MECHANICAL BEHAVIOUR OF CYANATE ESTER/EPOXY BLENDS AFTER REACTOR IRRADIATION TO HIGH NEUTRON FLUENCES

R. Prokopec, K. Humer, H. Fillunger, R. K. Maix, and H. W. Weber

Atomic Institute of the Austrian Universities,
Vienna University of Technology, 1020 Wien, Austria

ABSTRACT

The mechanical strength of conventional epoxy resins drops dramatically after irradiation to a fast neutron fluence of $1x10^{22}$ m^{-2} (E>0.1 MeV). Recent results demonstrated that cyanate ester / epoxy blends were not affected at this fluence level. The aim of this study is to investigate the performance potential of these blends at higher fluence levels without significant degradation of their mechanical properties.
Short-beam shear as well as static tensile tests were carried out at 77 K prior to and after irradiation to fast neutron fluences of up to $4x10^{22}$ m^{-2} (E>0.1 MeV) in the TRIGA reactor at ambient temperature (340 K). In addition, load controlled tension-tension fatigue measurements were performed, in order to simulate the pulsed operation conditions of a tokamak. Initial results show that only a small reduction of the mechanical strength under static and dynamic load is observed at a fast neutron fluence of $2x10^{22}$ m^{-2} (E>0.1 MeV). After exposure to $4x10^{22}$ m^{-2} (E>0.1 MeV) the interlaminar shear strength of materials with a cyanate ester content of 40 % or more is only reduced by 20 % to 30 %.

KEYWORDS: Fiber reinforced composites, Cyanate ester, Mechanical properties, Neutron irradiation

INTRODUCTION

In order to find a suitable insulation system for the ITER toroidal field coils, which would withstand high radiation levels, extensive research was carried out over the past years [1-6]. It turned out that innovative resin mixtures containing cyanate ester (CE) showed excellent properties after exposure to the ITER design fluence of $1x10^{22}$ m^{-2} (E>0.1 MeV) compared to traditional epoxy resins. Even with a CE content of only 20 %, no degradation of the mechanical properties was found [7, 8]. However, the costs of the CE resins are higher by a factor of about 10 compared to the epoxies and the industrial

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handling experience is less developed. Based on the improved radiation resistance, a CE/epoxy blend containing 40 % or 30 % CE is foreseen for the ITER TF coil insulation.

Depending on the shielding concepts of upcoming fusion devices, the radiation dose, to which the magnet insulation will be exposed to, will be higher than for ITER. Therefore, it is important to investigate the mechanical properties of these blends at higher radiation level in order to establish, whether they can be used in future devices or alternatives have to be found.

This work addresses the mechanical behavior of different glass fiber reinforced composites impregnated with a mixture of cyanate ester and epoxy at 77 K before and after fast neutron irradiation to a fast neutron fluence up to $4x10^{22}$ m^{-2} (E>0.1 MeV). Tests in tension and interlaminar shear were carried out under static and dynamic load conditions, in order to assess the material performance under ITER relevant conditions.

EXPERIMENTAL DETAILS

Materials

The investigated insulation systems were fabricated by Marti-Supratec Corporation, Switzerland, using the vacuum pressure impregnation (VPI) technique. The reinforcement of the composite consists of R-glass fiber (0.24 x 40 mm) / Kapton H tapes, which were wrapped half-overlapped around a steel plate, 7 layers of glass / Kapton in total and one pure glass layer.

For the impregnation, pure CE as well as mixtures with different ratios of CE to epoxy were used. Both resins were supplied by Huntsman, Switzerland [9]. After the impregnation, the material was pressed to increase the fiber content and to obtain a thickness of 4 mm. A short summary of the insulation systems investigated in this study can be found in TABLE 1. The curing cycle was chosen according to the recommendations of the supplier and the needs of ITER.

Irradiation and Test Procedures

The neutron irradiation was done in the TRIGA reactor (Vienna) at ambient temperature (340 K) to fast neutron fluences of up to $4x10^{22}$ m^{-2} (E>0.1 MeV), which corresponds approximately to a total absorbed dose of 200 MGy [10].

All static and dynamic tests were carried out at 77 K using a servo-hydraulic MTS 810 testing device, which was modified for measurements in a liquid nitrogen environment. The ultimate tensile strength (UTS) was measured according to DIN 53455 and ASTM D638. The interlaminar shear strength (ILSS) was determined by the short-beam-shear (SBS) test according to the ASTM D2344 standard on samples which showed interlaminar fracture. Therefore, span-to-thickness ratios of 4:1 and 5:1 were used. To simulate the pulsed tokamak operation tension-tension fatigue measurements (ASTM D 3479) were carried out in the load controlled mode at a frequency of 10 Hz and a minimum to peak stress ratio of R=0.1. Each data point refers to 4 or more samples. After 10^6 load cycles the tests were stopped manually.

Because of the wrapping procedure the materials have anisotropic properties. Therefore, short-beam-shear specimens were cut parallel (0°) and perpendicular (90°) to the winding direction of the reinforcing glass fiber tapes. For the tensile tests, samples were only cut in 90° direction. In this direction the influence of radiation damage is more

TABLE 1. Overview of cyanate ester based insulation systems

Type	Cyanate Ester	DGEBF
Resin	AroCy-L10	PY306
Hardener	----	----
Additives	Mn Acetylacetonate in nonylphenol	
Reinforcement	R-glass / Kapton	
Curing Temp.	4 h @ 100 °C 5 h @ 160 °C	

Insulation System	CE/Epoxy Ratio
T1 (100)	100:0
T2 (40)	40:60
T8 (30)	30:70
T10 (20)	20:80

pronounced, because the mechanical strength is mainly determined by the fiber/resin interface and bonding.

RESULTS

Ultimate Tensile Strength

In the unirradiated state the investigated materials show no significant influence of the UTS on the CE content. The results are in the range from 250 to 270 MPa. Only in the system with a CE content of 40 % (T2) the UTS is slightly higher, 313 MPa. This is in good agreement with expectations expressed by the resin supplier, where the best mechanical properties should be reached with 40 % CE because of the chemical structure of both resins. However, delamination was found for the pure CE material, where failure occurred at the location of the Kapton foils. No such behavior was observed for the three blends. Therefore, the admixture of epoxy to CE enhances the bonding strength between Kapton and resin.

After irradiation to the ITER design fluence no reduction of the UTS is found. Only when the fluence was doubled, the 20 % CE system (T10) showed a slightly lower UTS, which can be related to radiation damage, whereas the other systems with a higher CE content (T1 (100), T2 (40), T8 (30)) are hardly affected.

The results of the static tensile tests are summarized in TABLE 2.

Fatigue Behavior

To study the influence of the CE content on the material performance under dynamic load, tension-tension fatigue measurements were carried out before and after irradiation to neutron fluences of up to $2x10^{22}$ m^{-2} (E > 0.1 MeV). FIGURE 1 shows the absolute and normalized stress-lifetime diagrams (S-N curves, Wöhler curves) before irradiation.

In general, the CE content does not have a big influence on the lifetime of the material. The Wöhler curves of all CE/epoxy blends are characterized by a slow and continuous decrease up to 10^6 load cycles. Only the pure CE system (T1) shows a life endurance limit σ_D at 0.5 UTS (=125 MPa). The slight variations at high load levels are

TABLE 2. Ultimate tensile strength (UTS) measured at 77 K before and after irradiation to fast neutron fluences up to $2x10^{22}$ m^{-2} (E>0.1 MeV)

Insulation system	T1 (100) UTS 90° (MPa)	T2 (40) UTS 90° (MPa)	T8 (30) UTS 90° (MPa)	T10 (20) UTS 90° (MPa)
unirr.	250 ± 19	313 ± 18	269 ± 19	265 ± 16
$1x10^{22}$ m^{-2}	250 ± 22	296 ± 10	274 ± 6	243 ± 12
$2x10^{22}$ m^{-2}	228 ± 13		260 ± 7	218 ± 8

mainly related to differences in the initial strength, as can be seen from the normalized curves. Regarding the ITER operation, where 30000 load cycles are expected, the differences between the insulation systems are even smaller. The residual strength of all four materials is ~130 MPa, which is more than adequate for ITER. Recent calculations presented at the ITER TF coils insulation review group showed that stresses up to 20 MPa are expected [11]

After neutron irradiation no dramatic changes of the material performance are observed at 1 nor at $2x10^{22}$ m^{-2}. To illustrate these facts, FIGURE 2 shows absolute stress-lifetime diagrams (Wöhler curves) for the pure CE system (T1) and for one CE/epoxy blend (T8). The Wöhler curves of the other two systems T2 (40) and T10 (20) show the same behavior. At high load levels (in the range of σ= 0.85 to 0.7 σ_{max}) the lifetime of the materials is slightly reduced, whereas the change of the mechanical properties caused by radiation effects is smaller below. Especially at the ITER point ($3x10^4$ cycles) and above the residual strength is not reduced by irradiation. Contrary, all three CE/epoxy blends tend to have a marginally higher residual strength in this region.

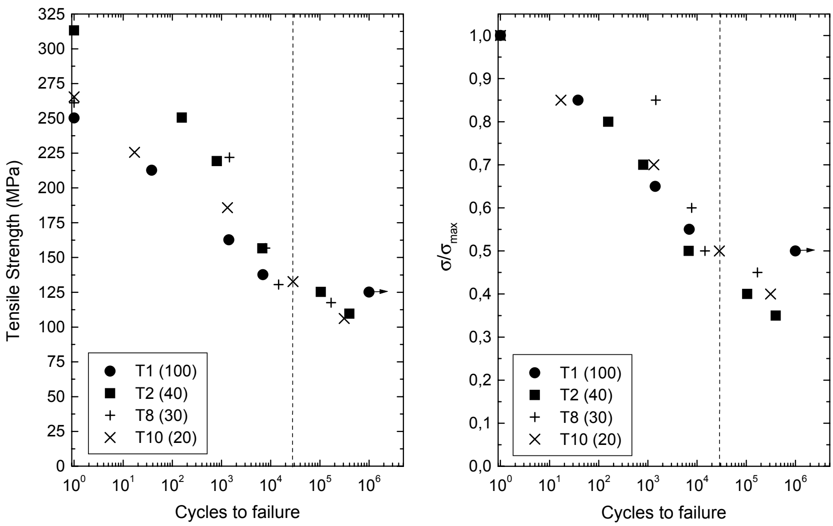

FIGURE 1. Absolute (left) and normalized (right) tension-tension stress-lifetime diagrams before irradiation measured at 77 K. All measurements were stopped manually above 10^6 cycles, as indicated by the arrows.

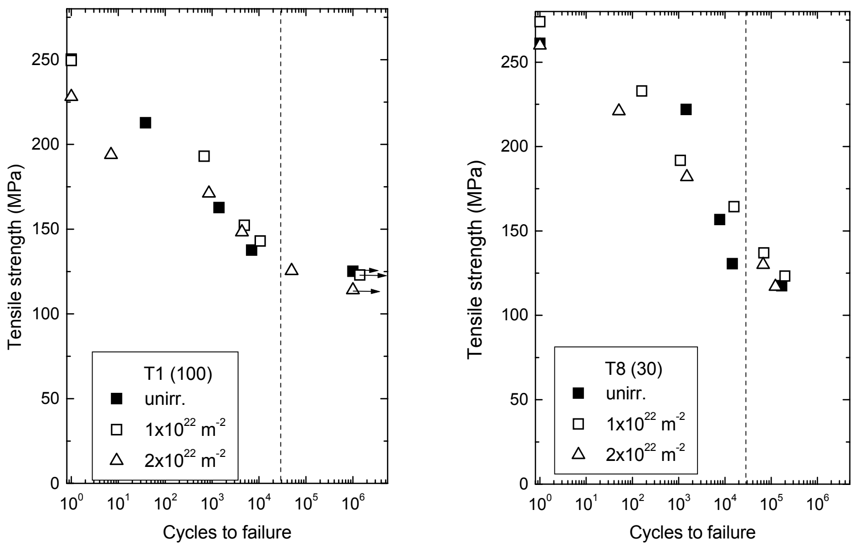

FIGURE 2. Absolute tension-tension stress-lifetime diagrams of T1 (100) and T8 (30) before and after irradiation to fast neutron fluences of up to $2x10^{22}$ m^{-2} (E > 0.1 MeV) measured at 77 K. All measurements were stopped manually above 10^6 cycles, as indicated by the arrows.

Up to a neutron fluence of $2x10^{22}$ m^{-2} (E>0.1 MeV) the change of the mechanical properties caused by irradiation is not significant. The smallest effect is found for the pure CE system (T1).

Only for the 20 % CE system (T10) some differences were observed at $2x10^{22}$ m^{-2} (E>0.1 MeV). Whereas, the shape and the absolute values of the Wöhler curve were hardly affected, the scatter of the data points increased significantly at this neutron fluence, which indicates an enhancement of material inhomogeneities.

Interlaminar Shear Strength

The ILSS was determined in both load directions. A detailed summary of results of the short-beam-shear tests can be found in TABLE 3. They are in good agreement with those obtained from the tensile tests.

In general, the ILSS in 0° direction lies between 60 and 80 MPa, whereas in 90° direction the ILSS is lower by approximately 10 to 15 MPa. As expected from the previous section the system with a 40 % CE has slightly higher values, but the CE content does not have a big influence on the mechanical properties.

To make the irradiation effects more obvious, FIGURE 3 shows the relative ILSS compared to the unirradiated state. Up to a neutron fluence of $2x10^{22}$ m^{-2} (E>0.1 MeV) the reduction of the ILSS is not pronounced. At $1x10^{22}$ m^{-2} (E>0.1 MeV) the deviations are caused by material inhomogeneities, whereas at $2x10^{22}$ m^{-2} (E>0.1 MeV) radiation damage starts to degrade the mechanical properties, which confirms the results of the tensile tests. The observed degradation lies between 0 and 20 % at $2x10^{22}$ m^{-2} (E>0.1 MeV). No distinct correlation between radiation resistance and CE/epoxy ratio is found.

TABLE 3. Interlamninar shear strength (ILSS) for both directions measured at 77 K before and after irradiation to fast neutron fluences of up to $4x10^{22}$ m^{-2} (E>0.1 MeV)

Insulation system	T1 (100)		T2 (40)		T8 (30)		T10 (20)	
	0°	90°	0°	90°	0°	90°	0°	90°
unirr.	59 ± 8	42 ± 10	77 ± 4	57 ± 3	74 ± 4	63 ± 9	62 ± 6	48 ± 9
$1x10^{22}$ m^{-2}	68 ± 4	48 ± 5	66 ± 5	58 ± 3	69 ± 8	58 ± 7	65 ± 4	48 ± 5
$2x10^{22}$ m^{-2}	50 ± 2	46 ± 1			62 ± 3	51 ± 3	53 ± 6	48 ± 3
$4x10^{22}$ m^{-2}	46 ± 2	37 ± 2	52 ± 2	45 ± 6	43 ± 3	37 ± 5	36 ± 4	26 ± 4

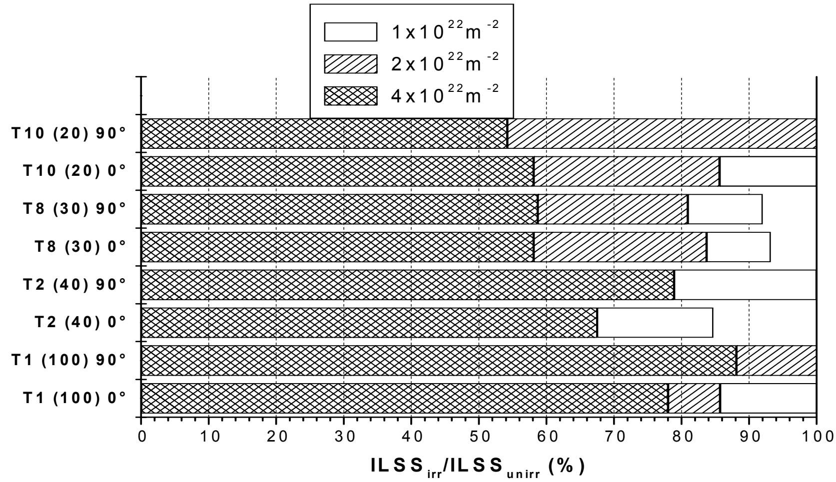

FIGURE 3. Normalized interlaminar shear strength after irradiation to fast neutron fluences of up to $4x10^{22}$ m^{-2} (E>0.1 MeV).

After irradiation to $4x10^{22}$ m^{-2} (E>0.1 MeV) the ILSS is reduced depending on the insulation system. Especially the 30% (T8) and the 20% CE systems (T10) are more severely affected by irradiation than the others. The ILSS lies between 36 MPa and 52 MPa for the 0° direction and between 26 MPa and 45 MPa for the 90° direction. Taking the variations of the initial shear strength into account, the normalized values demonstrate the good performance of these materials. The ILSS of the insulation systems impregnated with pure CE is only reduced by approximately 20%. Also the 40 % system (T2) shows quite a similar radiation resistance, whereas the ILSS of systems with a lower CE content (T8 (30) and T10 (20)) drops by 45 %. Compared to the results of conventional epoxy resins, such as the TFMC systems, the least radiation resistant blend (T10) has still better mechanical properties, even after exposure to a 4 times higher neutron fluence [1, 2, 6].

Based on these results, we conclude that composites containing more than 40 % CE have the potential to withstand neutron fluences beyond $4x10^{22}$ m^{-2} (E>0.1 MeV).

SUMMARY

Fiber reinforced composites based on a mixture of cyanate ester and epoxy resin have demonstrated their radiation resistance up to a radiation level, which will be accumulated over the ITER lifetime. For future applications, where higher radiation levels are expected, it is of special interest to find limits of these new systems depending on the CE concentration.

In this work several cyanate ester/epoxy insulation systems were investigated under static and dynamic load conditions before irradiation as well as after exposure to the ITER design fluence of $1x10^{22}$ m^{-2} (E > 0.1 MeV) and far beyond (up to $4x10^{22}$ m^{-2}). The results may be summarized as follows:

- The best static mechanical properties were obtained on a material, which consists of 40 % cyanate ester, but in general the influence of the cyanate ester content is low.
- Under dynamic load, the cyanate ester content does not have a big influence on the material performance. Especially at the ITER load cycle and above, all investigated systems are nearly equal.
- After irradiation to a neutron fluence of $2x10^{22}$ m^{-2} (E > 0.1 MeV) slight reductions of the interlaminar shear strength as well as of the ultimate tensile strength are observed, especially for the 20 % cyanate ester system.
- Fatigue measurements showed, that the lifetime after irradiation of all materials is not reduced at load levels below $\sigma = 0.7\ \sigma_{max}$. In addition, for the system with the lowest cyanate ester content (20%) an increase of material inhomogeneities was found, which indicates radiation damage.
- Irradiation to a neutron fluence of $4x10^{22}$ m^{-2} (E > 0.1 MeV) leads to an ILSS reduction by only 20 to 30 %. Materials with a cyanate ester content below 40 % are less radiation resistant.

With respect to applications under severe radiation conditions, the CE/epoxy laminates with a cyanate ester content down to 20 % showed an improved performance even up to neutron fluences of $4x10^{22}$ m^{-2} (E > 0.1 MeV), when compared to conventional epoxy materials exposed to $1x10^{22}$ m^{-2} (E > 0.1 MeV). Especially materials with a cyanate ester content between 40 to 100 % show the potential to withstand even higher neutron fluences and to retain acceptable mechanical properties.

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