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RADIATION EFFECTS ON EPOXY/CARBON-FIBER COMPOSITE

E.N. Hoffman, T.E. Skidmore
Savannah River National Laboratory: SRS Road 1, Aiken, SC, 29808, Elizabeth.Hoffman@srnl.doe.gov

Carbon fiber-reinforced bisphenol-A epoxy matrix composite was evaluated for gamma radiation resistance. The composite was exposed to total gamma doses of 50, 100, and 200 Mrad. Irradiated and baseline samples were tested for tensile strength, hardness and evaluated using FTIR (Fourier transform infra-red) spectroscopy and DSC (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 FTIR results with increasing gamma irradiation. The results suggest the epoxy within the composite can be affected by exposure to gamma irradiation.

I. INTRODUCTION

The Department of Energy (DOE) Savannah River Site (SRS) 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[1]. Carbon fiber-reinforced epoxy composites 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)[2] for post-construction maintenance and is DOT-compliant per 49CFR 192 and 195 (Refs. 3,4). The proposed carbon fiber/epoxy composite reinforcement system was originally 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[5-7]. The majority of available data are based on traditional exposures to gamma irradiation at high dose rates (~1E+06 rad/hr) 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 degradation of 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 epoxy matrix composite reinforced with carbon fibers are presented herein.

II. 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 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 8 x 1 x 1/16" were used for the mechanical testing.

The test exposure conditions for both high and low dose rate exposures are given in Table I.

TABLE 1. Radiation Exposure Conditions

Dose/Condition	Dose Rate	Irradiation Time
Baseline	n/a	n/a
50 Mrad	5e+05 rad/hr	100 hours
100 Mrad	5e+05 rad/hr	200 hours
200 Mrad	5e+05 rad/hr	400 hours

Target radiation doses of 50, 100, and 200 Mrad were selected to meet typical nuclear qualification doses and to bound the 20-year service dose expected in DWPF. IN addition, the piping will be exposed to a bounding dose rate of 500 rad/hr leading to an annual total dose of 4.38E+06 rad (4.4 Mrad) and a 20-year service dose of 8.76E+07 rad (88 Mrad). The tensile bars were also irradiated to total doses of 50, 100, and 200 Mrad, typical of testing used to qualify electric motors, cables and

related equipment in commercial nuclear service[8-10]. Exposures and experiments were performed in duplicate.

Six irradiated composite 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 4" grip separation. A load cell of 20 kips was used with a crosshead speed of 0.05 in/min. Each bar was tested until failure by fracture. The ASTM D7205 (Ref. 11) standard for testing fiber-reinforced epoxy composites 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 surface and determine any microstructural or fracture mode changes after gamma irradiation.

Differential scanning calorimetry (DSC) was performed on epoxy resin from the baseline and 200 Mrad 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 by an aluminum pan of approximately equal weight. The heating rate was set at 10 ºC/min. A flow of 30 ccm Ar was used. Three consecutive runs were performed for each sample from 30 to 150 ºC.

Fourier transform infrared spectroscopy (FT-IR) analysis was performed on composite bars of baseline, 50, and 100 and 200 Mrad 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 FT-IR instrument, employing a Michelson interferometer with a KBr beamsplitter to accomplish frequency discrimination. The spectral resolution of the instrument was nominally 2 cm^{-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.

III. RESULTS AND DISCUSSION

IIIA. Tensile Test Results

A comparison of the tensile properties of the materials exposed to the various radiation doses showed no substantial difference in tensile behavior with the exception of the 200 Mrad test in which the curve showed evidence of slipping during testing as shown in Figure 1. The strain at failure and moduli values taken from the stress/strain curves are given in Table II.

TABLE II: Moduli of Tensile Test Bars

Bar #	Dose (Mrad)	Modulus (ksi)	Strain at Failure	Fracture Stress (ksi)
13	0	162.1	0.70	115.5
15	0	170.2	0.70	112.2
16	50	137.2	0.64	86.8
17	50	132.7	0.72	89.4
18	100	154.5	0.70	110.4
19	100	169.1	0.69	117.5
20	200	158.0	0.66	86.4
21	200	131.0	0.68	75.6

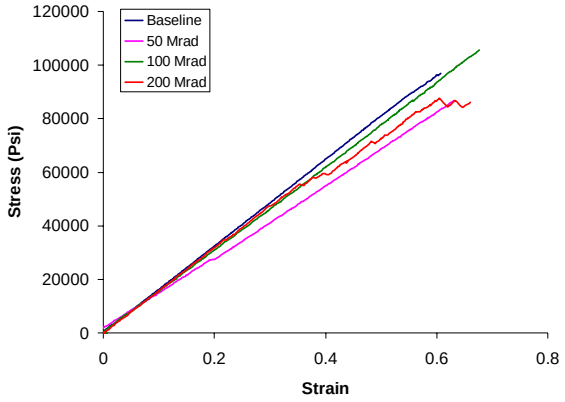

Fig. 1. Stress strain curves of representative of composite bars irradiated to doses of 0, 50, 100, and 200 Mrad.

IIIB. Tensile Fracture Surfaces

Photographs of the fracture surfaces of the tensile bars are shown in Figures 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 Figure 3a. The baseline tensile samples fractured approximately perpendicular to the length of the tensile bar. Further visual examination revealed visible protruding fibers as shown in Figures 3b, c and d. Minimal evidence of delamination between the resin and carbon fibers is visible.

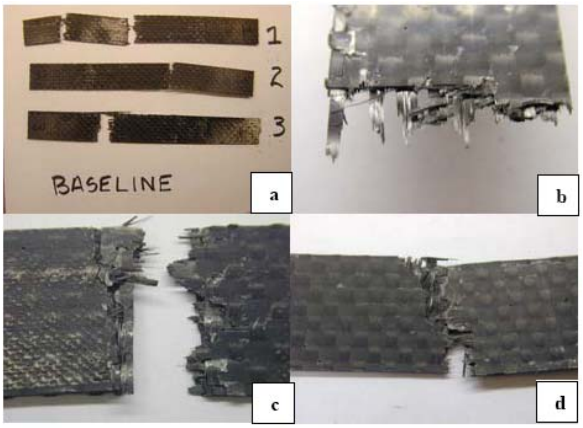

Fig. 2. Baseline fracture tensile test bars (a), fractured surface with protruding carbon fibers (b) and (c), minimal evidence of delamination are visible adjacent to the fracture region (d).

The resin underwent a color change from clear/transparent to light yellow after exposure to a gamma radiation dose of 50 Mrad, typical of polymers exposed to gamma irradiation.[12] 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 Figure 3b, protruding fibers were found at the Minimal delamination or other damage exists was found outside the fracture area.

The resin showed an increased color change with a visibly darkened yellow color, after exposure to total 100 Mrad gamma dose as shown in Figure 4. The tensile bars fractured with visible damage primarily contained to the fracture area as shown in Figure 4a. Similar to the baseline and 50 Mrad samples, protruding fibers are visible at the fracture site shown in Figs. 4 b and c.

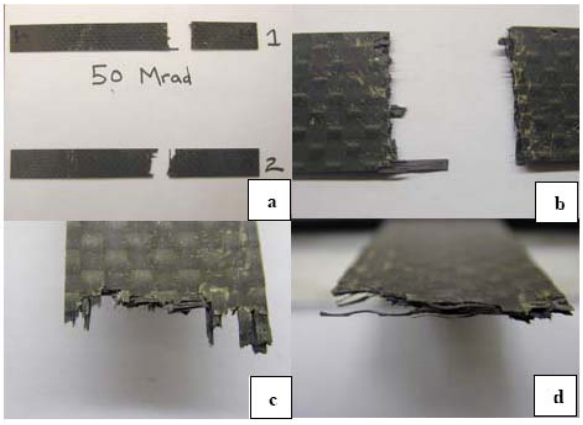

Fig. 3 Fractured tensile test bars after 50 Mrad (a), fractured surface with protruding carbon fibers with slight evidence of delamination on the surface of adjacent area to the fractures surface (b), minimal evidence of delamination (c). The resin has developed a slight yellow color visible in delamination areas (d).

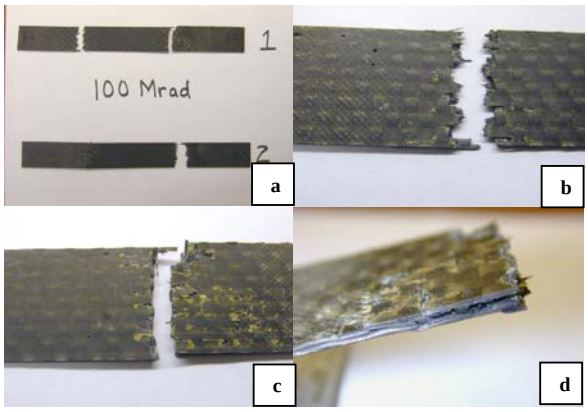

Fig. 4 Fractured tensile test bars exposed to 100 Mrad (a), fractured surface with minimal protruding carbon fibers (b), increased surface delamination adjacent to the fracture area with a darker yellow color (c), increased delamination along the length of the bar (d).

Visible delamination exists at the fracture site, with minimal damage extending beyond the fracture area as shown in Figure 4d.

At the higher dose of 200 Mrad, the resin underwent a significant color change with a visible dark yellow color as shown in Figure 5. Damage extends along the length of the tensile bar and is not confined to the fracture site, Figure 5a. In addition to color changes, pockets of resin are missing at the interface between carbon fiber woven points, Figure 5b. This damage extends several inches 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, Figure 5d. Weight measurements were taken for a bar from each radiation dose. While baseline, 50 Mrad, and 100 Mrad samples weighed between 7.7 and 7.9 g, the 200 Mrad weighed

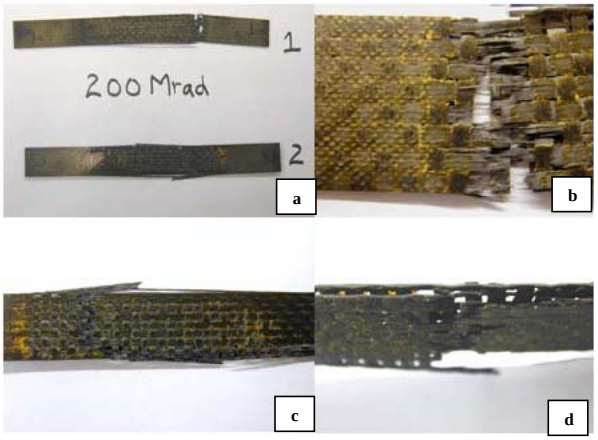

Fig. 5 Fractured tensile test bars exposed to 200 Mrad (a), fractured surface with protruding carbon fibers and a visible deep yellow color (b), void formation is visible at the adjacent to the fracture surface (c), significant delamination throughout the core of the bar (d).

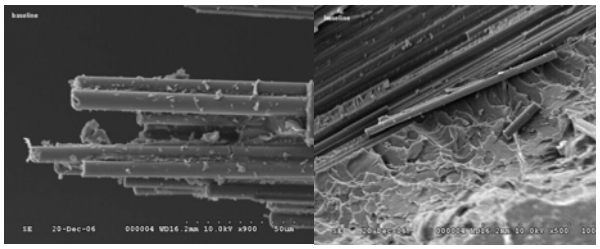

Fig. 6 Baseline tensile bar with carbon fibers with small amount of resin debris (left), fractured resin surface at failure site. Fractured surface contains evidence of fracture with a significant degree of ductility (right).

7.5 g, which is a more significant weight loss.

IIIC. Scanning Electron Microscopy

Scanning electron micrographs of the fracture surfaces of the tensile bars are shown in Figures 6-10. The virgin composite exhibited significant amounts of interfacial failure. Fiber pullout found in the baseline samples contained minimal polymer debris, Figure 6, suggesting failure at the interface of the fibers and the epoxy. The epoxy matrix exhibited a dimpled fracture surface suggestive of ductile fracture.

After 50 Mrad of 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 Figure 7.

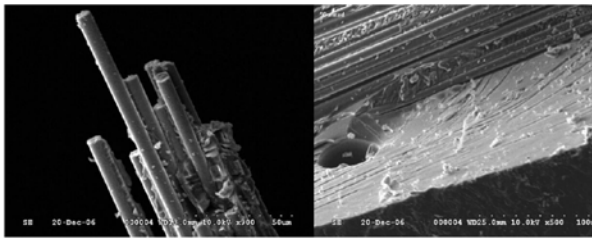

Fig. 7. Tensile bar subjected to 50 Mrad gamma radiation with carbon fibers with small amount of resin debris (left), fractured resin surface at failure site. Fractured surface suggests a fracture with a smaller degree of ductility compared to baseline samples shown in Figure 5 (right).

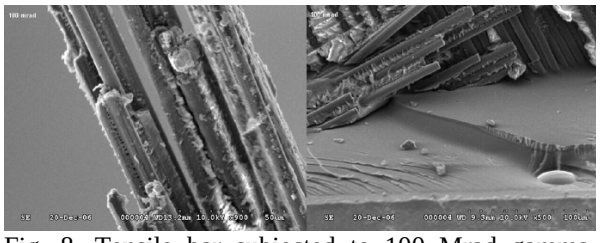

Fig. 8. Tensile bar subjected to 100 Mrad gamma radiation with carbon fibers coated with substantial amount of resin (left). The fracture surface of the resin is mostly brittle in nature (right).

At radiation doses of 100 Mrad, Figure 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 200 Mrad, the integrity of the composite is substantially diminished. Significant epoxy debris remains on carbon fibers and numerous cracks run through the epoxy core, Figure 9.

As further evidence of increased degradation after a 200 Mrad 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. Offgassing of polymers during radiation exposure is expected. Additional images of radiation damage are shown in Figure 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**.**

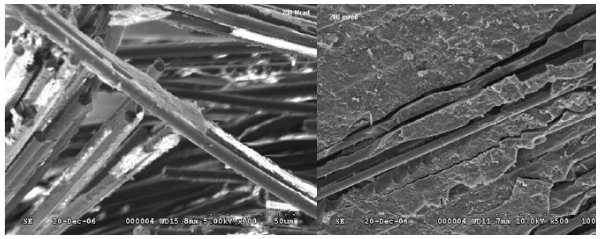

Fig. 9. Tensile bar subjected to 200 Mrad gamma radiation with carbon fibers coated with substantial amount of resin (left). Numerous fractures are present within the resin parallel to the length of the fibers (right).

Fig. 10 Epoxy surface on tensile bar subjected to 200 Mrad gamma radiation.

IIID. Differential Scanning Calorimetry (DSC)

Figure 11 shows the results for the baseline and 200 Mrad samples, respectively. The DSC curves between the baseline and 200 Mrad resin are clearly different. The first DSC run for both baseline and 200 Mrad removed the thermal history by heating to 150 ºC. 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 20C higher than the service temperature or the substrate temperature during the repair. The downward slope in the DSC baseline curve starting at ~60 ºC is the onset of the glass transition. The T_g can be estimated as ~72 ºC and 84 ºC for the baseline and 200 Mrad samples, respectively, see Figure 11. From these data, the T_g of the epoxy has apparently shifted approximately 10 ºC 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.

III E. Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectrum contained peaks consistent with the presence of a bisphenol-A-based epoxy resin, see Figure 12. Changes were observed with increasing dose in the carbonyl region near 1700 cm^{-1} indicating oxidation.

III. F. Hardness Testing

Hardness testing was performed as a standard epoxy characterization method. Rockwell M scale 0.25 diameter ball indenter with 10 kg minor load, and 100 kg major load was used per ASTM D785-03 (Ref. 13). The hardness results of the epoxy and composite can be found in Tables III and IV, respectively.

TABLE III. Hardness values for epoxy

Unirradated	100 Mrad Irradiated
44.4	70.6
50.3	71.8
49.2	72.5
49.5	72.0
40.1	71.9

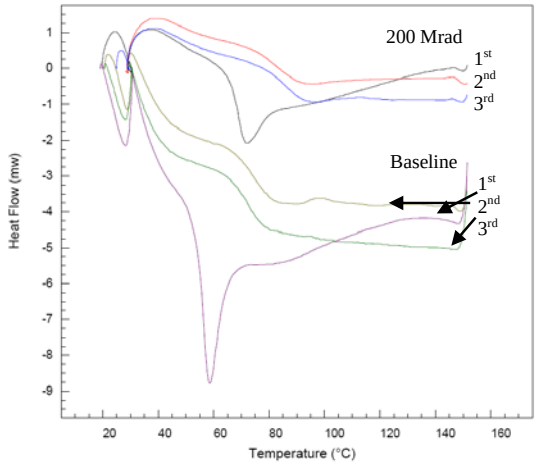

Fig. 11 DSC curves of baseline resin and 200 Mrad irradiated resin.

TABLE IV. Hardness values for composite

Condition	Test #1	Test #2	Test #3
Baseline	102.1	103.3	102.3
50 MRad	100.3	98.9	101.8
100 MRad	106.1	101.5	104.2
200 MRad	105.4	100.9	107.4

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.

II. CONCLUSIONS

Mechanical and thermal testing followed by microstructural analysis was performed on candidate epoxy-reinforced composite materials to determine the gamma radiation effects on their functionality for use in the DWPF. The mechanical testing revealed no substantial trends from the modulus or strain at failure data, although the microstructural orientational effects were not accounted for. The reliability and accuracy of the stress/strain curves is unknown due to the highly

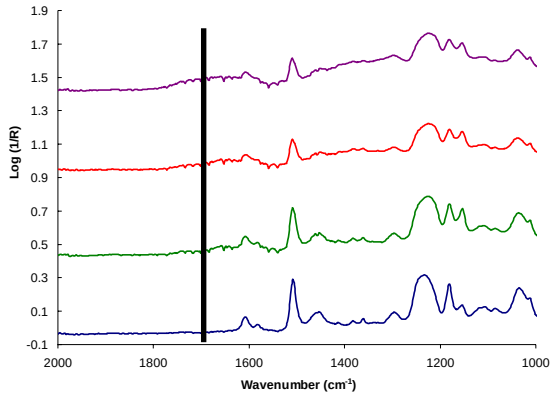

Fig. 12 Bisphenol A epoxy resin – duplicate analyses of the irradiated and control samples. Dotted line depicts region associated with oxidation upon irradiation.

directional nature of the fiber composite. 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 ~0.4 and above, suggesting the failure mechanism is different for highly irradiated samples and should not be discounted.

Radiation doses up to 200 Mrad gamma do not affect the carbon fibers significantly. This is typical and expected behavior for graphite or carbon fiber materials. The damage threshold dose for the epoxy used in the composite is unknown, but the resin appears to be slightly degraded at a dose of 50 Mrad, with increased changes at higher doses. At 50 Mrad, 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 100 Mrad, 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 200 Mrad, 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, composite appears to be resistant to a dose of 50 Mrad and should function similarly to non-irradiated material. Effects on properties and interfacial behavior are more significant for samples irradiated to doses of 100 Mrad 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 50-100 Mrad 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.

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