value. The fracture surface is shown in figure 14. The somewhat rougher surface beyond the crack tip indicates increased energy dissipation compared to the system described in the next section.



SikaBiresin® PU system

Araldite® CY-192-2 Aradur® HY 918-1

Figure 14: Comparison of the fracture surfaces from testing in liquid nitrogen for two of the other tested systems.

3.4.2 Araldite[®] CY192-1 / Aradur[®] HY 918-1

This system is a two-component epoxy system produced by Huntsman. It is the resin system currently in use at CEA (France). The plates were prepared by mixing the two components in a 50/50 weight ratio and curing using the following curing schedule: Ramp to 80 °C in 1 h, plateau of 24 h at 80 °C, ramp to 120 °C in 2 h, plateau of 34 h at 120 °C, ramp to 130 °C in 2 h, plateau of 12 h at 130 °C, cooldown (free). The obtained fracture toughness at room temperature was 0.80 ± 0.10 MPa \sqrt{m} and in liquid nitrogen 1.73 ± 0.14 MPa \sqrt{m} . As many formulations tested in this work, the fracture toughness at -196 °C is considerably higher than at room temperature.

3.4.3 CTD-701X

This is a newer polyolefin system from Composite Technology Development. It was also tested at both room temperature and in liquid nitrogen. The obtained fracture toughness at room temperature was 3.23 ± 0.05 MPa \sqrt{m} and in liquid nitrogen 6.2 ± 0.32 MPa \sqrt{m} . As many formulations tested in this work, the fracture toughness at -196 °C is considerably higher than at room temperature.

4 Conclusion and outlook

An extensive study was performed directed towards the goal of finding new epoxy resin formulations for cryogenic SC magnet applications. New resin compositions that match the high toughness at cryogenic temperature of commercial formulations, but with a much better pot-life, were identified by using aromatic amines, such as MPD, as hardeners. A detailed study of network parameters has resulted in several findings. First, a general trend of increasing toughness with decreasing crosslink density was observed at -196 °C. However, inside groups of chemically similar systems differing only in polymeric backbone chain lengths, the trend appeared to be very weak or insignificant. Second, the addition of flexibilizer (glycidyl end-capped aliphatic polyglycols) was found to promote toughness. Third, increasing the polydispersity of the distribution of crosslink chain lengths did not always increase the toughness. Notably, the addition of longer poly(propylene glycol) chains into the network even decreased the toughness, while the addition of longer poly(DGEBA) chains into the network increased the toughness significantly. Together with the second finding, we conclude that the addition of flexibilizer increases the toughness by another mechanism than by promoting extensibility to the network. In the future, we want to find out if flexibilizers are needed at all to achieve high toughness at cryogenic temperature. Furthermore, one or two resins will be selected and characterized thermally and by rheology in order to bring them to application.

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