

STUDY OF IMPREGNATING EPOXY RESINS FOR HIGH FIELD NMR SUPERCONDUCTING MAGNETS

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ABSTRACT

NMR magnet coils are usually quite long, thick, and tightly wound with thin superconducting wires. The successful vacuum/pressure impregnation of such kind of coils demands the use of epoxy resins with superior properties such as low viscosity, long pot life, and high cracking resistance etc.. In order to find the most appropriate impregnating epoxy resin for the fabrication of high-field NMR magnet coils, we have studied several promising epoxy resins by viscosity, thermal shock, bonding/de-bonding measurements. The results of these measurements are presented. Model coils have been vacuum/pressure impregnated with selected epoxy resins and analyzed with scanning electronic microscope (SEM). It was found that among all of the studies epoxy resins the CTD- 101K epoxy resin is most suitable for impregnation of coils. The test results of the model NbTi superconducting coil show that coils potted with CTD-101K do not quench until critical current of the superconductor is reached. This epoxy and the impregnation technique have been successfully applied to the first 400 Mhz/89 mm actively shielded high resolution NMR magnet developed at Houston Advanced Research Center.

INTRODUCTION

Vacuum-pressure impregnation (VPI) of magnet coils with epoxy has been a widely used technique in building high field superconducting magnets. The purpose of epoxy impregnation is to prevent the conductor motion caused by the Lorentz force. Such motion is one of the main sources for the premature quench of the superconducting magnets^{1,2}. A high field NMR superconducting magnet usually involves the fabrication of long and thick coils which are tightly wound with very thin wires. Thus, the use of the most appropriate epoxy formulation and reliable VPI technique plays the key role in magnet construction.

In 1992, the Houston Advanced Research Center (HARC) started its project of developing the first actively shielded 400 MHz 89 mm bore NMR spectrometer magnet and other higher field magnets. Special coil design/winding features and conductor wire size of the 400 MHz magnet demanded the use of suitable epoxy formulation and impregnation technique. At that time, there had been only very few epoxy formulations reported in the literature³ for vacuum impregnation of NMR magnet coils and they appeared not appropriate for our project. The goal of our research was to find the most appropriate epoxy resins for the successful impregnation of the 400 MHz NMR magnet coils.

SELECTION OF EPOXY FORMULATIONS

Criteria for Epoxy Selection

The selection of the epoxy resins was based on the following six criteria: 1. low viscosity ($\leq$ 100 centistokes at 60 °C); 2. long pot life ($\geq$ 20 hours at 60°C); 3. high crack resistance; 4. appropriate cure schedule and temperature (5 - 24 hours and maximum 125°C); 5. low toxicity (epoxy containing carcinogens should be avoided); and 6. Good vacuum and mechanical properties such as high fracture toughness and tensile strength etc..

The pot life here is defined as the time required for the viscosity of the epoxy to rise to 1000 centistokes (cSt). One of the main reasons for the criterion 4 above is that longer time high temperature curing could induce significant degradation of the critical current I_c , especially in high field. Our field dependent I_c measurement on the NbTi wires (for the 400 MHz magnet) had shown that there was an about 7% I_c degradation at 9 Tesla after the wires were annealed at 110-125 °C for about 20 hours.

Viscosity Measurements

Viscosity measurement is necessary for determining the pot life of the epoxy. The viscosity as a function of time and temperature were measured with a set of calibrated BOEKEL Zahn cup-type viscometers for more than ten epoxy formulations. These epoxide resins were pre-screened (based on the available information related to above criteria) from commercial products of Ciba-Geigy, the E. V. Robert & Associates, and Shell Chemical. In Fig. 1, we show the viscosity data measured at 60 °C for seven epoxy formulations listed in Table 1. It is seen that the four samples A1 and A2 (Resin CY179 with accelerator XU183 $\leq$ 2.5 parts by weight), B (GY6010), and C (CTD-101K) have pot life longer than 20 hours at 60 °C and thus they were chosen for further model coil potting study and thermal shock test. All of the epoxy samples shown in Table 1 and Fig. 1 were from Ciba-Geigy except the sample C which was from the E. V. Robert & Associates. The CTD-101K is an anhydride cured epoxy originally developed for cryogenic applications down to liquid helium temperature⁴.

VPI EQUIPMENT AND PROCEDURE

Equipment for VPI of Coils

Two VPI systems were built for this study. The first system was a smaller one for potting smaller model coils with size up to 8 inches in diameter and 14 inches in length. It consisted of an epoxy deaeration chamber (EDC) made of stainless steel and a vacuum-pressure impregnation chamber (VPIC) modified from a Galvanized steel paint tank which

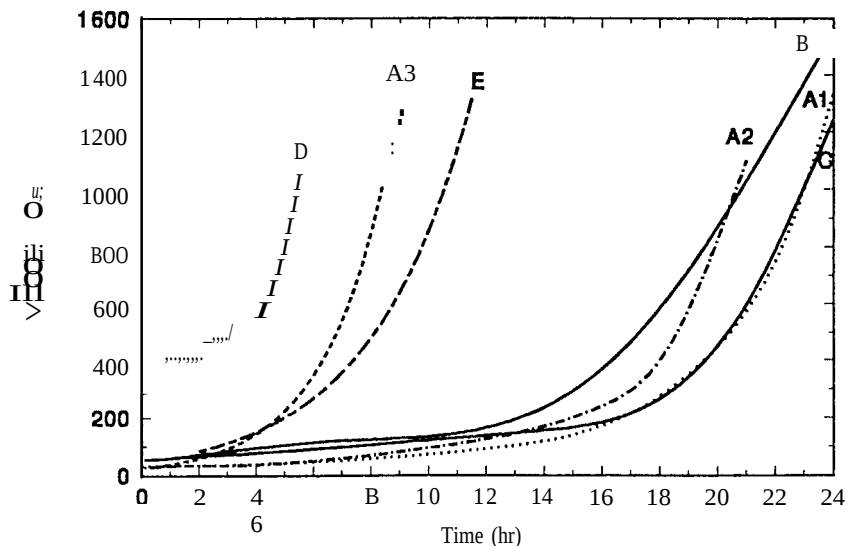


Figure 1. Viscosity as a function of time for selected epoxy samples at 60 °C.

can withstand 115 psi pressure. Both of them were equipped with vacuum/pressure, temperature controlling, heating, and window/lighting systems. An epoxy tank for mixing the epoxy and a mold tank for sitting the coil were placed inside the EDC and VPIC, respectively, both of these two tanks were wrapped with heating tapes. The second system is an enlargement of the first one with similar construction features. The larger system was used for potting the 400 MHz NMR magnet coils.

Table 1. Several selected epoxy formulations

Experiment Sample	Composition		Parts By Weight
A1	Araldite Hardener Accelerator	CY179	100.0
		HT907	105.0
		XU183	1.6
A2		CY179	100.0
		HT907	105.0
		XU183	2.5
A3		CY179	100.0
		HT907	105.0
		XU183	6.0
B		GY6010	100.0
		HT907	85.0
		XU183	1.4
c	Resin Hardener Accelerator	PART A	100.0
		PART B	90.0
		PART C	1.5
D		CY225	100.0
		HY227	100.0
E		GY6005	100.0
		HY906	80.0
		DY062	1.0

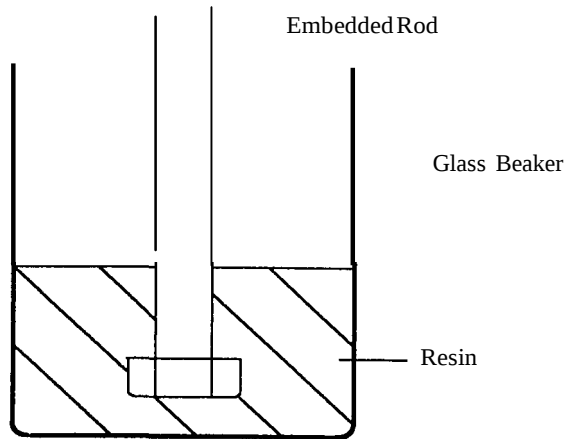


Figure 2. Schematic drawing of a epoxy sample.

Epoxy VPI Procedure

A typical procedure for VPI of model coils can be described as the following, taking epoxy CTD-101K as an example:

(1) Place the coil in the mold tank and bring the temperature up to about 70°C, degas the VPIC for about 12 hours at a vacuum of about 20 microns.

(2) Mix the resin, hardener, and accelerator together in the epoxy tank and warm the mixture up to about 60°C. Deaerate the mixture by a vacuum pump while stirring the epoxy with a motorized stirrer. Continue this process for about 45 minutes until the small bubbles completely cease to produce and pressure is about 20 microns.

(3) Transfer the epoxy from the epoxy tank (in EDC) into the mold where the coil is sitting. Stop the transferring as soon as the epoxy reaches a desired level. Set temperature of the coil at 60 °C.

(4) Deaerate the epoxy in the mold until vacuum goes down to about 20 microns. Pressurize the epoxy with nitrogen gas slowly for about 20 minutes until the pressure reaches 100 psi. Maintain this pressure and 60 °C for about 8 hours.

(5) Depressurize the VPIC to atmospheric pressure. Take out the coil and rotate it in a oven (or furnace) with temperature already set at 60 °C.

(6) Increase the temperature of the oven to 110 °C at a rate of about 2 °C/min. Cure the epoxy at this temperature for about 4-6 hours and then at 125 °C for about 15 hours.

THERMAL SHOCK EXPERIMENTS

Sample Preparation and Experimental

The purpose of our thermal shock experiment was to find the appropriate cure schedule which would yield high cracking resistance for the epoxy resins. Thermal shock specimens of the four long pot-life epoxy resins A1, A2, B, and C (see Table 1) were prepared in four different geometric configurations as following.

(1) The specimens were made approximately cylindrical shape using glass beakers as the epoxy mold. The diameters of the specimens have two sizes: 62 mm and 51 mm. The thickness ranges from 10 mm to 50 mm. Table 2 listed some selected specimens, where A1 and A2 specimens are the same epoxy resins as listed in Table 1; A3 is the same as A2 but

Table 2. Thermal shock result for selected samples in configuration (I)

Epoxy Sample	Dia, Length (mm), (mm)	Crack at First	Cycles prior to	Curing Schedule
A1	51,15	N	>25	120°C x 8 h
A2	62,12	Y	0	100°C Y. 0.5 h + 120 °C x6 h
A3	62,20	Y	0	80°C x 4.5 h +120°C x 15 h
B1	62,16	Y	0	r20°c x 3 h
B2	62,30	Y	0	r20°c x 3 h
B3	62,16	N	>26	120°C x 12 h
B4	62,30	N	>26	r20°c x 12 h
BS	62,16	Y	0	120°C x 19 h
R6	62,30	Y	0	r20°c x 19 h
CI	62,16	Y	0	135°C x 1.5 h
C2	62,16	N	>14	110°C x 6 h + 125°C x 2.S h
C3	62,16	N	>14	110°c x 6 h + 12s ^U c x 10 h
C4	62,30	Y	0	13S°C x 1.5 h
cs	62,30	N	8	110°c x 6 h + 12s ^U c x 2.s h
CG	62,30	Y	0	110°C x 6 h + 125°C x JO h
C7	62,14	N		120°c x 11 h
C8	62,32	Y	0	120°c x 11 h
C9	51,14	Y	0	110°C x 4 h + 125°C x 23 h

with a different cure schedule; B1-B6 and CI-C9 are resins B and C in Table I, respectively, with different cure conditions.

(2) The specimens were the same as in configuration (1) except that each specimen contains a cylindrical steel insert of about 12 mm diameter, as shown in Fig. 2.

(3) The specimens were prepared using 1/4 inch diameter U-shaped copper tubing as mold. Only CTD-10IK specimens were tested for this configuration.

(4) The specimens were the vacuum-pressure impregnated model coils which were wound with copper wires of various diameter (0.5-1.0 mm). They were cut and examined by scanning electronic microscope (SEM) after thermal shock test. Only CTD-10 I K and CY 179 were tested for this configuration.

Mold release were applied on the interior surfaces of the mold so that the specimen can be removed from the mold after curing. The deaeration of the resins was as described in previous section. The thermal shock experiments were made by plunging the epoxy samples into liquid nitrogen and then warming them up. Sign of cracking was checked after each wormmg up.

Thermal Shock Results

Almost all of the specimens prepared in configuration (2) were cracked in the first shock cycle, and all the specimens prepared in configuration (3) were non-cracked (examined for 10 cycles). This result shows that the insert induce large stree in the epoxy and the specimens with smaller volume have much higher cracking resistance. The thermal shock results of the potted coils, i.e., the configuration (4), will be discussed later. Table 2 presents the thermal shock results for some of the selected specimens in configuration (1).

The data in Table 2. supports the following conclusion. First, moderate cure time and temperature could maximize the cracking resistance. For example, the B3 and B4 cured at 120 °C for 12 hours did not crack but those cured at shorter time (3 hours) and longer time (19 hours) cracked. Similar results were observed for the CDT-10IK (CI-C9) specimens.

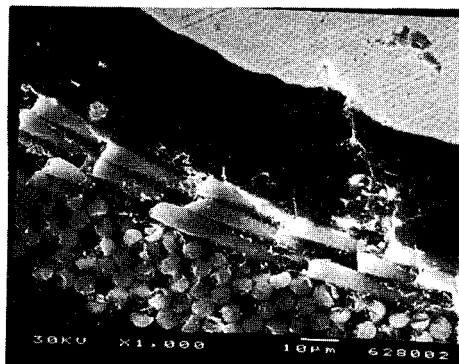
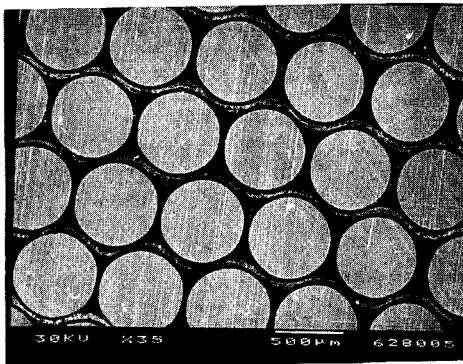


Figure 3. The SEM photographs of a section of the potted coil at two magnifications: 35 for the left and 1,000 for the right. Left photo: the circles are copper wire cross-section, the wavy bands are the E-glass cloth, the rest is the epoxy and formvar. Right photo: the up-right part is the copper wire, the left-bottom part is the mixture of E-glass and epoxy, and the band-like part between copper and E-glass is Formvar.

Second, larger specimens were easier to crack. Third, based on our overall cracked to non-cracked specimen ratio, it appeared that cracking resistance decreases in the order of CTD-IOLK, GY6010, and CY179. Thus, CTD-IOLK was chosen to be the primary candidate for other tests.

OTHER TESTS AND ANALYSIS

Bonding and De-bonding

Four kinds of mold-release have been tested. The surfaces of glass beaker, G-10 sheets, mylar, and steel rods were sprayed or coated with the mold release, put in contact with deaerated CTD-IOLK epoxy, and then annealed with the epoxy cure schedule. It was found that one of the FREKOTE mold-releases is very good for de-bonding the epoxy from steel, glass and mylar.

The bonding strength between CTD-IOLK epoxy and the formvar insulation layer were tested for some formvar insulated copper wires of about 1 mm diameter. The wires were inserted into the epoxy about 1 cm in a similar way as the embedded rod shown in Fig. 2. Tension was increasingly applied to a wire to pull it out of the epoxy. No slipping between the wire and the epoxy was observed until the wire was broken by the tension. This showed that the bonding between CTD-IOLK and the wires is extremely strong.

Coil Potting Performance Analysis

Eight coils wound with formvar insulated copper wires were potted according to the procedure described previously. Seven of them were potted with CTD-IOLK and one with CY 179 formulation. The coils were fabricated exactly the same way as the designed 400 MHz NMR magnet coils: the same wire diameter range (0.64 and 0.89 mm) and thickness (about one inch). The inner diameter of the coil ranges from one inch to six inches and the length varies from 1.5 inch to 14 inches. E-glass cloth of two mil thickness was placed between neighboring conductor layers to facilitate the longitudinal percolation of the epoxy. Mold release was sprayed on the surface of the coil bobbin; mylar film was wrapped on the coil forms, and G-10 disks were placed against the flanges of the bobbin. Three potted copper coils were sliced and analyzed by SEM technique (with magnification up to 2000) after thermal shock cycles were made. Fig. 3 shows two of the SEM photographs.

Table 3. Specification of the NbTi test coil

Bore Material	Stainless Steel Mylar
Material Between Bore and Coil	E-glass
Material Between Coil Layers	G-10
Material Between Coil and flange	7.635
Inner Radius	cm
Radius	10.235c
Length	m
Tums/Layer	6.375 cm
Winding Prestrain Material	160
Bare Diameter	22 N
Final Diameter	NbTi / Cu
Insulation	0.75 mm
Cu / Sc Ratio	0.795 mm
No. Filaments	Formvar
le (4.2K, ST)	1.35 : I
le (4.2K, 9T)	54
	200A
	103A

The following was found: Both CTD-IO I K and CY!79 epoxide resins worked well for their penetration inside the coils. No voids was found inside the coils. All of the SEM photographs showed that there were no any micro cracks inside the epoxide resins after thermal shock. With the use of a specific mold release that we found through our research, the potted coil can be completely detached from the coil form.

TRAINING CHARACTERISTICS OF NbTi COILS

A 36 layer test coil was wound with Oxford formvar insulated NbTi wire and then potted with CTD-IO I K resin. The specifications of the coil are presented in Table 3. The coil was tested at 4.2 K with four excitations. The four quenching currents measured were 195.33 A, 195.12 A, 195.07 A, and 194.77 A. This 195 A current corresponds to a 8.0 Tesla peak field in the coil and a 6.5 Tesla field at the center. This shows that the quench current is 97.5% of the short-wire critical current (i.e., 200 A at 8 Tesla from Table 3) for the conductor. This test thus successfully demonstrated the excellent potting properties and performance of CTD-10IK resin and our VPI technique.

The eight main coils of the 9.4 Tesla 400 MHz NMR magnet were also potted with CTD-IO I K resin. The specifications of the coils are listed in Table 4. The training characteristics of the magnet were measured and is shown in Fig. 4. The magnet quenched twelve times before it reached the full field current. The first several quenches are believed to be caused by unbalanced forces due to the axial misalignments during magnet assembly. Whether the rest of the quenches is related to the epoxy or not is currently unclear.

Table 4. Specifications of the main coils of the 400 MHz magnet

Parameter	Sec. 1	Sec. 2	Sec. 3	Sec. 4,5	Sec. 6	Sec. 7,8
Tums / Layer	460	732	118	373	98	114
Layers	24	38	38	38	30	30
Wire diameter (mm)	1.073	0.706	0.552	0.552	0.644	0.644
Cu / Sc ratio	1.35	2.0	3.0	3.0	7.0	7.0
Peak field (T)	9.49	7.75	3.40	4.71	2.41	2.33
J. (A / mm ²)	122.0	261.0	539.6	405.0	327.6	331.4

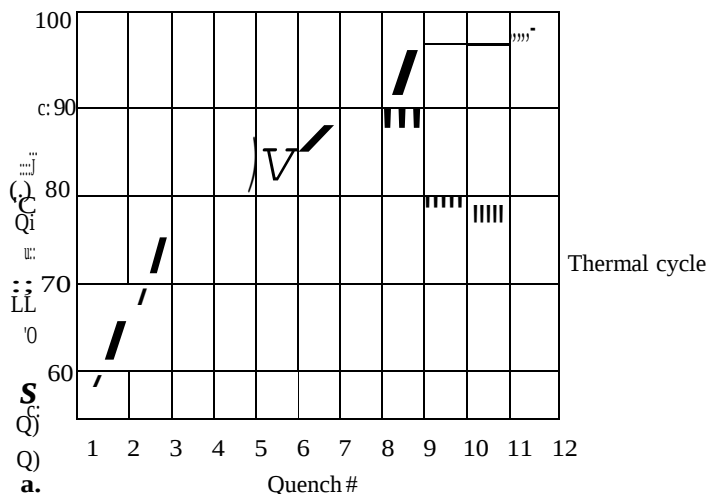


Figure 4. The training curve of the 400 MHz/900 mm NMR magnet.

CONCLUSIONS

Several epoxy formulations have been studied by viscosity, thermal shock, bonding/de-bonding, SEM measurements and model coil tests. Our study shows that among all of the epoxy formulations studied in this project, the CTD-101 K is the most appropriate resin for vacuum-pressure impregnation of high-field NMR magnet coils. The CTD-101K resin has been successfully applied to the fabrication of the 400 MHz/89 mm actively shielded high resolution NMR magnet. This research also developed a reliable vacuum-pressure impregnation technique which involves the combination of appropriate coil winding method, potting procedure, and potting equipment.

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