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New Technologies for Repairing Aging Cables in Nuclear Power Plants

M3LW-14OR0404015 Cable Rejuvenation Report

September 2014

KL Simmons
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U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
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Richland, Washington 99352

Summary

The goal of this project is to conceptually demonstrate techniques to repair cables that have degraded through subjection to long-term thermal and radiation exposure in nuclear power plants. Physical degradation of the aging cables is manifested primarily as visible cracking and increased brittleness of the polymeric electrical insulation. The targeted cable-repair concept comprises development of techniques to impart a softening or strengthening agent within the deteriorated polymer insulation jacket to enable recovery of the ability of the insulation to stretch without failing and possibly to heal existing cracks in the insulation.

In fiscal year 2014 we focused on commercially available ethylene-propylene rubber (EPR) as the relevant test material, isolated a high surface area form of the EPR material to facilitate chemical treatment screening and characterization, and measured chemical changes in the material due to aging and treatment using Fourier Transform Infrared (FTIR) spectroscopy. Nuclear grade pink EPR insulation was cut from medium voltage cable and machined into a powder of ribbon-like particles. The smallest particle sizes (< ~1mm) were then obtained by removing larger particles using standard mesh sieves. The isolated particles were aged in a circulating air oven at 140°C to produce specimens corresponding to the full range of cable age-performance points from new (>350% elongation at break) to end-of-life (<50% elongation at break). The EPR powder was characterized through change in visible appearance with aging, change in mass with aging, and change in FTIR absorbance spectra. A treatment method to induce chemical functional groups onto the undamaged polyolefin backbone was conceived and demonstrated on the EPR powder. This approach to adding functional groups might serve as a basis for constructive cross-linking or for covalent attachment of internal plasticizing function in the matrix.

The developed powderized form of EPR insulation proved to be an effective screening platform for chemical treatment and characterization of the otherwise intractable rubber. Initial rounds of thermal aging of the powders exhibited a couple of interesting and unexpected results. After only ~1 day in the oven at 140°C the pink powder, though exhibiting no visible color change or FTIR-observable spectral change, appeared to exhibit association between particles eliminating free flow of the powder. As the EPR does not melt at this temperature, this result may indicate that the material begins cross-linking or other inter-molecular association very early on in the thermal aging process. In previous studies aging 5-mm-thick EPR specimens at 140°C it was observed that the pink EPR material turns a dark reddish brown toward the second half of the aging spectrum, corresponding to elongation at break values less than ~100%. Similarly, the EPR powder transformed from its initial light pink eraser color to dark reddish brown at ultimate aging times. Surprisingly, however, the piles of particulate in each sample pan did not undergo this transition uniformly, but rather spots of dark color appeared heterogeneously in the material and grew until the material became uniformly dark. This observation may support an understanding that aging does not proceed uniformly throughout the volume of insulation in a given cable. In addition to non-uniformity in local environmental conditions stressing the cable material (i.e., hotter regions of cable exposure), there may also exist non-uniformity in the dispersion of components within the cable insulation material as manufactured including, for instance, the inorganic filler and anti-oxidant.

A treatment was developed to add chemical functionality to the EPR polymer backbone selectively at ambient temperatures. The treated was demonstrated on EPR powder and chemical reaction was confirmed by observation of the added chemical group signature on the modified EPR. Next steps in the development of this promising chemical route include demonstrating the same reaction in a suitable

carrier solvent that might be used to apply the treatment to intact cable and application of the treatment to EPR forms amenable to tensile mechanical testing. As elongation at break is a standard method for assessing cable degradation state, assessment of the effect of the treatment in recovering elongation at break in an aged sample will be important for demonstrating its rejuvenation utility. Further treatments including covalently attaching chemical functionality to the newly formed anchor points within the rubber matrix will be developed and ultimately demonstrated on full size (thickness) specimens of insulation material to confirm restoration of the ability of degraded EPR to be compliant and resist fracture.

Acronyms and Abbreviations

DSC	differential scanning calorimetry
EPR	ethylene-propylene rubber
FTIR	Fourier-transform infrared (spectroscopy)
PNNL	Pacific Northwest National Laboratory
SEM	scanning electron microscopy
SNL	Sandia National Laboratory
TGA	thermogravimetric analysis
UV-Vis	ultraviolet-visible spectroscopy

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1.0 Cable Insulation Particle Form

Chemical methods to rejuvenate aging cable insulation in cables installed in nuclear power plants will need to be effectively applied to intact cable systems including conductor, shielding, jacket, etc. We are initially pursuing the development and demonstration of proof-of-concept methods to restore insulation properties lost with age on the rubber insulation material, isolated from the cable system. In previous work we measured the kinetics of uptake of a series of chemical treatments including plasticizers into ethylene-propylene rubber (EPR) cable insulation specimens cut from Okonite Company-brand Okoguard Aerial Jumper Cable (Catalog number 303-21-1944) (Simmons et al. 2013). The EPR insulation on the ~25-mm diameter cable investigated is ~5.5-mm thick and is easily cut into 100-mm long tensile specimens to evaluate thermal aging extent and restoring effect from chemical treatment through measurement of elongation at break according to ASTM D412. The dog bone-shaped tensile specimens have low surface area and it was concluded that screening of covalent chemical approaches to modify the material and investigate chemical changes in the material with thermal oxidative aging would be assisted with a high surface area form of the EPR material. A high surface form of the EPR facilitates rapid access to the material by applied chemical treatment and extraction experiments and spectroscopy to evaluate aging and treatment. Due to the proprietary nature of the nuclear grade EPR formulation in the Okoguard cable, it has not been possible to obtain raw material from the manufacturer for calendaring, compounding and processing into arbitrary test forms ourselves. Consequently, we were led to develop a high surface area test form of the cable EPR material from the commercially available cable itself.

In Okoguard Aerial Jumper Cable, the EPR insulation does not have a surrounding of either a shielding layer or an additional jacket material. The outside of the EPR layer has printed ink and other contaminates introduced during the production, shipping and handling of the cable. The inside of the EPR layer is adhered to black, semiconducting tape that surrounds the metal conductor. To produce a clean, uncontaminated version of EPR for less ambiguous testing, the outer and inner layers of EPR strips cut from the cable were abraded away. The isolated EPR material strips were milled through careful trimming using a multi-fluted router bit. The fine flake/powder cut from the strips was collected and shifted through standard mesh sieves to obtain approximate particle size-controlled EPR powder.

Figure 1.1. EPR Material Cut from Cable (Left) and Milled into Powder (Right)

The controlled milled material was used for spectroscopic analysis, including FTIR, and exploratory chemical treatments which were applied directly to this tractable form of higher surface area EPR solid material.

2.0 Insulation Particle Aging

Accelerated aging in circulating air ovens has been used to produce EPR samples of various effective ages, defined by degradation of initial material performance, to demonstrate recovery of material properties with chemical treatment. This rejuvenation of aged material returns its performance to that of an earlier effective age. EPR tensile specimens were previously aged at Pacific Northwest National Laboratory (PNNL) (Simmons et al. 2013) and at Sandia National Laboratory (SNL) (6-9-2014 Mata memo) to produce a series of samples with effective ages from un-aged to end-of-life. Samples reached and equivalent advanced state are ~50 days at 140°C at PNNL (Figure 2.1), and ~55 days, ~120 days and >200 days at SNL at 138°C, 124°C and 109°C (Figures 2.2, 2.3, and 2.4), respectively.

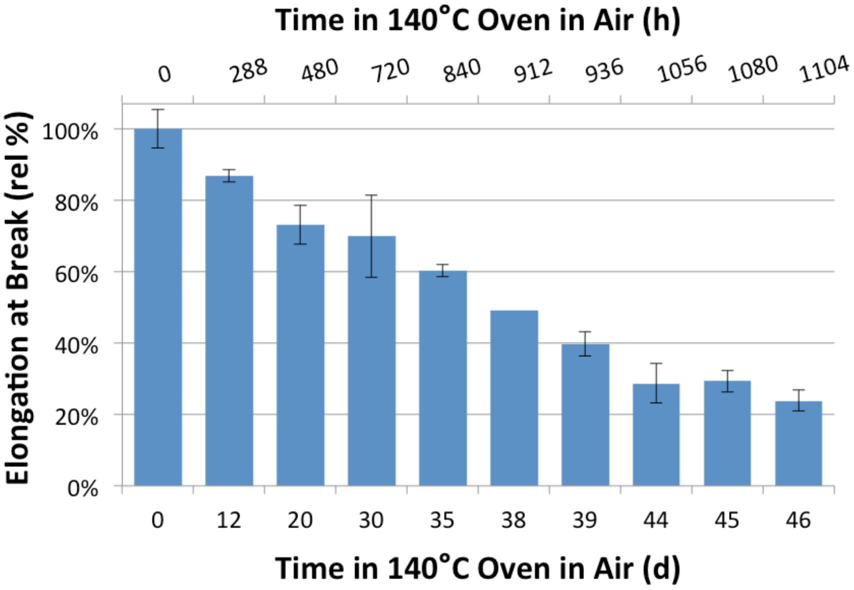

Figure 2.1. Elongation at Break of EPR with Aging at 140°C

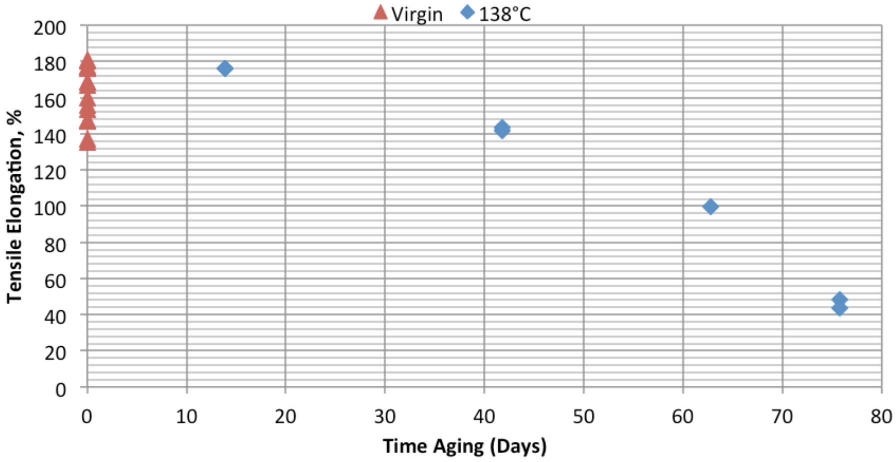

Figure 2.2. Elongation at Break of EPR with Aging at 138°C

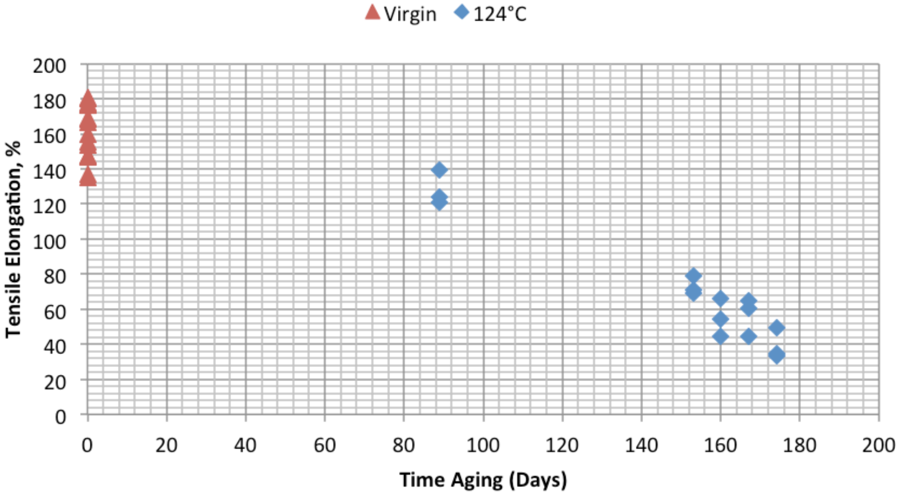

Figure 2.3. Elongation at Break of EPR with Aging at 124°C

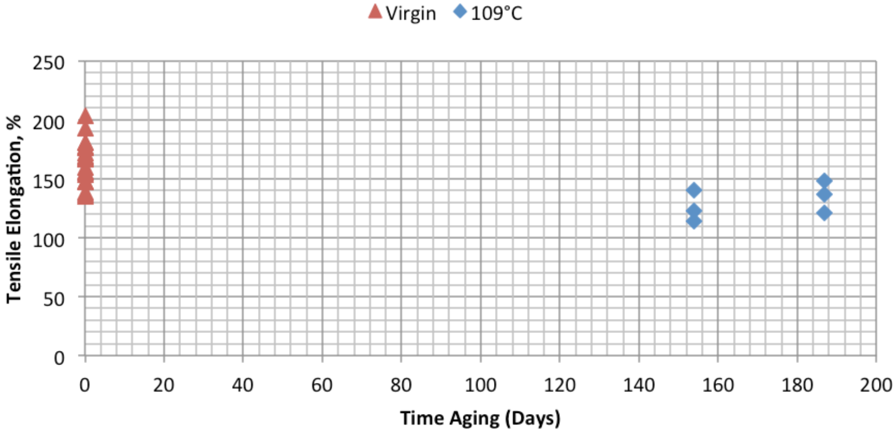

Figure 2.4. Elongation at Break of EPR with Aging at 140°C

It was hypothesized that the use of less than 1-mm thick produced EPR particles would age (degrade) at a faster rate than the ~ 5-mm thick specimens cut directly from the cable proportional to their higher surface area. It was not possible to directly compare aging rates of the two EPR forms using elongation at break since tensile specimens could not be prepared from the particles. However, based on the clear visual transition from light pink un-aged EPR particles to dark reddish brown advanced age EPR particles observed in EPR particle samples aged at 140°C the aging rates were very similar. Rather than the aging only taking a few days, as might be expected from the greater than order of magnitude increase in surface area, the visual transition required the same ~50 days for particles as the elongation at break did for the thick tensile specimens. Quantification of aging rates for difference forms of EPR material will help to inform an understanding of the degradation mechanisms including contributions from loss of material; i.e., plasticizer, consumption of anti-oxidant, and presence of diffusion limitations on oxidation.

In Figure 2.5 EPR particles were aged in a circulating air oven in ~1-g portions in aluminum weigh pans. It was observed that the samples darkened faster in certain regions of the oven, presumably due to differences in exposure temperature in different regions of the oven. We were surprised to observe that the particulate sample portions in each pan often did not age uniformly, but the visible discoloration initiated at apparently random spots with each pan and expanded outward through the sample until the entire sample in the pan was discolored. In comparing Figures 2.6 and 2.7, the growth of the aging spots grew as a function of time. Rather than a result of inhomogeneous heating, this appears to indicate that the aging mechanism is also affected by apparently inhomogeneous composition of the material. Initiation points for the degradation, as evidenced by the discoloration, may be non-dispersed inorganic filler, pockets of advanced anti-oxidant consumption, or points of residual catalyst or peroxide. These indicators of inhomogeneous degradation were not so readily visible in the larger, aged tensile specimens previously investigated and may serve to elucidate fundamental degradation mechanisms of the EPR material.

Figure 2.5. Trays of Un-aged EPR Powder in Aluminum Pans for Oven Aging

Figure 2.6. Aging EPR Powder Showing Inhomogeneous Aging Spots

Figure 2.7. Aging EPR Powder Showing Inhomogeneous Aging Spots with Further Aging

After only a day or two of aging in the oven at 140°C, the particulate EPR piles in each aluminum weigh pan exhibited another surprising behavior. The free flowing, un-ages powder loaded into the oven became somewhat monolithic. In Figure 2.8 shows when dumping the material out of the pan it all came out at once and pieces of the pile could be pulled away with tweezers. This result demonstrated apparent association between the surfaces of the freshly cut pieces of EPR powder loaded into the oven. This apparent bonding between EPR surfaces may be related to cross-linking or non-covalent interactions between polymer chains. Further analysis of this observed result might inform the degradation mechanism of the EPR material including better understanding of the interplay between polymer chain scission and crosslinking following thermal stress.

Figure 2.8. EPR Particulate Removed from Pans at Different Extents of Aging at 140°C in Air

Analysis of the aged versus un-aged EPR particulate by Fourier transform infrared (FTIR) spectroscopy, ultraviolet-visible spectroscopy (UV-Vis), and scanning electron microscopy (SEM) revealed chemical and morphological changes in the material with oxidative thermal stress. In attenuated total reflectance FTRI measurement the un-aged, light pink EPR samples exhibited unsaturated carbon peaks around 2900-cm^{-1} that went away with aging. Aged, dark brown EPR samples showed the appearance of carbonyl peaks near 1700-cm^{-1} and a broad hydroxyl manifestation between 3000 and 3500-cm^{-1}. Changes were also observed between the samples in initial diffuse reflectance UV-Vis measurements consistent with chemical changes including growth of absorption at low wavelengths due to increase carbonyl content. Intermediately aged EPR particulate samples exhibited inhomogeneous aging that began with darkening spots in the material that grow in size until the entire sample looked dark. FTIR spectra of the dark and light regions within one of these intermittently aged samples resembled the spectra of light, un-aged and completely darkened samples, respectively.

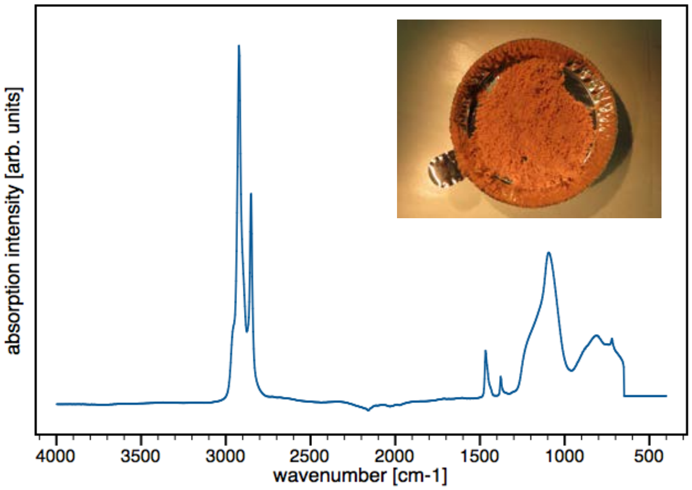

Figure 2.9. FTIR of Light, Un-aged EPR Particulate

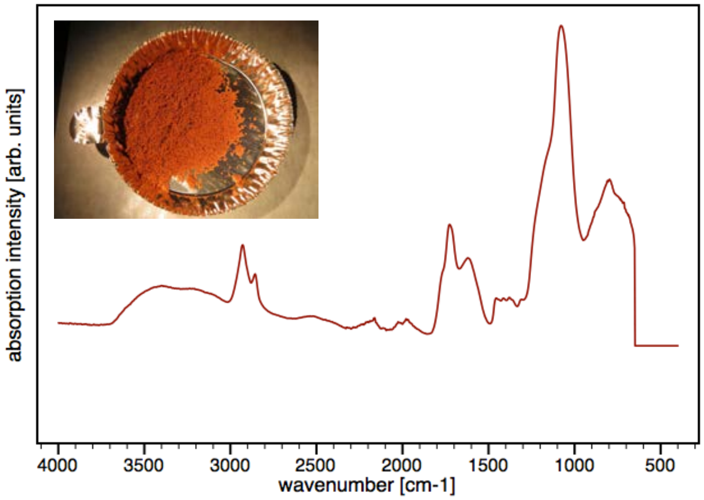

Figure 2.10. FTIR of Dark, Aged EPR Particulate

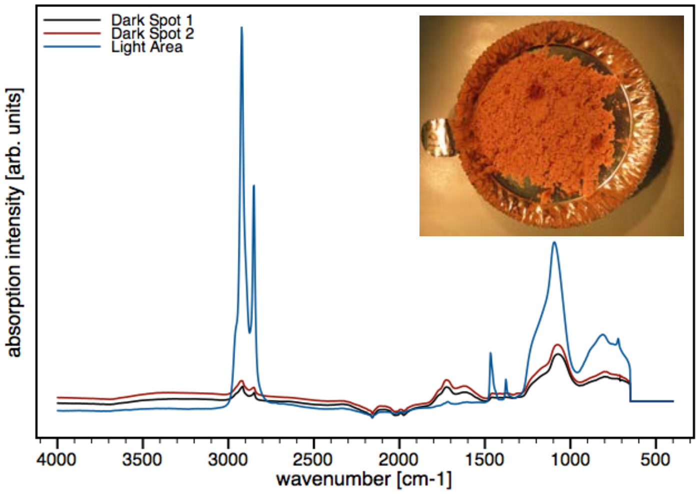

Figure 2.11. FTIR of Regions of Heterogeneously Age EPR Particulate

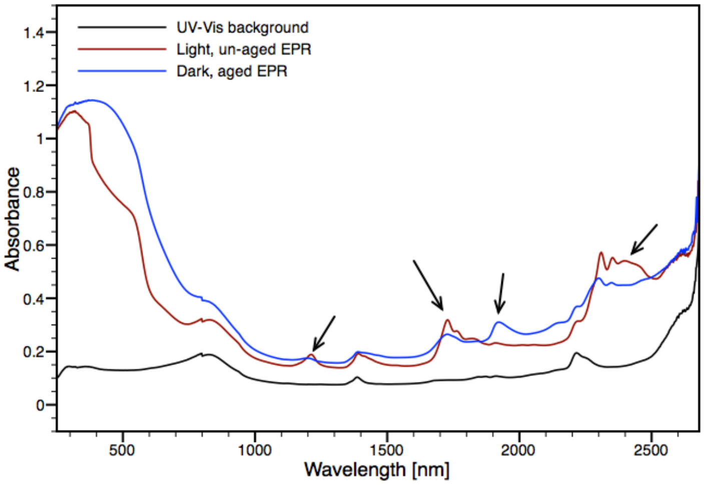

Figure 2.12. Arrows Indicating Differences in EPR UV-Vis Spectra Before and After Aging

Thermal gravimetric analysis (TGA) combined with differential scanning calorimetry (DSC) of a chunk of the same un-aged EPR material was performed with ramped heating of the sample to 600°C in nitrogen, followed by ramped heating to 800°C in air. The ~50% of the initial mass remaining after this heating represents inorganic content and is white in color.

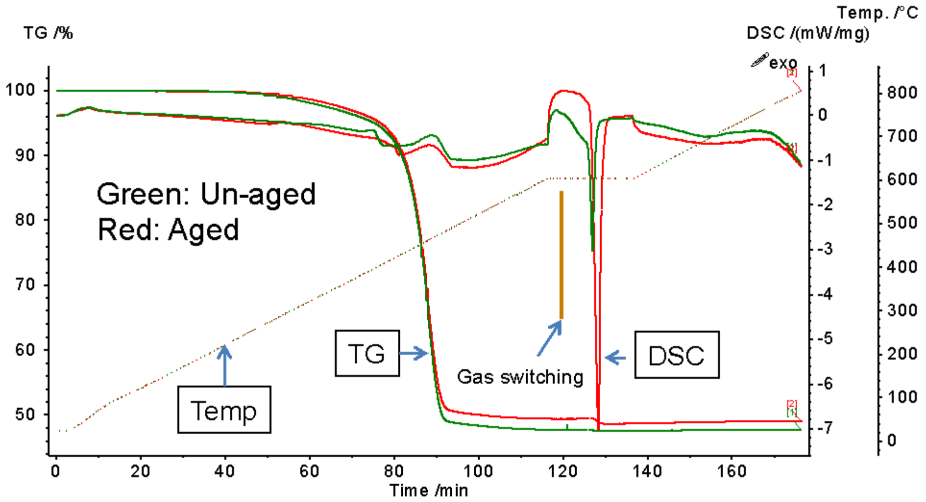

Figure 2.13. TGA of EPR Ramped at 5°C/min, 25–600°C in Nitrogen, 600–800°C in Air

SEM images of the un-aged (Figure 2.14) and aged (Figure 2.15) particles revealed the inorganic filler in an organic matrix. The matrix appears to contract around the filler more after aging, perhaps resulting from loss in organic material and/or restructuring of the material with thermal oxidative aging where the density of the material undergoes change.

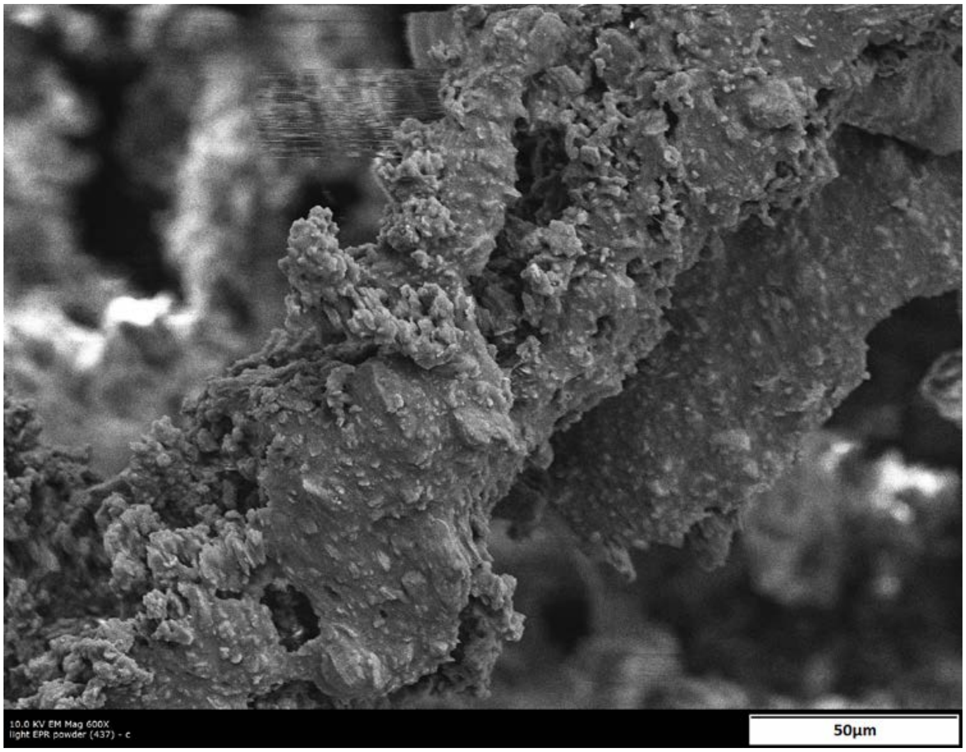

Figure 2.14. SEM of Un-aged EPR Particles

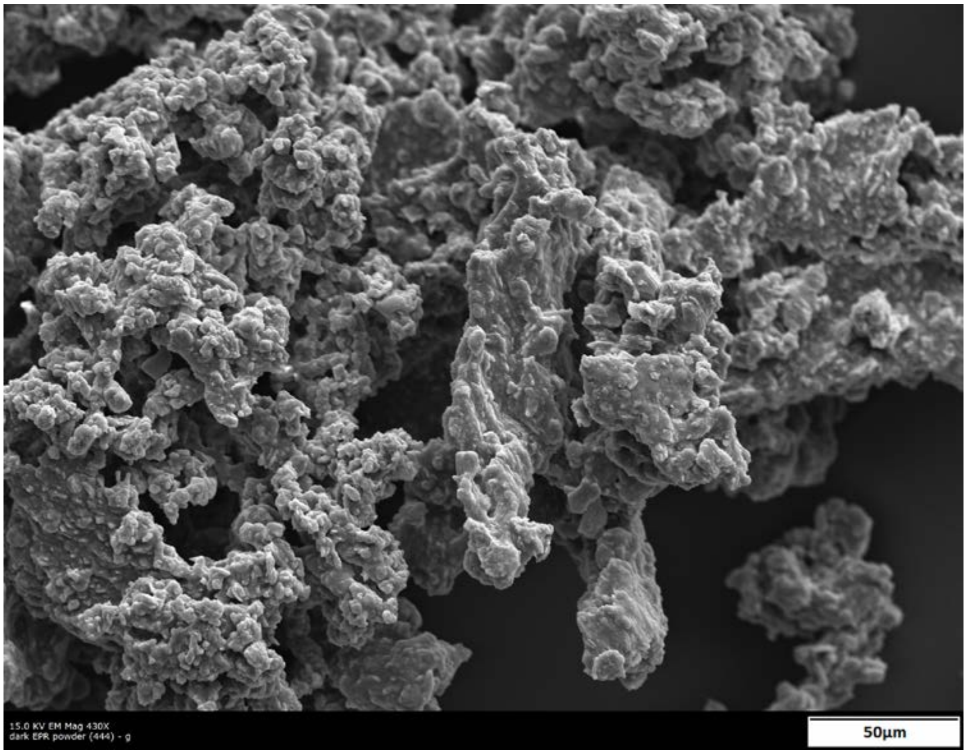

Figure 2.15. SEM of Aged EPR Particles

3.0 Covalent Chemistry on Insulation Particles

Decreases in performance of nuclear-grade electrical cable polymer insulation relative to performance of the as-produced and as-qualified material may be due to thermal oxidative degradation mechanisms including consumption of anti-oxidant, loss of plasticizer, polymer chain scission, polymer chain cross-linking and/or changes in the crystallinity of semi-crystalline materials (Fifield et al. 2014). Chemical strategies to recover lost performance and rejuvenate aged cable polymer insulation may include replacement of anti-oxidant, replacement of plasticizer or polymerization of an added monomer within the cable polymer matrix. These strategies involve non-covalent chemistry with the insulation polymer; no chemical bonds of the insulation polymer chain backbones are formed or broken during the treatment. Covalent approaches involving breaking or forming bonds directly with the cable matrix might include reactions with induced defects such as oxidation groups or polymer ends resulting from chain scission. We are pursuing a strategy for altering the mechanical behavior of aging cables that involves the creation of chemical reaction points along the polyolefin backbone of EPR. These reaction points may be used to add chemical functionality to cross-link neighboring polymer chains or impart plasticizing behavior. The goal of this work is to return the performance of EPR in a cable to that of material that has experienced a lower degree of damage.

Recognizing that we have an ambitious goal, we are developing cable rejuvenation chemical treatments with attention to the following contextual constraints: Treatments will ideally be applicable to commonly used cable materials such as EPR and must be able to be applied to existing, intact cables. Reaction conditions should preferably be mild. They should proceed close to room temperature, close to atmospheric pressure, and should result in minimal side products and side reactions. Also, the kinetics of induced chemical reactions should be fast so as to make cable treatment feasible.

An EPR modification scheme was developed and initially demonstrated in which a platform functional group was grafted directly onto the intact ethylene-propylene backbone of the insulation polymer, illustrated in Figure 3.1. The three traces in the plot of Figure 3.1 represent the absorption spectrum of (un-aged) unmodified EPR, the spectrum of the functional group alone, and the spectrum of the modified EPR. The peak in the modified EPR confirms the presence in the material of the functional group, and the slight shift in peak location confirms covalent attachment to the EPR matrix. This successful proof-of-concept reaction was demonstrated using high surface area EPR particles. The next step for developing this reaction is confirmation that the reaction proceeds in a solvent amenable to large-scale treatment of intact polymer. The reaction will also be applied to thin EPR sheet and full-thickness EPR material to explore the effects of the treatment on EPR tensile mechanical performance.

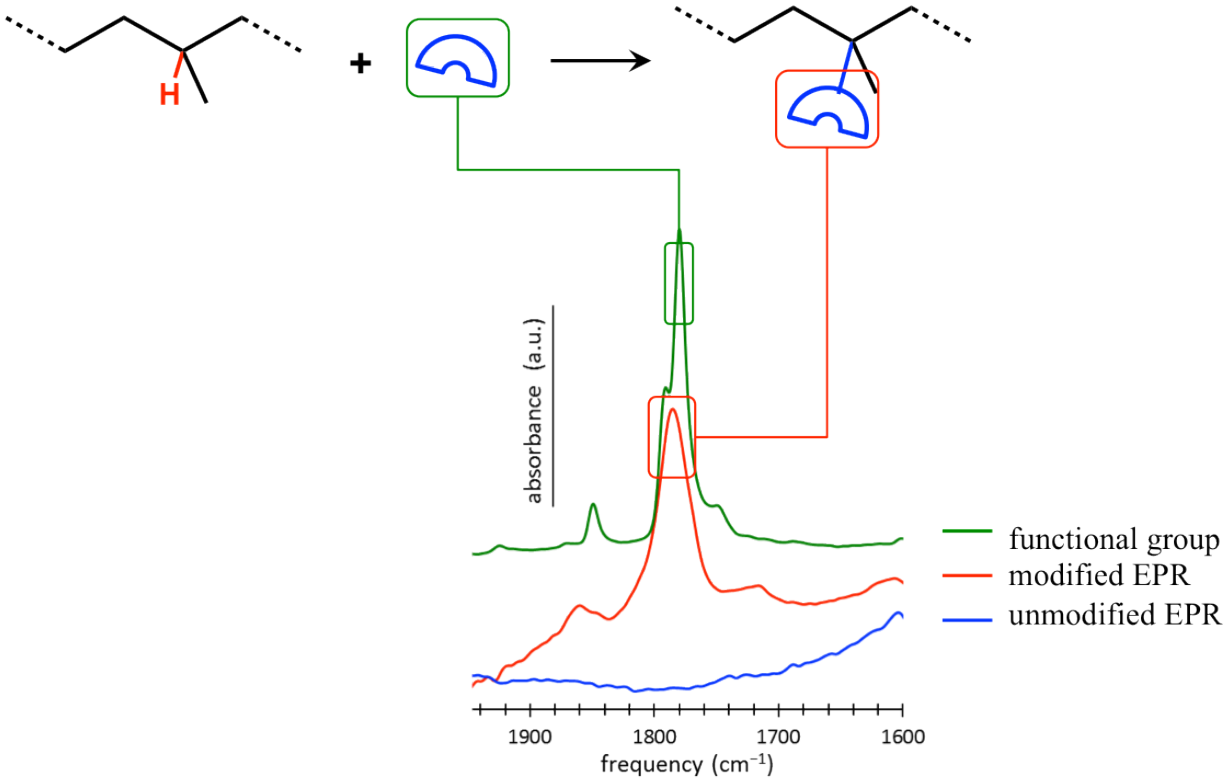

Figure 3.1. FTIR Spectroscopic Evidence of Grafting

4.0 Conclusions and Status

The motivation for this project comes from the need to extend the working life of in-containment cables at nuclear power plants. Replacement of existing safety-related power, instrumentation, and control cables represents significant costs in materials and plant shut down time. Therefore, it is of substantial importance to develop methods for lengthening the remaining useful life of existing cables.

During the past year we have successfully developed a high surface area form of the proprietary nuclear grade pink EPR insulation material to aid in characterization of aging effects in the material and screening of rejuvenation chemical treatments. This EPR particulate form has begun to produce new insight into the thermal oxidative aging process by exhibiting inter-particle bonding and heterogeneous discoloration phenomena not able to be observed in the previously studied thick EPR material.

A novel chemical treatment to introduce reaction points along undamaged portions of the ethylene-propylene EPR backbone has been conceived and demonstrated to effectively modify the EPR particulate form. The next step in the development of this promising approach is to confirm that the chemistry will proceed in a carrier solvent previously shown to facilitate diffusion into EPR rubber. The treatment will then be applied to EPR sheet material so that the effect of the treatment on EPR tensile properties may be evaluated. The treatment will be applied to aged and un-aged EPR to determine its rejuvenation potential. The approach involves introduction of a platform reaction site open to a wide range of chemical functionality. Chemical groups will be selected for the modification toward positively tuning the aged

EPR mechanical properties including modulus and strength. A successful treatment to recover EPR strength lost with aging might be applied to extend the life of installed cables and reduce the cost of continued nuclear plant operation.

Figure 4.1. Tensile Specimens of ~1.8-mm thick EPR Sheet

5.0 References

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