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On the mechanism of radiation and thermal-induced degradation of the insulation cables in nuclear power plants-The Presence of long-lived polyenyl C-centered Radicals

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Abstract

Radiolytically and thermally produced long-lived polyenyl C-centered radicals in the nuclear power plants' insulation cables are detected and measured after more than 45 months of aging since the irradiation and the thermal treatment. Electron Paramagnetic Resonance (EPR) results of the irradiated Cross-linked Polyethylene (XLPE) and Ethylene Propylene Rubber (EthProRu), used as primary insulation materials at Nuclear Power Plants (NPP), clearly demonstrate the presence of polyenyl radicals along with allyl and peroxyl radicals. The yields of these free radicals are dose-rate dependent. EPR results also show the presence of the long-lived polyenyl along with allyl and peroxyl free radicals in the thermally treated XLPE, and EthProRu. These free radicals can cause a major failure in the performance of these cables in NPPs. Besides, the results showed the enhancement in the oxidation reactions due to the migration of copper ions from the conductor to the bulk of the insulation.

This study also shows that the oxidation index (OI) and Elongation at Break (EAB) increases and decreases respectively at higher doses and temperatures.

Keywords

Insulation cables, Radiation and Thermal degradation, Long-lived polyenyl C-centered radicals

Introduction

The safe operation of Nuclear Power Plants (NPPs) is significantly dependent on the reliable function of cables which are responsible to transmit electricity and control signals to motors and control instruments respectively. [1], [2]

Environmental stresses such as heat, humidity, and radiation along with mechanical stresses such as bending can result in cable insulations' aging over time. It is of great importance that cables maintain their integrity over normal and accident conditions of operation at NPPs even when they are aged. [3]

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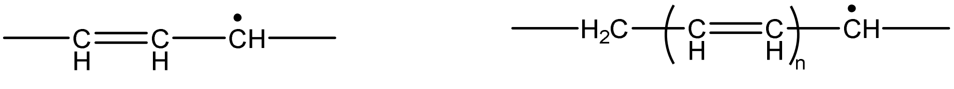
* Based on PhD dissertation in 2022 by Dr. Salimeh Gharazi

When polymers are exposed to ionizing radiation, excited states and cations are generated which ultimately forms alkyl free radicals and hydrogen atoms. The abstraction of hydrogen atom from an adjacent chain by the hydrogen atom product will form alkyl free radicals. Alkyl free radicals decay quickly due to their instability via three mechanisms: migration of two alkyl free radicals on the same chain which forms trans-vinylene unsaturation through disproportionation reactions, recombination of two alkyl free radicals via crosslinking reactions. and migration of alkyl free radical to an allylic position via hydrogen abstraction which forms allyl free radicals on vinylene and polyenyl free radicals on polyene unsaturation respectively. The conversion of alkyl radicals to polyenyl and allyl radicals happens in the crystalline regions.

Figure 1 shows the schematic of allyl and polyenyl free radicals. [4], [5]



$-\underset{H}{C}=\underset{H}{C}-\dot{C}H-$ $\qquad$ $-H_2C-\left(\underset{H}{C}=\underset{H}{C}\right)_n-\dot{C}H-$

(a) (b)

Figure 1. Schematic of molecular structure of (a) Allyl and (b) Polyenyl free radicals

Allyl and polyenyl free radicals are significantly more stable than alkyl free radicals due to resonance stability. Electron Paramagnetic Resonance (EPR) detects polyenyl free radicals by a singlet which is due to the highly conjugated nature of the free radical and the spectrometer cannot differentiate the multiple signals. [4], [6]

In the presence of oxygen, alkyl free radicals react with oxygen producing the corresponding peroxyl radicals. Peroxyl radicals ($RO_2^{\bullet}$) are unstable and undergo various types of reactions leading to the degradation of the polymer. The main reactions of $RO_2^{\bullet}$ are: propagation reactions by abstraction of hydrogen from adjacent polymer chains and termination reactions of bimolecular reactions to produce the unstable tetraoxides (ROOOR).

Hydroperoxides are produced in the propagation reactions. They decompose to alkoxyl and hydroxyl radicals as well as ketone and H_2O. Alkoxyl and Hydroxyl radicals are highly reactive components with important propagation reactions. Alkoxyl radicals through hydrogen abstraction and β scissions produce alkyl radicals. β scission reactions are illustrated in Figure 2.

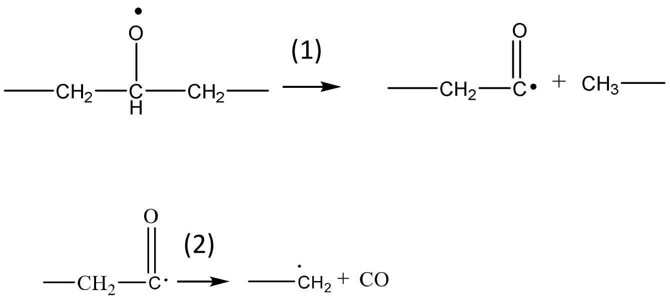


Figure 2. Schematic of β scission reaction

It should be mentioned that the ROOOR undergoes decomposition reactions to produce aldehyde, Oxygen and alcohol .[5]

It should be noted that the conversion of alkyl radicals to polyenyl and allyl radicals happens in the crystalline regions. The crystalline regions are 30-55% in XLPE and 0-50% in EthProRu respectively. The allyl and polyenyl free radicals may migrate to amorphous regions where they may react with oxygen. However, probability of the reactions is much less than that of alkyl radicals due to their conjugation stability. Oxidation reactions have been known as the most detrimental insulation degradation mechanism. [4], [6], [7],[8], [9]

A summary of all the corresponding reactions of alkyl radicals discussed above is illustrated in Figure 3.

As a result of the thermal, mechanical stress, and ionizing radiation, additionally, ruptures or scissions occur along the backbone of the chain, which lead to the decrease in the number average molecular weight ($\overline{M}_n$) and weight average molecular weight ($\overline{M}_w$). Obviously, the decrease in the $\overline{M}_n$ and $\overline{M}_w$ leads to the loss of mechanical properties.[10], [11]

While there are many investigations on understanding the aging mechanism of cable insulations in thermal and radiation environments, there is less clarifications on the type of the formed free radicals. The type of formed free radicals is significantly important in predicting the successive reactions. [12], [13],[14]

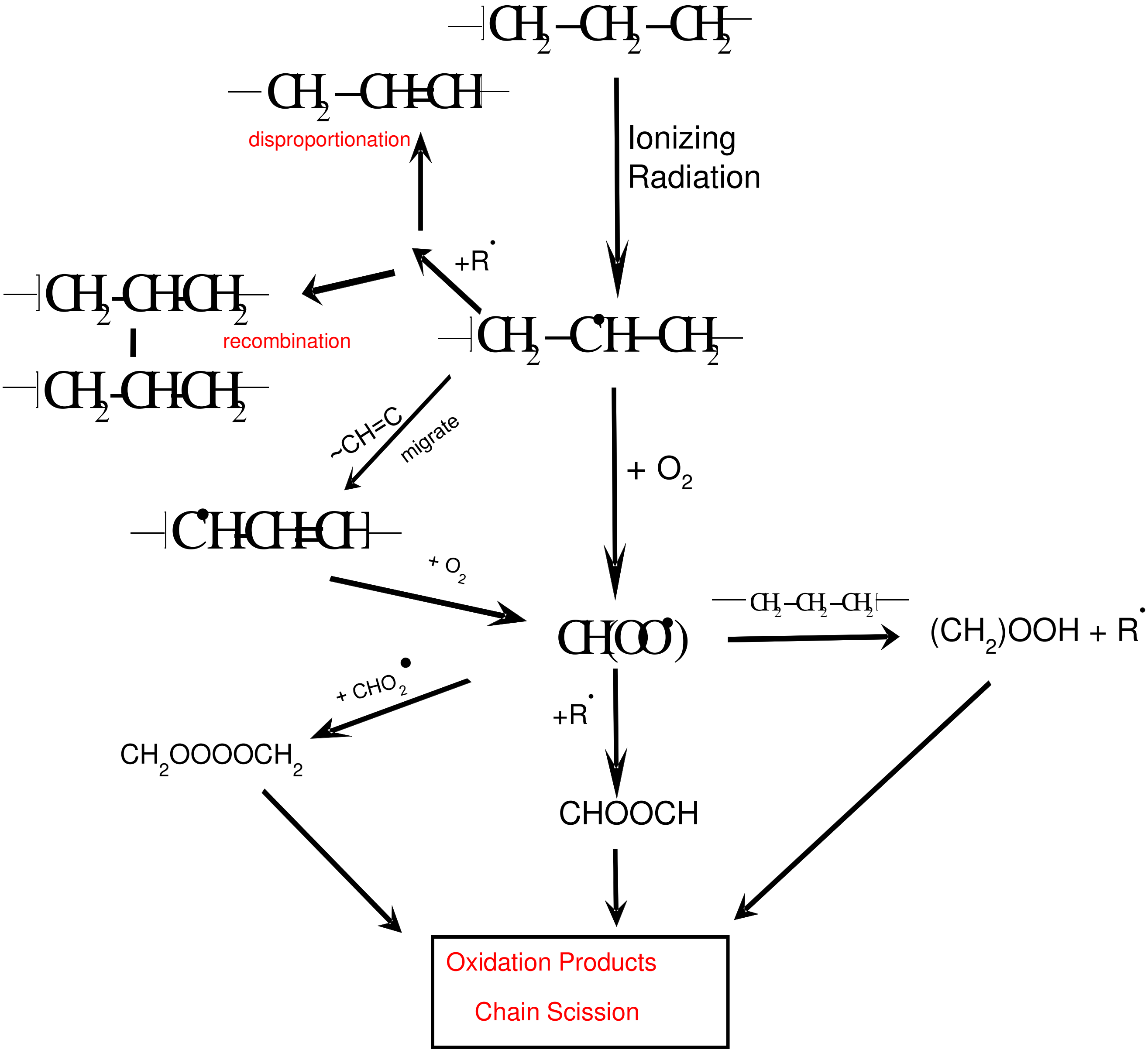


Figure 3. Schematic of oxidation reaction

In this work, polyenyl free radicals along with peroxyl and allyl radicals are detected by Electron Paramagnetic Resonance (EPR) spectroscopy in both thermally and irradicated aged specimens of XLPE and EthProRu insulation cables after 45 months of aging. The mechanical properties of all the aged specimens were measured with tensile tests. The results indicated that the mechanical properties decreased upon aging which is due to chain scission and crosslinking reactions. The Fourier Transform Infrared -Attenuated Total Reflectance (FTIR) results showed that Oxidation Index (OI) increases in most of the aged specimens.

Materials and Methods

We are donated commercial grade Cross-linked Polyethylene (XLPE) cables by General Cables and purchased Ethylene Propylene Rubber (EthProRu) commercial grade cables from Platt supply company. Nuclear-grade cables were donated and purchased from RSCC World Class Nuclear Cable Company which are commonly used in the nuclear industry. The characteristics of cables are summarized in Table1.

Table1- Cable Characteristics

Material	Grade	Insulation Thickness (mm)	Abbreviation
EthProRu	Nuclear	4.95	EthProRu-NU
XLPE	Nuclear	2.25	XLPE-NU
EthProRu	Commercial	7.50	EthProRu -Com
XLPE	Commercial	2.77	XLPE-Com

Thermal Treatment

Samples were prepared by cutting the cables into 6-inch-long sections using a bandsaw. The EthProRu and XLPE cables were then placed in ovens at temperatures of 90 °C, 120 °C which were extracted monthly up to 6 months. The samples aged at 90 °C did not reach the end of life after 6 months. Therefore, they were allowed to be aged for 45 months at 90 °C in the oven. Besides, the XLPE samples were aged at 140 °C, and extracted weekly up to four weeks.

After extraction, in order to strip the cables, the 6-inch-cut cables were again cut with bandsaw machines at the Institute for Research in Electronics and Applied Physics (IRIP) of University of Maryland to strip the cable.

Irradiation Treatment

Samples were irradiated using ^{60}Co gamma sources at the National Institute of Standards and Technology (NIST). Alanine dosimetry was used to measure the absorbed dose. Samples were irradiated in the presence of air with dose rate range from 0.074 to 3.5 kGy/hr for a total dose of 100kGy.

Characterization Techniques

Electron Paramagnetic Resonance (EPR)

EPR spectra were recorded on a EMX EPR spectrometer (Bruker corporation, USA) located at the University of Maryland. The working parameters of the instrument are as follows; Conversion time of 40.96 ms, time constant of 20.48 ms, modulation amplitude of 3.12 G, receiver gain of 6.32E3, MW power of 5 mW, MW attenuation of 16 dB and sweep width of 1000. The size of the samples in EPR tubes were 15mm×3mm×3mm. All the readings were normalized by dividing by their mass.

Tensile Test

Tinius Olsen Universal Testing Machine was used for tensile testing of our samples. The samples were tested at a strain rate of 13 mm/min. The RAY-RAN test equipment dog-bone press was used for cutting dog bones which uses dog-bone cutting die dimension according to TSC-ASTM D638-5 Dog Bone.

Fourier Transform Infrared -Attenuated total Reflectance (FTIR-ATR)

Fourier Transform Infrared (FTIR) spectra was obtained on Thermo Nicolet iS50, equipped with Attenuated total Reflectance (ATR) module. The FTIR-ATR spectra were used to analyze the structural changes of the insulations. The number of 128 scans from 650 cm^{-1} to 4000 cm^{-1} wavenumbers with a resolution of 2 cm^{-1} were averaged to make the ultimate FTIR-ATR spectrum after subtracting from the collected background.

The Oxidation Index (OI) is used to monitor/quantify the relative degree of oxidation.

The method used was to normalize the carbonyl peak absorption band (from 1700cm^{-1} to 1750cm^{-1}) relative to the reference peak, which is independent of aging, and calculate the area under the carbonyl peak. The reference peak for EPR was $A_{1155\ cm^{-1}}$ and the reference Peak for XLPE was $A_{720\ cm^{-1}}$ respectively. [15], [16]

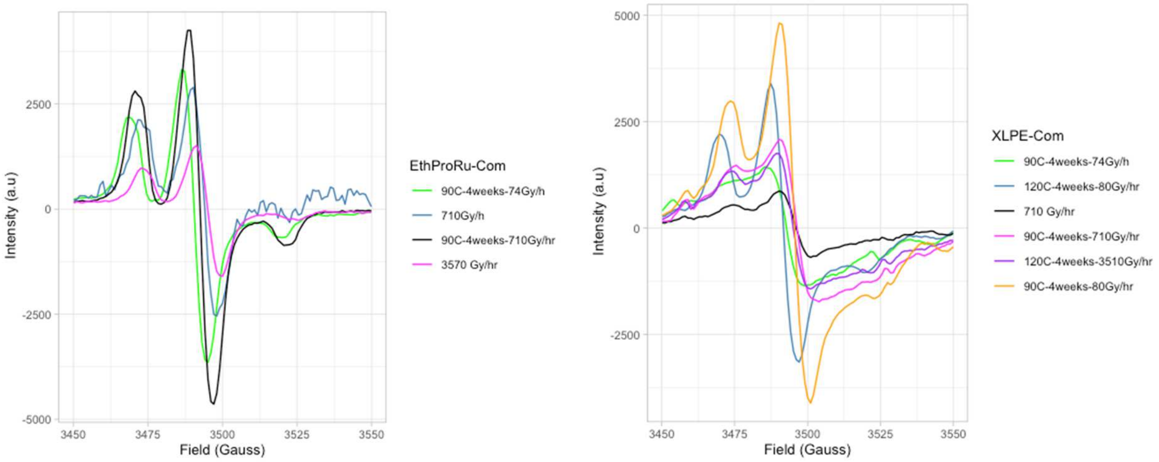
Results and Discussion

1. Irradiated Specimens

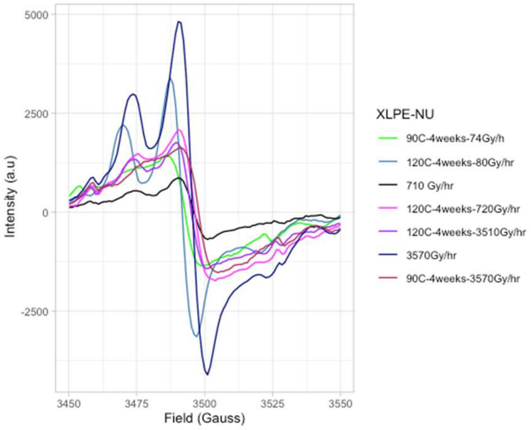
Identification of the long-lived free radicals

Figure 4a-c shows the EPR spectra of the long-aged, irradiated samples with various dose rates and temperatures of EthProRu-Com, XLPE-Com, and XLPE-NU respectively. All samples had received a total dose of 100 kGy. These samples were

irradiated in the presence of oxygen, and also aged in the presence of oxygen at various temperatures. All EPR spectra exhibit a broadened singlet pattern which is due to the presence of polyenyl radicals, peroxyl radicals and allyl radicals. [4], [5], [17], [18] and [19] As in the previous works, the radiolytically produced alkyl radicals in the crystalline region slowly transform to polyenyl radicals. The irradiated samples with higher dose rate exhibit lower amplitude of signal intensity indicating lower free radical concentration. This can be related to the fact that at higher dose rate, the alkyl radicals decay through second-order crosslinking reactions rather than transfer to allyl and polyenyl via first-order kinetics.



(a) (b)

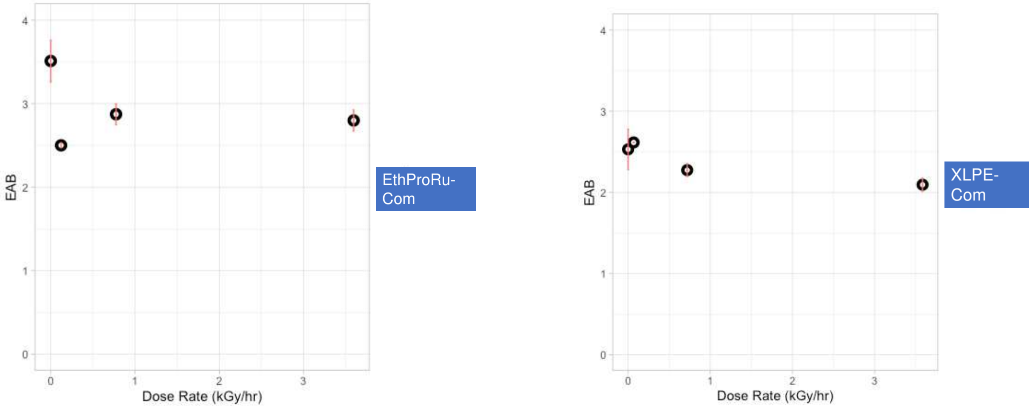


(c)

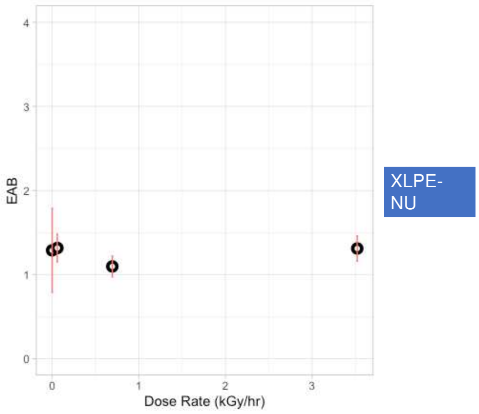
Figure 4. EPR spectra for (a) EthProRu-Com, (b) XLPE-Com, (c) XLPE-NU at different dose rate levels and temperatures.

Total dose and Dose rate effects on Elongation at Break (EAB)

Figure 5a-b show that the EAB decreases for EthProRu-Com and XLPE-Com with increasing dose-rate because of the progression of crosslinking reactions. These results suggest that at high dose rate, the crosslinking become the dominant reactions, even in the presence of oxygen. On the other hand, at lower dose-rate, the reactions of the radiolytically produced C-centered radicals with O_2 are the more prevailing, leading to the oxidative degradation.



(a) (b)



(c)

Figure 5. EAB versus dose-rate (kGy/hr) for (a) EthProRu-Com, (b) XLPE-Com and (c) XLPE-NU for the total dose of 100 kGy

Figure 5(c) shows that EAB of XLPE-NU slightly decreased which is due to the inhibition of crosslinking reactions because of radical scavenging of antioxidants present in the XLPE-NU specimens. Figure 6 is a schematic of the competition among the crosslinking reactions, reactions with O_2 and reactions with antioxidants of the radiolytically produced carbon center radicals.

The alkyl free radicals react with antioxidant, AH, which reduces the number of available free radicals for proceeding crosslinking and oxidation reactions. The reaction of antioxidants with peroxyl radicals produces hydroperoxides which inhibits chain scission reactions. As it was discussed in the introduction, the probability of reaction of allyl and polyenyl free radicals with oxygen and other chemicals such as antioxidants are much less than that of alkyl free radicals.

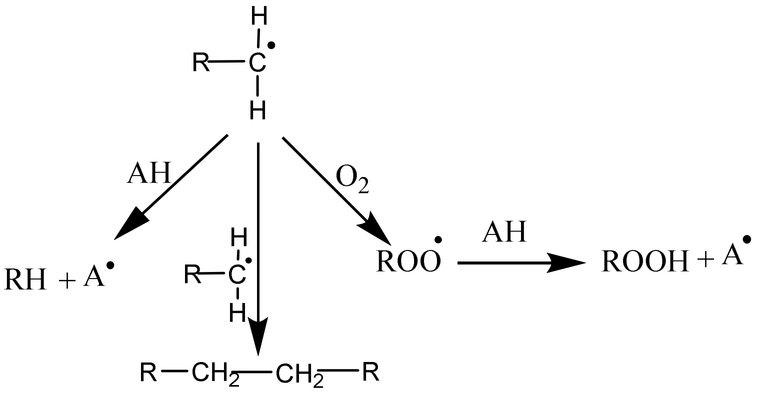


Figure 6. Schematic of the competition among the crosslinking reactions, reactions with O_2 , reactions with anti-oxidants of the radiolytically produced carbon center radicals

Total dose and Dose rate effects on Oxidation Index, OI

Figure 7 shows samples were taken from the inside [at the interface between the insulation interface and the copper conductor] and outside [at the interface between the insulation interface and the jacket] of the XLPE-NU cable insulation which were used for OI measurements.

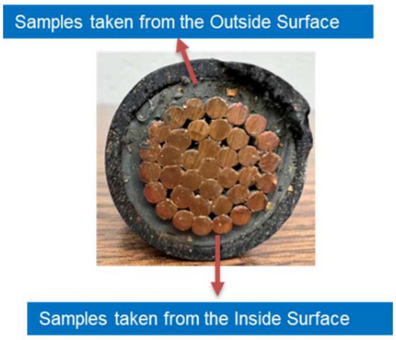
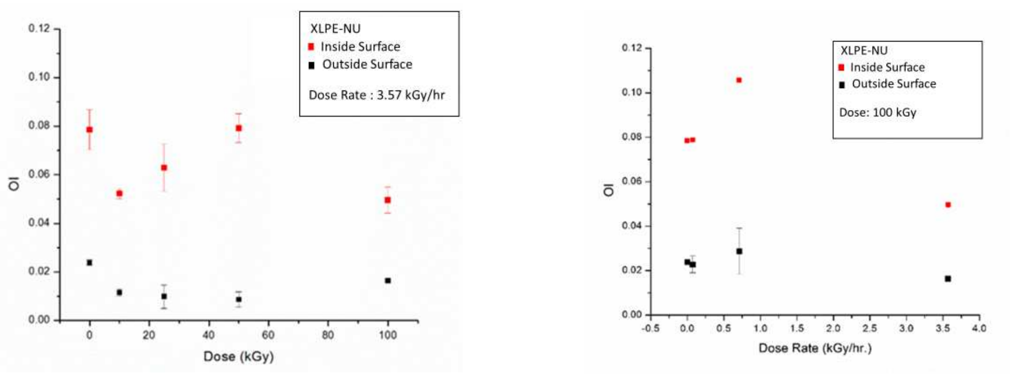


Figure 7. Specimens taken from the inside [at the interface between the insulation interface and the copper conductor] and outside surface [at the interface between the insulation interface and the jacket] of XLPE-NU cable insulation for OI measurements



(a) (b)

Figure 8. OI versus dose-rate for the total dose of 100 kGy (a) dose for the dose-rate of 3.57 (b) for the inside [at the interface between the insulation interface and the copper conductor]and outside surface [at the interface between the insulation interface and the jacket] of XLPE-NU cable insulation

Figure 8a-b show the OI measurements in the inside surface [at the interface between the insulation interface and the copper conductor]is much higher than the outer side, even though the outer surface is more exposed to air. The inside surface is in contact to the copper conductor which enhances the oxidation reactions by migration of copper ions into the insulation bulk. The OI measurements on the outside surface, Figure 8a, shows almost no changes. The slight change is in the experimental error range.

Figure 9 shows the schematic of oxidation induced due to copper ions. Figure 9 demonstrates that Cu^{+} is oxidized to Cu^{2+} by reaction with hydroperoxides produced from the oxidation of the radiolytically produced carbon center radicals which ultimately produces peroxyl radicals.

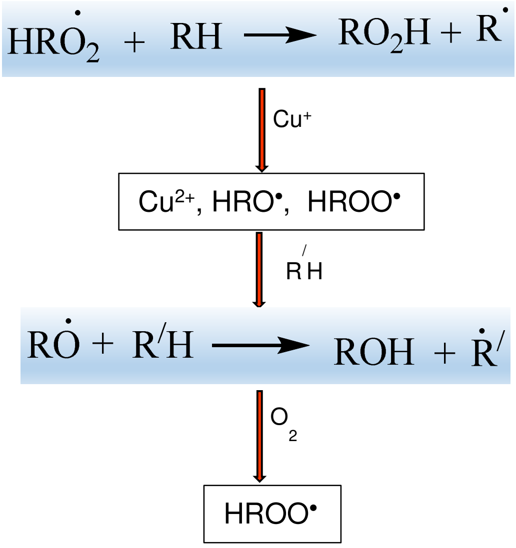
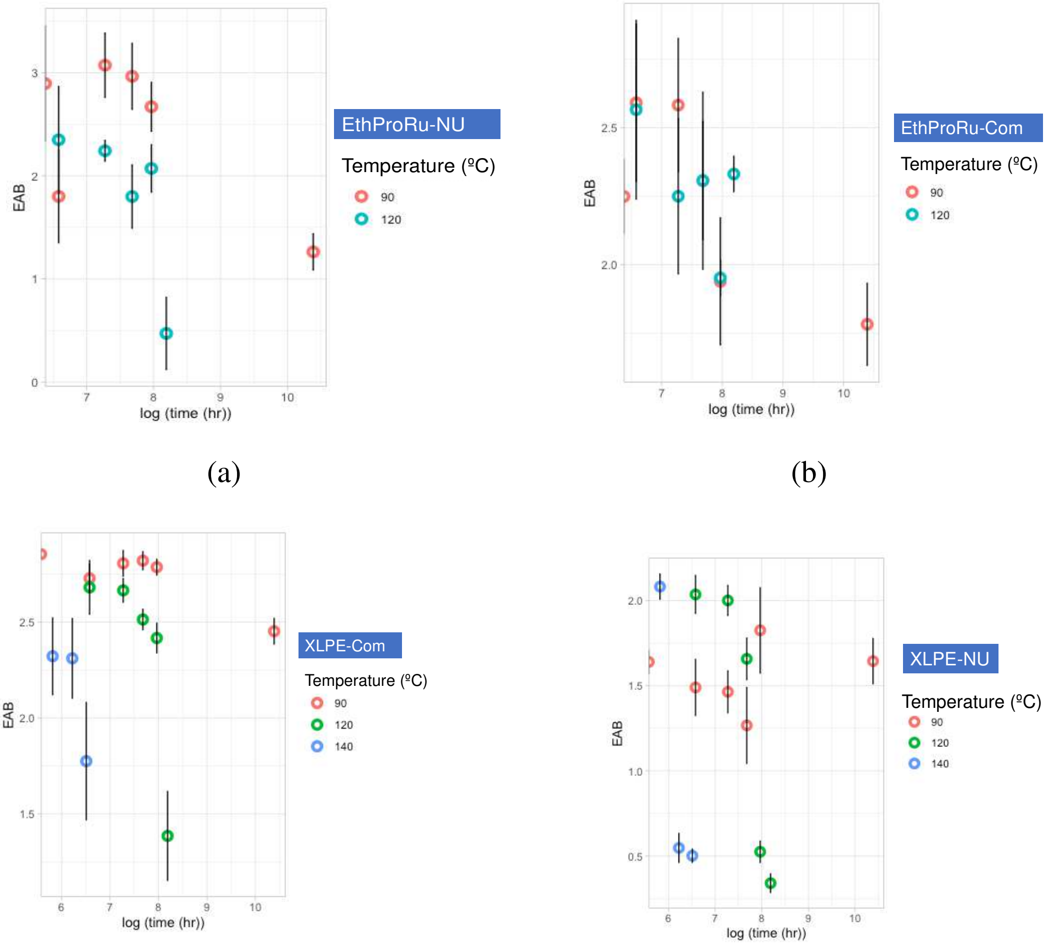


Figure 9. Oxidation induced due to copper ions at the interface between the insulation interface and the copper conductor

2. Thermally Aged Specimens

Thermal effect on Elongation at Break (EAB)

Figure 10 a-d shows the decrease of EAB versus time for all cases which is due to the enhancement of brittleness as a result chain scission and crosslinking. It should be noted that chain scission can generate alkyl radicals which can convert to more stable radicals or react with oxygen and produce peroxyl radicals. The ductility will drop when the movement of chains are limited in crosslinking reactions and shorter chain length does not support the plastic deformation in chain scission reactions.



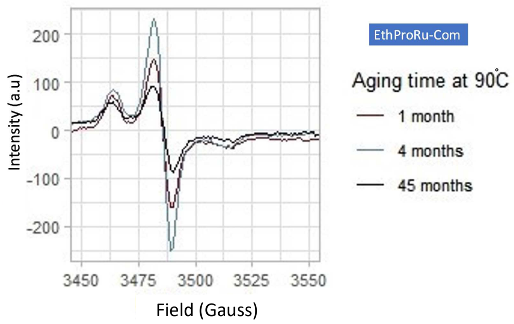
(a) (b)

(c) (d)

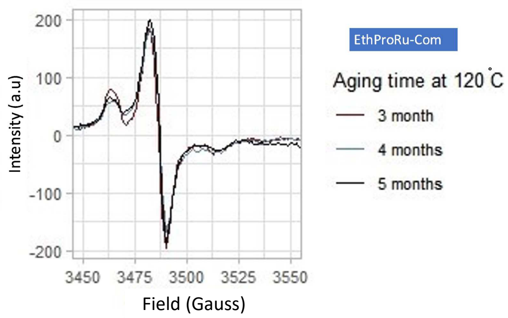
Figure 10. EAB versus time at different temperatures for (a) EthProRu -NU, (b) EthProRu-Com, (c) XLPE-Com and (d) XLPE-NU

Thermally produced polyenyl free radicals

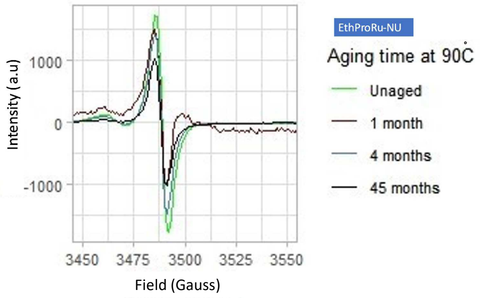
Figure 11 shows the EPR spectra of long-aged thermally treated samples of EthProRu-Com, EthProRu-NU, XLPE-Com, and XLPE-NU. Similar to the irradiated samples, all EPR spectra exhibit a broadened singlet pattern which is due to the presence of polyenyl radicals, peroxyl radicals and allyl radicals. It is worthy of noticing that even at higher temperatures, these polyenyl free radicals along with peroxyl and allyl radicals are still present. This suggests that the reactions of these polyenyl radicals via crosslinking or with oxygen are very slow or inconsiderable due to the conjugate nature of the polyenyl radicals.


EthProRu-Com
Aging time at 90°C
1 month
4 months
45 months
Intensity (a.u)
200
100
0
-100
-200
3450
3475
3500
3525
3550
Field (Gauss)

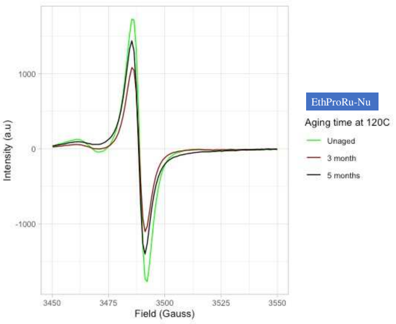
(a)


EthProRu-Com
Aging time at 120°C
3 month
4 months
5 months
Intensity (a.u)
200
100
0
-100
-200
3450
3475
3500
3525
3550
Field (Gauss)

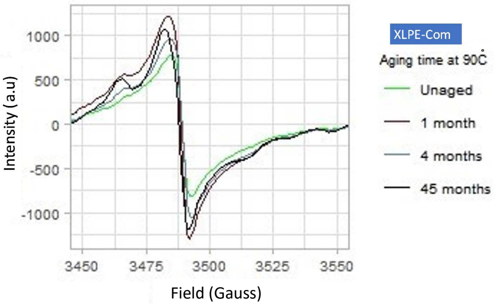
(b)


EthProRu-NU
Aging time at 90°C
Unaged
1 month
4 months
45 months
Intensity (a.u)
1000
0
-1000
3450
3475
3500
3525
3550
Field (Gauss)

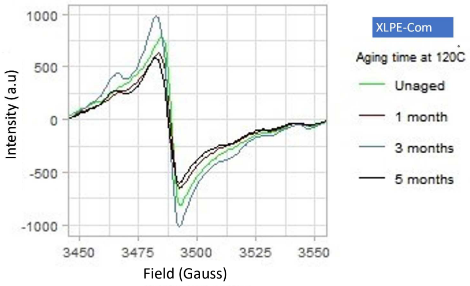
(c)


EthProRu-Nu
Aging time at 120C
Unaged
3 month
5 months
Intensity (a.u)
1000
0
-1000
3450
3475
3500
3525
3550
Field (Gauss)

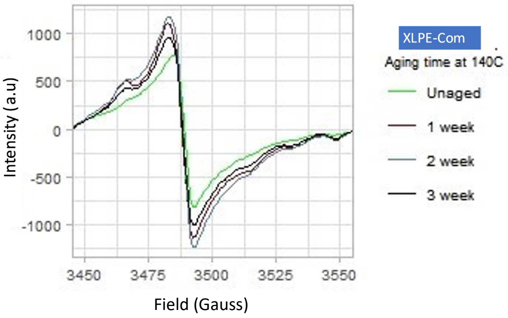
(d)


XLPE-Com
Aging time at 90°C
Unaged
1 month
4 months
45 months
Intensity (a.u)
1000
500
0
-500
-1000
3450
3475
3500
3525
3550
Field (Gauss)

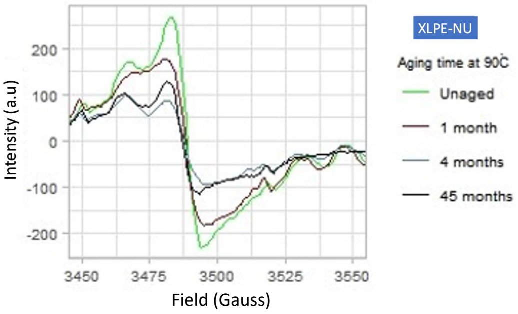
(e)


XLPE-Com
Aging time at 120°C
Unaged
1 month
3 months
5 months
Intensity (a.u)
1000
500
0
-500
-1000
3450
3475
3500
3525
3550
Field (Gauss)

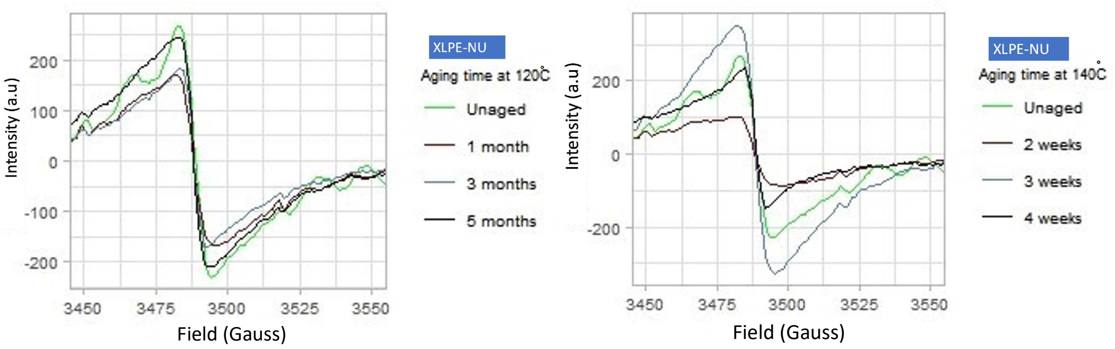
(f)


XLPE-Com
Aging time at 140°C
Unaged
1 week
2 week
3 week
Intensity (a.u)
1000
500
0
-500
-1000
3450
3475
3500
3525
3550
Field (Gauss)

(g)


XLPE-NU
Aging time at 90°C
Unaged
1 month
4 months
45 months
Intensity (a.u)
200
100
0
-100
-200
3450
3475
3500
3525
3550
Field (Gauss)

(h)



(i) (j)

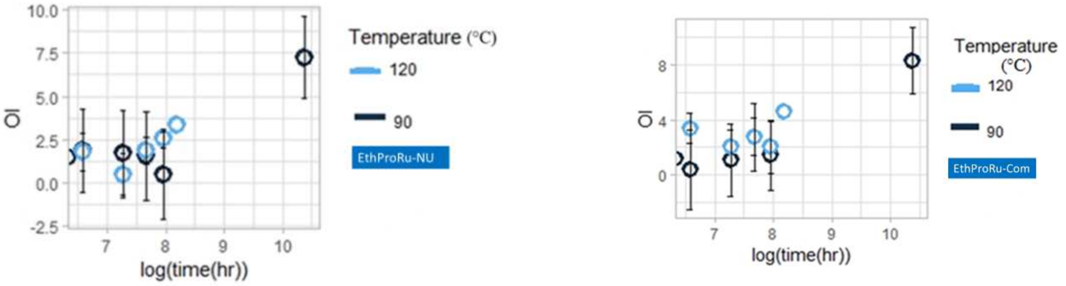
Figure 11. EPR spectra for EthProRu-Com at 90 °C (a) and 120 °C (b), EthProRu-NU at 90 °C (c) and 120 °C (d), XLPE-Com at 90 °C (e), 120 °C (f) and 140 °C (g), XLPE-NU at 90 °C (h), 120 °C (i) and 140 °C (j).

Thermal effect on Oxidation Index, OI

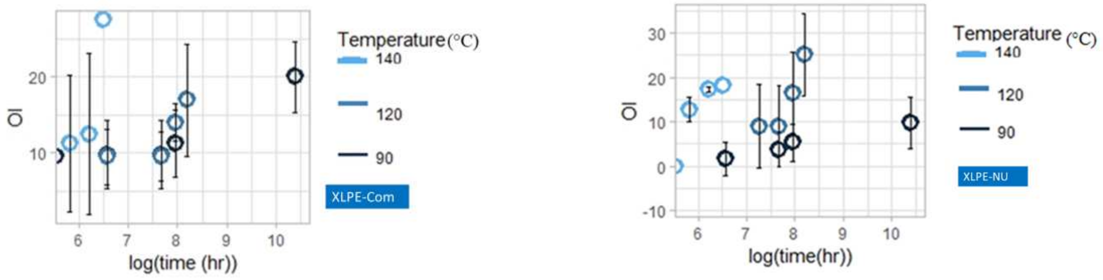
Figure 12 shows the OI measurement versus time which demonstrates that OI increases with time for different temperatures in all cases.

The immediate decrease in the OI is directly related to the initial thermal induced decomposition of the organic oxides, leading to the formation of volatile carbon dioxide. This process is followed by an increase in OI as a function of temperature.

Figure 12 c-d shows that the increase in the OI at 140 °C is higher than that at 120 °C and 90 °C, thermally treated for the 1,6- and 45-months period respectively. These results are attributed to the high molecular mobility of polymeric chains at 140 °C and the presence of oxygen in the amorphous regions which has extended to crystalline areas above meting the point temperature.[7] It should be mentioned that the samples were not softened even at 140 °C and 120 °C because they are heavily crosslinked.[20]



(a) (b)



(c) (d)

Figure 12. OI versus time at different indicated temperatures for (a) EthProRu-NU, (b) EthProRu-Com, (c) XLPE-Com, (d) XLPE-NU

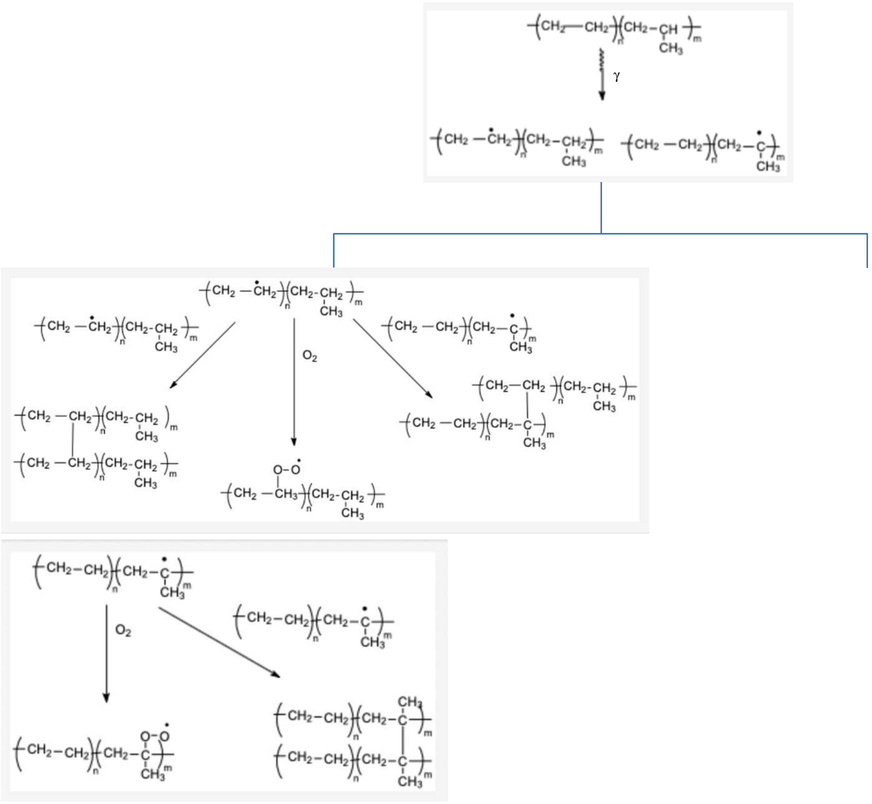


Figure 13. The schematic of free radical formation, crosslinking, and oxidation reactions of EthProRu

Figure 13 shows the main reactions of two types of radiolytically produced radicals in the EthProRu. These two types of free radicals are formed on the ethylene and propylene parts of the EthProRu. We expect that the alkyl radicals in the ethylene parts undergo more crosslinking reactions than the propylene part. This can be explained by the fact that the steric effect of the methyl group can impede the crosslinking reactions. In addition, the electron-donating methyl groups are expected to enhance the reaction with oxygen leading to less crosslinking. As it was explained before the probability of the allyl and polyenyl free radicals' reaction with oxygen are much less than that of alkyl radicals.

Conclusion

We concluded that the radiolytically and thermally produced alkyl radicals in XLPE and EthProRu can be transferred to relatively stable polyenyl and allyl radicals as well as peroxyl radicals. These findings are important to elucidate the failure mechanism of the insulation cables used in nuclear power plants. Most likely, these polyenyl and allyl radicals are in the crystalline structures of the insulators, where the concentrations of oxygen are negligible. However, there is also a contribution of peroxyl radicals in the amorphous regions at the steady state concentration. In addition, the highly conjugated structures of these polyenyl radicals react very slowly with oxygen. Clearly, these radiolytically and thermally produced alkyl radicals undergo the following three types of competing reactions: reaction with oxygen, transferring to polyenyl and allyl radicals, scission, disproportionation, and even crosslinking reactions. The evidence of the cross-linking reactions resides in the decrease of EAB, as the increase in the crosslinking enhances the brittleness of the insulators.

Another important conclusion is that even the presence of very small amounts of Cu^+ and Cu^{+2}, produced on the surface of the copper metal conductor, can enhance the oxidation of the insulators. This explains why the OI at the outer surface of the insulators is smaller than the inside OI, which is located at the interfaces between the copper metal conductor and the insulator.

Finally, the weak or the absence of the dependence of the OI on dose rate, demonstrates the effect of the antioxidants by scavenging the radicals and impeding the reaction of the alkyl radical with oxygen, even at low dose-rate.

Acknowledgment

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