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Design of a High Toughness Epoxy for Superconducting Magnets and Its Key Properties

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***Abstract*—Nb_3Sn accelerator magnets are poised to enable the luminosity upgrade of the Large Hadron Collider (LHC) at CERN, improving its potential for exploring physics beyond the standard model of particle physics. The prototype Nb_3Sn magnets consistently need 10–25 quenches to achieve their best performance. A hypothesis is that the long training of these magnets may at least be partially induced by epoxy cracking and bonding failures. In 2018, we showed that several existing epoxies have a higher toughness and less tendency to crack at low temperatures than CTD-101K, the epoxy resin with which almost all Nb_3Sn accelerator magnets have been impregnated. Here we explore a new high toughness formulation for reducing quench training of Nb_3Sn accelerator magnets, through combining two amine curing agents to achieve a good glass transition temperature (T_g), adding a viscosity reducer to achieve low viscosity, and experimenting a coupling agent for improved bonding strengths. We report results of comprehensive materials tests, including thermal shock, tensile, compressive, shear tests, viscosity and T_g tests.**

I. Introduction

To provide mechanical integrity for Nb_3Sn superconducting accelerator magnets, epoxy resin is employed as an electrical insulation as well as an encapsulation material [1] to minimize the movement of superconductors under Lorentz forces [2]. However, Nb_3Sn accelerator magnets still exhibit a long quench training and a lack of reproducibility of achieved performance, and there is a gap between the performance that is predicted on paper (the so-called short-sample-limit, SSL) and that which is achieved for produced magnets [3]–[8]. The term training refers to the increase of peak current observed in a magnet when it undergoes a series of tests where the current is ramped up until the magnet quenches. For example, CERN-Fermilab 11 T dipole magnets reached their nominal current (~20% of SSL along load line) at 1.9/4.3 K after 6–22 quenches [8]. So far Nb_3Sn accelerator magnets have shown a good memory of their training between thermal cycles; therefore training adds expenses but is noncritical for the high luminosity upgrade of LHC that only needs tens of such magnets [5]–[8]. Training is a critical issue [9], for future 12–16 T class Nb_3Sn magnets based high energy proton-proton colliders [10] that need thousands of such magnets. Training is also relevant for many other applications of Nb-Ti and Nb_3Sn superconducting magnets fabricated by epoxy impregnation, ranging from MRI [11], NMR [12], fusion, undulator magnets for light sources [13], to ion source magnets [14], [15].

For impregnating superconducting coils, the following epoxy system characteristics are generally sought: (1) Long pot life at least >3 hours [16]. (2) Low viscosity for void free impregnation. (3) Low temperature cure to reduce internal thermal stresses. (4) Easy to use. (5) Acceptable strength and flexibility after irradiation. For Nb_3Sn accelerator magnets, a hypothesis is that the long training may at least be partially induced by epoxy cracking, and bonding failures [17]–[19], driven by mismatches of thermal contraction between epoxy resin and magnet components and high Lorentz forces. There are pockets of neat resin between strands inside a Nb_3Sn Rutherford cable and they can crack on cooldown. Therefore, in selecting the resin formation to be used for Nb_3Sn accelerator magnets, account should be taken especially of toughness and resistance to cracking, i.e., work of fracture. In addition, Nb_3Sn accelerator magnets based on the cosine-theta design also need to withstand a maximum compression stress, i.e., preload, of ~90 MPa at room temperature (RT). Therefore, the glass transition temperature T_g of an epoxy needs to be carefully selected because an epoxy with T_g near RT tends to be soft at RT whereas a too high T_g (>150 °C) results in large internal thermal stress, and also because if hot spot temperature during quenches [20] exceed the T_g of epoxy, the magnet's mechanical properties may change locally, resulting in an unknown change of its performance.

Our previous study sorted epoxies used for major Nb-Ti and Nb_3Sn superconducting magnets into three groups and analyzed their key properties [21]. The formulations include the CTD-101K [22] used for almost all prototype Nb_3Sn accelerator magnets, the epoxy designed for the ITER Central Solenoid (ITER-CS) [23], the epoxy used for the NHMFL 900 MHz NMR Solenoid [24], and the epoxy developed for ATLAS End Cap Toroid (ATLAS-ECT) [25]. CTD-101K exhibits a pot life around 13 hours at 50 °C and the ITER-CS epoxy has a pot life of >20 h at 50 °C. The pot life of an epoxy resin in this work is defined as the time that passes from initial mixing to reaching a viscosity of 200 cps. But they show low thermal cracking resistance, a typical behavior exhibited by an anhydride cured epoxy resin. The epoxies for the NHMFL 900 MHz NMR magnet and the ATLAS-ECT magnet represent another amine-cured group and they have much better thermal shock

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TABLE I
EPOXY FORMULATIONS TESTED

	Formulation ID	F_A	F_B	F_C	F_D	F_E	F_F	F_G	F_H	F_I
Ratio of curing agents (by weight)	D230	2	2	2	2	1	3	2	2	2
	HY5200	8	8	8	8	9	7	8	8	8
	T5000	0	0	0	0	0	0	0.5	1	2
Parts by weight (resins)	GY282	100	95	90	80	90	90	90	90	90
	H61	0	5	10	20	10	10	10	10	10

resistances, though showing a shorter pot life of less than 4 hours. A third group is a room-temperature cured, Jeffamine cured epoxy that has the best thermal shock resistances but has the shortest pot life around 1 h and a T_g near RT.

To further improve the toughness of the epoxy and explore a formulation that has a better overall performance, this study examines several new formulations. The base epoxy resin was chosen as GY282 because it's a low-viscosity and unmodified bisphenol-F epoxy resin and it was used in ITER CS epoxy and ATLAS ECT epoxy, whose formulations can be found in [21]. Compared to bisphenol-A based resins, bisphenol-F based resins show similar mechanical properties, but with a longer pot life and a lower viscosity [26]. Its viscosity was further reduced by a reactive modifier, HELOXY 61(H61), a monoepoxide with a relatively low molecular weight effective with reducing viscosity. Curing agents were chosen to be a mix of HY5200 and Jeffamine D230 [21]. HY5200 was an aromatic amine curing agent used in the epoxy for ATLAS ECT epoxy. Compared to the anhydride hardeners, the incorporation of HY5200 increases viscosity but improves toughness. The cured epoxy with HY5200 also has a high T_g. For further raising the toughness, HY5200 was mixed with D230, a RT cured Jeffamine with a flexible backbone exhibiting high toughness but with low T_g. Bond failure is another source for quenches in superconducting magnets [19]. Therefore, to improve the adhesion property of the epoxy formulation, a coupling agent, Jeffamine T5000, was added. T5000 is a polyoxypropylene triamine that can be used to improve peel strength and tensile shear strength without degrading other properties. Table I details the formulations.

II. EXPERIMENTAL METHODS

Thermal shock test was used to investigate the toughness and the thermal cracks resistance of the formulations. The detailed method was introduced previously [21]. Simply, the epoxy sample with or without a brass bolt were immersed in liquid nitrogen and then brought back to room temperature for 20 times. Tensile properties of neat resins were evaluated according to the ASTM D638 standard [27]. A table top SEM (JEOL Neoscope JCM-5000) was used to investigate the micromorphology of the fractured surfaces. Viscosity of epoxy formulations was determined by a Brookfield DV2T-LV viscometer at 50 °C. Differential scanning calorimetry (DSC) (TA Q1000) was employed to analyze the T_g. The heating process was set from 5 °C to 150 °C at 10 °C/min [28]. Single lap shear test was used to study the bonding strength according to the ASTM D1002 standard [29] and the 6061 Aluminum was chosen as the test metal panels. Compression properties were evaluated according to the standard ASTM D695 [30].

III. RESULTS

A. Thermal Shock Test

The odd-number samples are neat resin blocks and the even-number samples contain a brass bolt to induce a large thermal differential strain. The thermal shock results of the even number samples after the 1st and the 20th cycle to 77 K are shown in Fig. 1. All samples showed cracks after the 1st cycle, except sample #14, #16 and #18 (F_G, F_H and F_I). After the 20th cycle, small cracks were observed on the surface of the sample #16 (F_H) and #18 (F_I). Sample #2 to sample #14 (F_A to F_G) had extensive cracks or even fractured to several pieces.

B. Tensile Test

The results of tensile tests at RT are shown in Fig. 2. As shown in Fig. 2(a), the viscosity reducer H61 improved the toughness at RT. Fig. 2(b) and (c) show the results of the tested samples with different ratios of the curing agents under 10 parts by weight (pbw) H61. The F_F with 3:7 (D230:HY5200) showed an engineering strain of 7.3%.

The fracture morphology of the formulations after tensile test was investigated by SEM, as shown in Fig. 3. In general, on increasing the epoxy toughness, the surface roughness increases. The Fig. 3(a) exhibits a relatively smooth surface, revealing a low toughness of F_C and low resistance for the fracture propagation. Fig. 3(b) and (c) are similar morphology, showing textured surface with higher roughness than Fig. 3(a). The roughest surface is observed in Fig. 3(d), which means that F_H is with high toughness and has the highest resistance for the fracture propagation. In sum, the fracture morphology agrees with the results of engineering strain shown in Fig. 2.

C. Viscosity Test

The viscosity comparison of the designed formulations at 50 °C is shown in Fig. 4. As shown in Fig. 4(a), under identical ratio of the curing agents (D230 and HY5200), H61 reduced the viscosity and raised the pot life. Fig. 4(b) presents the results of the different ratios of the curing agents with 10 pbw H61, showing that HY5200, compared to D230, was effective with reducing the viscosity. As for the Fig. 4(c), the T5000 with various ratios was blended with the other two curing agents and the T5000 increased the viscosity slightly.

D. Glass Transition Temperature

The results of the heat flow versus temperature are shown in Fig. 5. In these figures, the T_g is defined as the mid-point of the glass transition temperature region. As shown in Fig. 5(a), under identical ratio of the curing agents (D230 and HY5200), increasing H61 decreased the T_g. As for the Fig. 5(b) and (c), we found that the HY5200 was an effective component for increasing the T_g and the epoxy formulations blended with different ratios of the T5000 had similar T_g.

E. Single Lap Shear Test

As shown in Fig. 6, the results of the single lap shear test verified that the T5000 was useful for improving the shear

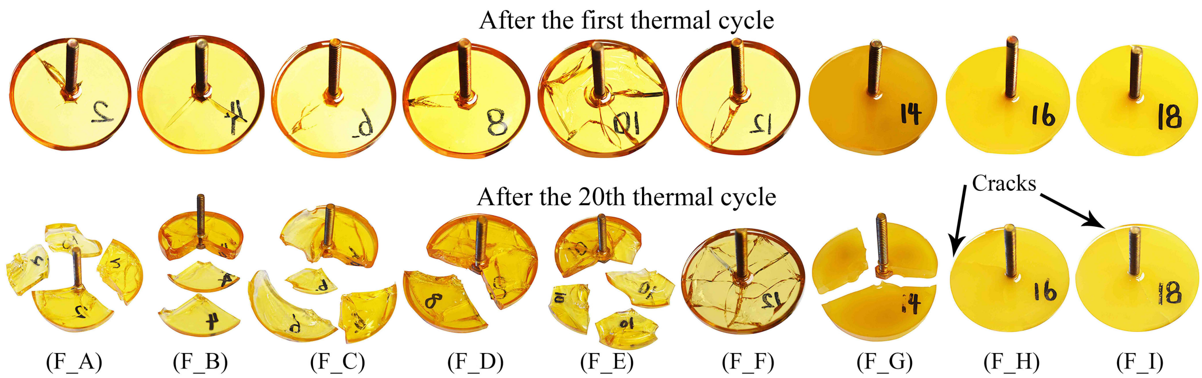

Fig. 1. Thermal shock samples (from left to right, #2, #4, #6, #8, #10, #12, #14, #16, and #18) with brass bolts after the 1st thermal cycle and the 20th thermal cycle. Formulation IDs of these samples are F_A to F_I, arranged from left to right.

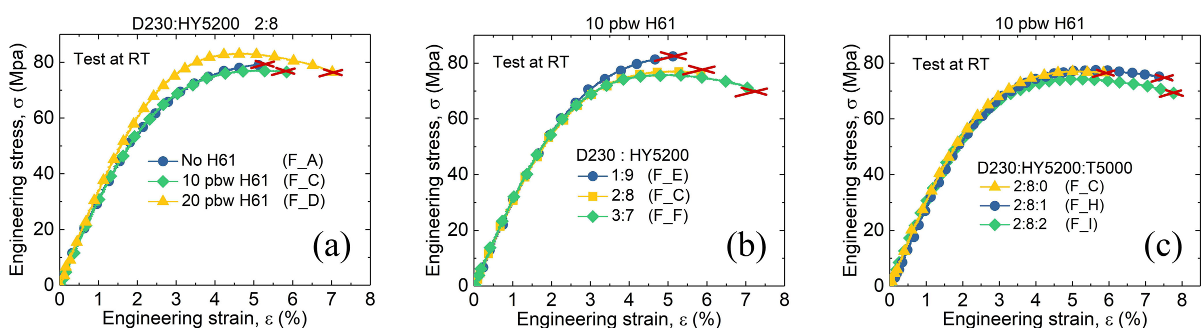

Fig. 2. Tensile stress-strain curves for the designed formulations (a) 2:8_(D230:HY5200) with different amount of H61 (F_A, F_C, and F_D). (b) 10 pbw H61 with different ratios of the D230 to HY5200 (F_E, F_C, and F_F). (c) 10 pbw H61 with different ratios of D230, HY5200 and T5000 (F_C, F_H, and F_I).

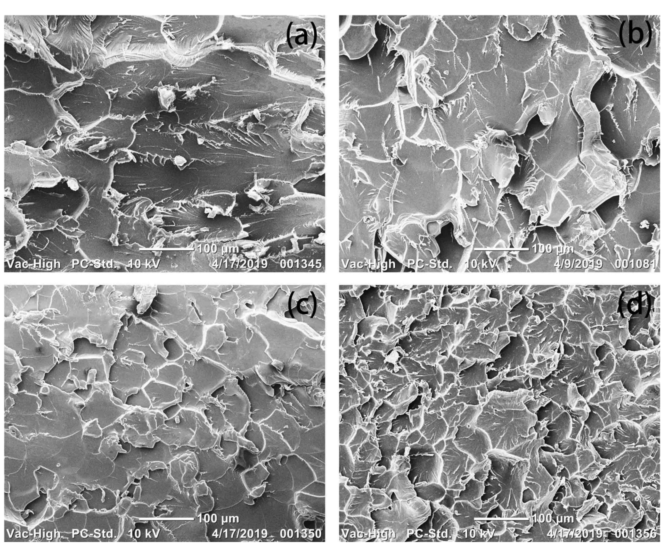

Fig. 3. Microstructure analysis of the fractured surface from tensile tests (a) F_C. (b) F_F). (c) F_D. (d) F_H.

strength both at RT and 77 K. At 77 K, F_H with addition of T5000 had 30% higher strength than F_C without addition.

F. Compressive Test

Comparisons of compressive stress versus displacement at room temperature or 77 K are shown in Fig. 7. Under identical ratio of the curing agents (D230 and HY5200), compressive strength decreased with increasing H61. Fig. 7(c) and (d) show the results for different ratios of the curing agents when the H61 was 10 pbw. The ratio of the D230 to HY5200 had almost no effect on the compressive strength, but the adding of the T5000 lowered the strength.

IV. Discussion

Table II summarizes key properties of epoxy resin formulations in this work with other formations in use [19]. Formulations F_D and F_H, bolded in Table II, are recommended for Nb_3Sn accelerator magnets for their well-balanced overall combination of properties. Formulation F_D shows a pot life of ∼10 hours at 50 °C, smaller than that of CTD-101K (∼13 hours), but higher than those of NHMFL mix-61 and ATLAS ECT (<4 hours). F_D has a thermal shock resistance larger than that of CTD-101K. F_D and F_H have T_g around 100 °C, higher than that of NHMFL mix-61. The RT compressive yielding stress is ∼100 MPa for F_D and F_H, smaller than ∼125-150 MPa for CTD-101K [31], but larger than ∼25 MPa for NHMFL mix-61.

Our work reveals impacts of each epoxy modifier for further fine tuning formation. Adding D230 could increases the toughness but in the meanwhile, increases viscosity and reduces T_g. The viscosity reducer H61 did not negatively impact the toughness, contrary to the previous suggestion that this chain stopper may present no advantages at low temperatures [32]. But increasing H61 also decreases the T_g. The bonding agent T5000 was effective with raising the shocking resistance. The results of the single lap shear test shown in Fig. 6 confirmed that T5000 could increase the shear strength at both RT and 77 K.

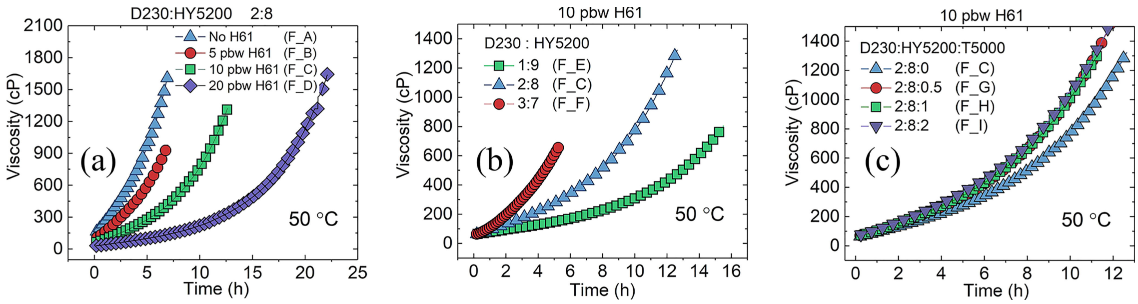

Fig. 4. Comparisons of viscosity development versus time at 50 °C. (a) 2:8_D230:HY5200 with different pbw of H61 (F_A to F_D). (b) different ratios of D230 to HY5200 with 10 pbw H61 (F_E, F_C, and F_F). (d) different ratios of D230, HY5200 and T5000 with 10 pbw H61 (F_C, F_G, F_H, and F_I).

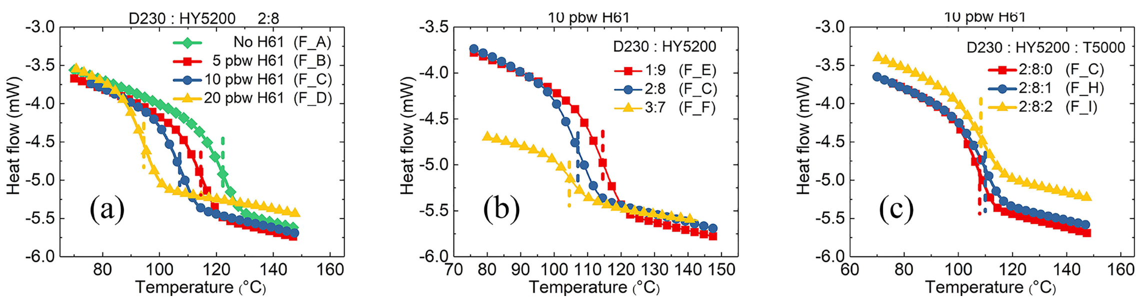

Fig. 5. Results of T_g from DSC tests. (a) 2:8_D230:HY5200 with different pbw of H61 (F_A to F_D). (b) different ratios of D230 to HY5200 with 10pbw H61 (F_E, F_C, and F_F). (c) different ratios of D230, HY5200 and T5000 with 10pbw H61 (F_C, F_H, and F_I).

TABLE II
SUMMARY OF PROPERTIES OF EPOXY RESIN FORMULATIONS TESTED IN THIS STUDY AND IN PRACTICAL USES. ENGINEERING STRAIN AND ULTIMATE TENSILE STRENGTH WERE OBTAINED AT RT

Formulations	CTD-101K	ITER CS	NHMFL mix-61	ATLAS ECT	F_A	F_C	**F_D**	F_E	F_F	**F_H**	F_I
RT Engineering strain at break (%)	0.9	1.3	39.3	10.6	5.3	5.9	**7.1**	5.2	7.3	**7.7**	7.8
RT ultimate tensile strength (Mpa)	29.6	43.7	20.9	75.0	79.5	77.0	**83.1**	82.4	75.8	**77.5**	74.3
Pot life at 50 °C (h)	12.9	>20	2.7	3.4	0.5	3.5	**9.4**	7.1	2.1	**2.8**	2.6
T_g (°C)	105	85	65	123	122	107	**94**	115	104	**110**	108

Data for CTD-101K, ITER CS, NHMFL mix-61 and ATLAS ECT was obtained from our previous study [19].

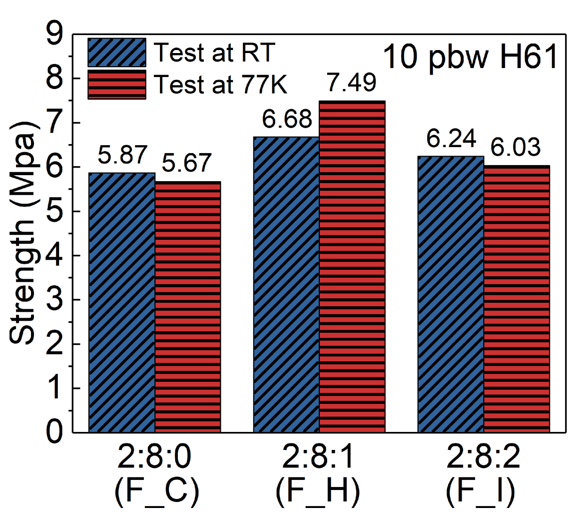

Fig. 6. Results of the single lap shear tests for the different ratios of the D230, HY5200 and T5000 with 10 pbw H61 (F_C, F_H, and F_I) at RT and 77 K.

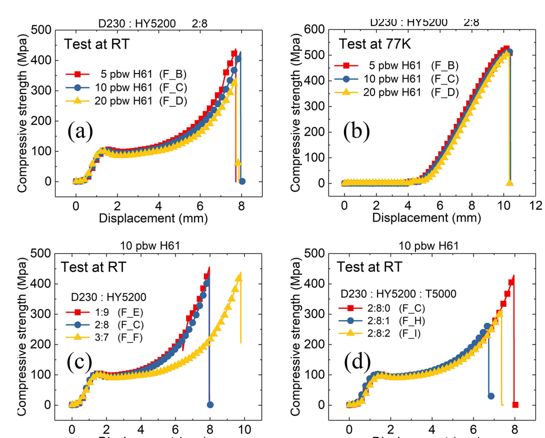

Fig. 7. Compressive strength versus displacement of formulations with different amounts of H61 (F_B, F_C, and F_D), at (a) RT and (b) 77K, (c) with different ratios of D230 to HY5200 with 10pbw H61 (F_E, F_C, and F_F), and (d) with different ratios of D230, HY5200 and T5000 with 10pbw H61 (F_C, F_H, and F_I). Data in (c) and (d) was obtained at RT.

V. CONCLUSION

We tested several new epoxy formulations used for vacuum impregnating Nb_3Sn superconducting magnets and found two formations that show a healthy combination of low viscosity, long pot life, and relatively high toughness and are potentially useful for impregnating superconducting magnets. The effectiveness of these new formulations for reducing quench training will be examined in future works.

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REFERENCES

[1] D. Evans, J. Morgan, and G. Stapleton, "Epoxy resins for superconducting magnet encapsulation," Rutherford High Energy Lab. Rep., RHEL/R251, 1972.
[2] Y. Iwasa, "Experimental and theoretical investigation of mechanical disturbances in epoxy-impregnated superconducting coils. 1. General introduction," *Cryogenics*, vol. 25, no. 6, pp. 304–306, 1985.
[3] H. Felice *et al.*, "Design and test of a Nb_3Sn subscale dipole magnet for training studies," *IEEE Trans. Appl. Supercond.*, vol. 17, no. 2, pp. 1144–1148, 2007.
[4] P. Ferracin, "LARP Nb_3Sn quadrupole magnets for the LHC luminosity upgrade," *AIP Conf. Proc.*, vol. 1218, 2010, Art. no. 1291.
[5] P. Ferracin *et al.*, "The HL-LHC low-β quadrupole magnet MQXF: From short models to long prototypes," *IEEE Trans. Appl. Supercond.*, vol. 29, no. 5, 2019, Art. no. 4001309.
[6] J. Muratore *et al.*, "Test results of the first two full-length prototype quandrupole magnets for the LHC Hi-Lumi Upgrade," *IEEE Trans. Appl. Supercond.*, to be published, doi: 10.1109/TASC.2020.2981269.
[7] H. Song, "Test results of the HL-LHC low-β quadrupole magnet MQXFA03," private communication, 2020.
[8] F. Savary *et al.*, "The 11 T dipole for HL-LHC: Status and plan," *IEEE Trans. Appl. Supercond.*, vol. 26, no. 4, 2016, Art. no. 4005305.
[9] S. Gourlay *et al.*, "The US magnet development program plan," 2016, [Online]. Available: https://escholarship.org/content/qt5178744r/qt5178744r.pdf
[10] A. Abada *et al.*, "FCC-hh: The hadron collider, future circular collider conceptual design report volume 3," *Eur. Phys. J. Special Topics*, vol. 228, pp. 755–1107, 2019.
[11] C. Wang, Q. Wang, and Q. Zhang, "Multiple layer superconducting magnet design for magnetic resonance imaging," *IEEE Trans. Appl. Supercond.*, vol. 20, no. 3, pp. 706–709, 2010.
[12] R. Fu *et al.*, "Ultra-wide bore 900 MHz high-resolution NMR at the national high magnetic field laboratory," *J. Magn. Reson.*, vol. 177, no. 1, pp. 1–8, 2005.
[13] Y. Ivanyushenkov, "Development and operating experience of a 1.1-m-long superconducting undulator at the advanced photon source," *Phys. Rev. ST Accel. Beams*, 20, 2017, Art. no. 100701.
[14] C. Taylor *et al.*, "Magnet system for an ECR ion source," *IEEE Trans. Appl. Supercond.*, vol. 10, no. 1, pp. 224–227, 2000.
[15] D. Arbelaez *et al.*, "Test results for a superconducting 28-GHz ion source magnet for FRIB." *IEEE Trans. Appl. Supercond.*, vol. 29, no. 5, 2019, Art. no. 4100605.
[16] P. E. Fabian *et al.*, "Properties of candidate ITER vacuum impregnation insulation systems," *Adv. Cryog. Eng. Mater.* Springer. pp. 1007–1014, 1994.
[17] E. Bobrov, J. Williams, and Y. Iwasa, "Experimental and theoretical investigation of mechanical disturbances in epoxy-impregnated superconducting coils. 2. Shear-stress-induced epoxy fracture as the principal source of premature quenches and training theoretical analysis," *Cryogenics*, vol. 25, no. 6, pp. 307–316, 1985.
[18] Y. Iwasa *et al.*, "Experimental and theoretical investigation of mechanical disturbances in epoxy-impregnated superconducting coils. 3. Fracture-induced premature quenches," *Cryogenics*, vol. 25, no. 6, pp. 317–322, 1985.
[19] H. Maeda and Y. Iwasa, "Heat generation from epoxy cracks and bond failures," *Cryogenics*, vol. 22, no. 9, pp. 473–476, 1982.
[20] G. Ambrosio, "Maximum allowable temperature during quench in Nb_3Sn accelerator magnets," 2014, *arXiv:1401.3955*.
[21] S. Yin *et al.*, "Epoxy resins for vacuum impregnating superconducting magnets: A review and tests of key properties," *IEEE Trans. Appl. Supercond.*, vol. 29, no. 5, 2019, Art. no. 7800205.
[22] G. Chlachidze *et al.*, "Performance of the first short model 150-mm-aperture Nb_3Sn quadrupole MQXFS for the high-luminosity LHC upgrade," *IEEE Trans. Appl. Supercond.*, vol. 27, no. 4, 2017, Art. no. 4000205.
[23] R. Reed, D. Evans, and P. Fabian, "Development of a new resin system for the US ITER central solenoid model coil," *Adv. Cryog. Eng. Mater.* Springer, pp. 227–234, 2000.
[24] W. D. Markiewicz *et al.*, "25 T high resolution NMR magnet program and technology," *IEEE Trans. Mag.*, vol. 32, no. 4, pp. 2586–2589, 1996.
[25] R. P. Reed and D. Evans, "Low-viscosity, radiation-resistant resin system with increased toughness," *AIP Conf. Proc.*, vol. 711, no. 1. AIP, 2004.
[26] C. Baldan *et al.*, "Study of bisphenol-F epoxy resin system for impregnation of superconducting magnets," *Adv. Cryog. Eng. Mater.*, Springer. pp. 205–210, 2000.
[27] ASTM Standard D638-14, "*Standard Test Method for Tensile Properties of Plastics*," ASTM International, West Conshohocken, PA, 2014, doi: 10.1520/D0638-14.
[28] M. S. Madhukar and N. N. Martovetsky, "DGEBF epoxy blends for use in the resin impregnation of extremely large composite parts," *J. Compos. Mater.*, vol. 49, no. 30, pp. 3741–3753, 2015.
[29] ASTM Standard D1002-10, "Standard test method for apparent shear strength of single-lap-joint adhesively bonded metal specimens by tension loading," ASTM International, West Conshohocken, PA, 2010, doi: 10.1520/D1002-10.
[30] ASTM Standard D695-10, "Standard test method for compressive properties of rigid plastics," ASTM International, West Conshohocken, PA, 2010, doi: 10.1520/D0695-10.
[31] B. Gold *et al.*, "Tough epoxy systems for the impregnation of high field superconducting magnets," presented at *Int. Cryogenic Mater. Conf.*, Hartford, 2019.
[32] D. Evans, "Resins for superconducting magnet construction – an overview of requirements, processing and properties," presented at *Int. Cryogenic Mater. Conf.*, Hartford, 2019.