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Light Water Reactor Sustainability Program

Progress in Characterizing Thermal Degradation of Ethylene-Propylene Rubber

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Date

SUMMARY

Ethylene-propylene rubber (EPR) is one of the two most common nuclear cable insulation materials. A large fraction of EPR-insulated cables in use in the nuclear industry were manufactured by The Okonite Company. Okoguard® is the name of the medium voltage thermoset EPR manufactured by The Okonite Company. Okoguard® has been produced with silane-treated clay filler and the characteristic pink color since the 1970's. EPR is a complex material that undergoes simultaneous reactions during thermal aging including oxidative and thermal cleavage, and oxidative and thermal crosslinking. This reaction complexity makes precise EPR service life prediction from accelerated aging using approaches designed for single discreet reactions such as the Arrhenius approach problematic. Performance data and activation energies for EPR aged at conditions closer to service conditions will improve EPR lifetime prediction. In this report pink Okoguard® EPR insulation material has been thermally aged at elevated temperatures. A variety of characterization techniques have been employed to track material changes with aging. It was noted that significant departure in EPR aging behavior seemed to occur at accelerated aging temperatures between 140°C and 150°C at around 20 days of exposure. This may be due to alternative degradation mechanisms being accessed at this higher temperature or to the need for longer aging times at lower temperatures to see the same effect. These results reinforce the need to perform accelerated aging for Okoguard® EPR service life prediction at temperatures below 150°C for exposure times much more than 20 days.

ACKNOWLEDGEMENTS

Plaques of press cured Okoguard® medium voltage compound and information on EPR testing and qualification at The Okonite Company were generously provided by Carl Zuidema and E.J. Bartolucci of The Okonite Company.

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ACRONYMS

AJC	Okoguard® Aerial Jumper Cable (15kV – 90°C Rating), Catalog Number 303-21-1944
CSPE	chlorosulphonated polyethylene
DSC	differential scanning calorimetry
EAB	elongation at break
EMDA	Expanded Materials Degradation Assessment (NUREG/CR-7153)
EPR	ethylene-propylene rubber
EPDM	ethylene-propylene-diene M-type (ASTM D1418, 2010)
FWIII	Firewall® III
FTIR	Fourier-transform infrared spectroscopy
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronics Engineers
IM	indenter modulus
NPP	nuclear power plant
OIT	oxidation induction time
OITP	oxidation induction temperature
XLPE	cross-linked polyethylene

INTRODUCTION

Ethylene-propylene rubber (EPR) materials represented more than one third of all low-voltage qualified, in containment cable insulation entries in a 1994 survey of US nuclear power plants (NPPs) [EPRI TR-103841]. The Okonite Company was noted to be the second most common EPR insulation manufacturer with Okonite-produced cable entries found in 26 of 2016 plants, following only Anaconda Wire and Cable, with cables in 35 plants. The Okonite Company currently produces two EPR-type insulation materials for the nuclear industry: Okoguard®, a premium thermoset EPR medium voltage (5 kV and above) insulation, and Okonite FMR-N, a thermoset low voltage flame, moisture and radiation resistant EP insulation [Okonite Cables brochure]. Okoguard® is used in medium voltage cable with either chlorinated polyethylene (CPE) or chlorosulphonated polyethylene (CSPE) jacket [NEI 06-05]. Black EPR, containing calcined clay filler, began to be replaced with water-enhanced aging-resistant pink EPR, containing silane-treated clay filler, in the 1970s [EMDA vol5, NEI 06-05]. EPR insulation was indicated to be more susceptible to thermal-only damage, in the absence of gamma radiation, than cross-linked polyolefin (XLPO) insulation [EMDA vol5, NEI 06-05].

The Expanded Materials Degradation Assessment, Volume 5, "Aging of Cables and Cable Systems" (EMDA) [NUREG/CR-7153] reflects that despite the common use of the Arrhenius relationship to predict long-term performance from the results of accelerated aging, the approach is well-suited only for materials and conditions for which the same degradation reactions occur at both the elevated accelerated aging temperatures and at service temperatures. If degradation mechanisms differ under different exposure conditions, then the accuracy of prediction of one using the other is diminished. Certain polychloroprene (neoprene) and chlorosulphonated polyethylene (CSPE) jacket materials have been observed to exhibit different activation energies (E_a) at lower aging temperatures than they exhibit at higher temperatures [Gillen, *et al* 2005] This observation has raised the potential concern that material lifetime may be overestimated using the Arrhenius approach with too high of temperatures used for accelerated aging. The EMDA concluded that, particularly in the context of the complex thermal aging behavior exhibited by some EPR materials, insufficient lower-temperature aging data exist to confirm the presence or importance of non-Arrhenius behavior in EPR. Determination of EPR E_a for temperatures below 100°C using sensitive degradation detection methods was suggested as a target for further research.

In their Environmental Qualification Report for Okoguard Insulated Cables [NQRN-3], first report revision produced in 1982 and fourth report revision produced in 1988, a discussion of The Okonite Company's position and approach for longevity demonstration for 90°C-rated materials including pink EPR Okoguard® insulation is provided. Limitations of the Arrhenius approach to predicting EPR lifetime are presented therein, including the fact that thermal aging of EPR involves at least four simultaneous reactions—1) oxidative cleavage, 2) oxidative crosslinking, 3) thermal cleavage, and 4) thermal crosslinking—rather than a single, discreet chemical reaction with a single rate constant and activation energy. A straight line in a plot of the logarithm of the reaction rate of EPR thermal degradation versus reciprocal temperature is described as fortuitous, rather than having physical meaning or to be expected. Arrhenius lifetime predictions at mild temperatures from accelerated extension data at higher temperatures for material examples including Okolite (natural rubber oil-based insulation), natural rubber, and butyl rubber were found to be much lower than actual experimental data reflected. Other observations include the reflection that lifetime of insulation, as defined by 40% elongation retention, was greater for insulation aged in finished cable form rather than apart from multiple conductors and jacket as bare single conductors. Also, though they differ in formulation, the various EPR materials trend with essentially identical logarithm-of-time versus reciprocal temperature slopes.

The EPR insulations investigated in this report consist of pink Okoguard® EPR from Aerial Jumper Cable (AJC) and pink Okoguard® medium voltage material in pressed sample slabs provided directly by The Okonite Company. It is assumed that the aging and degradation of the material considered herein is similar to that of pink Okoguard® EPR present in cables installed in NPPs since the early 1970s and relevant to black Okoguard® EPR installed in NPPs before and after that time.

Degradation of EPR specimens described here was accomplished through accelerated thermal aging using advanced protocol forced-convection laboratory ovens [ASTM D5423-14, ASTM 5374-13, IEC 60216-4-1] in the absence of gamma or UV irradiation. The majority of the specimens, including all plaque specimens, were individually hung by hooks to allow free air flow around them or sandwiched on rack. Certain cable-derived specimens were aged lying flat, sandwiched between racks to prevent curling during heating. Aging temperatures explored with partial and complete datasets included here are 60°C, 90°C, 115°C, 130°C, 140°C, and 150°C. Techniques used to observe changes in the EPR material with exposure time include tensile elongation at break, oxidation induction temperature, Fourier-Transform Infrared spectroscopy, gel/swell analysis, dynamic mechanical analysis, and indenter modulus. Characteristic signals from these techniques were seen to track with exposure temperature and time.

ETHYLENE-PROPYLENE RUBBER (EPR) SOURCE MATERIALS

EPR used in this study consisted of "pink" medium voltage Okoguard® insulation. In the first instance, EPR specimens were obtained from Okoguard® Aerial Jumper Cable (AJC) (15kV – 90°C Rating) (15kV – Okoguard Insulation: #4/0 AWG, 210 mils, Catalog Number 303-21-1944) using the following method. AJC was cut into ~4-inch lengths through the conductor using an horizontal table saw. Insulation was manually cut from the conductor into ~0.8-inch wide strips using a box cutter. The interior of the strips retain black semiconductor layer residue and undulating features from being molded onto the underlying conductor. Strips were prepared into standard tensile "dog bone" or "dumbbell" shapes using a Tensilkut tabletop router with specimen template. AJC was purchased from The Okonite Company through a local distributor. AJC Okoguard® insulation is assumed to be similar to that used in cables such as Okoguard®-Okolon® TS-CPE Type MV-105 15kV Shielded Power Cable.

In the second instance, EPR specimens were obtained from nominally 6-inch by 8-inch by 0.060-inch, press cured plaques of Okoguard® medium voltage insulation compound. Each plaque was crosslinked under heat and pressure in the laboratory using factory-produced compound. Tensile "dog bone" or "dumbbell" shaped specimens were stamped from the EPR plaques using a standard ratio NAEF punch. Strips of 0.125-inch width were also cut from the plaques using a razor blade and cutting mat. The plaques were generously provided to this research program by The Okonite Company's Materials Research Laboratory.

THERMAL AGING

EPR test specimens were prepared from source material prior to thermal exposure so as to avoid material damage during specimen preparation after aging. All stamped and cut specimens from the press cured plaques were hung from hooks or clamps during aging in forced-air convection ovens. Routed specimens from the AJC were aged in forced-air convection ovens either hung from hooks, or sandwiched between racks. Specimens were aged in advanced protocol ovens with good temperature uniformity and flowing air to prevent local regions of oxygen depletion [IEC 60216-1, ASTM D573].

INDICATORS OF AGED CONDITION

EAB is the standard metric of degradation state for elastomers including EPR [IEC/IEEE 62582-3, ASTM D412]. EPR elongation-to-break (strain-to-break) is defined as the ratio of specimen (gauge section) length when it fails as specimen ends are pulled apart, to the starting specimen (gauge section) length. As a measure of sample age, EAB can either be expressed as an absolute value, or as a percentage of the EAB value of the unaged specimen—retained EAB. The latter may be more meaningful as a general value for comparing material age since original EAB of unaged materials varies significantly between materials and, despite attempts at use of standard methods, absolute EAB values may be somewhat dependent on equipment used to measure it.

Several methods were used to track changes in EPR specimens with exposure to 140°C. The results from these methods were normalized based on values of the initial unaged material for plotting together in Figure 1. Some quantities such as EAB and indenter modulus are observed to undergo an induction period before experiencing a rapid change while others, such as mass loss, are observed to change less and less significantly over time. Specimen density and oxidation induction temperature may represent quantities that change consistently over the full range of EPR life. End of service life for Okoguard® EPR, as defined by The Okonite Company for EAB that is 40% of the unaged value, is indicated in the figure.

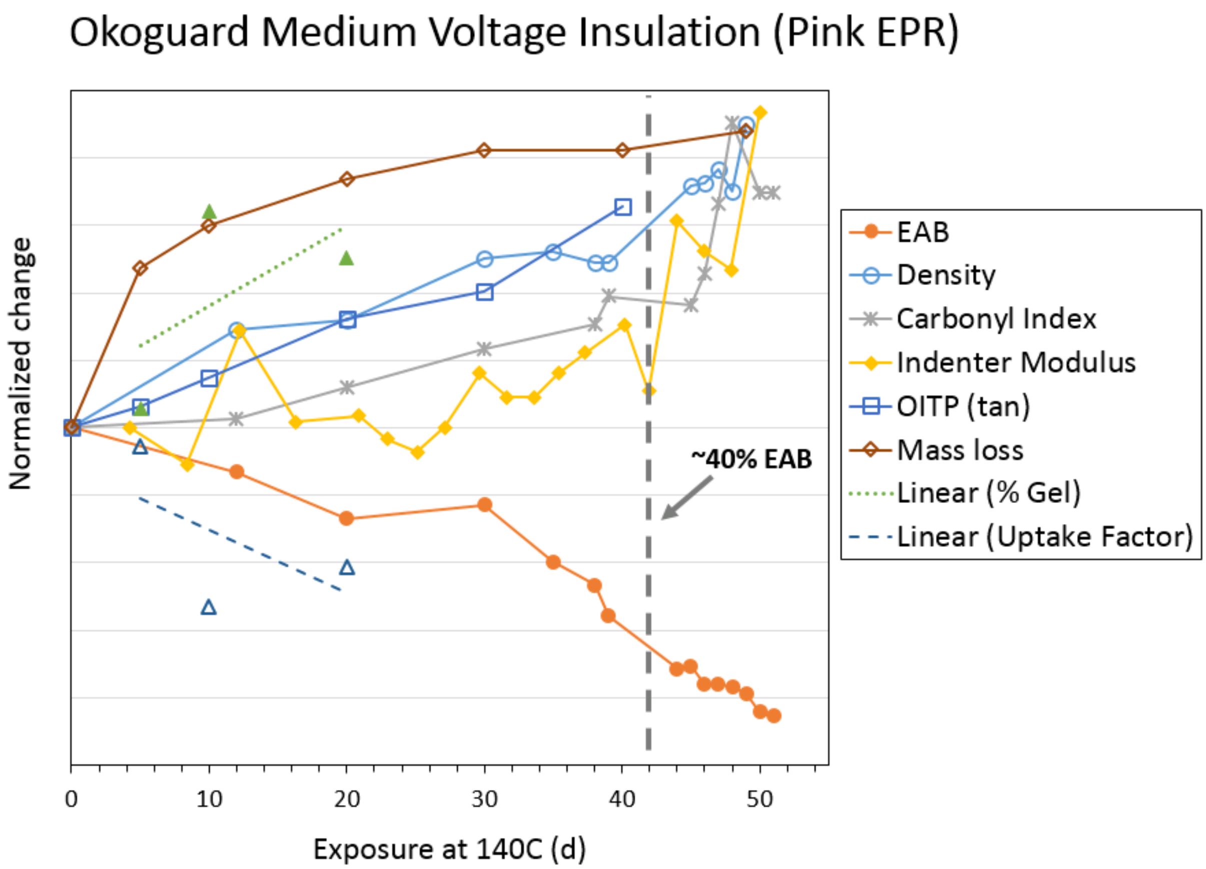

Figure 1. Correlation of normalized aging metrics for EPR at 140°C.

INDICATION OF TEMPERATURE DEPENDENT MECHANISMS?

Oxidative damage from thermal exposure of polyolefins, including polyethylene and polypropylene, may be tracked with Fourier-transform infrared spectroscopy (FTIR) using a figure of merit known as carbonyl index (CI). CI is defined here as the ratio of absorption values as the ~1710 cm^{-1} stretch corresponding to the C=O bond, and the ~2850cm^{-1} stretch corresponding to C-C bond. In Figure 2 the carbonyl indexes of EPR specimens aged for 20 days at various temperatures are plotted. The plotted curve appears to be bi-modal, increasing nearly linearly from 60°C to 140°C, before rising rapidly at 150°C.

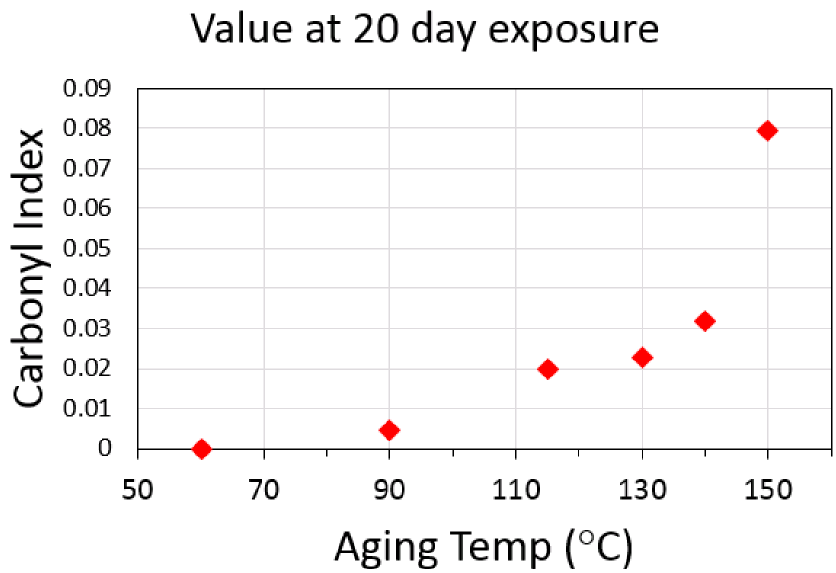

Figure 2. Carbonyl index at 20 day exposure to various temperatures.

The EPR CI with exposure time for a series of temperatures is plotted in Figure 3. CI is seen to increase nearly linearly with exposure time at temperatures of 140°C and below. The same data is plotted in Figure 4 at a different scale to reveal the rapid departure of this linear behavior by EPR exposed at 150°C.

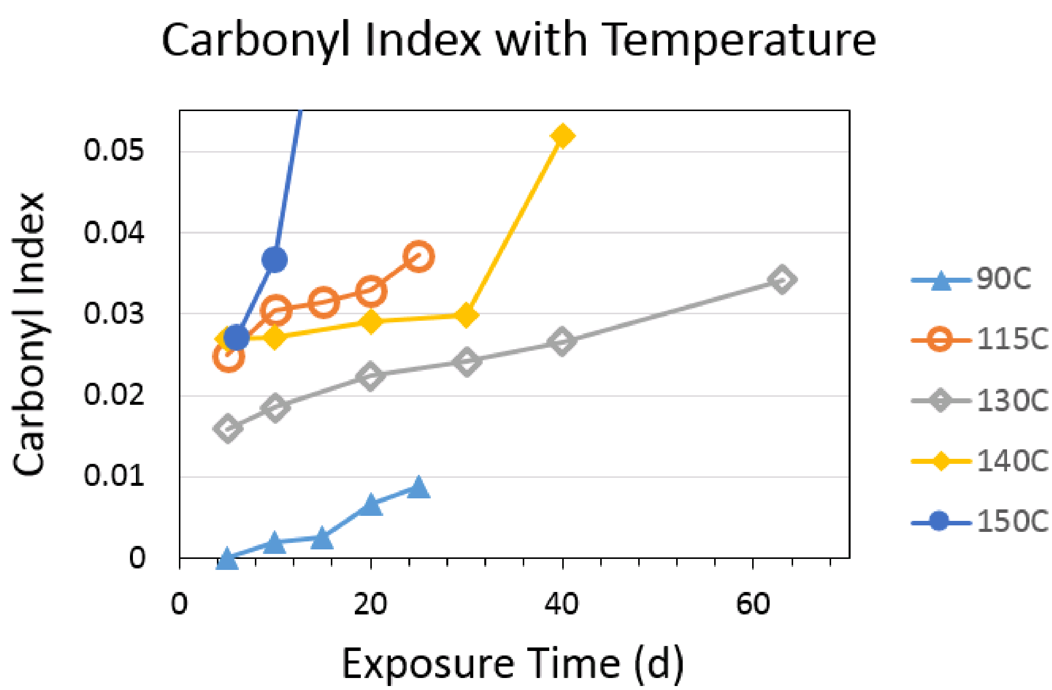

Figure 3. Carbonyl index versus exposure time for various temperatures, zoomed in.

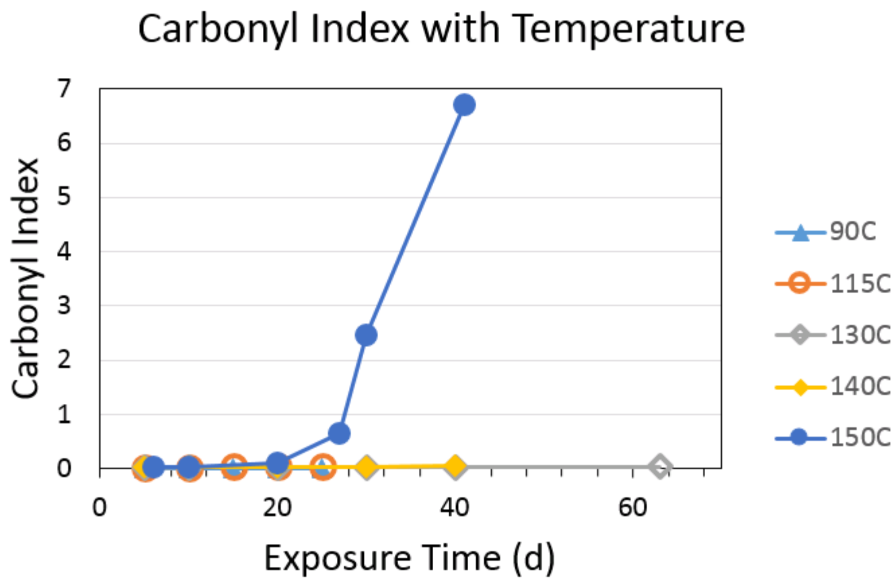

Figure 4. Carbonyl index versus exposure time for various temperatures, zoomed out.

Oxidation induction temperature (OITP) is the temperature at which exothermic transitions occur when heating a rubber specimen in air. The temperature of the OITP is observed to decrease linearly with exposure time in Figure 5 for EPR heated at 130°C and 140°C. The OITP curve for 150°C aging of EPR, however, exhibits an abrupt change in direction and begins increasing at 20 days of exposure. This may be evidence of chemical reactions that are only accessed at this higher temperature. An alternative explanation might be that the aging curves for the lower temperatures will exhibit similar departures as the 150°C aging, but the exposure times at which these transitions occurs have not be reached in the present experiments. Future research will investigate longer aging times of EPR at lower temperatures to identify if CI data point to similar oxidation behavior. This will help to confirm the presence of distinct degradation mechanisms.

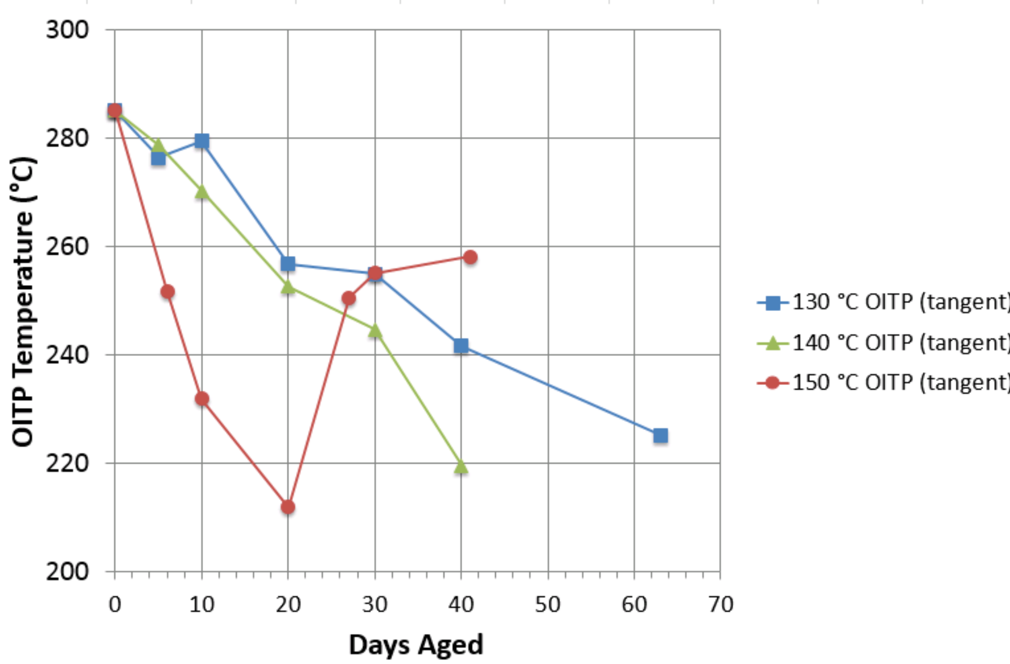

Figure 5. OITP curves for EPR aged at 130°C, 140°C and 150°C.

Dynamic mechanical analysis (DMA) is a technique that we use here to monitor the tensile response of an EPR specimen to an oscillating applied force as a function of temperature. The out-of-phase (loss) and in-phase (storage) response of the material, and the ratio of these two (tan delta or dissipation factor) with applied temperature can reveal phase transitions and differences in materials between specimen with different thermal histories. Similar to the CI and OITP data portrayed above, the storage modulus data at 23°C of EPR aged for various times at 130°C, 140°C and 150°C and plotted in Figure 6 show a distinct departure in trend for the 150°C data after 20 days exposure. The peak loss modulus temperature plotted in Figure 7 show a similar bimodal before for 150°C data above 20 days aging as other data sets above. Unlike the other data, however, this plot shows one data point at 50 days of 140°C exposure that may support the explanation that the 150° C degradation behavior not seen at lower temperatures may occur at those temperatures given sufficient exposure time. Interestingly, the tan delta peak temperatures, representing the ratio of loss modulus to storage modulus, shown in Figure 8 seem to track monotonically with exposure time for all three temperatures explored.

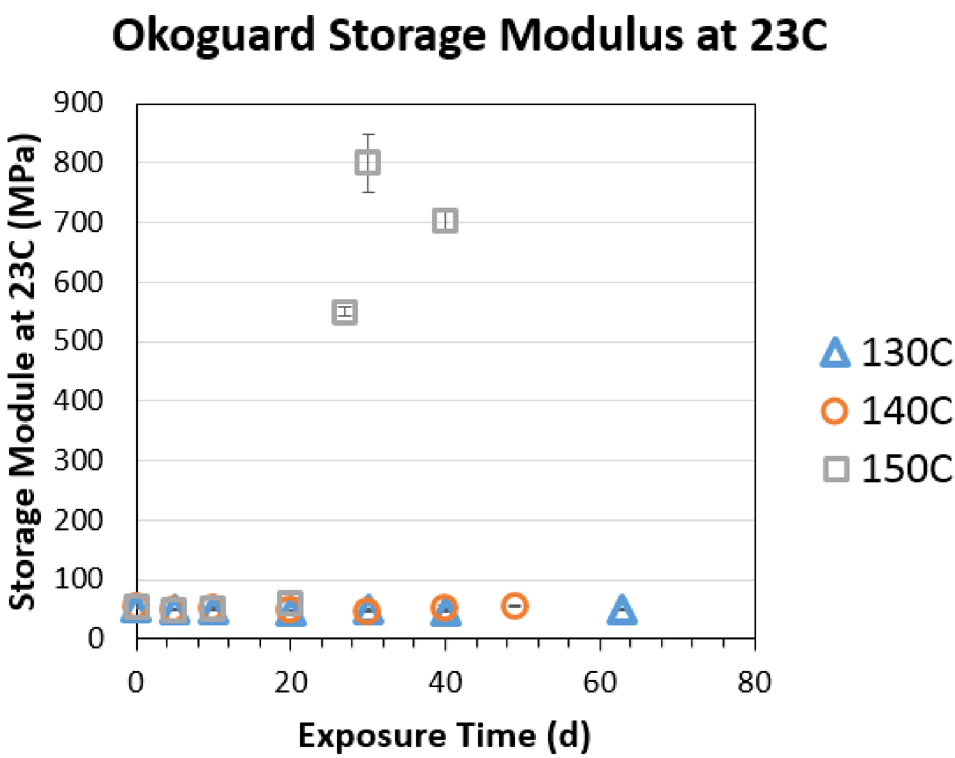

Figure 6. Storage modulus at 23°C for EPR aged at 130°C, 140°C and 150°C.

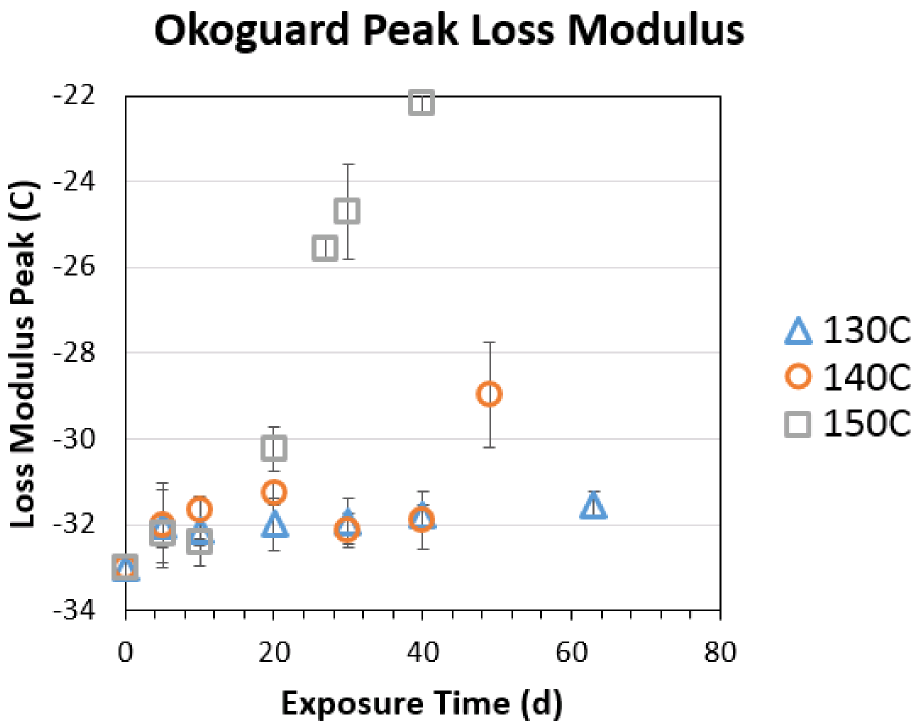

Figure 7. Loss modulus peak temperature for EPR aged at 130°C, 140°C and 150°C.

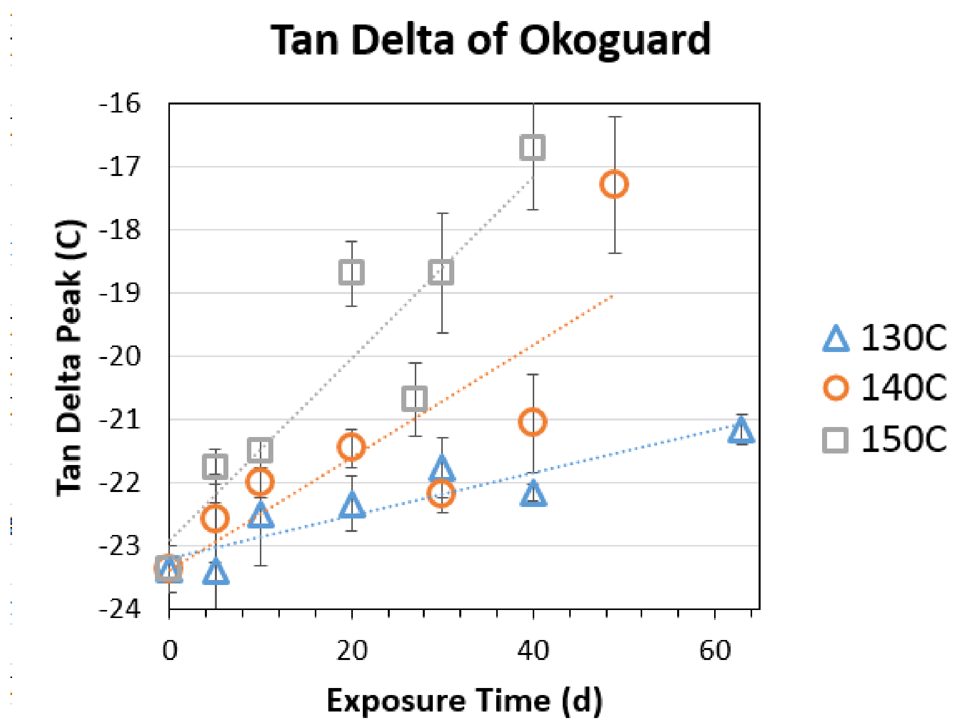

Figure 8. Tan delta (dissipation factor) peak temperature for EPR aged at 130°C, 140°C and 150°C.

CONCLUSION

EPR is a commonly found insulation material in nuclear power plants and understanding EPR degradation under long-term service conditions is important for cable aging management. Concerns have been raised regarding simple extrapolation of accelerated aging results for EPR to predict extended performance such as the Arrhenius approach that assumes a single discreet degradation reaction. Further study of EPR aging at temperatures closer to service temperatures using sensitive techniques to track early stages of degradation have been suggested. In this report we explore and demonstrate some of the variety of methods available to track material changes in EPR with thermal aging, including techniques that track continuously from early stages such density and OITP. Using DMA, OITP and CI we have observed stark differences in degradation of EPR materials aged at 150°C at around 20 days from those aged at lower temperatures and shorter times. This may be due to the appearance of unique degradation mechanisms above this temperature threshold. This would confirm the need to perform accelerated aging at temperatures below 150°C for times beyond around 20 days. An alternative explanation to the presence of different chemical degradation mechanism at 150°C for Okoguard® EPR is that the lower temperatures explored herein require longer aging times than have been explored to exhibit the same behaviors. Investigation of longer EPR aging at lower temperatures using the methods described here, including CI, DMA, and OITP, will help to confirm distinctions between degradation mechanisms at higher and lower temperatures.

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