ACCELERATED THERMAL AGING OF HARVESTED HYPALON JACKET FOR REMAINING USEFUL LIFE DETERMINATION AND DIAGNOSIS

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ABSTRACT

For nuclear power plants (NPPs) considering second license renewal for their operation beyond 60 years, knowledge of long-term operation, condition monitoring, and viability for the reactor components including reactor pressure vessel, concrete structures, and cable systems is essential. Such knowledge will provide NPPs with a game plan to predict performance and to estimate costs that are associated with monitoring or replacement programs for the affected systems. For cable systems that encompass a wide variety of materials, manufacturers, and in-plant location, accelerated aging of harvested cable jacket and insulation can provide insight as to remaining useful life and methods for monitoring. Accelerated thermal aging in air at temperatures between 80°C and 120°C was carried out on a multi-conductor control rod cable that had been in-service for over 30 years and was made by Boston Insulated Wire with Hypalon™ cable jacket and ethylene-propylene rubber insulation. From elongation at break (EAB) measurements and supporting Arrhenius analysis of the jacket material, an activation energy of 97.84 kJ/mol was estimated and the time to degradation, as represented by 50% EAB at the expected maximum operating temperature of 45°C, was estimated to be 80 years. These values were slightly below previous measurements on similar BIW Hypalon cable jacket and could either be attributed to in-service degradation or variations in material properties from process variations. In addition, results from indenter modulus measurements and Fourier transform infrared spectroscopy suggest possible markers that could be beneficial to monitor cable conditions.

Key words: cable aging, cable insulation, Hypalon, second license renewal

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1 INTRODUCTION

In nuclear power plants (NPPs), instrument and control (I&C) cables play a critical role in maintaining safe and efficient operations. The reliability of these cables from a material integrity standpoint for long-term operation beyond their initial 40-year qualified life is an issue as utilities in the United States like Dominion Energy, Inc. and Exelon Generation prepare for a second license renewal that will extend the operation of NPPs from 60 to 80 years [1]. While limited monitoring data in current NPPs have suggested that the dose, dose rate, and temperature that the I&C cables have been subjected to during their initial 40-year operation was considerably less than assumed in their qualification standards [2,3], the amount of margin remaining in the cable presents a level of uncertainty. To address this uncertainty, the implementation of formal cable aging management programs at NPPs [4,5] and active forums on current cable related issues [6] have been established. In support of these programs, the Nuclear Regulatory Commission (NRC), the Electric Power Research Institute and the Department of Energy's (DOE's) Light Water Reactor Sustainability program are actively pursuing research to address knowledge gaps identified in the NRC/DOE Extended Material Degradation Assessment [7] with regard to harvested, low and medium voltage I&C cables to further reduce uncertainty, increase confidence level, and identify specific cable jacket and insulation materials that could be an issue for long-term, safe and reliable NPP operation.

In order to address the knowledge gaps, accelerated aging with respect to temperature and radiation were carried out on harvested I&C cable jacket and insulation materials to assess the extent of degradation relative to as-installed specifications, and to develop or refine non-destructive evaluation techniques to quantify and track degradation. To focus efforts on materials that are relevant to current NPPs, and to set programmatic priorities, databases compiled from previous surveys to identify the NPP employed I&C cable materials with respect to insulation and manufacturer [8,9] were used as guidance. Tables I and II show the breakdown of the results from this survey with respect to manufacturer and insulation.

Table I. Top Ten manufacturers used in NPPs [8].

Rank	Manufacturer	Database Entries	Percentage of Total
1	Rockbestos/Cerro	363	23
2	Okonite	359	23
3	Boston Insulated Wire	150	9
4	Anaconda Wire and Cable	128	8
5	Kerite Company	109	7
6	Brand-Rex	98	6
7	Samuel Moore	77	5
8	General Electric	69	4
9	Raychem	46	3
10	Continental Wire & Cable Corporation	37	2
	Subtotal of top ten manufacturers	1,436	90%
	Total Database Entries	1,590	100%

This paper summarizes the results from accelerated thermal aging at temperatures between 80°C and 120°C that was performed on a harvested, Boston Insulated Wire (BIW)-manufactured cable. The mechanical and chemical properties of the Hypalon™ cable jackets were assessed to determine the extent of its performance change after 30 years of operation and to understand the changes in its chemical structure. When compared to results from previous Hypalon™ cable jacket measurements, the dependence of mechanical properties such as elongation at break (EAB) and indenter modulus (IM) with

Table II. Ten corresponding insulations used in NPP [8,9].

Rank	Insulation	No. of NPPs
1	Firewall® III XLPE*	23
2	EPR*	23
3	XLPE	9
4	EPR	8
5	HTK*	7
6	Coax XLPE	6
7	XLPE	5
8	EPR	4
9	Bostrad 7E EPR	90%
10	Flame retardant EPR	100%

* XLPE = cross-linked polyethylene, EPR = ethylene-propylene rubber, HTK = high temperature Kerite (EPR-like)

respect to temperature were observed to be similar save that the onset of degradation appears to be initiating sooner.

2 CABLE HARVESTING AND CHARACTERIZATION

2.1 Boston Insulated Wire Control Rod Cable

A cross-section of the harvested BIW-manufactured I&C cable is given in Fig. 1. This cable, which was used in an auxiliary space outside the missile barrier of the NPP was rated for operation at 600 V with two 12 AWG insulated wires and twenty-two 20 AWG insulated wires. This cable, which had an overall diameter of 25.4 mm, consists of a 2.74 mm thick jacket of Hypalon™ - a chlorosulfonated polyethylene (CSPE) - a thin foil ground shield, and multiple conductors with EPR insulation of thicknesses between 1.1 mm to 1.3 mm. In addition to the insulation, the EPR insulated conductors were covered with a 0.4 mm thick dyed coating of CSPE to assist circuit connection discrimination and further protection of the EPR.

Figure 1. Cross section of BIW control rod cable.

2.2 Accelerated Aging and Arrhenius Analysis

In order to determine the performance of I&C cables that have an expected lifetime on the order of tens to hundreds of years at maximum operating temperatures at installed locations ranging between 30°C and 60°C, accelerated aging at higher temperatures is employed to extrapolate I&C cable performance. This is done by assuming that the degradation mechanism and the rate of degradation is functionally related to the exposure temperature of the cable. For I&C cables that are qualified for NPPs as well as many other polymers, an Arrhenius analysis is utilized in which the rate of degradation, k, is expressed as

$$k \sim e^{\left[-E_a/_{RT}\right]} \tag{1}$$

where E_a is the activation energy, R is the ideal gas constant 8.314 kJ/kmol-K, and T is the temperature. The rate of degradation is found through the comparison of a measured property, which is often EAB for I&C cables, across different temperatures over a period of time as with the data presented in Fig. 2 [10]. The data in Fig. 2b is obtained from a Hypalon™ cable jacket that was manufactured by a different company, Eaton. A reference temperature of 100°C is selected and the remaining data is multiplied by a constant, C, until it overlaps the reference (Fig 2b). The constant, which is related to the rate of degradation, is plotted as a function of inverse temperature as shown in Fig. 3 and the activation energy is obtained from its slope. Using (1), E_a is 111 kJ/mol for the Eaton Hypalon™. This activation energy along with the time for degradation to 50% EAB at the reference temperature is utilized to determine the expected time to degradation at the maximum expected operating temperature. For this case with a maximum operating temperature of 45°C, the time to degradation is estimated as ~ 400 years. Note that

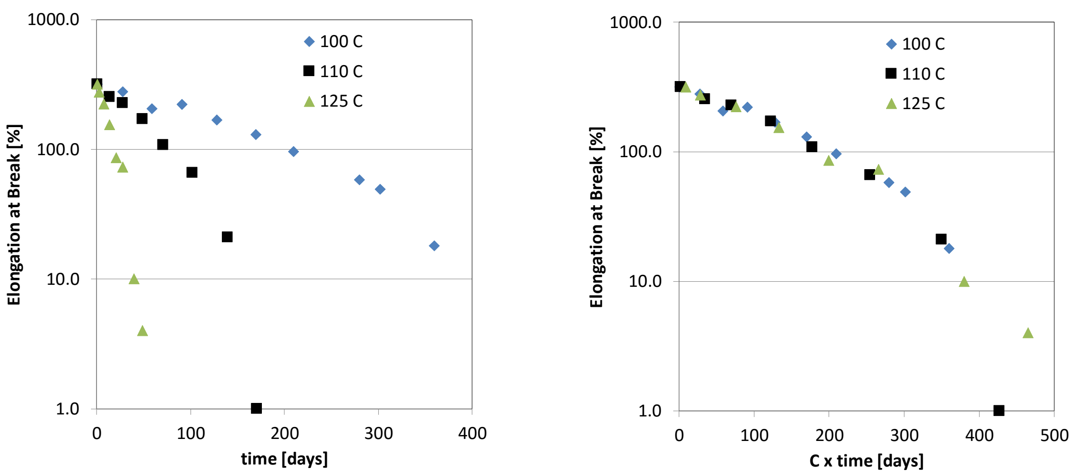

Figure 2. (a) EAB for CSPE jacket after accelerated aging at temperatures between 80°C and 130°C as a function of time and (b) EAB for Hypalon™ jacket after multiplying each temperature by a constant, *C*, assuming a reference temperature of 100°C [10]. Hypalon™ for this case was manufactured by Eaton.

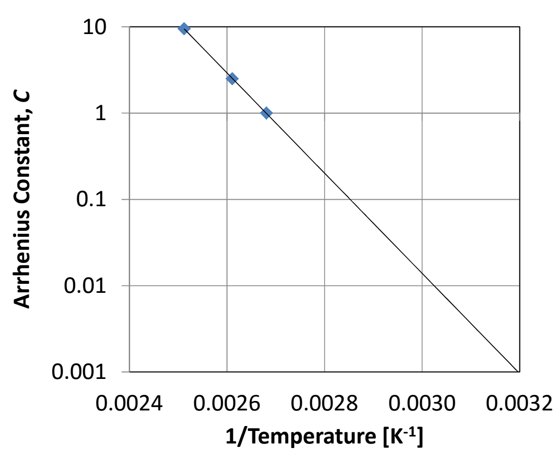

Figure 3. Arrhenius plot of constants that were found from EAB measurements in Fig. 2 for Hypalon™ jacket as a function of inverse temperature [10]. Hypalon™ for this case was manufactured by Eaton.

effects of diffusion limited oxidation and non-Arrhenius degradation with respect to temperature could impact this prediction [7].

For the BIW cable, short sections of cable and cable jacket specimens, which were prepared according to ASTM standard D638-14 [11], were placed into several different air convection furnaces

Figure 4. Example of furnace (left) and sample arrangement (right) utilized in accelerated thermal aging of BIW cable and jacket samples.

(Fig. 4) at temperatures ranging between 80°C to 120°C. Cable and jacket specimens were removed periodically over the course of several hundred days and the samples were kept at ambient conditions for 24 to 48 hours (per IEC/IEEE standard 62582) before commencing the measurements [12].

Mechanical properties of the Hypalon™ cable jacket over the duration of the accelerated thermal aging were tracked through EAB and IM techniques. Using the guidance from IEC/IEEE 62583-3 [12], dog bone shaped cable jacket samples with lengths of 63.5 mm and widths of 9.53 mm were placed in a Instron 4450 Tensile Tester and the stress as a function of strain measured at the rate of 1.27 mm/s until failure occurred. This EAB assessment process was repeated for five samples at each temperature to average out possible material variations. For IM, an Indenter Polymer Aging Monitor (IPAM) was used on cable jacket samples prior to EAB measurements. Using IEC/IEEE 62582-3 guidelines [13], the same dog bone shaped cable jacket samples were placed onto un-aged, 10-mm diameter cable samples to recreate the cable geometry. The indenter force during the measurements was ramped from 0 to 9 N. The indenter modulus of the cable jacket is calculated from the slope of the change in deformation with respect to the force applied. Specifically, it is the difference in force of 4 N and 1 N (3N) divided by the difference in deformation at 4 N and 1 N.

In addition to mechanical characterization, chemical analysis of each cable jacket sample was performed utilizing Fourier transform infrared (FTIR) spectroscopy to correlate mechanical changes with the changes in the chemical structure of the cable jacket. Given that portable FTIR systems are under consideration for use in cable monitoring programs, the FTIR response could prove viable for a non-destructive evaluation of the jacket. FTIR analysis was carried out with a Digilab FTS 7000 equipped with DTGS detector and a PIKE MIRacle ATR accessory equipped with a diamond crystal. FTIR examines the formation of oxidized species and changes to the chemical bonds through the absorption of infrared energy. More detailed information on FTIR techniques and their use in characterizing polymers can be found in [14-16].

3 RESULTS & ANALYSIS

3.1 Elongation at Break

The EAB as a function of time for different aging temperatures between 80°C and 120°C for the BIW Hypalon™ as well as reported data for Gillen *et al* (Hyp-08) cable jackets are shown in Fig. 5. When compared to the previous measurements of BIW Hypalon™ cable jacket evaluated by Gillen *et al* (Hyp-08) [9], the amount of time required to see the drop in EAB at a given temperature is shorter. For example, to reach 50% EAB at a temperature of 100°C, which is often used as the definition of cable end-of-life performance, it was estimated that it takes ~ 130 days for the harvested BIW cable jacket and 220 days for the Hyp-08. It should be noted that while Hyp-08 was manufactured by BIW and is of the same

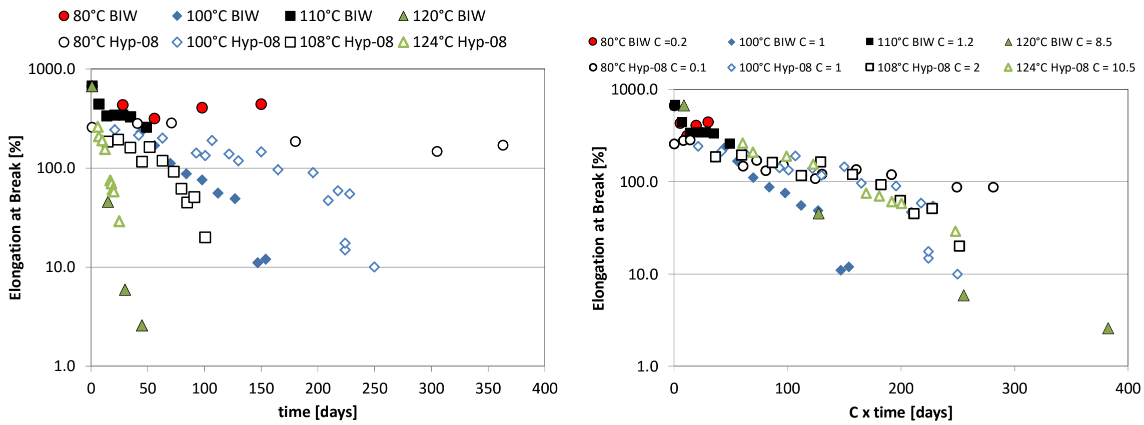

Figure 5. Comparison of EAB for BIW Hypalon™ as a function of time at different aging temperatures to previous BIW Hypalon™ data [9] (right) and comparison of the two data sets after an Arrhenius constant, C, is applied to each data set with 100°C as the reference point (C=1) (left).

vintage of the harvested cable jacket, the Hyp-08 originated from a different cable type consisting of three conductors instead of multiple conductors. Hence, there could be subtle changes in the chemical formulation to accommodate the different cabling that could have impacted this result. Future work is planned as harvested cables are obtained.

To compare the performance of these two types of cable jackets, Arrhenius constants, C, were obtained (Fig. 5) assuming a reference temperature of 100°C where C = 1. When the constants were compared to each other for both cables as well as to the constants obtained for another type of Hypalon™ in the Gillen database (Hyp-06), their functional dependence appears to be similar (Fig. 6). Using (1) and the slope of the exponential curve fit in Fig. 6, the activation energy was estimated to be 97.84 kJ/mol for the harvested BIW cable jacket and 103.92 kJ/mol for the Hyp-08. The exponential curve fit was utilized to calculate the Arrhenius constant at the maximum expected operating temperature of 45°C. Dividing the

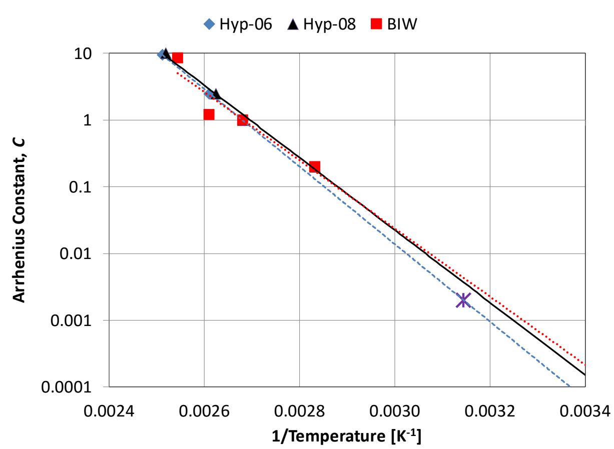

Figure 6. Arrhenius constants as a function of inverse temperature that were found for BIW Hypalon™ cable jackets (BIW & Hyp-08) from Fig. 5. Additionally, Arrhenius constants for the Eaton Hypalon™ are also given (Hyp-06). The lines are the exponential curve fits for each Hypalon™ cable jacket.

time to 50% EAB by this constant, the time to 50% EAB at the maximum expected operating temperature is estimated as ~80 years for the harvested BIW cable jacket and ~150 years for the Hyp-08 cable jacket.

While 50% EAB is often selected to indicate end-of-life degradation, there are several factors to consider when comparing this result to previous measurements. First, the types of BIW could have chemical variations that could lead to different accelerated aging performance. The harvested cable was a multiconductor cable, while Hyp-08 was an extruded three-conductor cable. Differences could be present due to the functional nature of the jacket in each case and comparative testing would be needed. Second, the estimated Arrhenius constants for 80°C and 110°C were found from data with no noticeable degradation toward 50% EAB that could impact the curve fit for calculation of activation energy. The activation energy drives the constant for determination of time to 50% EAB. For example if the activation energy increased from 97.84 kJ/mol to 103 kJ/mol, the resultant time to 50% EAB at the maximum expected operating temperature would increase to 95 years. Third, the failure of the jacket does not necessarily coincide with electrical failure of the I&C cable given its complex structure. Comparison of the insulation performance as a function of jacket degradation needs to be addressed before any judgement on the entire cable performance is rendered. Finally, current standards are built not on 50% EAB comparison, but on testing of materials that have been subjected to design basis events [17,18]. Clearly, more detailed analysis is required before drawing definitive conclusions on the mechanism(s) underlying the observed decrease in activation energy and time to 50% EAB.

3.2 Indenter Modulus

Indenter modulus data for the harvested BIW Hypalon™ jacket is presented in Fig. 7. When compared to previous measurements, the functional time dependence appears to be quite similar to EAB in that the degradation as indicated by an increase in indenter modulus occurs earlier. Like the EAB measurement for the harvested BIW Hypalon™ cable jacket, the indenter modulus appears to track the mechanical degradation as function of temperature and time. This is particularly evident when the EAB for two temperatures, 100°C and 120°C, is directly compared to the indenter modulus as a function of time in Fig. 8. This would support the ability of indenter modulus to serve as a method for non-destructive evaluation of cable condition for this type of cable.

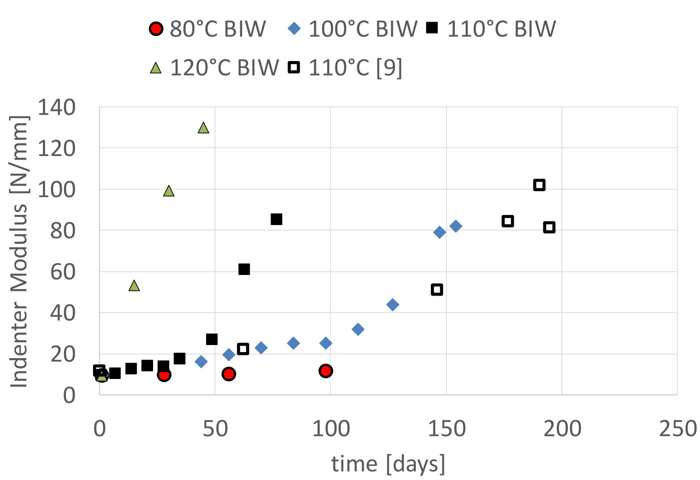

Figure 7. Indenter modulus as a function of time and temperature for harvested BIW Hypalon™ cable jacket. Data from a previously reported measurement of Hyp-08 at 110°C is provided for comparison [9].

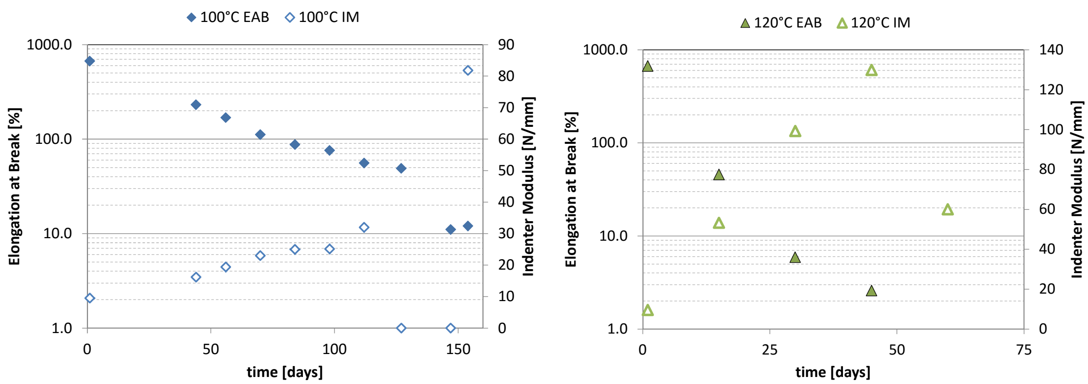

Figure 8. Comparison of EAB and indenter modulus as a function of time for harvested BIW Hypalon™ cable jacket aged in air at temperatures of 100°C and 120°C.

3.3 FTIR

An example of the FTIR spectrum for BIW Hypalon™ cable jackets for different exposure times at a fixed temperature is given in Fig. 9. While the carbon black filler and the overall black color makes meaningful FTIR measurements difficult due to the limited reflected light, notable changes in the FTIR spectra that seem to correlate to age-related chemical activity were observed. For example, formation of terminal vinyl groups (CH=CH) and evidence of oxidation as a function of exposure time are apparent by the increased absorbance near 1000 cm^{-1} and between 3200 cm^{-1} and 3600 cm^{-1}, respectively [19-20]. Additional changes of note are increases at 2848 cm^{-1} and 2916 cm^{-1} that are indicative of changes to C-H bonds. While the possibility of diffusion limited oxidation is small for Hypalon™, also known as CSPE, FTIR depth profile measurements might provide more conclusive information and resolve whether surface contamination could be causing some of these effects.

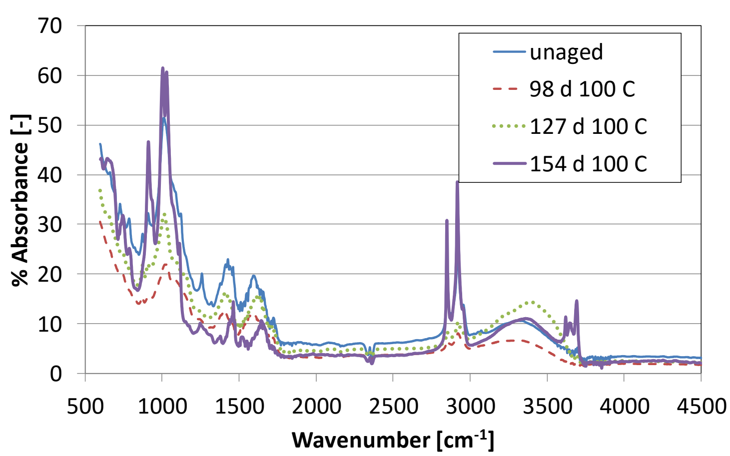

Figure 9. FTIR spectra for BIW Hypalon™ as a function of time from exposure to air at 100°C.

4 CONCLUSION

Accelerated thermal aging at temperatures between 80°C and 120°C was performed on a harvested BIW-manufactured cable to determine the extent to which cable jacket performance changed after being in operation for over 30 years. From mechanical characterization via EAB and IM, degradation appeared to occur sooner when compared to previously reported results on Hypalon-jacketed BIW cables of alternate construction. From the Arrhenius analysis, the dependence of degradation with respect to exposure temperature and time suggests that the mechanism(s) for chemical degradation are similar. Using FTIR measurements, these chemical changes were identified as the formation of terminal vinyl groups, oxidation products, and alterations in the C-H bonds. From the Arrhenius analysis, the activation energy was estimated to be 97.84 kJ/mol, which is slightly less than the values obtained for other Hypalon™ cable jackets. Future work is planned to better understand the functional dependence of the degradation within the BIW manufactured cable types of different cable geometries, including depth profiling FTIR to identify the possible chemical changes taking place within the cable jackets. The estimated time to reach 50% EAB if the cable were exposed to its maximum expected operating temperature is around 80 years for the harvested BIW cable jacket and 150 years for the Hyp-08 cable jacket. However, factors that are related to differences in BIW Hypalon™ chemical composition and uncertainty from accelerated thermal aging performed to date require additional testing and uncertainty analysis before definitive conclusions can be drawn.

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