SANDIA REPORT
SAND2012-3358
Unlimited Release
Printed April 2012

Neutron and Gamma Irradiation Damage to Organic Materials

Gregory Von White II and Robert Bernstein

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.

Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: http://www.osti.gov/bridge

Available to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online

SAND2012-3358
Unlimited Release
Printed April 2012

Neutron and Gamma Irradiation Damage to Organic Materials

Gregory Von White II and Robert Bernstein
Organic Materials Department
Sandia National Laboratories
P.O. Box 5800
Albuquerque, NM 87185-0888

Abstract

This document discusses open literature reports which investigate the damage effects of neutron and gamma irradiation on polymers and/or epoxies—damage refers to reduced physical chemical, and electrical properties. Based on the literature, correlations are made for an SNL developed epoxy (Epon 828-1031/DDS) with an expected total fast-neutron fluence of ~10^{12} n/cm^2 and a γ dosage of ~500 Gy received over ~30 years at < 200 °C. In short, there are no gamma and neutron irradiation concerns for Epon 828-1031/DDS. To enhance the fidelity of our hypotheses, in regards to radiation damage, we propose future work consisting of simultaneous thermal/irradiation (neutron and gamma) experiments that will help elucidate any damage concerns at these specified environmental conditions.

Table of Contents

1. INTRODUCTION **7**

2. DISCUSSION **11**

2.1 GAMMA IRRADIATION 11
2.2 NEUTRON IRRADIATION 17
2.3 OUTGASSING 25

3. CONCLUSIONS **27**

4. REFERENCES **29**

1. Introduction

Fundamental understanding of neutron and gamma irradiation effects on polymers is advantageous for successful long term application in extreme radiation environments. Reports demonstrate small doses of radiation can result in dramatic physical or mechanical property changes in polymers.[1-3] Epoxies—a class of thermosetting polymers—are broadly used in coatings, adhesives, and composites. Detailed insight to the radiation dose effects on epoxies is critical because they are employed as insulator and mechanical support materials in superconducting magnet applications.[4, 5] Enhancing the current knowledgebase of epoxies is necessary because they are used in high consequence applications such as nuclear reactors,[6] radiation processing facilities,[6] and military applications that support our national interests in energy and homeland security.

Understanding the underlying radiation degradation pathways is complex because the depth of penetration for neutrons is large and not limited to only the external surface of the material.[1] This is in part because neutrons scatter as a function of atomic composition and density,[7, 8] and therefore damage caused by radiation is considered composition dependent.[1] As an example, ten times more energy is lost from neutrons scattered by hydrogen atoms compared to an equal number of carbon atoms. Furthermore, the extent of materials damage is dependent upon the incident neutron energy, where lower energy neutrons are more likely to interact via scattering or absorption compared to higher (faster) energy neutrons. Polymers that absorb neutron and gamma radiation produce both free radical and ionic species.[2] These radicals readily participate in simultaneous and ongoing degradation chemistries; chain scission, crosslinking, and unsaturation. The chemical bonds most susceptible to cleavage due to irradiation are the C-H, and C-C bonds. Epoxies with certain chemical attributes (e.g., high numbers of aromatic[1] or heterocyclic rings modified with imide groups) minimize chemical degradation that affects performance by enhancing strength, thermal resistivity, and radiation resistance.[9] The addition of an amine containing hardener like diaminodiphenylsulfone (DDS) has also been shown to increase the thermal stability of epoxies.[10] Tailoring the atomic composition or formulation mixture of an epoxy can help alleviate typical radiation concerns like dynamic and static modulus, dimensional stability, internal friction, outgassing, debonding, and heat distortion temperature.[11]

Sandia National Laboratories (SNL) has interest in developing a fundamental understanding of the irradiation effects on epoxy materials. More explicitly, an unfilled Epon 828-1031/DDS system which is a 50/50 by weight mix of the Epons, where 100 parts Epons is added to 32 parts DDS. The DDS and Epon 1031 components were chosen to enhance thermal stability. The atomic composition is approximately H (45.8%), C (43.5%), N (1.5%), O (8.4%), and S (0.7%). For clarity, Figure 1 shows the molecular structure of the epoxy components and from this point in the manuscript will be referred to as Epon 828-1031/DDS, where n = 1 or 2 in Epon 828 (Figure 1A). As a reference, Epon 828 is a bisphenol A (BPA)-based resin.[11]

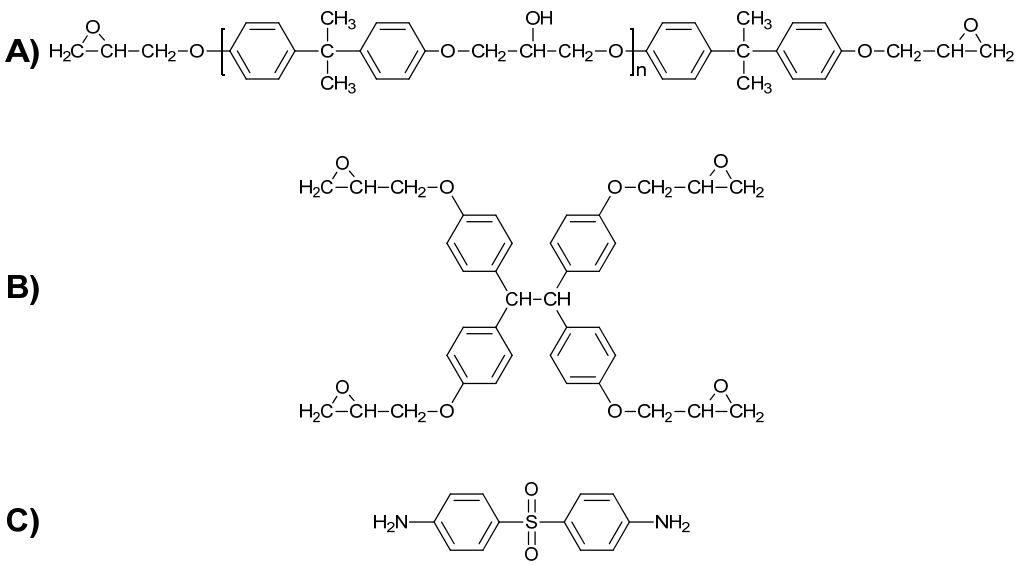

Figure 1. The molecular structures of A) Epon 828, B) Epon 1031, and C) DDS.

Neutron and γ irradiation studies on polymers and epoxies indicate that variation in T_g is linked to changes in polarity,[3] molecular architecture,[3] conductivity,[12-14] size of the macromolecular chains,[3] and variation of free volume.[15] Previous work by Anderson developed and characterized the thermal stability of Epon 828-1031/DDS and demonstrated that adhesion strength closely correlates to changes in glass transition temperature, T_g.[16] Thermal analysis of virgin Epon 828-1031/DDS showed that the ultimate T_g is 253 °C.[16] Accelerated aging studies performed on Epon 828-1031/DDS resulted in a calculated activation energy (E_a) of 43 kcal/mol (180 kJ/mol), assuming Arrhenius behavior (Figure 2A). The degradation activation energy obtained from time-temperature superposition of fractional adhesion force measurements (Figure 2B) was determined to be 44 kcal/mol (184 kJ/mol)—agreeing well with the thermal analysis derived E_a. Based on these results, Anderson and co-workers suggest that minimal degradation of the T_g will occur over decades of use. It is worthwhile to point out that while these thermal accelerated aging experiments were performed at temperatures above 200 °C;[16] curvature in Arrhenius shift factor plots has been observed for organic materials at low temperatures (e.g., 99 °C and lower).[17] At this time, curvature in the Arrhenius shift factor plots for TGA and adhesion force measurements at temperatures lower than 200 °C is unknown.

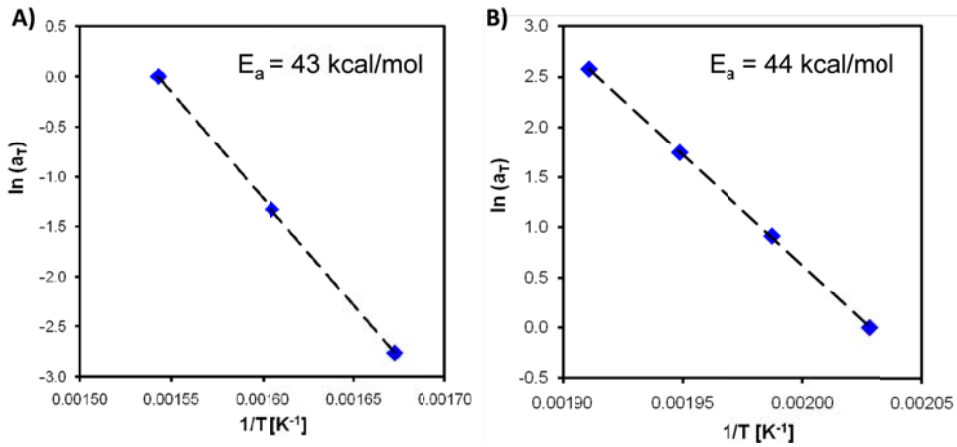

Figure 2. Arrhenius plot of the shift factors derived from A) isothermal TGA measurements and B) fractional adhesion strength of Epon 828-1031/DDS. Modified from Anderson.[16]

The intent of this manuscript is to identify and discuss open literature investigations which characterize neutron and gamma irradiation effects on polymer and epoxy materials as a means to make conclusions—where appropriate—for Epon 828-1031/DDS. The environmental conditions of interest are a neutron fluence of ~10^{12} n/cm^2 (E_{ave} ~2 MeV, neutron flux of ~10^3 n/s cm^2) and γ dose of 500 Gy (E_{ave} ~1 MeV with a dose rate ~10^{-3} Gy/hr) held at a normal operating temperature of < 200 °C.

2. Discussion

2.1 Gamma Irradiation

Advances in nuclear energy capability and efficiency (e.g., extending nuclear plant lifetimes, increasing power output, etc.) are the dominant driving forces for active neutron and gamma irradiation research with polymers. As a result, there has been extensive research investigating neutron and γ irradiation effects on organic material performance at radiation levels relevant to nuclear power plant (NPP) environments. In 1996 Brookhaven National Laboratory published a report (NUREG/CR-6384) for the NRC discussing the environmental qualification of safety-related electric cables.[18] This report includes a summary of the common operating conditions for boiling water reactor (BWR) and pressurized water reactor (PWR) plants (Figure 3).[18] NUREG/CR-6384 states that radiation dose rates vary with location in a NPP, where typical dose rates for cables experience ~1 Gy/hr for γ-rays and negligible neutron exposure occurs in both the BWR and PWR NPPs.[18] Subudhi commented that alpha and neutron radiation is not a concern for low voltage NPP cables—though gamma radiation should be considered, in particular rubber based materials.[18]

Per the literature, the high content of aromatic and imide structures in Epon 828-1031/DDS will increase radiation resistivity against γ radiation compared to typical NPP cable insulations. It is significant to point out that air and humidity are known to increase the rate/extent of material degradation in the presence of temperature[17] or radiation[19, 20]—both environmental factors are common for NPP cables. Based on NUREG/CR-6384, a discussion of other relevant studies concerning γ irradiation is required to understand dose effect on epoxies.

PWRs:	49°C
	0.1 - 200 rad/hr (gamma plus neutron)
BWRs:	65°C
	40-60% relative humidity
	0.3 - 160 rad (carbon)/hr (gamma)
	0.1 - 50 rad (ethylene)/hr (neutron)

Figure 3. Typical operating conditions in BWR and PWR NPPs. Reprinted from Subudhi.[18]

Research in the super conducting magnet field has also studied radiation effects on polymers and epoxies (albeit, the epoxies employed in super conducting magnet applications are typically glass fabric or boron filled).[5,21] Coltman and co-workers studied the γ irradiation effects on three variations of an epichlorohydrin bisphenol A based epoxy (Figure 4)—either glass fabric filled containing boron, boron-free glass filled, and glass fabric filled containing boron with aromatic amine hardener, respectively named G-10CR, G-10CR(BF), and G-11CR.[5,21]

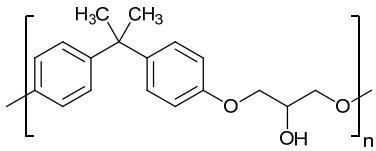

Figure 4. Molecular structure of epichlorohydrin bisphenol A

G-10CR, G-10CR(BR), and G-11CR were γ-irradiated up to 100 MGy at 5 K and then examined by optical microscopy and mechanical testing to identify delamination and flexural strength, respectively.[5] Figure 5 shows the epoxy specimens after irradiation and mechanical testing. It is quite evident that as the γ dose increases, the color darkens. Between 0 and 24 MGy white spots are evident, which are indicative of the glass fibers debonding from the epoxy. At the highest doses of γ irradiation, no white spots are visible due to extreme darkening (not the absence of delamination).

More closely related to the radiation environment expected for Epon 828-1031/DDS, at 3 MGy G-10CR(BR) exhibited no signs of debonding. However, G-10CR displays extensive delamination at 10 MGy, whereas G10-CR(BR) only exhibits slight signs of delamination. These optical microscopy results suggest that boron negatively impacts bond strength in glass fabric filled epoxies. The authors point out that a similar study had been performed on an unfilled polyimide (Vespel) up to 100 MGy, 8.7 x 10^{16} n/cm^2 of fast neutrons, and a thermal-neutron fluence of 3.1 x 10^{17} n/cm^2—*no debonding was observed.*[22] These results confirm that the presence of glass fillers (with or without boron) weakens the epoxy bond strength. The interface between the filler and organic material appears to be the most sensitive part of the material when exposed to γ irradiation.[5] The mechanical testing in this study shows that at 3 MGy, G-10CR(BR) retained ~15% more strength compared to G-10CR supporting a conclusion that boron also negatively impacts flexural strength.[5]

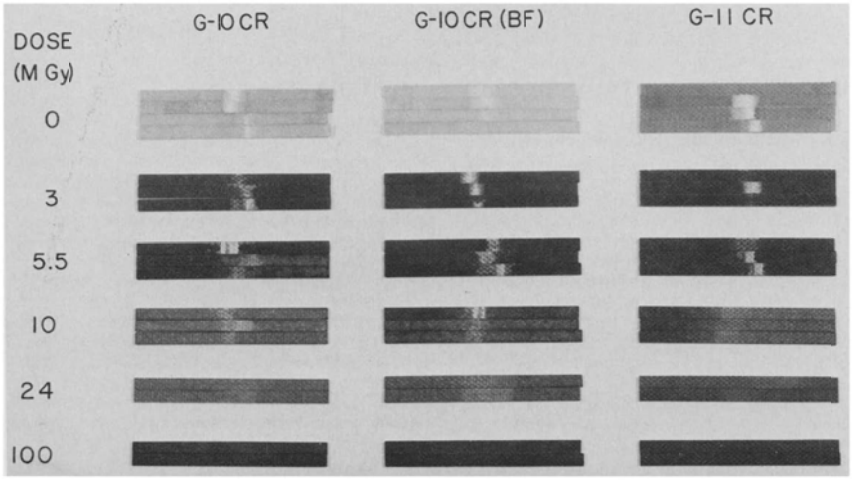

Figure 5. G-10CR, G-10CR(BF), and G-11CR epoxy samples after gamma irradiation and mechanical testing with varying dose between 0 MGy and 100 MGy. The white spots shown on the epoxy specimens indicate delamination between the glass fibers and the polymer. Reprinted from Klabunde and Coltman.[5]

A more rigorous investigation by Coltman and co-workers studied the effect γ radiation at 77 K on the same GC-10CR, GC-10CR(BR), and GC-11CR epoxies and measured flexural strength (Figure 6), linear flexure modulus (Figure 7), and compression strength (Figure 8).[21] Strength measurements for virgin G-10CR and G-11CR showed no difference, however the addition of the amine hardener to the epoxy (G-11CR) demonstrated an increased resistivity to irradiation.[21] In this study, the authors subject the samples in the worst case to gamma irradiation of 100 MGy, thermal neutron fluence of 3.1 x 10^{16} n/cm^2, fast neutron fluence of 8.7 x 10^{15} n/cm^2 (E > 0.1 MeV), and a total irradiation time of 19 hours; all irradiated at 77 K followed by incubation for 2 weeks at room temperature before being tested.[21] For compressive and flexure strength, as well as linear flexure modulus, G-11CR was more radiation resistant than G-10R, i.e. the amine enhanced the flexural strength.[21] G-10CR and G-11CR had a similar initial strength, but G-11CR had higher radiation tolerance.[21] The boron free sample, G-10CR(BR), showed little difference to that of the sister sample (G-10CR), which demonstrated that the boron fission fragments had little effect.[21]

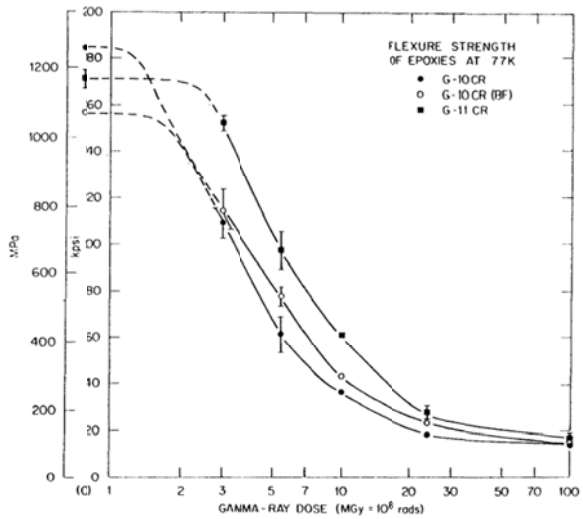

Figure 6. Measured flexure strength of G-10CR, G-10CR(BF), and G-11CR epoxy samples after gamma irradiation at 4.9K followed by a warm-up to 307K. Reprinted from Blazewicz et al.[21]

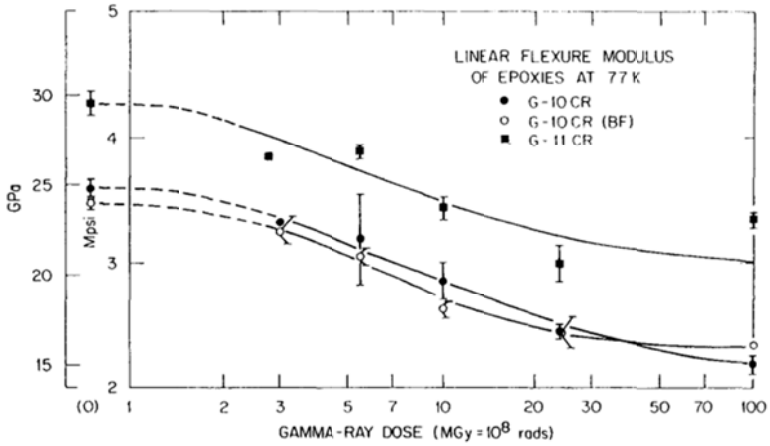

Figure 7. Linear flexure modulus of G-10CR, G-10CR(BF), and G-11CR epoxy samples after gamma irradiation at 4.9K followed by a warmup to 307K. Reprinted from Blazewicz et al.[21]

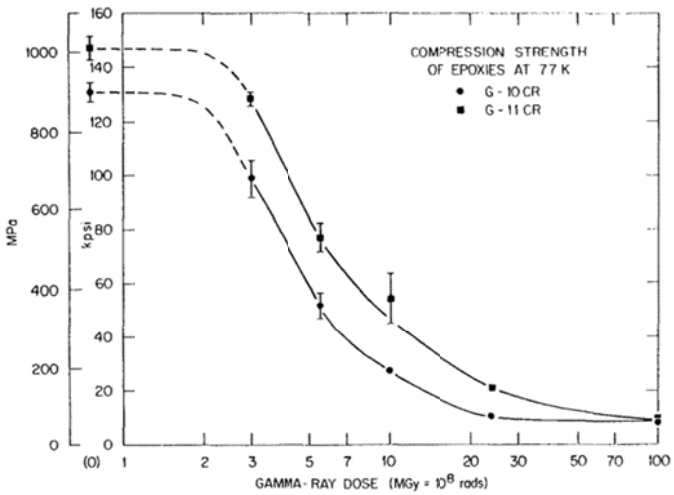

Figure 8. Compression strength of G-10CR, and G-11CR epoxy samples after gamma irradiation at 4.9K followed by a warmup to 307K. Reprinted from Blazewicz et al.[21]

More closely related to the Epon family, Fouracre studied the γ irradiation effects (^{60}Co) up to 2 MGy on two DGEBA (diglycidyl ether of bisphenol-A, see Figure 9) based epoxy systems that incorporated hardener in the final cured epoxy formulations (one of which was DDS).[14] The change in conductivity—measured by an electrometer and a photomultiplier as a function of γ dose and temperature—revealed E_a to be ~28 kcal/mol (119 kJ/mol);[14] thermal degradation experiments reported an activation energy of ~23 kcal/mol (96 kJ/mol).[23] Albeit the total dose is ~4,000 times what is expected for Epon 828-1031/DDS, Fouracre states the activation energy is a function of dose rate and γ dose (E_a increases with total dose).[14] This is critical to point out as the γ dose rates in this work were 500 – 2,500 Gy/hr, whereas the Epon 828-1031/DDS conditions are on the order of 10^{-3} Gy/hr.

Work by Gillen and co-workers suggest that high gamma irradiation dose rates (^{60}Co) can lead to diffusion limited oxidation (DLO) dependent upon the material type.[24] Under DLO conditions—extremely high dose rates and/or high temperature—the rate of oxygen consumption is greater than the rate at which oxygen can diffuse into the material. These conditions exhibit a reduction in oxygen concentration from its equilibrium sorption value from the sample surface to the value inside the material. This results in heterogeneous oxidation through the thickness of the polymer/epoxy, leaving the outside of the specimen "cooked" and the inside of polymer pristine.[24] Physical property data (e.g., tensile strength, adhesive strength, etc.) used to predict material properties as a function of time may be unrealistic and result in extremely conservative lifetimes—this can be dangerous! One may infer that the experimental conditions used by Fouracre[14] resulted in DLO and therefore large activation energies were measured which result in overestimates in physical property predictions as a function of time. No direct conclusions can be made from the results presented by Fouracre in relation to Epon 828-1031/DDS, but this work strongly suggests that if experiments are to be performed on the SNL epoxy to elucidate performance, attention should be given to the dose rate and total dose employed if oxygen is present.

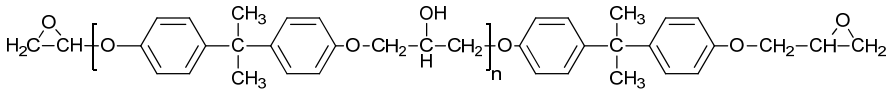

Figure 9. Structure of DGEBA. As shown, the atomic composition of DGEBA is approximately H (7.0%), C (74.7%), and O (18.3%).

In 1997, Huang et al. investigated radiation hardness effects caused by γ irradiation (^{60}Co) on Eccobond-24, a commercial optical glue which is comprised of 100 parts DGEBA and 30 parts diethyleneglycol bis-(3-aminopropyl) ether. After 1,000 Gy, the glue began to yellow, turning darker and eventually turned brown at ~10,000 Gy.[25] At less than 20 Gy the UV-VIS absorbance for wavelengths less than 400 nm were very high compared to higher doses.[25] Huang et al. point out that the DGEBA based epoxy is appropriate for radiation environments of 1 Gy/yr—the typical dose expected for epoxies employed as optical interfaces for CsI or BGO crystals in a photodiode read-out.[25] Due to the low γ doses studied, per the application of the glue, the experimental conditions are within an order of magnitude to the environment of the Epon 828-1031/DDS (much more relevant than the work discussed by Fouracre)[14]. <u>The conclusions of this work suggest that no radical changes are to be expected for the Epon 828-1031/DDS epoxy at a gamma dose of ~500 Gy.</u>

Per the results and discussion of open literature reports which study γ irradiation effects on polymers and epoxies, no concerns exist for Epon 828-1031/DDS. However, efforts should be directed towards elucidating the neutron irradiation effects of this system. The next section of this report will discuss open literature studies that investigate neutron and neutron + gamma irradiation effects on organic materials.

2.2 Neutron Irradiation

Rivaton and Arnold studied the structural effects of fast neutrons (average energy of 14 MeV, dose rate of ~2 x 10^8 n/s, 5 orders of magnitude greater than the flux expected for Epon 828-1031/DDS) on a wide range of polymers, including epoxy resins and quantified structural changes through physical and chemical analysis.[3] This investigation included ethylene propylene diene monomer (EPDM), polyoctenamer rubber, high and low density polyethylene (HDPE and LDPE, respectively), polypropylene (PP), polyethylene oxide (PEO), polyvinyl chloride (PVC), phenoxy resin (PKHJ®), poly[N-vinylcarbazole] (PVK), bisphenol-A polycarbonate (PC), poly[ethylene terephthalate (PET), and polystyrene (PS). Based on the geometries of the samples studied, the total neutron fluence ranged between 1.8 x 10^{12} n/cm^2 and 4.5 x 10^{13} n/cm^2 during a maximum of 40 hour exposure time.[3] To ensure the degradation mechanisms were representative of neat polymers, the processing anti-oxidants were removed by extraction before irradiation. The samples were studied either immediately after irradiation or after some time under air exposure. It was clear that after air exposure post-irradiation, all of the aliphatic polymers resulted in oxidation—evident by carbonyl and hydroxyl peaks measured by IR spectroscopy.[3] An intriguing fact was that double bonds (in EPDM and polyoctenamer rubber) were not the preferred reactive site after neutron irradiation; actually they appeared unaffected as measured before and after by IR spectroscopy.[3] This suggested that bond scission of the backbone is the primary damage mechanism for neutron irradiation resulting in radical formation, followed by oxidation upon exposure to air.[3]

Rivaton and Arnold also measured T_g for all of the polymers studied.[3] The materials with the most significant variation in T_g as a function of neutron irradiation time are shown in Table 1. Of note, the bisphenol-A polycarbonate did exhibit an increase in T_g with increasing irradiation time—a decrease in T_g may indicate reduced adhesion forces per the work by Anderson and co-workers,[16] thus these results are encouraging for the Epon 828-1031/DDS system. The authors pointed out that the materials not shown in Table 1 did not exhibit changes in T_g, i.e. the epoxy resin was not listed. More importantly, the total neutron fluence was nearly identical to what is expected for the Epon 828-1031/DDS epoxy; however, the neutron energy was 7x higher than the expected energy for Epon 828-1031/DDS. Hence, one would expect greater nuclear interactions with the lower energy neutrons employed in this study. The authors report that structural changes are expected for many organic materials after neutron irradiation.[3] Albeit structural changes were observed, they were small and were linearly associated with the neutron fluence.[3] This work indicates that radical formation is likely to occur for Epon 828-1031/DDS; however, storage of the epoxy in an inert (hermetically sealed) atmosphere significantly mitigates (eliminates) the negative degradation effects associated with polymer oxidation.

Table 1. Evolution of T_g (°C) for polymer samples under the impact of neutrons. Adapted from Rivaton and Arnold.[3]

Duration of Irradiation	0 hrs	16 hr	24 hrs	40 hrs
poly(N-vinylcarbazole), PVK	225	229	231	235
polystyrene, PS_g	92	94	95	97
bisphenol-A polycarbonate, PC	141	146	149	152
polyvinyl chloride, PVC	86	89	90	93
poly(ethylene terephthalate), PET	88	77	75	69

Kline investigated the thermal neutron (from an enriched uranium nuclear reactor at Pennsylvania State University) and gamma irradiation effects on Epon 828 (molecular weight estimated to be 340) with doses varying between 5 x 10^{14} n/cm^2 to 1 x 10^{16} n/cm^2 and 1.1 x 10^4 Gy to 2.2 x 10^5 Gy at 60 °C, respectively. The experimental conditions employed here (temperature, neutron fluence, γ dose, oxygenated atmosphere) rigorously investigated the environmental effects on Epon 828. Tensile testing demonstrated no changes in tensile strength as a result of neutron and gamma irradiation (T = 54 °C, neutron fluence = 1 x 10^{16} n/cm^2, and γ dose = 2.2 x 10^5 Gy).[11] Compared to the expected environmental conditions of Epon 828-1031/DDS, the thermal neutron fluence and γ irradiation dose applied to the Epon 828 in the study by Kline is substantially greater by orders of magnitude (four orders of magnitude larger for the total neutron fluence). The data in this work strongly suggests that there are no relevant thermal (low energy) neutron concerns for Epon 828-1031/DDS—particularly as these experiments were performed in an oxygen containing air environment and at a relevant elevated temperature. Discussion of more energetic neutrons are more relevant to the Epon 828-1031/DDS system, i.e. fast neutrons.

Liepens and co-workers at Los Alamos National Laboratory (LANL) studied three Epon 828 based epoxies and a model polyimide (see Figure 10 for the chemical structures) to elucidate fusion reactor material behavior after exposure to neutron radiation in vacuum.[1] The neutron source employed was 14.8 ± 0.8 MeV (fast and high energy neutrons), where the total neuron fluence varied from as low as 2.3 x 10^{16} n/cm^2 to as high as 5.4 x 10^{16} n/cm^2—four orders of magnitude larger than the expected neutron fluence for Epon 828/1031-DDS. The epoxy and polyimide samples were examined by IR spectroscopy, vapor phase osmometry (molecular weight), DSC, UV-VIS spectroscopy, and ESR spectroscopy. All of the irradiated samples discolored and had some degree of swelling (2 - 14%, indicative of chain scission) and some degree of gas bubbles.[1] All samples were irradiated at room temperature (298 K). Liepens suggested that the higher the hydrogen content, the more damage was noted, and that further studies are necessary with higher molecular weight material.[1] More explicitly, the polyimide model compound, with the highest number of hydrogen atoms and largest number of aliphatic carbon-hydrogen groups (Figure 10C), increased in molecular weight by 20%—indicative of significant free radical formation followed by free radical coupling.

ESR analysis demonstrated that the compound shown in Figure 10C had the largest decay of the total free radical density, a result of having the least aromatic functionality; it also

exhibited the most degradation. In short, a lower number of hydrogen atoms, minimal aliphatic groups, and high quantities of CH_2S and aromatic ring functionality greatly enhances neutron resistance.[1]

In the same report by Liepins, DSC analysis revealed two decreased crystalline phase transitions for one of the compounds studied that suggested degradation of the compound.[1] Table 2 shows the DSC data before and after neutron irradiation. Albeit, T_g values were not reported, the decomposition temperatures (T_{dec}) were, as shown in Table 2. Substantial decreases in T_{dec} are indicative of environments that may lead to decreased adhesion forces. Epon 828-1031/DDS is most chemically similar to compounds B and D in Figure 10. Per Table 2, these are not "substantial" decreases in T_{dec}. Based on the work performed by Liepins et al., one may conclude that <u>no significant concerns exist for the Epon 828-1031/DDS system in regards to neutron irradiation</u>—one might consider this report to be a margin test, particularly because the damage expected for such high energy neutrons is greater than the performance environment of Epon 828-1031/DDS.

Table 2. DSC data before and after neutron irradiation of Epon 828 based epoxies. Adapted from Liepens and co-workers.[1]

Sample		T_m, °C	T_{dec}, °C
A	Before	162	> 350
	After	162	> 350
B	Before	-	362
	After	163	> 353
C	Before	67, 77	321
	After	53, 67	293
D	Before	84	> 358
	After	-	> 342

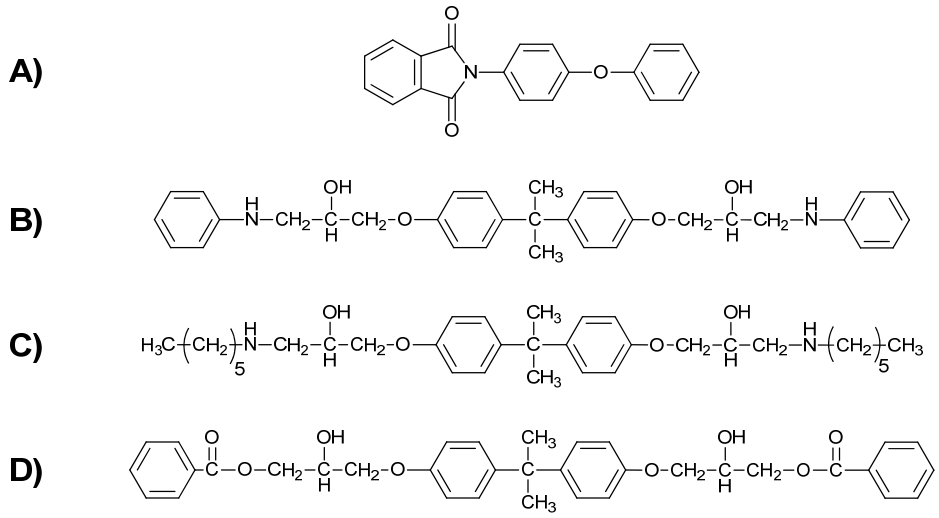

Figure 10. Model compounds used studied by Liepins and co-workers. Adapted from Liepens and co-workers.[1]

Imel et al. studied neutron damage effects on coil insulation materials (impregnated with epoxy) with the goal to reach the expected lifetime (4 years) doses (10^{16} to 10^{17} n/cm^2, 4.5 MeV average energy) in the Tokamak Fusion Test Reactor (TFTR) at a temperature of 62 °C. Imel showed that fast neutrons changed the flexural strength of a G-10 epoxy (the same material previously discussed in the work of Coltman and co-workers)[5,21] which decreased by 6% after 7 x 10^{16} n/cm^2 and 30% reduction after 1.4 x10^{17} n/cm^2, respecitvely.[26] Imel went on to further show that adding a plasticizer ("Hycar" 77) induced greater loss in flexural strength upon neutron irradiation. The most relevant conclusion to SNL is that the G-10 specimens exhibited a damage threshold of ~10^{16} n/cm^2 at a temperature of 62 °C; Epon 828-1031/DDS should not exhibit negative degradation effects because the environmental neutron fluence is ~4 orders of magnitude less. This study is even more relevant than those previously discussed, because it employs elevated temperature during neutron irradiation. <u>One may therefore conclude that there are no concerns Epon 828-1031/DDS when exposed to simultaneous fast-neutron/thermal aging conditions.</u>

An S2-glass fiber-epoxy (a diglycidyl ether bisphenol-A, DGEBA, based system with an anhydride curing agent) composite material (Composite Technology Development) was subjected to fast neutron and gamma irradiation.[27] In the end, the samples were subjected to three different irradiation conditions, 9 hours for a total neutron fluence of 0.9 x 10^{18} n/cm^2 (E. ~ 0.1 MeV), and gamma dose of 20 MGy, 17 hours for a total neutron fluence of 1.8 x 10^{18} n/cm^2 and gamma of 39 MGy and a maximum exposure of 30 hours which resulted in 3.1 x 10^{18} n/cm^2 and gamma dose of 67 MGy.[27] After a neutron fluence of 0.9 x 10^{19} n/cm^2, several cracks were observed in the material and the shear strength decreased from 120 to 85 MPa.[27] The shear strength was reduced to 45 MPa after a neutron fluence of 1.8 x 10^{18} n/cm^2 and was attributed to the loss in interface strength of the glass and epoxy matrix.[27] When the material was subjected to a neutron fluence of 3.1 x 10^{18} n/cm^2, there was extensive damage with regard to shear testing (reducing the shear strength of 10 MPa).[27] This damage was attributed to embrittlement of the epoxy and glass fibers as well as loss of interfacial strength between the epoxy and glass.[27] The

irradiation induced an increase in T_g for the material; attributed to cross-linking within the polymer. Megusar suggests that the epoxy remains amorphous up to a neutron fluence of 1 x 10^{19} n/cm^2, but that the T_g of the material clearly increased.[27] FTIR studies showed that the functional groups remained unchanged up to neutron irradiation of 3.1 x 10^{18} n/cm^2, except for the terminal epoxy group which disappeared.[27] Neutron irradiation causes crosslink formation and hydrogen evolution which become significant at neutron fluence of 1.8 x 10^{18} n/cm^2.[27] Out to a neutron fluence of 3.1 x 10^{18} n/cm^2, no evidence was found of nucleation of hydrogen bubble formation.[27]

Egusa et al. investigated mechanical property changes of cloth-filled organic composites as a function of fast neutron (> 0.1 MeV) and gamma irradiation.[28] The materials were either an epoxy (Sumiepoxy ELM-434 cured with *p*-aminophenyl sulfone) or polyimide (Kerimide 601) resin filled with either an E-glass (Kanebo KS-1210) or carbon (Torayca #6142) fiber cloth.[28] In the case of the polyimide the atomic composition was H (5.1%), C (73.4%), O (11.5%), and N (10.1%)—containing a lower quantity of hydrogen than Epon 828-1031/DDS. These materials were irradiated to a total neutron fluence of 5.0 x 10^{18} n/cm^2 and it was found that the Young's (tensile) modulus was unchanged but the shear modulus and ultimate strength were changed for only the glass filled materials.[28] Albeit, the hydrogen content is much lower for the polyimide studied by Egusa et al. (the neutron damage should be less), the polyimide exhibited excellent neutron resistivity at neutron fluences 5 orders of magnitude larger than expected for Epon 828-1031/DDS. The results from this study are also encouraging because the polyimide epoxy was filled—something which typically induces delamination between the filler and the epoxy.[5, 21] As expected, the damage observed in the polyimide sample was at the interface of the glass and boron.[28]

Coltman and co-workers wrote a comprehensive report which investigated organic insulator materials to be used in superconducting magnet applications at liquid helium temperatures (~5 K).[29] Samples of Sylcast 2850 FT, Epon 828 (Epoxy, with 20pp-h-X curing agent, 0.5% Z6020 Silane couplant, filled with 40 wt% 400 mesh SiO_2 -80 °C cure and 150 °C post cure), G-10 CR, G-10 CR (BF), G-11 CR, Nomex 410, and Kapton H were studied with regard to fast neutrons and gamma irradiation.[29] The samples were exposed to two different doses of fast neutrons and γ irradiation; 1) 2.2 x 10^{16} n/cm^2 and 24 MGy over 2 days or 2) 8.7 x 10^{16} n/cm^2 and 100 MGy over 8 days.[29] Due to reduced Cd shielding, all samples were irradiated with a thermal neutron flux of 4.7 x 10^{11} n/cm^2 s; however, due to the much smaller neutron capture cross section and primary atom-recoil energies for organic materials for thermal neutrons (compared to fast neutrons) the damage is considered negligible—with the exception of glass/boron filled materials.[29] The apparatus had a neutron energy spectrum similar to ^{235}U fission (but with a higher amount of high-energy neutrons) and had an intensity of 1.25 x 10^{11} n/cm^2 s.[29] In this apparatus most thermal neutrons are converted to gamma rays.[29]

Resistivity measurements were performed after the exposures; the Stylcast was unaffected, Epon 828 exhibited some decrease, both the G-10 and the G-11 showed little change under the low dose, but significant changes at the high dose—the Nomex and the Kapton showed little change even after the highest dose.[29] At the lower dose, none of the materials had much change in voltage breakdown.[29] At the higher dose, it appears that the Sylcast, G-10, and G-11 had significant lowering of the high voltage breakdowns.[29]

Physical property testing was consistent at the lower dose, in particular the Epon 828 exhibited virtually no change in flexure strength between the irradiated and lower dose. Epon 828 did show signs of "end of life" at the higher combined doses 8.7 x 10^{16} n/cm^2 fluence and 100 MGy. The particle filled epoxies demonstrated a steady decrease in strength with dose. Comparatively, the glass filled showed a step-function like decrease in flexure strength with dose—G-11CR retained its strength the best compared to G-10CR. Figure 11 shows the compressive strength data for all of the samples studied.

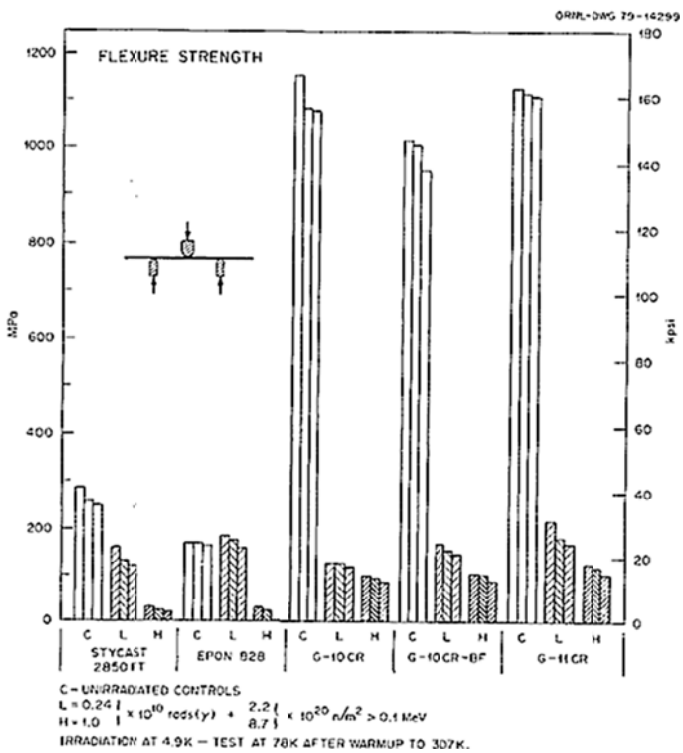

Figure 11. Flexure strength of organic insulator materials with varying neutron fluence and gamma dose performed, irradiated at 4.9 K—physical properties measured at 307 K. Reprinted from Coltman and co-workers.[29]

Compression testing was also performed on the same materials (see Figure 12). Epon 828 was the best performer under compression testing, with substantial strength remaining after exposure exhibiting no "end of life" behavior as it did with flexure testing.[29] Most relative to the performance criteria for Epon 828-1031/DDS, Cotlman and co-workers submit these same materials to shear strength bond testing (cast materials bonded to Cu plates). Up to the lower dose, Epon 828 showed superior strength (~120 MPa shear strength bonded to Cu); however, it did demonstrate an end of life behavior at the higher dose. Figure 13 summarizes the shear bond strength experimental results. Recall that the higher dose is 4 orders of magnitude greater neutron fluence and 2 million times more γ dose compared to the environment expected for the Epon 828-1031/DDS system. <u>This study indicates that there are no adhesion concerns for the expected environmental conditions of Epon 828-1031/DDS.</u> When this data was compared to previous results, it was summarized that no measurable effect on the outcome of the results was observable when the ratio of fast-neutron flux to the gamma dose rate was increased by a factor

of 17.[29] Recall that Fouracre reported that the degradation activation energy correlates to dose rate.[14]

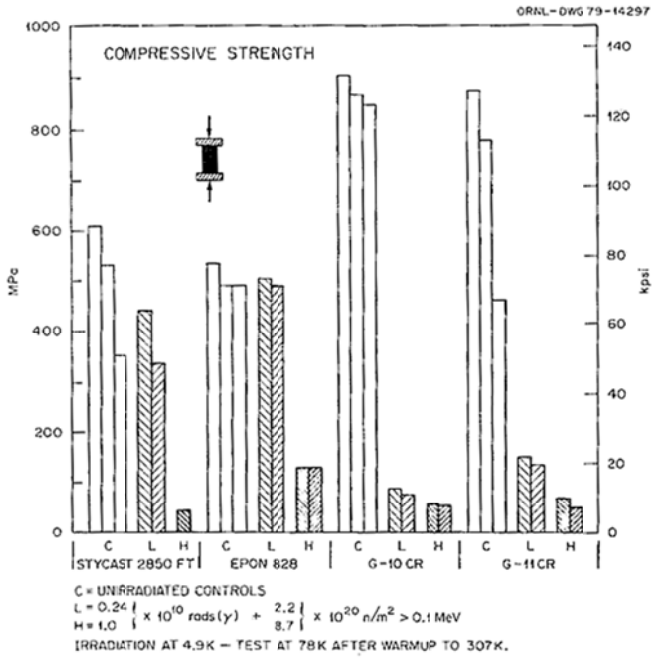

Figure 12. Compressive strength of organic insulator materials with varying neutron fluence and gamma dose performed, irradiated at 4.9 K—physical properties measured at 307 K. Reprinted from Coltman and co-workers.[29]

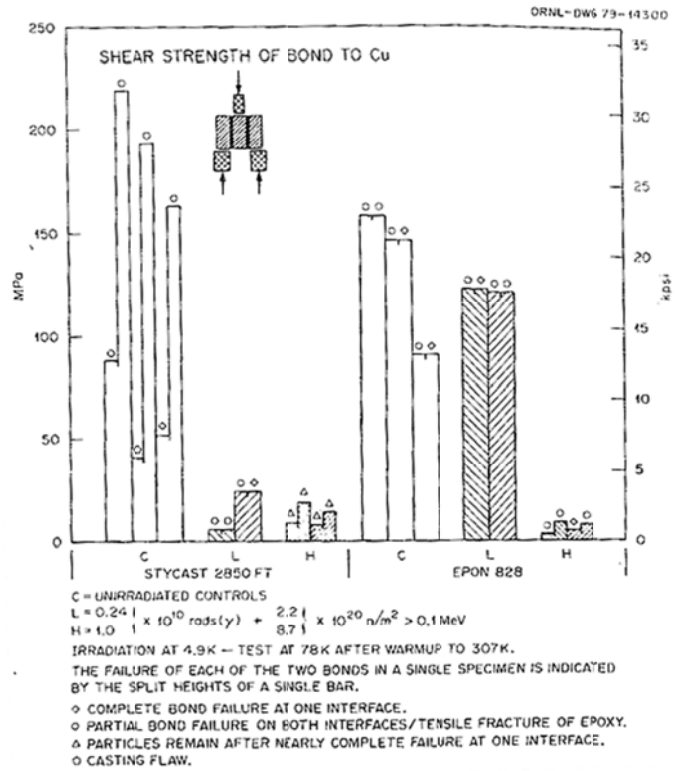

Figure 13. Shear strength bond of organic insulator materials to Cu with varying neutron fluence and gamma dose performed, irradiated at 4.9 K—physical properties measured at 307 K. Reprinted from Coltman and co-workers.[29]

Cotlman and co-workers also did a comparison study of glass fabric filled epoxies, Vespel (unfilled polyimide), Spaulrad (Spauldite –a high pressure aromatic polyimide laminate reinforced with E-glass woven fabric 70 - 71% by weight), and Norplex (formerly Kerimid; a resin of bismaleimide and aromatic diamines reinforced with E glass 40 - 60% by weight.[22] In general it was found that the glass filled polyimides were 5 - 10 times more radiation resistant than glass filled epoxies (G-11CR containing amine hardener).[22] However, Coltman and co-workers cite previous work where fast neutrons at 8.7 x 10^{16} n/cm^2 (> 0.1 MeV) and gamma irradiation of 100 MGy had no detectable change to the mechanical strength of the glass fabric filled epoxies.[22] This comparison study for the glass filled epoxy has the closet experimental conditions to the expected radiation environment for the Epon 828-1031/DDS epoxy (same order of magnitude for the dose of both γ and neutron irradiation with similar neutron energies). Per the work by Coltman and co-workers, there are no concerns for the Epon 828-1031/DDS system in terms of strength retention.

2.3 Outgassing

In addition to changes in T_g or physical properties (adhesion force), one must also consider the effect of epoxy outgassing, particularly if the application of an epoxy is in a hermetic environment. Coltman performed a study on several different polyimides, filled and unfilled, with a gamma dose of 100 MGy, thermal-neutron fluence of 3.1 x 10^{17} n/cm^2, fast neuron fluence of 8.7 x 10^{16} n/cm^2 with a total irradiation time of 189 hours—very aggressive compared to the application conditions of Epon 828-1031/DDS.[22] After 1 day, H_2, CH_4, H_2O, N_2 and CO, O_2, CO_2, C_2H_4 were observed —a cumulative mass of 35.2 x 10^{-4} grams gas/gram resin after 6 days, though ~92% of all outgassing products were formed within the first day of irradiation.[22] At a higher neutron flux to gamma dose rate ratio, 79% of the gas products evolved with the first 24 hours.[29] In the later study, the major species outgassed were H_2, CH_4 and some traces of low MW organics (acetylene, ethylene, propylene, butane, benzene).[29]

Comparatively, Megusar irradiated an S-2-glass-fiber epoxy composite with both fast neutrons and gamma irradiation and showed that the hydrogen content decreases with exposure to neutrons—approximately 7% loss of hydrogen per 1 x 10^{18} n/cm^2 fluence.[27] Table 3 is a modified summary from the work reported by Megasar, where H count rate for the expected peak position of hydrogen per prompt gamma neutron activation analysis (PGNAA), and the normalized count rates corrects for hydrogen counts from the background.[27]

Table 3. Hydrogen outgassing for an S-2-glass filled epoxy composite with varying neutron fluence, adapted from Megusar.[27]

Sample Fluence, n/cm^2	Weight, mg	H Count Rate, cps	Normalized Count Rate, cps
Unirradiated	399.4	16.78	11.47
9 x 10^{17}	359.6	16.01	11.88
1.8 x 10^{18}	407.3	15.43	9.92
3.1 x 10^{18}	393.6	14.2	9.02

A review of all Epon 828 epoxy formulations in the Outgassing Database for Selecting Spacecraft Materials Online[30] indicates that in general Epon 828 is considered a low outgassing epoxy. As expected, no outgassing exists for Epon 828-1031/DDS; however, low outgassing materials emit less than 0.1% of collected volatile condensable materials (CVCM). CVCM is defined as the difference in mass of the condensable matter outgassed onto a collector plate compared to a clean collector plate when an epoxy is exposed to a temperature of 125 °C.[30] Only specific formulations which employ Epon 828 are not considered low outgassing species—though these formulations do not include Epon 1031 or DDS. DDS is only present in one Epon based epoxy formulation in the database and has a CVCM of 0.01%, substantially lower than the limits for a low outgassing material. Based on the data present in the NASA database and work performed by Coltman and co-worker[22] and Megusar,[27] there is no outgassing concern for the Epon 828-1031/DDS epoxy.

3. Conclusions

A rigorous review of the open literature concerning gamma and neutron irradiation effects on epoxies suggests that no concerns exist for the Epon 828-1031/DDS system. An overwhelming number of reports discussing epoxy materials, including Epon 828, irradiate to neutron fluences several orders of magnitude greater than the performance environment of Epon 828-1031/DDS, some with more energetic (and therefore more damage inducing) neutrons. Most of these studies exhibited no or minimal change in physical (flexure and compressive strength, adhesion force, etc.) and chemical properties (e.g., glass transition temperature). Furthermore, all of the studies were performed in air—free radical oxidative chemistry induces far more severe degradation to polymers than those in an inert or hermetically sealed environment. An oxygenated atmosphere may also lead to a higher yield in outgassing species, compared to those in an inert or hermetic environment. Albeit, combined temperature and irradiation concerns were not discussed—the expected performance environment of Epon 828-1031/DDS is not particularly aggressive and some of the studies discussed were performed at room temperature or higher. At this time, simultaneous temperature irradiation effects appear to be negligible, but should be considered in future experimental work.

To enhance the veracity of the conclusions made in this report for Epon 828-1031/DDS, future work should include a thorough experimental investigation employing fast neutrons, gamma irradiation, and elevated temperature. This may include identifying changes in T_g (measured by dynamic mechanical analysis—DMA) and adhesion forces (napkin ring specimens) as a function of neutron irradiation dose from a fast neutron source up to a fluence of $\sim 10^{12}$ n/cm^2 (with margin tests up to $\sim 10^{13}$ n/cm^2), a gamma dose of ~500 Gy, and temperature maintained below 200 °C. Dose rate concerns can and should be addressed by irradiating specimens to $\sim 10^{12}$ n/cm^2 over extended periods of time (e.g., 1, 3, 6, or even 12 months).

4. References

(1) Liepins, R.; Wood, L. J.; Tucker, D. S.; Clinard Jr., F. W. *Radiat. Phys. Chem.* **1990**, *36*, 383-391.

(2) Reichmanis, E.; Frank, C. W., Eds.; In *Irradiation of Polymeric Materials: Processes, Mechanisms, and Applications;* American Chemical Society: Washington DC, 1993.

(3) Rivaton, A.; Arnold, J. *Polym. Degrad. Stab.* **2008**, *93*, 1864-1868.

(4) Egusa, S. In *In Effects of neutrons and gamma-rays on polymer matrix composites as low-temperature materials;* Proceedings of an International Symposium on Radiation Chemistry of Polymers, March 29, 1990 - March 31; Tokyo, Jpn, 1991; Vol. 37, pp 147-152.

(5) Klabunde, C. E.; Coltman Jr., R. R. *J. Nucl. Mater.* **1982**, *117*, 345-350.

(6) Blazewicz, S.; Piekarczyk, J.; Chlopek, J.; Blocki, J.; Michalowski, J.; Stodulski, M.; Zychowski, P. *Carbon* **2002**, *40*, 721-727.

(7) Hammouda, B. Probing Nanoscale Structures: the SANS Toolbox. *book available online at: www.ncnr.nist.gov/staff/hammouda/the_SANS_toolbox.pdf* (accessed October 20, 2010).

(8) White II, G. V.; Mohammed, F. S.; Kitchens, C. L. *J. Phys. Chem. C* **2011**, *115*, 18397-18405.

(9) Chin, W.; Hwu, J.; Shau, M. *Polymer* **1998**, *39*, 4923-4928.

(10) McGroarty, J. A. *Ind. Eng. Chem.* **1960**, *52*, 17-18.

(11) Kline, D. E. *J. Polym. Sci.* **1960**, *47*, 237-249.

(12) Al-Attabi, A.; Fouracre, R. A.; Banford, H. M.; Tedford, D. J. *Radiat. Phys. Chem.* **1992**, *40*, 411-19.

(13) Fouracre, R. A.; Al-Attabi, A.; Given, M. J.; Banford, H. M.; Tedford, D. J. In *In Effects on the thermally stimulated discharge-current spectra of a cured epoxy resin system exposed to up to 2 MGy of gamma and neutron radiation;* Proceedings of the 3rd Trilateral Meeting on Radiation Chemistry and Physics of Solids, September 7, 1992 - September 11; Pergamon Press Inc: Lodz, Pol, 1995; Vol. 45, pp 9-15.

(14) Fouracre, R. A.; Banford, H. M.; Tedford, D. J.; Gedeon, S.; Cao, X.; Wu, S.; Fu, L. In *In The effect of gamma-irradiation on the electrical properties of two typical epoxy resin systems;* First Trilateral Meeting on Radiation Chemistry and Physics of Solids, November 7, 1988 - November 10; Publ by Pergamon Press Inc: Pavia, Italy, 1991; Vol. 37, pp 581-588.

(15) Fox, T. G.; Flory, P. J. *J. Appl. Phys.* **1950**, *21*, 581-591.

(16) Anderson, B. J. *Polym. Degrad. Stab.* **2011**, *96*, 1874-1881.

(17) Bernstein, R.; Gillen, K. T. *Polym. Degrad. Stab.* **2010**, *95*, 1471-1479.

(18) Subudhi, M. , Literature Review of Environmental Qualification of Safety-Related Electric Cables NUREG/CR-6384 BNL-NUREG-52480 Vol. 1 **1996**.

(19) Mead, J. W.; Mead, K. E.; Auerbach, I.; Ericksen, R. H. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 158-163.

(20) Bernstein, R.; Thornberg, S. M.; Irwin, A. N.; Hochrein, J. M.; Derzon, D. K.; Klamo, S. B.; Clough, R. L. *Polym. Degrad. Stab.* **2008**, *93*, 854-870.

(21) Coltman Jr., R. R.; Klabunde, C. E. *J. Nucl. Mater.* **1983**, *113*, 268-272.

(22) Coltman , R. R.; Klabunde, C. E. *J. Nucl. Mater.* **1982**, *103*, 717-721.

(23) Fouracre, R. A.; Banford, H. M.; Tedford, D. J.; Cao, X.; Gedeon, S. *Radiat. Phys. Chem.* **1991**, *37*, 589-597.

(24) Gillen, K. T.,Assink, R. A.,Bernstein, R., Nuclear Energy Plant Optimization (NEPO) Final Report on Aging and Condition Monitoring of Low-Voltage Cable Materials Sandia National Laboratories, SAND2005-7331 **2005**.

(25) Huang, H. C.; Peng, K. C.; Sahu, S. K.; Ueno, K.; Chang, Y. H.; Wang, C. H.; Hou, W. S. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1997**, *385*, 559-560.

(26) Imel, G. R.; Kelsey, P. V.; Ottewitte, E. H. *J. Nucl. Mater.* **1979**, *85-86, Part 1*, 367-371.

(27) Megusar, J. *J. Nucl. Mater.* **1996**, *230*, 233-241.

(28) Egusa, S.; Kirk, M. A.; Birtcher, R. C. *J. Nucl. Mater.* **1984**, *126*, 152-159.

(29) Coltman, R. R., Jr.,Klabunde, C. E.,Kernohan, R. H.,Long, C. J. , Radiation Effects on Organic Insulators for Superconducting Magnets. Annual Progress Report for Period Ending September 30, 1979 Oak Ridge National Laboratories, TNORNL TM-7077 **1979**.

(30) Viens, M. J. Outgassing Database for Selecting Spacecraft Materials Online *http://outgassing.nasa.gov/* (accessed 11/28, 2011).

Distribution List

3	MS 0888	Gregory Von White II, 01821
3	MS 0888	Robert Bernstein, 01821
1	MS 0888	James R. McElhanon, 01821
1	MS 0889	James M. Hochrein, 01825
1	MS 0614	Manuel M. Contreras, 02547
1	MS 0614	Tri Q. Trinh, 02547
1	MS 0614	William B. Chambers, 02547
1	MS 0958	Benjamin J. Anderson, 01833
1	MS 0899	Technical Library, 9536 (electronic copy)

Sandia National Laboratories