

Properties of Impregnation Resin Added to Multifunctional Epoxy at Cryogenic Temperature

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ABSTRACT: A multifunctional epoxy tetraglycidyl dibenz-methylamine and triglycidyl benzylamine were blended, respectively, into impregnation resin, which mainly consists of diglycidyl ether of bisphenol A (DGEBA) and acid anhydride hardener. This resin is expected to impregnate HT-7U superconducting Tokamak toroidal field coils and improve the fracture toughness of DGEBA–acid anhydride resin at cryogenic temperature. However, the experimental results reveal that resin lap shear strengths decrease remarkably

both at ambient and liquid nitrogen temperatures. After blending multifunctional epoxy for several hours, its viscosity increased quickly at room temperature. The usable potting life is too short to impregnate large coils such as those used in fusion reaction. By FTIR the possible reason was investigated. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1385–1389, 2003

Key words: multifunctional epoxy; viscosity; FTIR; resins

INTRODUCTION

The structural integrity of toroidal field (TF) magnet coils as well as the operational safety of HT-7U superconducting Tokamak apparatus, in general, relies on the adhesive strength formed between the superconductors and/or the coil support structure, a stainless-steel coil box. This resin/glass fiber material also forms the main electrical insulating barrier for the coils. Thus the importance of a proper resin to impregnate coils, especially a resin with high shear strength, is very clear. Many methods can be used to improve the resin shear strength, but for impregnating resin, in particular for fusion superconducting coils, it is difficult. For example, the curing temperature of impregnating resin should be lower than 200°C. It is known that the matrix intrinsic strength will be improved if the resin cures at high temperature, although high curing temperatures destroy the property of the superconductor. Besides high shear strength, the resin should also have high crack resistance. It should resist cracking when the coils cool from curing temperature to ambient temperature as well as to liquid helium working temperature (LHT, ~ 4.2 K), and still retain high bonding strength at this operating temperature. To our knowledge, it is impossible for normal epoxy resin not to crack and retain high strength at such temperature. Therefore many methods have been attempted to improve the fracture toughness of resin, such as dispersing of nanoscale silica filler in the resin

formulation,¹ modifying the diglycidyl ether of bisphenol A (DGEBA) by a long aliphatic resin,² applying tougher epoxy, such as diglycidyl ether of bisphenol F (DGEBF) as the main ingredient, and so on. Nishijima and Okada³ even mixed multifunctional epoxy tetraglycidyl-*meta*-xylenediamine (TGMXDA) in the formulation. They blended TGMXDA and DGEBA to improve the resin fracture toughness at cryogenic temperature. The experimental result indicated that both the resin's microscopic strength of molecular chain and its macroscopic fracture toughness K_{qi} were improved after being blended with the two epoxies. The improvement is attributed to the formation of an intensified three-dimensional network in molecular structure after curing. The local structure of the molecular chains, which relax stress concentration at cryogenic temperature, was also intensified. The matrix could not easily be ruptured at cryogenic temperature. Because of such a benefit, the multifunctional epoxy was chosen to be used in our resin formulation for HT-7U coil impregnation.

For large coils the resin processing parameters must be considered carefully. For example, in general resins with low viscosity and a long potting life are indispensable for large coils; the resin must fully impregnate the coil to form a good impregnation system. In practice for large coils the gel time (potting life) will be longer than 8 h, or the resin viscosity will be lower than 100 mPa · s and/or increase less than 10% during the entire impregnating period. In our work, two kinds of multifunctional epoxies, tetraglycidyl dibenz-methylamine (TGDMDA) triglycidyl benzylamine (TGBA) were chosen to blend with DGEBA and to produce impregnation resin, respectively. A resin of

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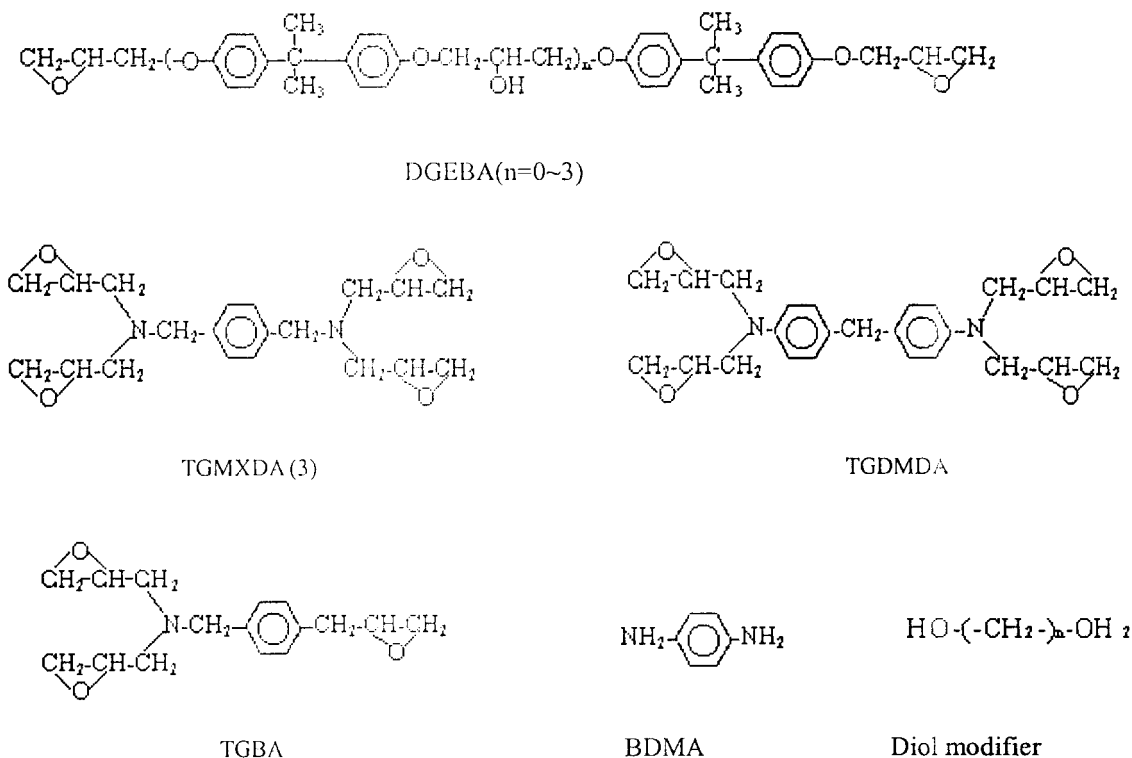


Figure 1 Molecular structures of materials.

satisfactory toughness to impregnate HT-7U TF coils operating at 4.2 K was expected. However, the experimental result shows that the viscosity of the resin mixed with these multifunctional epoxies was high and increased very quickly at room temperature. The measurement of resin gel time indicates that the resin has a short potting life, and it is impossible to fully impregnate the large coils before the resin gelatinizes. Moreover, the lap shear strength at both room and cryogenic temperatures also decreases after blending with multifunctional epoxy. A low shear strength cannot support the operation of large coils under conditions of immense shear force and cryogenic temperature. In this study the possible reason and suggestions are presented.

EXPERIMENTAL

Materials and samples

A normal DGEBA (Shanghai Polymer Resin Co., Shanghai, China) type epoxy resin was used as the main ingredient. The hardeners used were nadic-tetrahydric-methylanhydride (NA), nadic-sixhydric-methylanhydride, and another anhydride hardener based on NA but modified by diol molecule (commercial name HK-021). A silane coupling agent (commercial name A-178TM; Witco Company USA, China Ltd.) was also employed to improve the cryogenic properties. Figure 1 shows each molecular structure in for-

mulation, and their properties are shown in Table I. Table II lists all experimental resin components. Formulations 1, 2, and 3 alternate the hardeners. TGMDMA and TGBA were compared in formulation 4 and formulations 5 and 6. Formulations 5 and 6 have different ratios of TGMDMA. The curing schedule for all resins are as follows: 3 h at 100°C + 24 h at 160°C.

RESULTS AND DISCUSSION

Shear strength

Nishijima and Okada³ did not show the lap shear strength of the hybrid resins, but did examine K_{qi} . The fracture toughness increased continually with increasing ratios of TGMXDA in formulation and reached the highest at the ratio DGEBA : TGMXDA = 50 : 50 at liquid nitrogen temperature (LNT).

TABLE I
Properties of the Epoxy Resins and Hardeners

Material	Density (g/cm ³)	Viscosity (poise) (25°C)
DGEBA	1.1-1.2	25
TGBA	1.20-1.24	43
TGMDMA	1.22-1.28	34
NA	1.17-1.2	0.5-0.15
HHPA	1.18-1.24	0.7-2.0
HK-021	1.18-1.25	0.7-2.2

TABLE II
Formulations of Experimental Resins

Formulation number	Composition	Parts by weight (phr)
1	DGEBA	100
	NA	80
	A-178 TM	1
2	DGEBA	100
	HHPA	80
	A-178 TM	1
3	DGEBA	100
	HK-021	80
	A-178 TM	1
4	DGEBA	100
	TGBA	25
	NA	130
	A-178 TM	1
5	DGEBA	100
	TGDMDA	25
	NA	150
	A-178 TM	1
6	DGEBA	100
	TGDMDA	100
	NA	170
	A-178 TM	1

In our experiment, lap shear strength of the resin was one of the important parameters to be examined. The shear strength was investigated on copper samples with the geometry shown in Figure 2. The substrate was prepared by sandblasting, washing in acetone, then drying at 110°C. It is known that lap shear strength is not a precise method of calibrating resin ultimate strength because there is a stress concentration at the edge of the joint. For instance, for the test sample illustrated in Figure 2 with 0.1–0.2 mm glue thickness, the stress intensity factor at the joint was about $2\sqrt{2}$, which means the maximum shear stress at the edge of the joint is $2\sqrt{2}$ times greater than the mean stress calculated by dividing the force at rupture by the adhesive surface.⁴ However, just as the aforementioned TF coils bonded by resin will bear immense shear force during Tokamak operation, the resin shear strength is thus one of the necessary and important parameters.

Table III lists the shear strengths of all the resins. It reveals that the matrix cured by hardener HK-021 has a higher shear strength than that of the other two hardeners. This may be a benefit from the NA anhydride hardener modified by diol molecule to improve the molecular toughness.⁵ After blending with multifunctional epoxy, however, the lap shear strengths decrease, (Table III), not only at room temperature but also at LNT. With a greater ratio of multifunctional epoxy in formulation, such as formulation 6 mixed with 100-phr TGDMDA, its lap shear strength decreases remarkably at room temperature and even more at LNT, compared to formulation 5 or formulation 1, with only 25 or 0 phr of TGDMDA and the

same hardener. The table also indicates that TGDMDA seems better than TGBA in retaining resin shear strength at room temperature and LNT.

Thermal test

The thermal cycling test consists of dipping lap joint samples into a bath of liquid nitrogen (77 K) for 5 min, then drying at room temperature (293 K) for the same interval and so on before the measurement of shear strength at room and/or cryogenic temperature.

The other thermal cycle test, thermal shock resistance (TSR), must also be taken to ensure the structural integrity of the coils under operating conditions. The TSR test sample, the bolt-in-sample whose bolt is embodied by resin, was prepared according to Evans.⁶ The cured sample was cycled between liquid nitrogen and ambient condition until failure or 25 survivals.

The results, as shown in Table III, indicate that all samples are cracked and failed at less than 25 cycles. By addition of multifunctional epoxy, TSR values are obviously extended as shown in a comparison of formulations 4, 5, and 6 with formulation 1, which has the same hardener, although the extension was limited, at only 4 to 8 cycles. A greater ratio of multifunctional epoxy does not improve the resin cryogenic characteristics of TSR in formulation 5 compared to that in formulation 6. TGBA and TGDMDA seem to have the same efficiency to extend resin TSR. From these data one can deduce that the increased formation of an intensified three-dimensional network in molecular structure cannot prevent the resin from cracking at LNT. It is also noted that formulation 3, cured by HK-021 hardener (NA modified by diol), has the longest life in TSR, even though it was not blended with a multifunctional epoxy.

Viscosity

Isothermal viscosity profiles of all six formulations are shown in Figure 3. The results at room temperature show that, because of the high intrinsic viscosity of multifunctional epoxy, the viscosity of resin blended with multifunctional epoxy is higher than that without one. It is also noted that the intrinsic viscosity of TGBA is high, and the resin viscosity of formulation 4, which

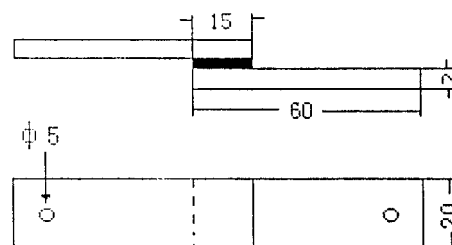


Figure 2 Lap joint sample (units in mm).

TABLE III
Properties of Lap Shear Strength (MPa) and Thermal Test

Property	Formulation number					
	1	2	3	4	5	6
Shear strength						
Initial						
at 293 K	6.6	4.7	8.2	5.0	5.2	5.2
at 77 K	7.1	5.5	9.7	4.5	6.3	5.2
After 15 cycles						
at 293 K	6.4	4.5	8.3	4.9	5.0	5.2
at 77 K	6.8	5.1	9.6	4.5	6.1	5.2
TSR (cycles before failure)	4-5	1-2	12	7-8	7-8	7-8

is blended with TGBA, is the highest in all six samples. Moreover, multifunctional TGBA seems to be very active because the viscosity of resin blended with it increases very quickly after 50 h storage at room temperature compared to other formulations, as Figure 3(b) shows. It also reveals that the greater the ratio of multifunctional TGDMDA in formulation, the higher the resin viscosity. Furthermore, with a greater ratio of TGDMDA, the resin viscosity increases quickly during storage. For example, when formulation 6 is mixed with 100-phr TGDMDA at room temperature, the viscosity increases from 80 to 132 mPa · s after 4 days, whereas for formulation 5 with only 25-phr TGDMDA its viscosity increases by only half this range of values.

At high temperature (e.g., at 50°C), which may be the temperature used for the coils' vacuum pressure impregnation (VPI) processing, because of the reduction in molecular intra-action, the viscosity was decreased at the beginning, as Figure 3(a) shows. For formulations 1-3 without a multifunctional epoxy, the viscosity at 50°C was lower than that at room temper-

ature. However, by blending these formulations with a multifunctional epoxy, the result is different. The hybrid resin viscosity increased dramatically after only short-term storage, even the viscosity at the beginning is lower than that at room temperature. Figure 3(a) shows that the viscosity of formulation 5 blended with 25 phr TGDMDA increases from 90 to 400 mPa · s after 6 h. The viscosity of formulation 6 with 100-phr TGDMDA increases steeply after 7 h.

To explain these results, the chemical structure of multifunctional epoxy must be studied. For TGBA, as shown in Figure 1, besides the three epoxy groups that react with anhydride groups, there is one amine species in the molecule, TGDMDA, which has two amine groups. It is well known that for the DGEBA-acid anhydride system adding an amine group decreases the curing temperature. For example, benzyl dimethyl amine (BDMA; molecular structure shown in Fig. 1, with two =N-group) is often used as a catalyst for this resin to decrease the curing temperature and accelerate the reactive rate. However, the BDMA mass

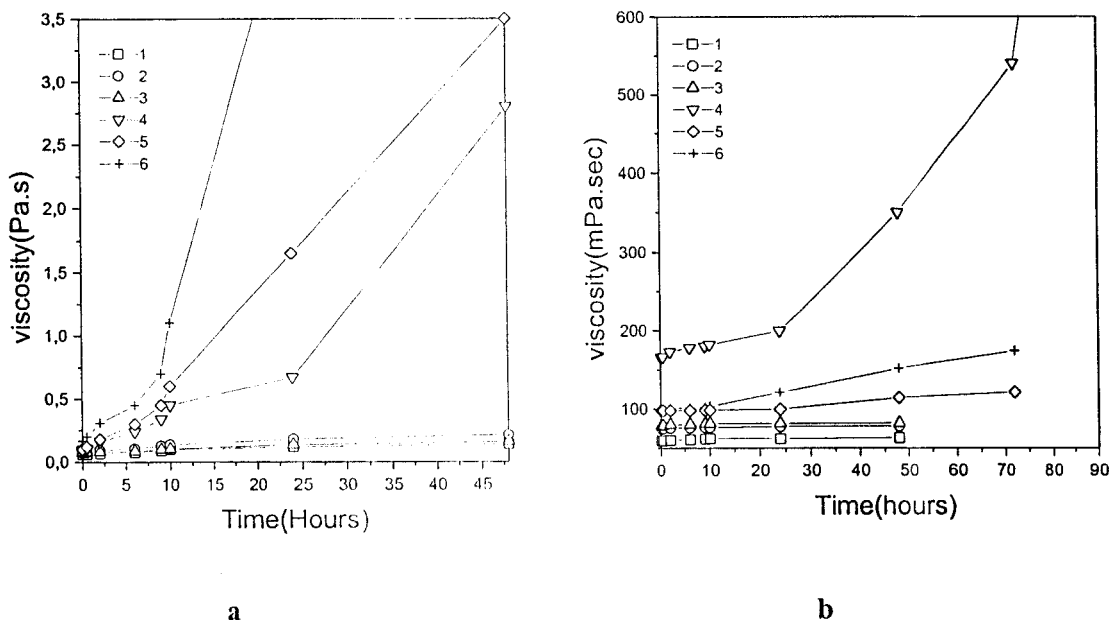


Figure 3 Isothermal viscosity characteristics of the resins at (a) 50°C and (b) 25°C.

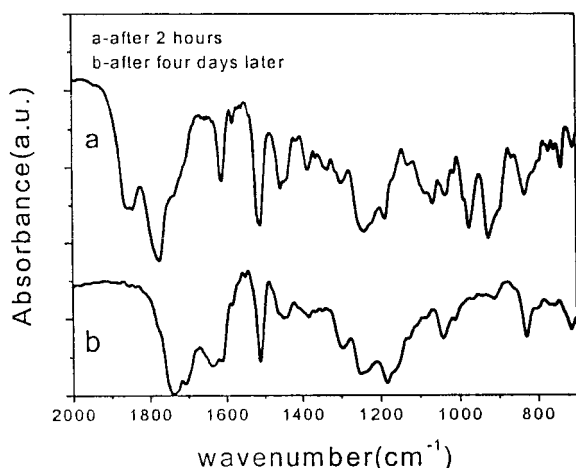


Figure 4 FTIR spectra of formulation 6 (a) after 2 h blending and (b) 4 days later at room temperature.

ratio in this formulation is small, less than 1 phr. A greater ratio of BDMA will destroy the resin system by rapid reactive rate and uncontrollable thermal release from the chemical reaction. From Table II, however, it is noted that for formulation 4 the mass ratio of TGBA is 25 phr and for formulation 5 the mass ratio of TGDMDA is 25 phr; furthermore, it is 100 phr TGDMDA in formulation 6. The stoichiometric ratio of $\equiv\text{N}$ -species in resin is responsible for accelerating the reactive rate and shortening the storage time, as shown in Figure 3. The increase of resin viscosity at room temperature (Fig. 3) is attributed to the pre-reaction between the anhydride and the epoxy group promoted by the amine species from the multifunctional epoxy.

In a comparison of different storage times of formulation 6, FTIR analysis provides enough evidence of epoxy group and anhydride pre-reacting during storage, as shown in Figure 4. After storage for 4 days at room temperature, the bands at 1774, 950, and 856 cm^{-1} typical for the epoxy group are characterized by a varied, weak shift. In particular, the peak at 1774 cm^{-1} in curve a of Figure 4 shifts to 1735 cm^{-1} in curve b. The peaks at 1885 and 1640 cm^{-1} , assigned to the anhydride species, are intense in curve a but disappear and deform in curve b. The peaks at 1480, 1440, and 1380 cm^{-1} are attributed to the CH deformation vibration of CH_2 and CH_3 groups; the weak peaks at 1240 and 1187 cm^{-1} , to the epoxy group; and the peak at 1260 cm^{-1} , to the C—O stretch mode; all peaks shift after the resin storage. These results mean that the pre-reaction between the epoxy group and the anhydride is inevitable and intense if a multifunctional

epoxy, which contains the amine group, is blended into the chemical chain. The pre-reaction is the reason that the viscosity at room temperature increases quickly in multifunctional resin blends.

CONCLUSIONS

A series of multifunctional epoxies added to the impregnation resin were developed and fully evaluated as to their suitability to impregnate HT-7U superconducting TF coils in this study. Results of lap shear strength and viscosity indicate that the resins are not suitable for large-coil VPI processing. The resin viscosity was high at ambient and increased very quickly at 50°C compared to that without multifunctional epoxy in the temperature. Because the viscosity increased with the storage time, its storage life was short, the reason for which was the pre-reaction between epoxy and anhydride in the resin during storage. It was confirmed by FTIR spectra, that the anhydride group disappeared, and the epoxy group shifted after the hybrid resin was stored for 4 days. The multifunctional epoxy not only caused the multigroup epoxy to react with acid anhydride to form a three-dimensional network in the molecular structure, but also caused the amine species to intensify the pre-reaction of epoxy and anhydride, thus decreasing the reactive temperature. This phenomenon was particularly significant with the greater stoichiometric ratio of $\equiv\text{N}$ -groups in formulation used in this investigation. We conclude that the multifunctional epoxy with the amine group in the molecular chain cannot be used to improve the characteristic cryogenic shear strength of the matrix, particularly at a high stoichiometric ratio.

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