Journal of Nuclear Materials 392 (2009) 371–378

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Radiation effects on epoxy/carbon-fiber composite

E.N. Hoffman *, T.E. Skidmore

Savannah River National Laboratory, 773-A, Savannah River Site , Aiken SC 29808, USA

A B S T R A C T

Carbon fiber-reinforced bisphenol-A epoxy matrix composite was evaluated for gamma radiation resistance. The composite was exposed to total gamma doses of 0.5, 1.0, and 2.0 MGy. Irradiated and baseline samples were tested for tensile strength, hardness and evaluated using Fourier transform infra-red spectroscopy and differential scanning calorimetry for structural changes. Scanning electron microscopy was used to evaluate microstructural behavior. Mechanical testing of the composite bars revealed no apparent change in modulus, strain to failure, or fracture strength after exposures. However, testing of only the epoxy matrix revealed changes in hardness, thermal properties, and spectroscopy results with increasing gamma irradiation. The results quantify the changes in the epoxy within the composite as a result of exposure to gamma radiation at doses relevant to service.

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1. Introduction

The Department of Energy Savannah River Site vitrifies nuclear waste incident to defense programs through its Defense Waste Processing Facility (DWPF). The piping in the DWPF seal pot jumper configuration must withstand the stresses during an unlikely but potential deflagration event, and maintain its safety function for a 20-year service life. Carbon fiber-reinforced epoxy composites (CFR) were proposed for protection and reinforcement of piping during such an event. The proposed CFR materials have been ASME-approved (Section XI, Code Case N-589-1) [1] for post-construction maintenance and is DOT-compliant per 49CFR 192 and 195 [2,3]. Originally, the CFR was developed for pipeline rehabilitation and post-construction maintenance in petrochemical, refineries, DOT applications and other industries.

The effects of ionizing radiation on polymers and organic materials have been studied for many years [4–6]. The majority of available data are based on traditional exposures to gamma radiation at high dose rates (~10 000 Gy/h) allowing high total dose within reasonable test periods and general comparison of different materials exposed at such conditions. However, studies in recent years have shown that many polymers are sensitive to dose rate, with more severe degradation often observed at similar or even lower total doses when exposed to lower dose rates. This behavior has been primarily attributed to diffusion-limited oxidation which is minimized during very high dose rate exposures. Most test standards for accelerated aging and nuclear qualification of components acknowledge these limitations.

The results of testing to determine the radiation resistance and microstructural effects of gamma irradiation exposure on a bisphenol-A based CFR are presented. This work provides a foundation for a more extensive evaluation of dose rate effects on advanced CFRs.

2. Experimental

A combination of mechanical testing, thermal testing, and microstructural analysis were used to determine the effect of gamma irradiation on the degradation of the candidate materials. Experiments were performed on polyacrylonitrile based carbon fibers woven into a plain weave cloth. A two-part epoxy based on bisphenol-A epoxy resin and modified aliphatic amine hardener was used to saturate the cloth and provide structural reinforcement and impermeability. A primer layer consisting of a two part epoxy and hardener was applied to the piping to prepare the surface prior to the application of the carbon weave and bisphenol-A epoxy resin. Tensile test bars of carbon fiber/epoxy matrix composite nominally 30.50 × 2.54 × 0.15 cm were used for the mechanical testing.

Target radiation doses of 0.5, 1.0, and 2.0 MGy were selected to meet typical nuclear qualification doses and to bound the 20-year service dose expected in DWPF. Gamma radiation exposure conditions are given in Table 1. The tensile bars were also irradiated to total doses of 0.5, 1.0, and 2.0 MGy, typical of testing used to qualify electric motors, cables and related equipment in commercial nuclear service [7–9]. Exposures and subsequent experiments were performed in duplicate.

Six irradiated CFR bars and three baseline bars were tensile tested in a universal testing machine (Sintech 1125). Sample bars were loaded in a swivel upper grip with a 10 cm grip separation.

* Corresponding author. Tel.: +1 803 725 5475; fax: +1 803 725 7369.
E-mail address: Elizabeth.Hoffman@srnl.doe.gov (E.N. Hoffman).

0022-3115/$ - see front matter Published by Elsevier B.V.
doi:10.1016/j.jnucmat.2009.03.027

Table 1
Radiation exposure conditions.

Dose/condition (MGy)	Dose rate (Gy/h)	Irradiation time (h)
0	n/a	n/a
0.5	5.0×103	100
1.0	5.0×10^3	200
2.0	5.0×10^3	400

A load cell of 88 900 N capacity was used with a crosshead speed of 0.127 cm/min. Each bar was tested until failure by fracture. The ASTM D7205 [10] standard for testing CFRs was used due to limitations on sample availability and geometry. The samples were visually examined and photographed to determine any macroscopic property changes. Scanning electron microscopy was used to examine fracture surfaces and determine any microstructural or fracture mode changes after gamma irradiation.

Differential scanning calorimetry (DSC) was performed on epoxy resin from the baseline and 2.0 MGy tensile bars to determine structure/property relationships in polymers and to identify thermal transitions and possible modes of degradation. Specimens weighing 5 mg were used for the measurements, referenced to an aluminum pan of approximately equal weight. The heating rate was set at 10 °C/min. A flow of 30 ccm Ar was used. Three consecutive runs were performed for each sample from 30 to 150 °C.

Fourier transform infrared spectroscopy analysis was performed on composite bars of baseline, 0.5, and 1.0 and 2.0 MGy samples to provide a 'fingerprint' of organic and polymeric materials. The material was analyzed by the attenuate total reflection (ATR) method. Each sample was analyzed in duplicate. Spectra were obtained using a Nicolet 210 FTIR instrument, employing a Michelson interferometer with a KBr beamsplitter to accomplish frequency discrimination. The spectral resolution of the instrument was nominally 20 mm^{-1}. Background scans were obtained prior to sample scanning, and improvement in the signal to noise ratio was obtained by averaging multiple interferograms for background and sample spectrum.

3. Results and discussion

3.1. Tensile test results

A comparison of the tensile properties of the materials exposed to the various radiation doses showed minimal difference in tensile behavior with the exception of the 2.0 MGy tests in which the curve showed evidence of slipping during testing as shown in Fig. 1. The strain at failure and moduli values taken from the stress/strain curves are given in Table 2. Both bars exposed to 2.0 MGy had initial fiber failures at 396 MPa associated with grip slip indicated in the stress/strain curves. The percent elongation to failure held constant between 1.2% and 1.4% for all irradiation levels.

3.2. Tensile fracture surfaces

Photographs of the fracture surfaces of the tensile bars are shown in Figs. 2–5. The tensile bars before exposure to radiation were shades of gray in color with some lighter patches most likely due to the presence of excess cured resin as shown in Fig. 2(a). The baseline tensile samples fractured approximately perpendicular to the length of the tensile bar. Further visual examination revealed visible protruding fibers as shown in Fig. 2(b–d). Minimal evidence of delamination between the resin and carbon fibers is visible.

The resin underwent a color change from clear/transparent to light yellow after exposure to a gamma radiation dose of

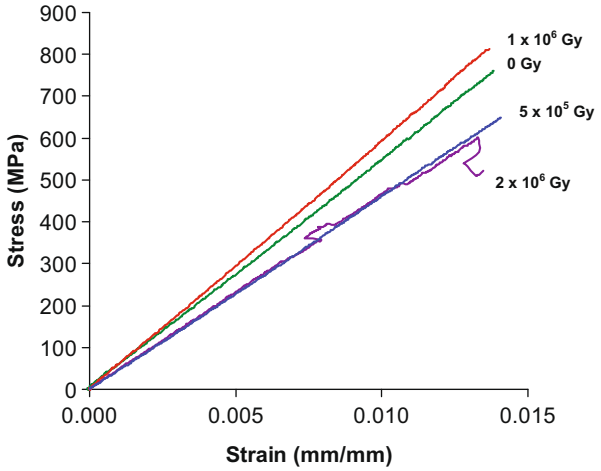

Fig. 1. Stress/strain curves of representative of composite bars irradiated to doses of 0, 0.5, 1.0, and 2.0 MGy.

Table 2
Moduli of tensile test bars.

Bar #	Dose (Gy)	Modulus (GPa)	Strain at failure	Fracture stress (MPa)
13	0	56.7	0.014	761
15	0	59.6	0.013	772
16	5×10^5	47.5	0.012	597
17	5×10^5	46.4	0.014	616
18	1×10^6	54.1	0.014	761
19	1×10^6	59.2	0.014	812
20	2×10^6	55.3	0.013	599
21	2×10^6	45.8	0.013	565

0.5 MGy, see Fig. 3, typical of polymers exposed to gamma irradiation, [11]. The fractures were nominally perpendicular to the tensile stress (length of the bar). Visual examination revealed that damage due to fracture was primarily limited to the fracture area. Similar to Fig. 2, protruding fibers were found at the fracture surface, however, minimal delamination was observed outside the fracture area.

The resin showed an increased color change with a visibly darkened yellow color, after exposure to total 1.0 MGy gamma dose as shown in Fig. 4. The tensile bars fractured with visible damage primarily contained within the fracture area as shown in Fig. 4(a). Similar to the baseline and 0.5 MGy samples, protruding fibers are visible at the fracture site shown in Fig. 4(b) and (c). Visible delamination exists at the fracture site, with minimal damage extending beyond the fracture area as shown in Fig. 4(d).

At the higher dose of 2.0 MGy, the resin underwent a significant color change with a visible dark yellow color as shown in Fig. 5. Damage extends along the length of the tensile bar and is not confined to the fracture site, Fig. 5(a). In addition to color changes, pockets of resin are missing at the interface between carbon fiber woven points, Fig. 5(b). This damage extends several centimeters from the fracture site down the length of the tensile sample. Noticeable volume of resin is also absent from the interior of the tensile bars, Fig. 5(d).

3.3. Scanning electron microscopy

Scanning electron micrographs of the fracture surfaces of the tensile bars are shown in Figs. 6–10. The virgin composite exhibited significant amounts of interfacial failure. Fiber pullout found in the baseline samples contained minimal polymer debris, Fig. 6,

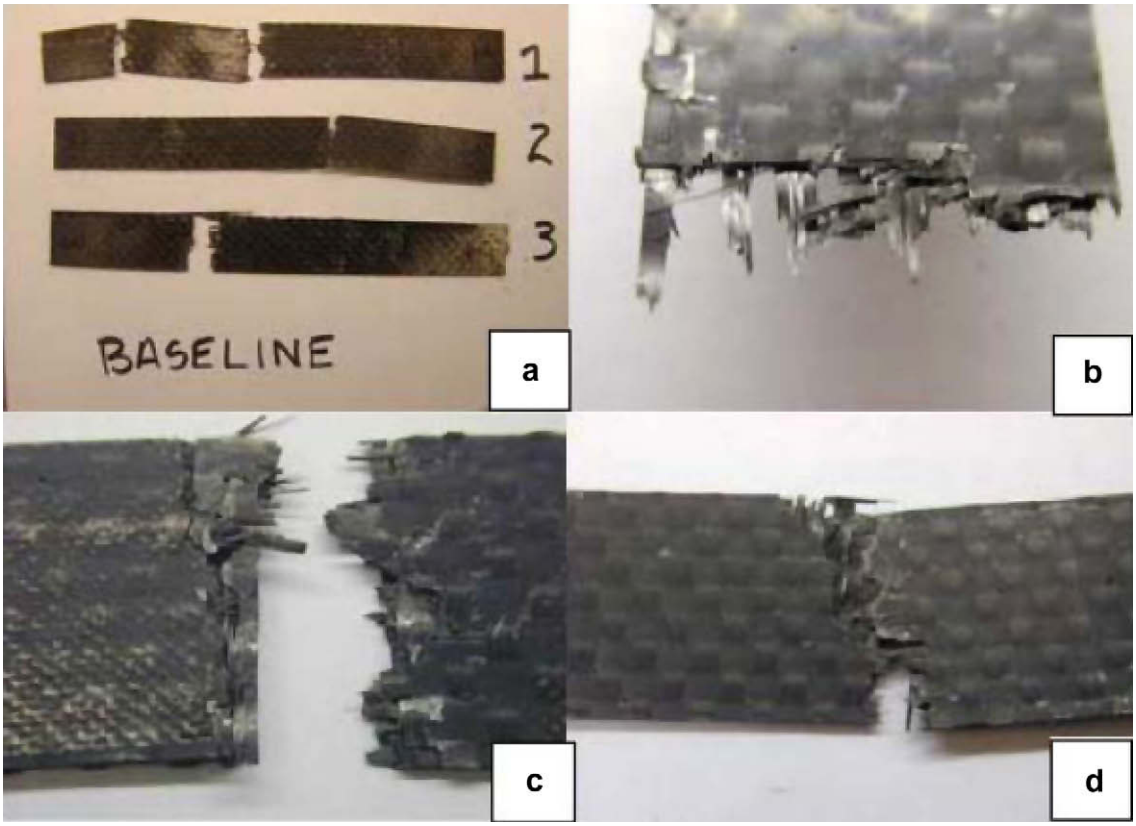

Fig. 2. Baseline fracture tensile test bars (a), fractured surface with protruding carbon fibers (b) and (c), minimal evidence of delamination are visible adjacent to the fracture region (d). Width of bar = 2.54 cm.

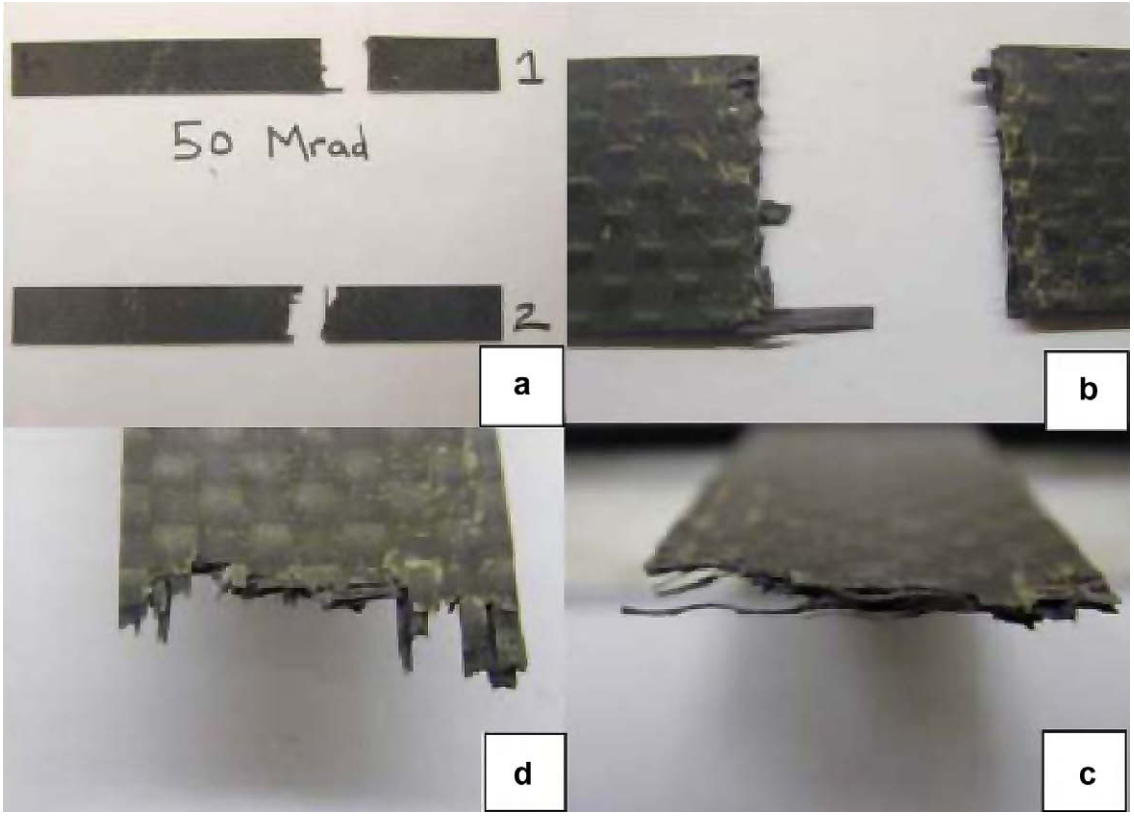

Fig. 3. Fractured tensile test bars after 0.5 MGy (a), fractured surface with protruding carbon fibers with slight evidence of delamination on the surface of adjacent area to the fractures surface (b), minimal evidence of delamination (c). The resin has developed a slight yellow color visible in delamination areas (d). Width of bar = 2.54 cm.

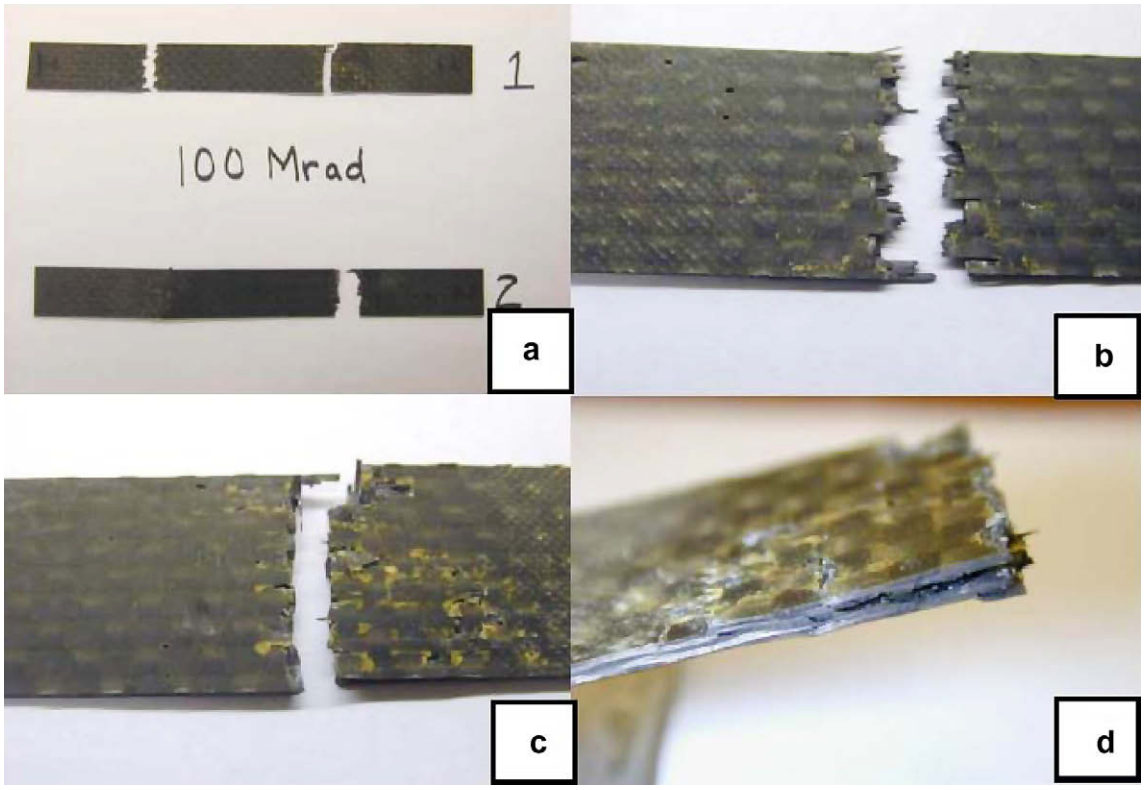

Fig. 4. Fractured tensile test bars exposed to 1.0 MGy (a), fractured surface with minimal protruding carbon fibers (b), increased surface delamination adjacent to the fracture area with a darker yellow color (c), increased delamination along the length of the bar (d). Width of bar = 2.54 cm.

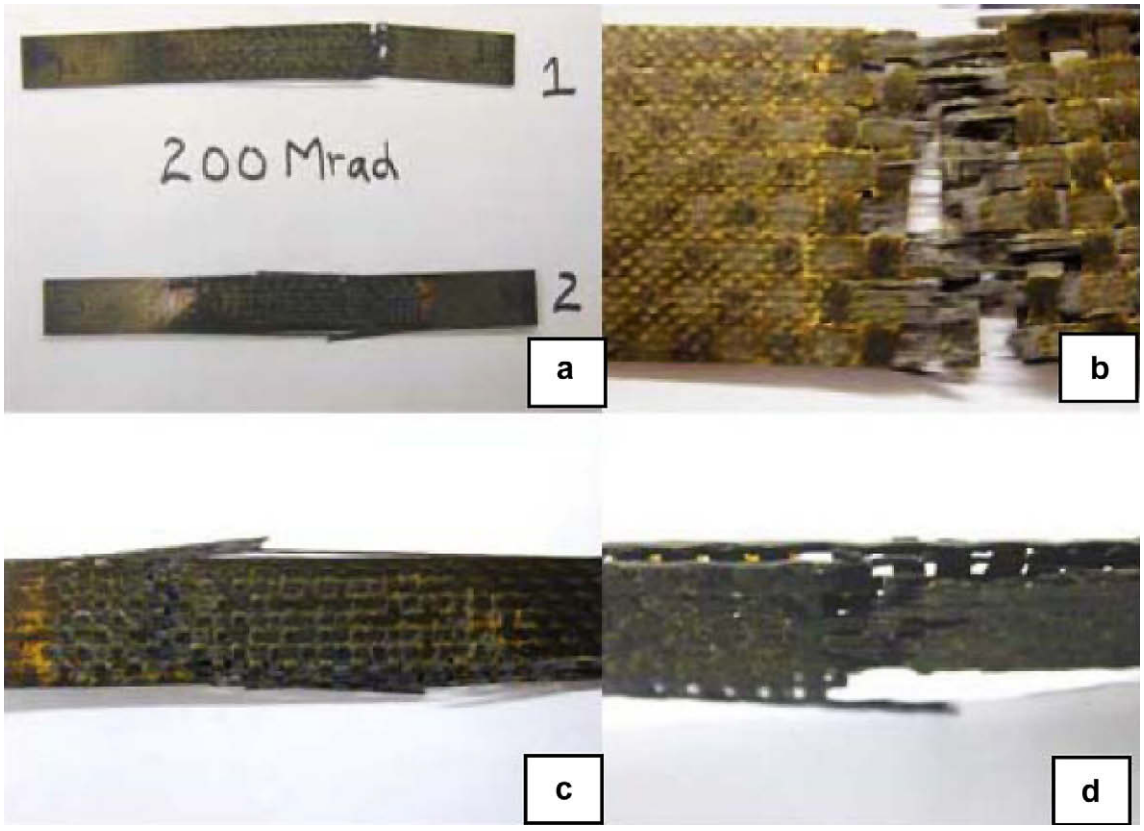

Fig. 5. Fractured tensile test bars exposed to 2.0 MGy (a), fractured surface with protruding carbon fibers and a visible deep yellow color (b), void formation is visible at the adjacent to the fracture surface (c), significant delamination throughout the core of the bar (d). Width of bar = 2.54 cm.

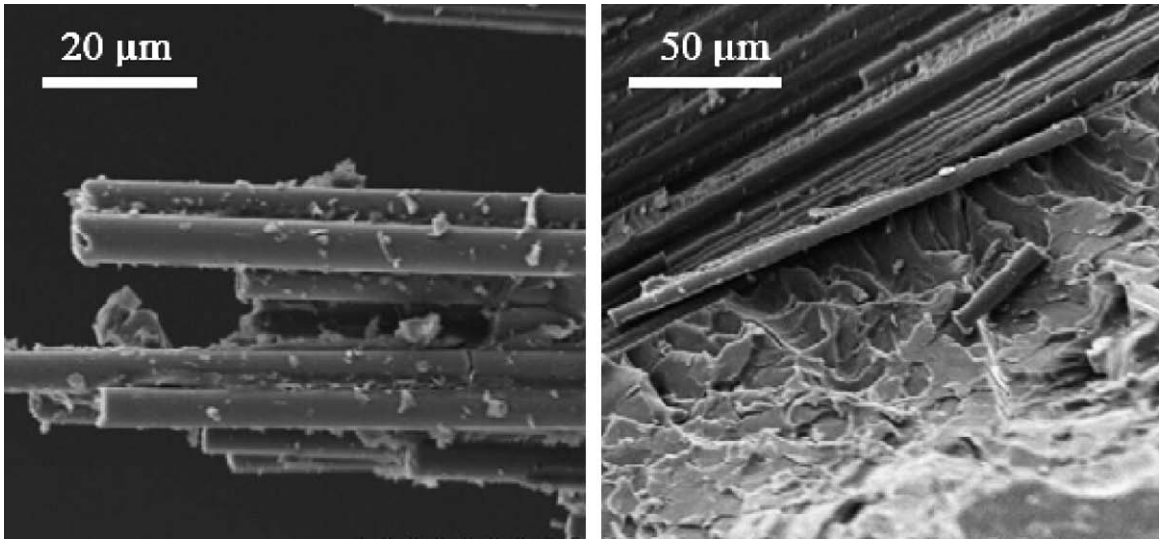

Fig. 6. Baseline tensile bar with carbon fibers with small amount of resin debris (left), fractured resin surface at failure site. Fractured surface contains evidence of fracture with a significant degree of ductility (right).

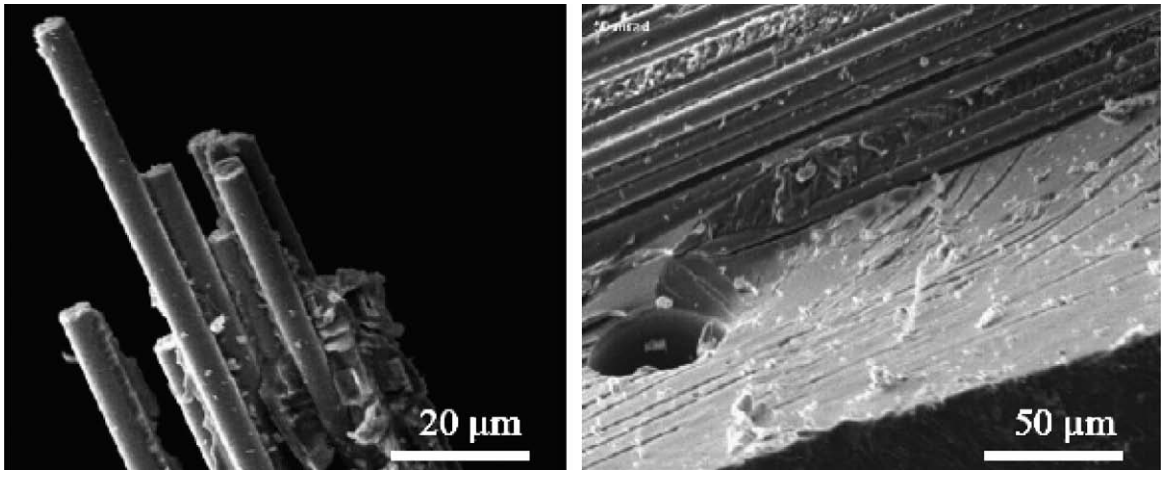

Fig. 7. Tensile bar subjected to 0.5 MGy gamma radiation with carbon fibers with small amount of resin debris (left), fractured resin surface at failure site. Fractured surface suggests a fracture with a smaller degree of ductility compared to baseline samples shown in Fig. 5 (right).

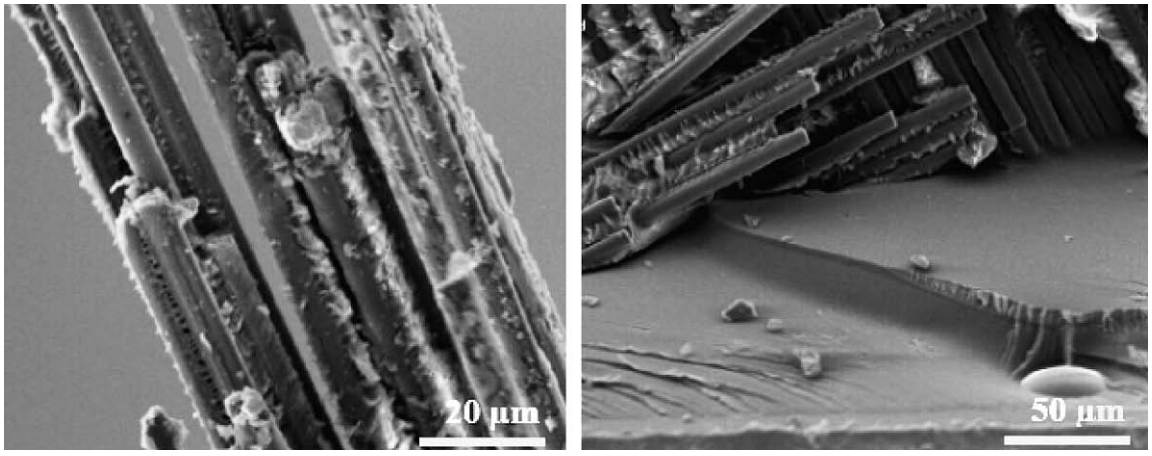

Fig. 8. Tensile bar subjected to 1.0 MGy gamma radiation with carbon fibers coated with substantial amount of resin (left). The fracture surface of the resin is mostly brittle in nature (right).

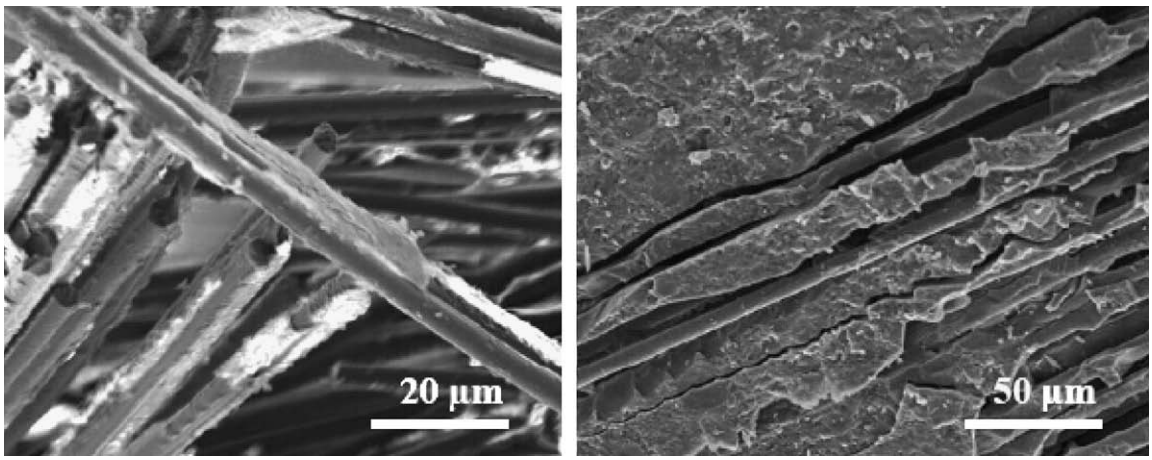

Fig. 9. Tensile bar subjected to 2.0 MGy gamma radiation with carbon fibers coated with substantial amount of resin (left). Numerous fractures are present within the resin parallel to the length of the fibers (right).

Fig. 10. Epoxy surface on tensile bar subjected to 2.0 MGy gamma radiation.

suggesting failure at the interface of the fibers and the epoxy. The epoxy matrix exhibited a dimpled fracture surface suggestive of ductile fracture.

After 0.5 MGy gamma radiation, minimal debris on fibers suggest interfacial failure as the primary failure mechanism, however, the fracture mode of the epoxy has undergone a transformation to a more brittle fracture, evidenced by the facets on the fracture surfaces as shown in Fig. 7. At radiation doses of 1.0 MGy, Fig. 8, significant amounts of polymer debris are present on the carbon fibers, with limited evidence of interfacial failure. The primary failure mechanism is through the epoxy rather than along the interface of the carbon fibers and epoxy. The fracture surface of the epoxy is increasingly brittle in nature. At radiation doses of 2.0 MGy, the integrity of the composite is substantially diminished. Significant epoxy debris remains on carbon fibers and numerous cracks run through the epoxy core, Fig. 9.

As further evidence of increased degradation after a 2.0 MGy gamma irradiation, several bulges covered in cracks have formed on the irradiated sample. These are possibly due to the release of gases from the epoxy upon radiation decomposition or a post-cure phenomenon. Off-gassing of polymers during radiation exposure is expected. Additional images of radiation damage are shown in Fig. 10, depicting the macroscopic disconnect between sections of epoxy on the carbon fiber weave. Macrocracks form at the interface of carbon fiber bundles as well as along the length of the carbon fiber bundles. The crack formation suggests the epoxy has lost significant reinforcing properties.

3.4. Differential scanning calorimetry (DSC)

Fig. 11 shows the DSC results for the baseline and 2.0 MGy samples, respectively. The DSC curves from the baseline and 2.0 MGy resin are clearly different. The first DSC run for both baseline and 2.0 MGy samples removed the thermal history by heating to 150 °C. The second and third runs are used to determine the T_g (glass transition temperature) value of the material, with the third run performed to show repeatability. The glass transition temperature of polymers is a critical parameter for thermal stability. Per ASME PCC-2, the T_g value of the product should be 20 °C higher than the service temperature or the substrate temperature during the repair. The downward slope in the DSC baseline curve starting at ~60 °C is the onset of the glass transition. The T_g can be estimated as ~72 and 84 °C for the baseline and 2.0 MGy samples, respectively, see Fig. 11. From these data, the T_g of the epoxy has apparently shifted upward approximately 10 °C due to irradiation. A slight increase in the T_g value alone does not always indicate severe degradation. However, in combination with mechanical test results and microscopic examination, this increase is consistent with resin degradation.

3.5. Fourier transform infrared (FT-IR) spectroscopy

The FT-IR spectrum contained peaks consistent with the presence of a bisphenol-A-based epoxy resin, see Fig. 12. Changes were

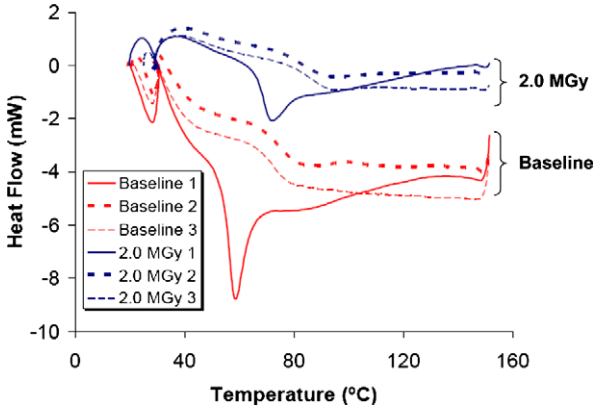

Fig. 11. DSC curves for three consecutive runs of baseline and 2.0 MGy irradiated resins.

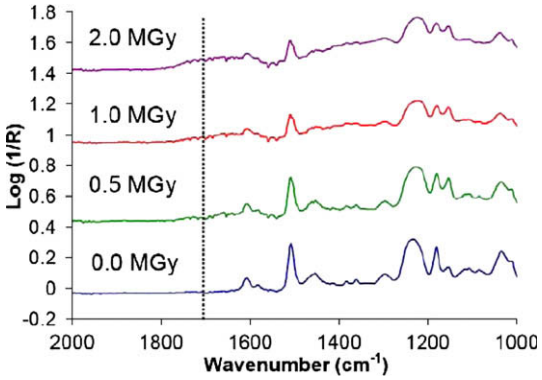

Fig. 12. Bisphenol A epoxy resin – duplicate analyses of the irradiated and control samples. Dotted depicts region associated with oxidation upon irradiation.

Table 3
Hardness values for epoxy irradiated at 1.0×10^6 Gy.

Unirradiated	Irradiated
44.4	70.6
50.3	71.8
49.2	72.5
49.5	72.0
40.1	71.9

Table 4
Hardness values for composite.

Condition (Gy)	Test #1	Test #2	Test #3
0	102.1	103.3	102.3
5.0×10^5	100.3	98.9	101.8
1.0×10^6	106.1	101.5	104.2
2.0×10^6	105.4	100.9	107.4

observed with increasing dose in the carbonyl region near 1700 cm^{-1} indicating oxidation.

3.6. Hardness testing

Hardness testing was performed as a standard epoxy characterization method. Rockwell M scale 6.35 mm diameter ball indenter with 10 kg minor load, and 100 kg major load was used per ASTM D785-03 [12]. The hardness results of the epoxy and composite can be found in Tables 3 and 4, respectively.

The hardness values for the epoxy change considerably compared to the hardness values of the composite, adding further evidence that the epoxy was affected by the radiation, while the carbon fibers were unaffected as the total composite hardness is heavily influenced by the properties of the carbon fiber.

4. Conclusions

Mechanical and thermal testing followed by microstructural analysis was performed on candidate CFRs to determine the gamma radiation effects on their functionality for use in the DWPF as piping reinforcement. The mechanical testing revealed no substantial trends from the modulus or strain at failure data, although the microstructural orientation effects were not accounted for. The reliability and accuracy of the stress/strain curves is unknown due to the highly directional nature of the CFR. Even with the use of a pivot cross-head, a fraction of a degree difference in alignment of sample during the tensile testing can dramatically change the results. However, stress/strain curves from samples exposed to high radiation doses do show erratic behavior, particularly at strains of ~0.015 and above, suggesting the failure mechanism is different for highly irradiated samples.

Gamma radiation doses up to 2.0 MGy do not affect the carbon fibers significantly. The damage threshold dose for the epoxy used in the CFR is unknown, but the resin appears to be slightly degraded at a dose of 0.5 MGy, with increased changes at higher doses. At 0.5 MGy, the epoxy fracture surface shows signs of less ductility. The failure mechanism associated with the composite failure, however, remains interfacial failure. Therefore, the strength of the irradiated epoxy is still stronger than the bond between the fibers and epoxy. At 1.0 MGy, the epoxy fracture mechanism becomes increasingly brittle. At this dose, the overall failure mechanism appears to have changed from interfacial failure to failure of the epoxy based on the significant amount of epoxy lining the carbon fibers. The exact transition dose is unknown.

At 2.0 MGy, the epoxy degrades in strength dramatically. It is evident from fracture surface examination and visual observation that the epoxy has undergone a transformation and significant amounts of resin are lost due to crumbling and falling off the composite weave from the degradation.

From these limited results, this composite appears to be resistant to a dose of 0.5 MGy and should function similar to non-irradiated material. Effects on properties and interfacial behavior are more significant for samples irradiated to doses of 1.0 MGy or higher. Based on the limited testing performed, performance of the material with regard to pipe repair (pressure retention, leak integrity, etc.) under specific conditions cannot be determined. Correlation of quasi-static mechanical properties to performance under more dynamic conditions (major pressure change or deflagration event) in combination with radiation exposure is difficult and must be given additional consideration.

These tests only provide relative indications of radiation resistance. In low pressure/temperature applications and those not subject to significant thermal changes or vibration, doses higher than 0.5–1.0 MGy are likely tolerable. However, additional testing is needed to qualify the product for particular applications. For service life prediction, samples should also be irradiated to similar doses at much lower dose rates to evaluate dose rate effects.

For higher dose applications, alternative epoxy resins, such as bisphenol-F or novolac epoxies, with higher functionality and degree of cross-linking may also be needed. Resin selection must balance all needed properties such as adhesion, fiber wetting, viscosity, thermal stability, chemical resistance and other properties as well as radiation tolerance.

Acknowledgments

The contributions of the following Savannah River National Laboratory personnel to this effort were invaluable: D.C. Beam (irradiation), G.K. Chapman (tensile testing), P.S. Korinko (DSC analysis), T.L. White (FT-IR analysis). Samples were provided by Citadel Technologies (M. Green). Input from J.T. Gee, Defense Waste Processing Facility Engineering was also provided.

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