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Influence of various catalysts on the radiation resistance and the mechanical properties of cyanate ester/epoxy insulation systems

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

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

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ABSTRACT

Fiber reinforced composites impregnated with mixtures of various cyanate ester and epoxy resins demonstrated their excellent performance at the ITER design fluence and beyond. The insulation systems consist of a wrapped R-glass/Kapton reinforcement, vacuum impregnated with a cyanate ester/epoxy blend. For the fabrication of the insulation a long pot-life of the resin is of great importance, which is mainly determined by the amount and the composition of the catalyst needed for curing the resin. However, the catalyst, which amounts to 1–2% of the resin, may also affect the mechanical properties as well as the radiation hardness of the material. In order to investigate these effects, two different composites were fabricated using a Mn- and a Co-catalyst, respectively.

The mechanical properties are characterized prior to and after irradiation to a fast neutron fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV) in tension and interlaminar shear at 77 K.

1. Introduction

In the past few years extensive work has been done to find radiation resistant insulation systems for the ITER TF coils [1–3]. While the dielectric properties of comparable fiber reinforced composites was not affected up to the ITER design fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV), the mechanical properties were affected significantly [4].It turned out that the mechanical strength of glass fiber reinforced composites impregnated with pure cyanate ester (CE) as well as with mixtures of CE and epoxy resins was hardly influenced by fast neutron irradiation up to the ITER design fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV). Especially materials containing more than 40% CE showed an excellent performance. Their mechanical strength is only reduced by 30% after exposure to 4×10^{22} m^{-2} ($E > 0.1$ MeV) [5,6]. This offers a large safety margin with respect to possible extensions of the ITER operation. However, because of the high reactivity of pure CE, which may cause problems in case of mishandling the system, a blended resin system seems to be favourable.

Apart from the radiation resistance also technological aspects have to be taken into account for large scale applications. For impregnating the TF coils a long pot-life (defined as the period where the viscosity stays below 100 mPa s), of at least 24 h is desired, in order to ensure a homogeneous resin distribution without un-wetted parts inside the structure before the network formation starts. Unfortunately, this demand could not be fulfilled by the previously investigated systems using a Mn-catalyst to start chemical reaction. Measurements of the viscosity showed a pot-life in the range of 6–8 h.

For this reason a new catalyst was developed by Huntsman Switzerland, using Co-acetylacetonate instead of Mn-acetylacetonate. By varying the concentration and modifying the curing cycle it was possible to obtain a new system, which offers a pot-life of up to 50 h [7]. Regarding the entire quantity of the blended resin system the catalyst plays only a minor role (about 1–2%), but it has a significant effect on the glass transition temperature. Therefore, the exchange of the catalyst may influence the mechanical properties as well as the radiation resistance and has to be carefully checked.

This work addresses the influence of the catalyst on the mechanical properties of glass fiber reinforced composites at 77 K before and after irradiation to a fast neutron fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV). Two insulation systems based on 40% CE and 60% epoxy resin were fabricated using a Mn- and a Co-catalyst. The ultimate tensile strength (UTS) and the interlaminar shear strength (ILSS) were measured under static and dynamic load conditions, in order to assess the material performance under ITER relevant conditions.

2. Materials

Two CE/epoxy blends (40:60) were fabricated by Marti-Supratec Corporation, Switzerland, using the vacuum pressure impregnation (VPI) technique. One R-glass fiber (0.25 mm thickness) layer and seven layers of glass/Kapton H tape sandwiches were wrapped

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* Corresponding author. Tel.: +43 1 58801 14188 fax: +43 1 58801 14199.
E-mail address: rprokopec@ati.ac.at (R. Prokopec).

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Table 1
Overview of the investigated insulation systems.

	T2		T12	
Type	Cyanate ester about 40%	DGEBF about 60%	Cyanate ester about 40%	DGEBF + catalyst about 60%
Resin	AroCy-L10 (LMB6653)	PY306	AroCy-L10 (LMB 6653)	PY306 + catalyst (LMB 6622)
Hardener	–		–	
Catalyst	Mn-acetylacetonate in nonylphenol		Co-acetylacetonate in pentylphenol	
Reinforcement	R-glass/Kapton		R-glass/Kapton	
Curing temperature	4 h @ 100 °C 5 h @ 160 °C		6 h @ 100 °C 4 h @ 120 °C 16.5 h @ 150 °C	

half-overlapped around an aluminium plate and impregnated with the resin. Contrary to the Mn-system, where the resins and the catalyst are delivered separately, the new Co-system consists of the pure CE and a catalyzed epoxy resin, where the exact quantity of the Co-catalyst is admixed to the PY306 epoxy resin. After a well-defined curing schedule according to the recommendations of the resin supplier as well as the needs of ITER, test specimens were cut from the final material plate with a thickness of about 4 mm [8]. A detailed summary of the resin components as well as the curing parameters is listed in Table 1.

The neutron irradiation was performed in the TRIGA reactor (Vienna) at ambient temperature (340 K) to fast neutron a fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV), which corresponds to a total absorbed dose of approximately 50 MGy [9], where 36 MGy results from γ-radiation. Now, reactor irradiation at 4.2 K is not existing, however, experiments from the past showed an increased damage by up to 20% compared to room temperature irradiation [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 UTS was measured according to the DIN 53455 and the ASTM D638 standards. In addition, an extensometer suitable for cryogenic temperatures was used to record the sample elongation during the tensile test, which allows conclusions on the quality of the matrix–reinforcement interface. The ILSS was assessed by the short-beam-shear (SBS) test according to the ASTM D2344 standard. Span-to-thickness ratios of 4:1 and 5:1 were used. For the simulation of the pulsed ITER operation, tension–tension fatigue measurements (ASTM D 3479) were done at a frequency of 10 Hz in the load-controlled mode up to 10^6 cycles at a minimum-to-peak stress ratio (R ratio) of 0.1. Each data point refers to four or more samples.

The materials have anisotropic properties because of the manufacturing process. Therefore, test specimens were cut parallel (0°) and perpendicular (90°) to the winding direction of the reinforcing glass fiber tapes. For tensile tests only the 90° direction was investigated, because the UTS in 0° direction is mostly dominated by the strength of the glass fibers and the influence of the irradiation is much smaller than for 90° samples.

3. Results

3.1. Static tests

The results are summarized in Table 2. Only slight differences between the two materials are found for the UTS. For the Mn-composite "T2" the UTS is about 45 MPa higher than for the Co-

Table 2
Ultimate tensile strength (UTS) and interlaminar shear strength (ILSS) measured at 77 K before and after irradiation to a fast neutron fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV).

Insulation system × 10^{22} m^{-2}	UTS 90° (MPa)		ILSS 0° (MPa)		ILSS 90° (MPa)	
	0	1	0	1	0	1
T2	313 ± 18	296 ± 10	77 ± 4	66 ± 5	57 ± 3	58 ± 3
T12	268 ± 9	280 ± 14	76 ± 3	73 ± 5	58 ± 6	60 ± 6

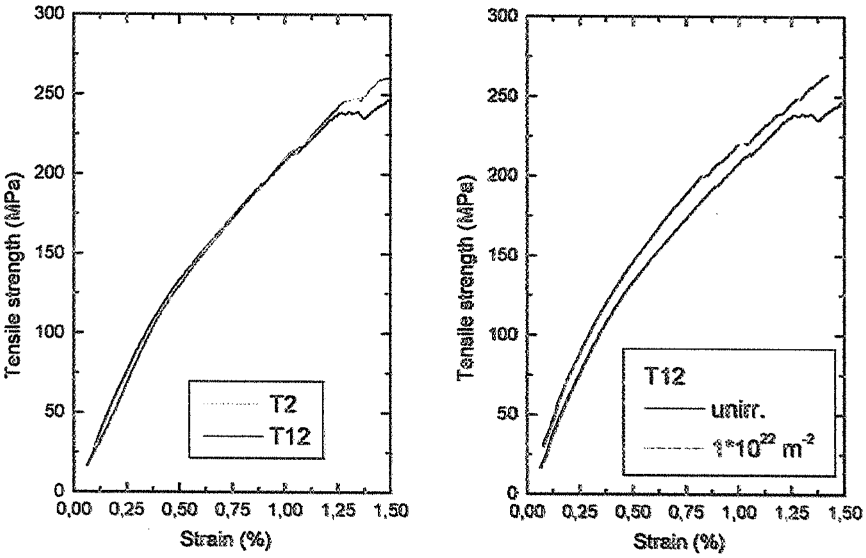

Fig. 1. Stress–strain curves measured at 77 K before ("T2", "T12") and after irradiation ("T12") to a fast neutron fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV).

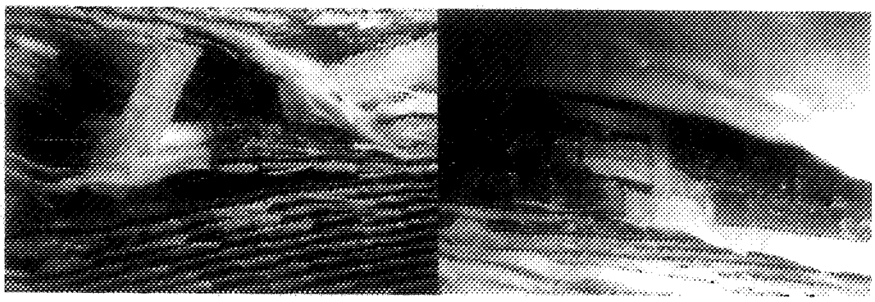

Fig. 2. Tensile specimen of "T2" (left) and "T12" (right) after test at 77 K.

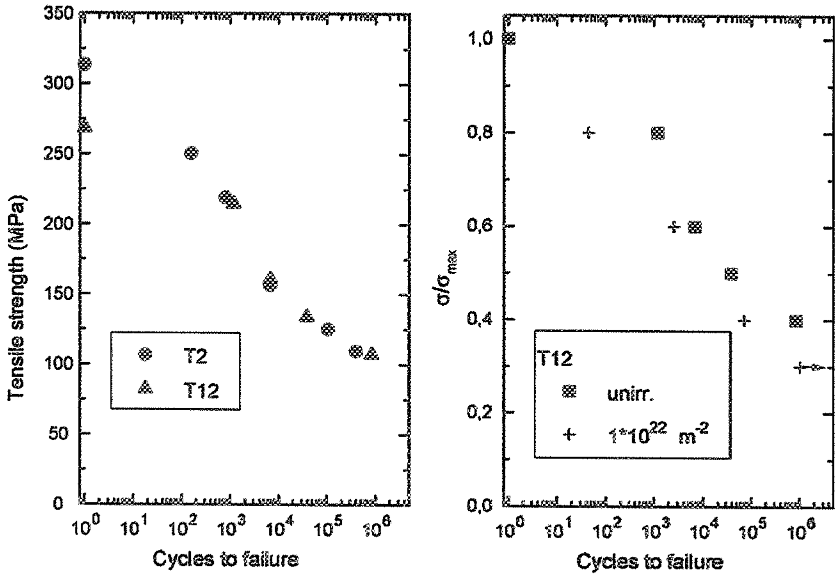

Fig. 3. Stress–lifetime diagrams measured at 77 K before and after irradiation to a fast neutron fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV).

based one. However, both materials are not significantly affected by irradiation to the ITER design fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV). Whereas a small decrease is found for "T2", "T12" tends to increase.

In order to qualify the interface between reinforcement and resin, the stress–strain relations are shown in Fig. 1. It turned out that the influence of the catalyst was negligible. As shown in the left part of Fig. 1 the stress–strain relations of both materials are nearly identical over a wide range before irradiation. Only at stress levels near the UTS small differences are observable. Moreover, the smooth curves without significant load drops indicate excellent bonding properties.

The samples were investigated in a microscope after the test. Fig. 2 shows parts of the specimen in through-thickness direction. In general, no evidence for delamination along the Kapton foils was found for both materials. Only the breakage of the glass fibers as well as of the Kapton foils is found. Also parts of resin are still attached to the Kapton surface.

Under interlaminar shear load, the results confirm the observed trend of the tensile tests. For both materials the ILSS in 0° direction is ~77 MPa, whereas in 90° the ILSS is lower by approximately 20 MPa. After irradiation the ILSS remains unchanged for both load directions, which also confirms that the catalyst does not significantly affect the mechanical properties as well as the radiation resistance.

3.2. Fatigue measurements

Tension–tension fatigue measurements were carried out, in order to simulate the pulsed ITER operation. The stress–lifetime diagrams (Wöhler curves) are shown in Fig. 3.

Apart from the differences at $\sigma = 0.8\sigma_{max}$, where "T12" survives significantly more load cycles (factor of 10), both materials behave similarly. At the ITER point of 30,000 cycles the residual strength is ~130 MPa, which is more than adequate for ITER. Also beyond the ITER level no differences were found.

After irradiation to 1×10^{22} m^{-2} ($E > 0.1$ MeV) both materials are hardly affected. As an example the Wöhler curves for "T12" are presented in Fig. 3. Only small lifetime reductions at a given load level were observed. For "T2" the irradiation effects are even smaller.

4. Summary

This work demonstrates that the exchange of the Mn- by a Co-catalyst, which was necessary to guarantee a sufficiently long pot-life for large scale impregnations, does not affect the mechanical properties of the composite. Characterization under tensile and interlaminar shear load showed similar results of the mechanical strength for both materials. Also the Co-catalyst is not more sensitive to irradiation compared to the Mn-catalyst. No significant degradation of the mechanical strength under static and dynamic load is observed after exposure to the ITER design fluence of 1×10^{22} m^{-2} ($E > 0.1$ MeV). T12 (Co-catalyst) combines the radiation resistance of the Mn-system with a long pot-life (up to 50 h) needed for large scale applications.

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References

[1] K. Bittner-Rohrhofer, K. Humer, Z.D. Wang, H.W. Weber, P.E. Fabian, N.A. Munshi, Radiation hardness of newly developed ITER relevant insulation systems, Fus. Eng. Des. 66–68 (2003) 1209–1213.

[2] K. Bittner-Rohrhofer, K. Humer, H. Fillunger, R.K. Maix, H.W. Weber, P.E. Fabian, N.A. Munshi, Radiation effects on the mechanical integrity of novel organic insulators for the ITER magnet coils, J. Nucl. Mater. 329–333 (2004) 1083–1087.

[3] P.E. Fabian, N.A. Munshi, S.W. Feucht, K. Bittner-Rohrhofer, K. Humer, H.W. Weber, Low temperature mechanical properties of cyanate ester insulation systems after irradiation, Adv. Cryog. Eng. 50 (2004) 289–296.

[4] K. Humer, H.W. Weber, R. Hastik, H. Hauser, H. Gerstenberg, Dielectric strength of irradiated fiber reinforced plastics, Physica C 354 (2001) 143–147.

[5] R. Prokopec, K. Humer, R.K. Maix, H. Fillunger, H.W. Weber, Mechanical behaviour of cyanate ester/epoxy blends after reactor irradiation to high neutron fluences, Adv. Cryog. Eng. 54 (2008) 182–189.

[6] K. Humer, R. Prokopec, R.K. Maix, H. Fillunger, H.W. Weber, Insulation systems for superconducting fusion magnets based on cyanate ester blends, SOFT, submitted for publication, doi:10.1016/j.fusengdes.2008.11.004.

[7] Provisional Datasheet LMB 6622/LMB 6653; Huntsman, 13.2.2008.

[8] P. Rosenkranz, K. Humer, H.W. Weber, Influence of the test geometry on the fatigue behavior of fiber reinforced plastics in tension and interlaminar shear at RT and 77 K, Adv. Cryog. Eng. 46 (2000) 181–187.

[9] H.W. Weber, H. Böck, E. Unfried, L.R. Greenwood, Neutron dosimetry and damage calculations for the TRIGA Mark-II reactor in Vienna, J. Nucl. Mater. 137 (1986) 236–240.

[10] K. Humer, S. Spießberger, H.W. Weber, E.K. Tschegg, H. Gerstenberg, Low-temperature interlaminar shear strength of reactor irradiated glass-fibre-reinforced laminates, Cryogenics 36 (1996) 611–617.