Light Water Reactor Sustainability Program

Investigation of Thermal Aging Behavior for Harvested Crosslinked Polyethylene and Ethylene-Propylene Rubber Cable Insulation

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SUMMARY

This Pacific Northwest National Laboratory (PNNL) milestone report describes investigation of the effects of accelerated thermal aging on two representative examples of low voltage electrical instrument cable insulation commonly found in nuclear power plants in the United States: Brand-Rex Ultrol cross-linked polyethylene (XLPE) and Anaconda Flame Guard ethylene-propylene rubber (EPR). The materials were harvested from Crystal River Unit 3 following 30 years of service for the Anaconda cable in the reactor coolant system and 21 years of service for the Brand-Rex cable in the main feed water service system.

Insulation samples extracted from the harvested cables were aged at 165°C, 150°C, and 136°C for up to 10 days, 30 days, and 41 days, respectively. Testing of intermediately aged samples was performed to determine mass change, elongation at break (EAB), indenter modulus, carbonyl index, and density as a function of aging temperature and aging time. While each of these measures was seen to trend with insulation material aging, mass change and indenter modulus were found to track most directly with aging and exhibit the least amount of scatter among the methods investigated for both the EPR and the XLPE materials considered.

Notably, the as-received Anaconda EPR insulation tested above 200% EAB and the as-received Brand-Rex XLPE insulation test around 350%, suggesting that the cables are not near their end of useful life despite their decades of service. Aging of the cable materials is currently underway at 121°C and analysis of data following further aging will enable estimation of the remaining useful life of these cables in the context of their qualified forty year life and the additional twenty and forty year periods that would be associated with the cables if they were installed in a plant seeking license renewal and subsequent license renewal.

ACKNOWLEDGMENTS

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ACRONYMS AND ABREVIATIONS

AWG	American wire gauge
CI	carbonyl index
CM	condition monitoring
CR3	Crystal River Unit 3
CSPE	chlorosulphonated polyethylene (Hypalon)
DOE	U.S. Department of Energy
EAB	elongation-at-break
EPR	ethylene propylene rubber
EPRI	Electric Power Research Institute
FRF	flame/fire retardant
FTIR	Fourier Transform Infrared Spectroscopy
IEC	International Electrotechnical Commission
IEEE	Institute of Electrical and Electronic Engineers, Inc.
IM	indenter modulus
IPAM	Indenter Polymer Aging Monitor
LWRS	Light Water Reactor Sustainability
mADC	milli Amps Direct Current
NDE	non-destructive evaluation
NPP	nuclear power plant
NRC	U.S. Nuclear Regulatory Commission
PNNL	Pacific Northwest National Laboratory
SLR	subsequent license renewal
XLPE	cross-linked polyethylene

1. INTRODUCTION

Over 80% of the hundreds of miles of electrical cable in a nuclear power plant (NPPs) is low voltage instrument and control (I&C) cable [1]. Moreover, one third (33%) of U.S. NPPs use Anaconda Y Flame-Guard FR brand cable with ethylene-propylene rubber (EPR) insulation inside their containment building and a similar number of plants (28%) use Brand-Rex cables with cross-linked polyethylene (XLPE) inside containment [1]. In fact, only Rockbestos Firewall III cable is more commonly found than these two. As leading NPPs begin to apply for subsequent license renewals (SLR) to operate for up to eighty years since original start-up, it is important to understand changes that occur to commonly found cable insulation materials in long term operation and methods to assess the health of cables in use to inform retest, repair, and replace decisions.

Harvested cables, i.e. cables that have been removed after being in service in operating NPPs, provide a unique opportunity to test assumptions regarding the effects of service operating and environmental conditions on cable materials. With assistance from the Electric Power Research Institute (EPRI), PNNL was able to obtain harvested cables from the decommissioned Crystal River Unit 3 (CR3) reactor [2] representing six of the eight most common cable manufacturers [1]. This resource provides both a snap shot of cable condition following actual service in a pressurized water reactor and a source of vintage cable materials relevant for SLR that are no longer manufactured nor easily obtainable for study.

A series of experiments are planned and underway at PNNL to utilize the valuable resource of these harvested cables to address the knowledge gaps previously identified in relation to electrical cables and SLR [3]. These include accelerated aging at elevated temperatures, aging with gamma irradiation, combined simultaneous exposure to thermal and radiation aging, and a wide range of mechanical, chemical, physical and electrical test and characterization methods. Thermal aging at a series of temperatures and characterization of the representative materials, a portion of which is reported here, is addressing knowledge gaps associated with the temperature dependence of calculated material degradation activation energies used for lifetime prediction and the importance of identified artefacts associated with accelerated aging such as diffusion limited oxidation.

2. MATERIALS

The Brand-Rex XLPE cable studied in this work, PNNL ID# XC25, was manufactured in 1986 and installed in the CR3 main feed water system in 1994. It was designated as 'maintenance rule', but not 'safety-related'. The cable jacket is labeled "BRAND-REX ULTROL INSTRUMENTATION CABLE 600V 1 SHIELDED PR #16 AWG 23XXX". As seen in Figure 1, it is constructed with a black CSPE overall jacket and two XLPE-insulated, 16-gauge conductors: one white and one black. It is 600V-rated cable, but operated at 24 VDC, with operational current of 4-20 mADC and 100% duty factor. The results described herein are for the white insulation, PNNL ID# XX28.

Figure 1. The Brand-Rex Ultrol 600V, shielded #16 gauge instrumentation cable

The Anaconda EPR cable studied in this work, PNNL ID# AC19, was manufactured in 1985 and installed in the CR3 reactor coolant system in the same year. It was designated as 'safety-related' and 'maintenance rule'. The cable jacket is labeled "ANACONDA-Y 4/C #16 FLAME-GUARD FR-EP 600V". It is constructed with a green, chlorosulfonated polyethylene (CSPE) overall jacket, seen in Figure 2, and four EPR-insulated, 16-gauge conductors: white, red, black, and green. It is 600V-rated cable, but had an operational voltage of 5 VDC and operational current less than 5 mADC with a 100% duty factor. The results described herein are for the white insulation, PNNL ID# AE21.

Figure 2. The Anaconda-Y 4/C #16 Flame-Guard FR-EP 600V cable components.

3.   METHODS

Specimens suitable for tensile testing, insulation 'straws' with metal conductor removed from the center of the insulation, were prepared from the received cable prior to thermal aging. Briefly, the overall jacket and fillers, wraps, etc. were carefully removed to expose the insulated conductors. One hundred millimeter length of insulated conductor were cut and aged for use for indenter measurements. The remaining insulated conductor was held in a vise while 50 mm or 100 mm length of insulation were removed in single 'straw' pieces using grips to strip the insulation from the bare conductor.

Specimens thus obtained were measured to determined initial mass and given a unique identification number labeled on a small clamp attached to each. Samples were hung by the clamp and a hook to freely suspend them during thermal aging. Samples were loaded in sets into digitally monitored, advanced protocol mechanic convection ovens at settings of 165°C, 150°C and 136°C. Each set included a 'with conductor' specimen and three 100 mm or five 50 mm straws. Sets were removed from the oven over time to produce series of specimens with increment aging to investigate insulation material changes with aging

3.1   Mass Change

After each sample set was removed from the oven, for example each week, and allowed to cool, the after-aging masses of the specimens were determined using an analytical balance. Though impractical for tracking aging of an installed cable, mass change of cable insulation specimens with exposure is a sensitive method to follow material degradation. Mass change with aging can be used to calculate activation energies of materials and thereby to predict rates of material change at untested temperatures [4].

3.2   Elongation at Break

Tensile EAB measurements were performed following guidance found in IEC/IEEE 62582-3 [5]. Specimens were tested with a Chatillon LF Plus Series digital testing machine. Samples were marked with a black felt pen to indicate a 15 mm gauge length, and then were loaded into grips to be tightened at 40 in. lb. using a torque screwdriver. Nexygen Software was used to enact a pull-to-break test with a pull speed of 50 mm/min, gauge length of 15 mm, and break condition of load dropping to 50%. Since the samples were of hollow cable geometry, end tabs were placed at each end (material of end cap depended on material of sample) before loading the sample to reduce stress concentration at the grips. A ruler placed adjacent to the grips, and a video camera was used to record the elongation. Canvas software was utilized to determine the length of the sample before and after the elongation.

3.3   Intender Modulus

Indenter modulus is a technology developed by EPRI [6] and is currently the most common method to quantify local degradation of cable installed in NPPs. The method consists of loading a section of accessible cable into the grip of a portable instrument. A small probe from the instrument contacts the cable exterior and records the force required to compress the surface in units of N/mm. This measure of compressibility of the cable exterior, usually the overall jacket, may be used to infer the state of the insulation inside of the intact cable.

Specimens were tested with an Ogden Indenter Polymer Aging Monitor IPAM2. Specimens were tested at five equidistant points along the length of the sample. The instrument measures the modulus at each point by using a probe to press against the sample, and then the average of the five points is reported as the modulus of that sample.

3.4 Carbonyl Index

Thermally-induced oxidation of the cable insulation polymer is manifest as changes in chemical bonding, breaking of C-C bonds and formation of C-O bonds, on the surface of the material observable using attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR). FTIR spectra were recorded over a range from 500-4000 cm^{-1} with a resolution of 8.0 cm^{-1} and 64 scans, using a Nicolet iS10 spectrometer (Thermo Scientific, Waltham, MA, USA). To measure absorbance of a peak the height tool of OMNIC software was used after baseline correction. The chemical changes due to oxidation are tracked through definition of a quantity termed 'carbonyl index' [7], defined as the ratio of the magnitude of FTIR absorption at wavenumber corresponding to C=O carbonyl stretching, 1740 cm^{-1}, to the wavenumber corresponding to –CH$_2$-CH$_2$- methylene-methylene stretching:

$$Carbonyl\ Index = \frac{A_{C=O}}{A_{C-H}} = \frac{A_{1715cm-1}}{A_{2850cm-1}}$$

3.5 Density

The density of insulation material changes due to polymer chain scission, crosslinking, and related processes that occur during thermal exposure. Density measurements were conducted according to the Archimedes method with a Sartorius (YDK 01) density determination kit. To avoid bubble formation when immersing polymer samples in water at $23.0°$C, samples were dipped in ethyl alcohol and wiped with a piece of paper before immersing into deionized water. Density calculation were as follows:

$$Density = \frac{Mass\ (g)}{Volume\ (cm^3)}$$

$$\rho = \frac{W_a}{V_s} = \frac{W_a}{V_{fl}} = \frac{W_a - \rho_{fl}}{W_a - W_{fl}} = \frac{W_a \cdot \rho_{fl}}{G}$$

$$\rho = \frac{W_a \cdot [\rho_{fl} - \rho_a]}{G \cdot Corr} + \rho_a$$

$$\rho = \frac{Wa(\rho_{fl} - 0.001192)}{0.99983G} + 0.00119278\ g/cm^3 \text{ at } 23.0°C$$

ρ : density of a solid

ρ_{fl} : density of the liquid, 0.99756 at $23.0°$C for water

W_a ; weight of the solid in air

ρ_a ; air density (buoyancy), 0.00119278 g/cm^3 at $23.0°$C

$G = W_a - W_{fl}$: buoyancy of the immersed solid

Corr = 0.99983 (buoyance correction factor): wires of the sample holder (d=0.7 mm) and liquid volume (beaker d=76 mm).

4. Results

4.1 Mass Change

After a brief initial period, not clearly visible in the higher temperature data traces since it occurs before the first sampling, the mass change is seen to proceed linearly with negative slope proportion to aging

temperature. The relatively low scatter in the mass change data of both cable insulations observed in Figures 3 and 4 suggest the possibility of using mass change condition monitoring (CM) for calculation of activation energy, especially following the collection of data at one or more temperature closer to service temperature (e.g. 121°C).
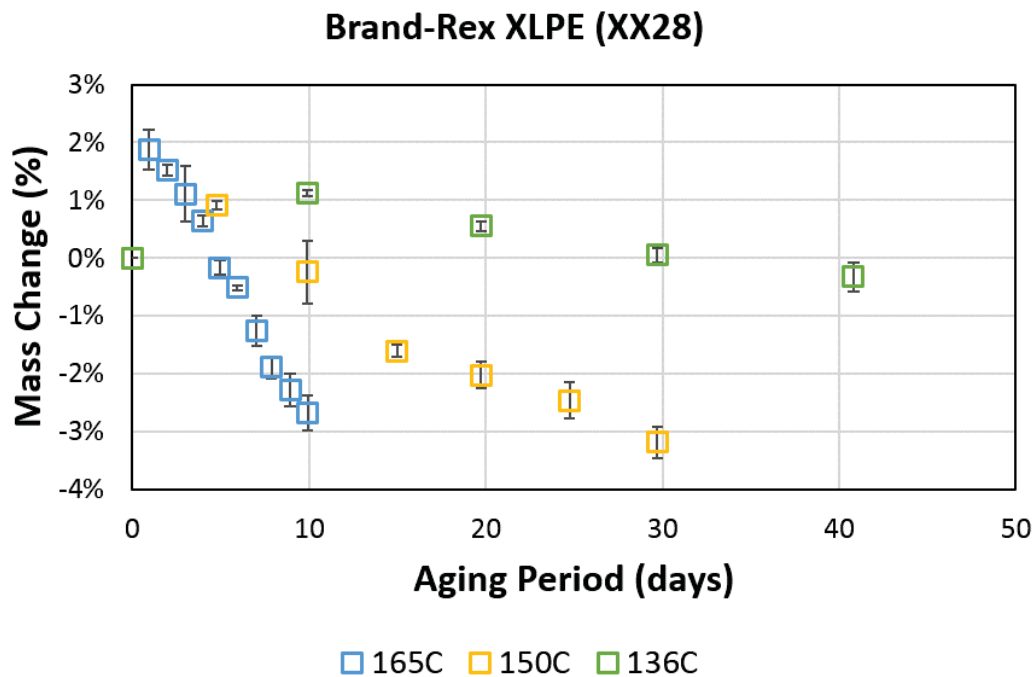
Brand-Rex XLPE (XX28)

Figure 3. EAB data of Brand-Rex XLPE aged at three temperatures
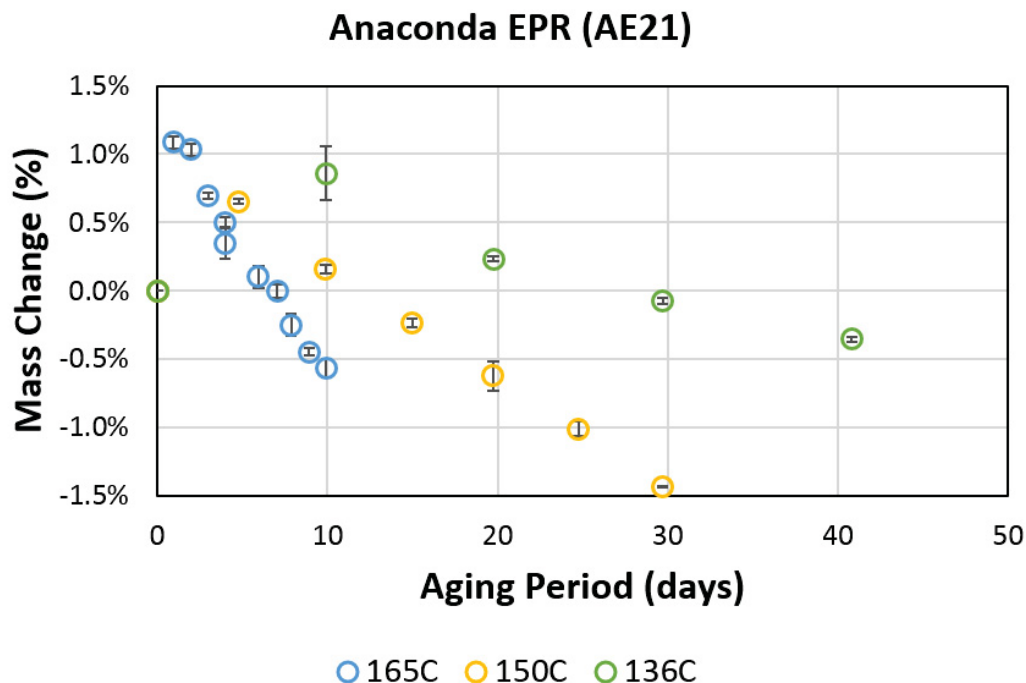
Anaconda EPR (AE21)

Figure 4. EAB data of Anaconda EPR aged at three temperatures

4.2 Elongation at Break

EAB is the quintessential measure of degradation in elastomeric materials and often used as the metric for cable insulation condition. EAB, especially for EPR, frequently exhibits a characteristic aging curve consisting of an initial plateau period with little change in the EAB value, known as the induction period, followed by a rapid decrease in EAB with leveling out near zero. The EAB data obtained for the Brand-Rex XLPE and Anaconda EPR materials plotted in Figures 5 and 6, however, do not exhibit this behavior, but rather trend linearly downward following initiation. Furthermore, the EAB data recorded is relatively noisy and with low linear correlation value compared to the mass change data above.
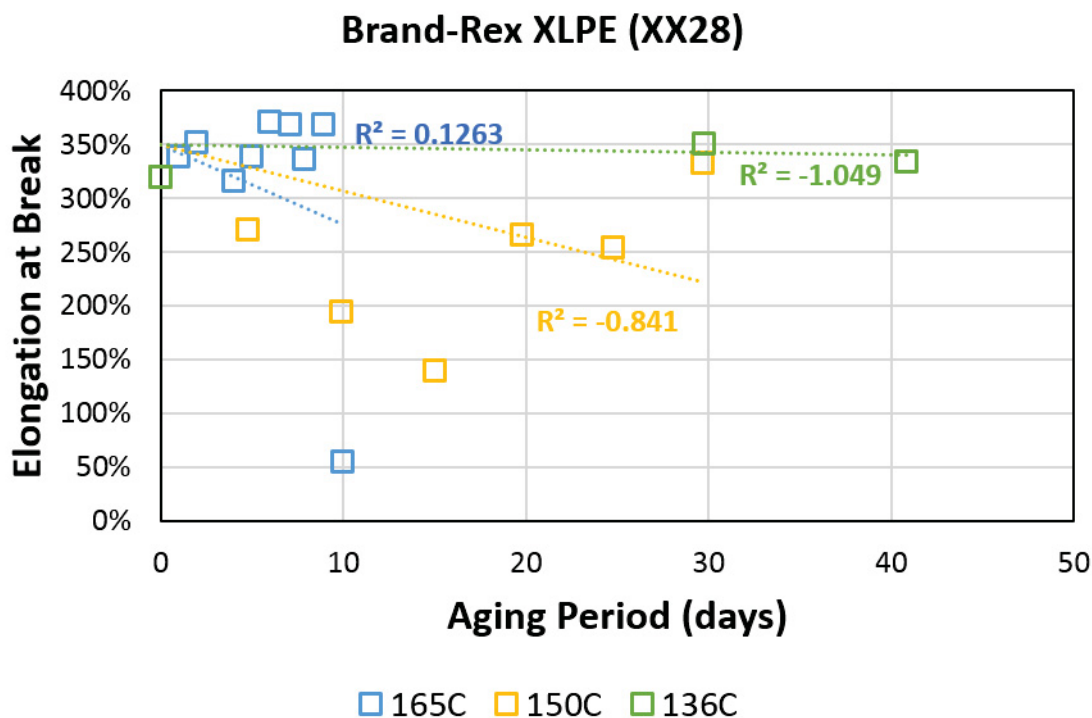
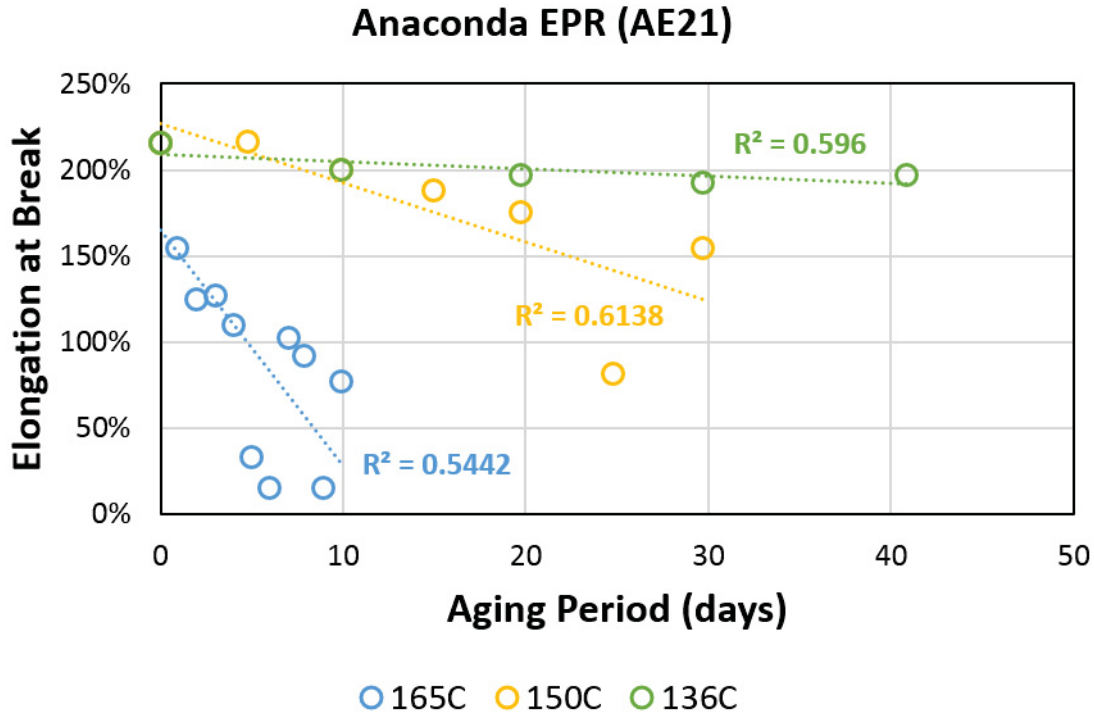Figure 5. EAB data of Brand-Rex XLPE aged at three temperatures.

Figure 6. EAB data of Anaconda EPR aged at three temperatures.

4.3 Indenter Modulus

The indenter modulus (IM) method produced mixed results as a CM technique for the two materials considered. It has been noted that "Indenter is not an effective tool for XLPE" [8] based on the low compliance of XLPE relative to EPR, CSPE, and other cable materials. The results here are consistent with that conclusion. While IM data generally trended with aging for Brand-Rex XLPE as seen in Figure 7, the linearity and consistency with aging were much better for the Anaconda EPR data seen in Figure 8.
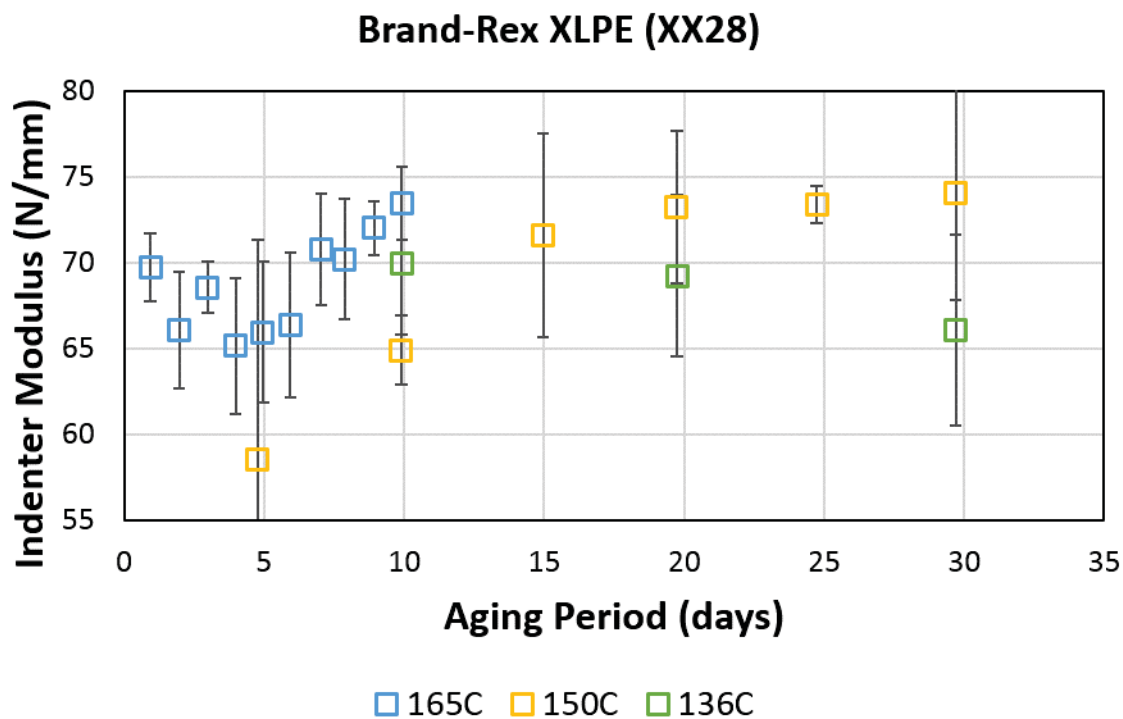
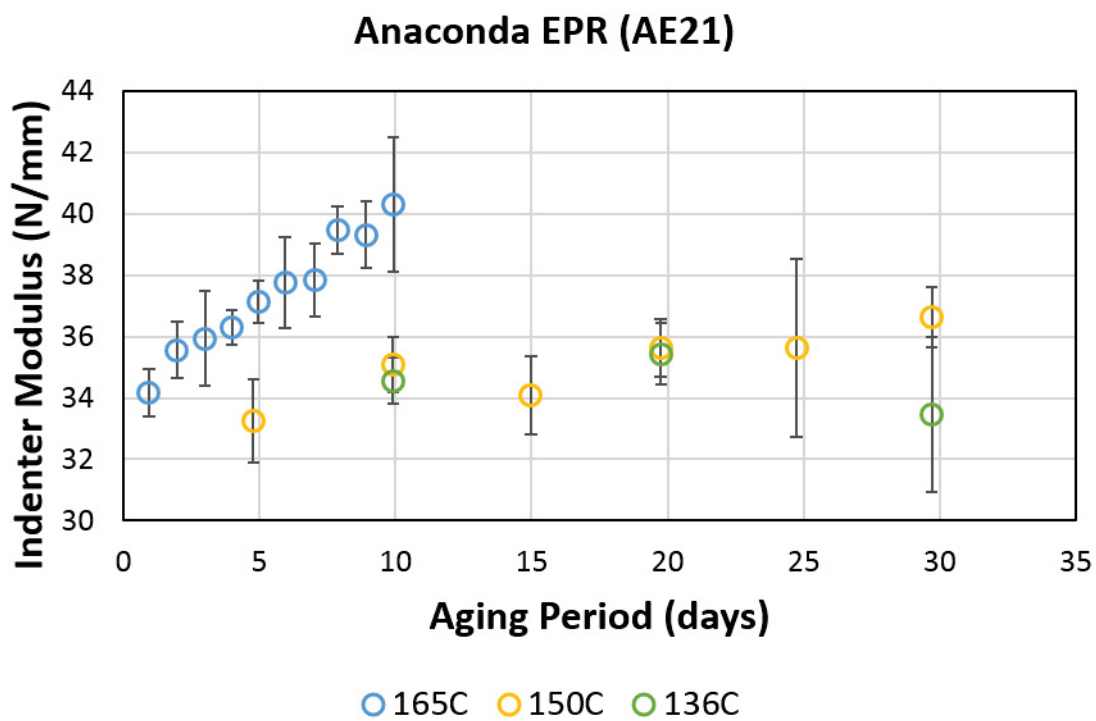**Figure 7. IM data of Brand-Rex XLPE aged at three temperatures.**

Figure 8. IM data of Anaconda EPR aged at three temperatures.

4.4   Carbonyl Index

While often an effective measure of thermal aging extent in electrical cable polymers, the carbonyl index (CI) did not appear to trend usefully with aging for neither the Brand-Rex XLPE data in Figure 9, nor the Anaconda EPR data in Figure 10. CI should trend positively as a polymer oxidizing with exposure to elevated temperature over time. Though scattered, CI does increase for the EPR oxidation in Figure 10. It is not obvious why no trend or even negative trend in CI is found for the XLPE data in Figure 9.
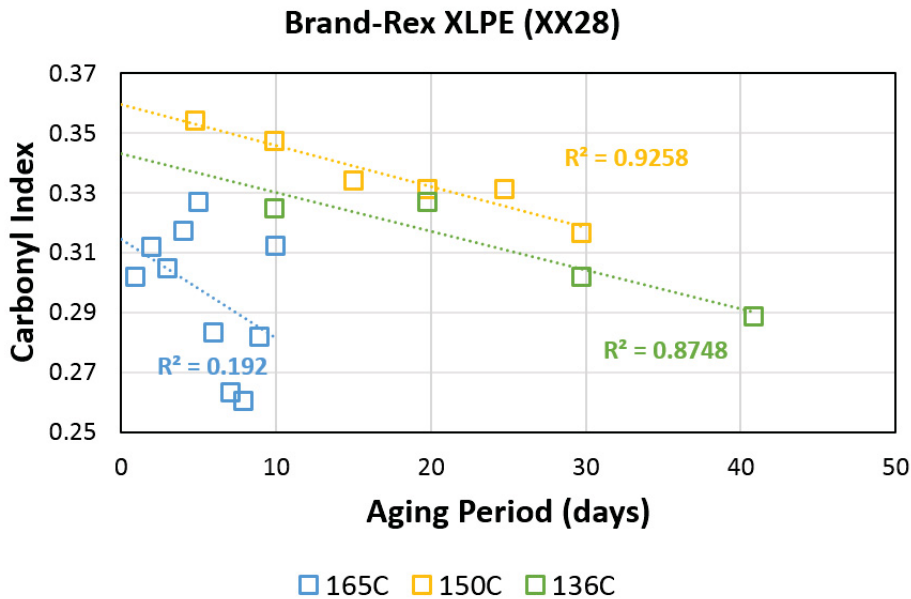

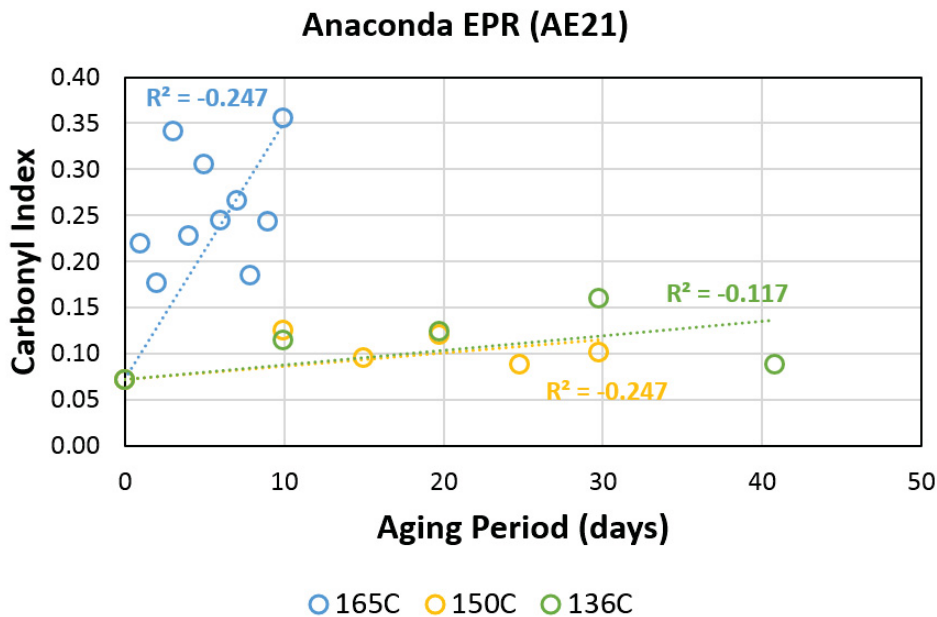**Figure 9. CI data of Brand-Rex XLPE aged at three temperatures.**

Figure 10. CI data of Anaconda EPR aged at three temperatures.

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4.5   Density

Like mass change, density is a laboratory technique for CM rather than a technique for use in tracking aging for cables in service. However, it is a convenient laboratory technique in that it requires only a small amount of material and is non-destructive. Density measurements plotted in Figures 11 and 12 below were measured on distinct samples for each data point, but a density trend could be obtained by measuring the same sample over time by removing it from and returning it aging between measurements. Density did not prove to be a fruitful metric for tracking aging in the Brand-Rex XLPE data in Figure 11 in that the density data was noisy for the 165°C samples, flat for the 150°C samples, and only trended well for the 136°C samples. With more data, perhaps density will be found to be useful for lower temperature aging for this material.
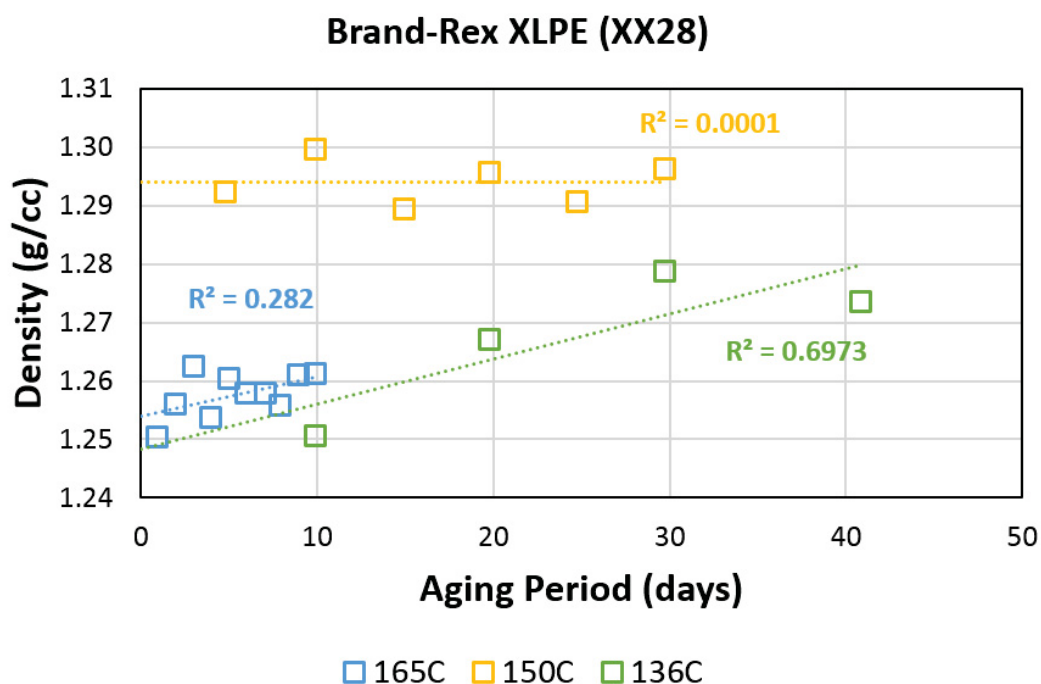
Brand-Rex XLPE (XX28)

Figure 11. Density data of Brand-Rex XLPE aged at three temperatures.

Density data tracked well with Anaconda EPR aging for 165°C and 136°C in Figure 12, but did not track for the 150°C data.
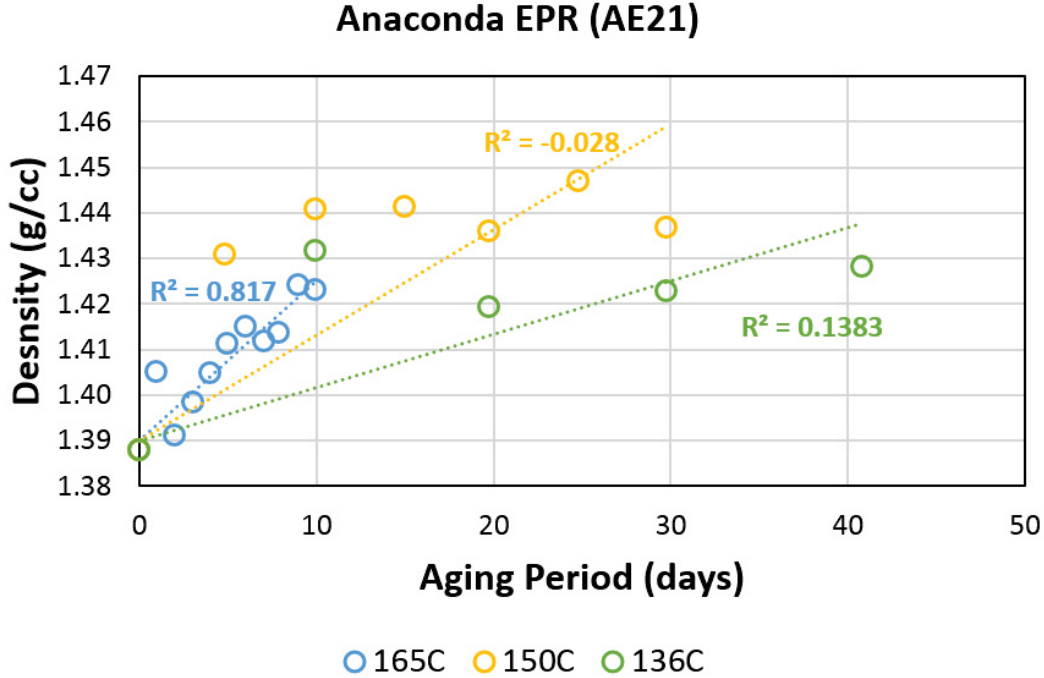
Anaconda EPR (AE21)

R² = -0.028

R² = 0.817

R² = 0.1383

○ 165C ○ 150C ○ 136C

Figure 12. CI data of Anaconda EPR aged at three temperatures.

5.   Conclusions

In this work we investigated the results of thermal aging on one XLPE and one EPR cable insulation material using five different measures of material change. The Brand-Rex XLPE material considered and the Anaconda EPR material considered represent two of the three most common cable insulation materials found in U.S. NPPs and thus are priority materials for study. The cables investigated were harvested from Crystal River 3, a decommissioned pressurized water reactor where they were installed for 21 years and 30 years, respectively. Study of these materials presents the opportunity to understand aging of relevant materials no longer available for purchase as well as the opportunity to evaluate the effects of long term operations on example cable materials. The techniques used here to evaluate aging include nondestructive and sensitive laboratory methods (mass change and density); the gold standard, but destructive EAB method; and two non-destructive methods suitable both for laboratory use and for use in the field (IM and FTIR) (though use in the field would commonly be done on outer jacket rather than directly on insulation).

For the thermal exposures (165°C, 150°C, and 136°C) and materials (Brand-Rex XLPE and Anaconda EPR) investigated here, mass change was found to be the most effective measure of insulation aging. Mass change tracked consistently with aging at each temperature and for both the XLPE and the EPR materials with little scatter. IM proved to be the second most useful method, tracking well with aging for EPR, especially at the higher 165°C temperature. However, IM data was much noisier than mass change data and did not trend as well for the XLPE. CI, density and EAB data exhibited heavy scatter and were not observed to consistently track with aging in the conditions considered here.

Based on these results, mass change may be the best candidate method for tracking thermal aging of polymer insulation in the pursuit of addressing the activation energy knowledge gap identified in the Expanded Materials Degradation Assessment [3] for these materials. Following completion of in-progress aging of the target materials at lower temperatures mass change will especially be used for activation energy analysis.

6.   References

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