Aging Mechanisms and Nondestructive Aging Indicator of Filled Cross-Linked Polyethylene (XLPE) Exposed to Simultaneous Thermal and Gamma Radiation

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Abstract Aging mechanisms and a nondestructive aging indicator of filled cross-linked polyethylene (XLPE) cable insulation material used in nuclear power plants (NPPs) are studied. Using various material characterization techniques, likely candidates and functions for the main additives in a commercial filled-XLPE insulation material have been identified. These include a mixture of brominated components such as decabromodiphenyl ether and Sb_2O_3 as flame retardants, ZnS as white pigment and polymerized 1,2-dihydro-2,2,4-trimethylquinoline as antioxidant. Gas chromatography-mass spectrometry, differential scanning calorimetry, oxidation induction time and measurements of dielectric loss tangent are utilized to monitor property changes as a function of thermal and radiation exposure of the cable material. The level of antioxidant decreases with aging by volatilization and chemical reaction with free radicals. Thermal aging at 90 °C for 25 days or less causes no observable change to the cross-linked polymer structure. Gamma radiation causes damage to crystalline polymer regions and introduces defects. Dielectric loss tangent is shown to be an effective and reliable nondestructive indicator of the aging severity of the filled-XLPE insulation material.

Keywords Filled cross-linked polyethylene · Aging mechanisms · Gas chromatography-mass spectrometry · Differential scanning calorimetry · Oxidation induction time · Dielectric loss tangent

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Introduction

Cross-linked polyethylene (XLPE)-based polymer composites are the most widely used cable insulation material in United States nuclear power plants (NPPs) [1]. The XLPE matrix in these materials contains various fillers and additives. Cables used in NPPs can be exposed to radiation at elevated temperatures. The integrity of the cable insulation is critical for the reliable operation of the cables and consequently for the safe operation of the NPPs. The study of the degradation of cable insulation materials under radiation and at elevated temperatures is important for gaining a fundamental scientific understanding of the aging mechanisms and for developing effective safety inspection methods. A review of prior work in this area was recently published by Bowler and Liu [2]. In this work, candidate components of the studied filled-XLPE insulation are identified, aging mechanisms are studied and a nondestructive indicator of the aging severity is identified.

Sample Preparation

White XLPE insulation material was obtained from a commercially available nuclear-grade instrumentation cable consisting of two 16AWG conductors, a laminated aluminum/polyester shield, drain wire, and a chlorosulphonated polyethylene jacket. The cable was purchased from RSCC (product code I46-0021). The cable jacket was removed to expose the XLPE-insulated wires. The average inner and out diameter of the XLPE insulation layer were measured under an optical microscope to be 1.46 and 2.76 mm, respectively, resulting in an average wall thickness of 0.65 mm. For accelerated aging, samples were hung by clips on a rack placed in an oven located in the exposure zone of a Co-60 source in the High Exposure Facility (HEF) at Pacific Northwest National Laboratory (PNNL). Simultaneous thermal and gamma radiation aging of the samples was achieved through placement of the oven in the radiation environment and control of the oven temperature. The dose rate to each individual sample was selected by controlling sample distance from the radiation source. Various radiation doses to the samples were achieved by aging them for different periods of time. Details of the accelerated aging process and sample preparation can be found in our previous paper [3].

Materials Characterization

A variety of materials characterization tests were conducted on pristine, 90 °C thermally-only aged and simultaneously thermal (90 °C) and gamma radiation (540 Gy/h) aged XLPE insulation materials in order to (1) identify the composition of

the filled-XLPE sample material; (2) study material aging mechanisms under these exposures; and (3) find a reliable and prominent nondestructive aging severity indicator.

Scanning Electron Microscopy (SEM)

SEM was conducted on the fracture surface of pristine XLPE material. The fracture surface was prepared by breaking the sample immediately upon removal from liquid nitrogen following 5 min immersion. The surface was coated with 5 nm of iridium prior to examination to avoid sample charging. The fracture surface was imaged using an FEI Quanta-FEG-250 SEM operated at 10 kV.

Pyrolysis Gas Chromatography—Mass Spectrometry (Pyrolysis GCMS)

An evolved gas analysis (EGA) using pyrolysis GCMS was conducted. The GCT is an accurate mass time-of-flight (TOF) mass spectrometer coupled to an Agilent 6890 gas chromatograph (GC). The Electron ionization (EI) source is used in this study. The Frontier 3030D pyrolyzer is mounted on the Back Inlet of the GC. A sample of 0.2 mg was heated in the pyrolyzer at 220 °C for 2 min and then heated to 700 °C at 20 °C/min. The GC was held isothermally at 320 °C during the run.

Oxidation Induction Time (OIT)

OIT was measured using a TA Instruments Q800 differential scanning calorimeter. Ten mg of sample material was heated at a rate of 15 °C/min from ambient temperature to 230 °C in helium flowing at 50 mL/min. When the temperature of 230 °C was reached, the specimen was held in helium isothermally for 2 min, after which the atmosphere was changed to oxygen maintained at the same flow rate. The specimen was then held at 230 °C until the oxidative reaction was revealed on the thermal curve. The threshold defining the oxidative reaction is heat flow of 0.1 W/g above the baseline.

Differential Scanning Calorimetry (DSC)

A DSC Q800 from TA Instruments was also used to perform standard calorimetry. In helium atmosphere, a temperature program of heating (cycle 1), cooling (cycle 2)

and re-heating (cycle 3) was performed using a sample mass of 5 mg. In cycle 1, the temperature was ramped from 20 to 160 °C at 10 °C/min, after which the temperature was held isothermally at 160 °C for 2 min. In cycle 2, the temperature was ramped from 160 °C back to 20 °C at 10 °C/min, after which the temperature was held isothermally at 20 °C for 2 min. In cycle 3, the temperature was ramped again from 20 °C up to 160 °C at 10 °C/min.

Dielectric Loss Tangent

Dielectric loss tangent is a dielectric property of an insulating material and is frequency-dependent. An Agilent 4980A LCR meter and 16451B dielectric test fixture were used to measure the dielectric loss tangent of the XLPE insulation materials. An electrode of 10 mm in diameter was used and the dielectric properties were measured over a frequency range of 10^5 to 10^6 Hz. For complex permittivity, at a particular frequency,

$$\varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \tag{1}$$

the dielectric loss $\varepsilon''(\omega)$ is the imaginary part of the permittivity, and the loss tangent is defined as

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{2}$$

Loss tangent of the pristine and aged XLPE insulation materials were measured in this study.

Results

Composition Analysis

An SEM image of the cross-section of the studied XLPE cable insulation material is shown in Fig. 1. It can be seen that the XLPE cable insulation is a composite material containing filler particles of various sizes. Further characterization of the material using energy dispersive X-ray spectroscopy (EDX, not shown), pyrolysis GC-MS, Fourier transform infrared spectroscopy (FTIR, not shown), carbon-hydrogen elemental weight ratio testing (C–H testing, not shown) and thermogravimetric analysis (TGA, not shown) indicate that the primary fillers consist of a mixture of brominated flame retardants such as decabromodiphenyl ether (DBDE), Sb_2O_3, ZnS and polymerized 1,2-dihydro-2,2,4-trimethylquinoline (pTMQ). The calculated weight percentages of these components are listed in Table 1. For brevity, detailed data
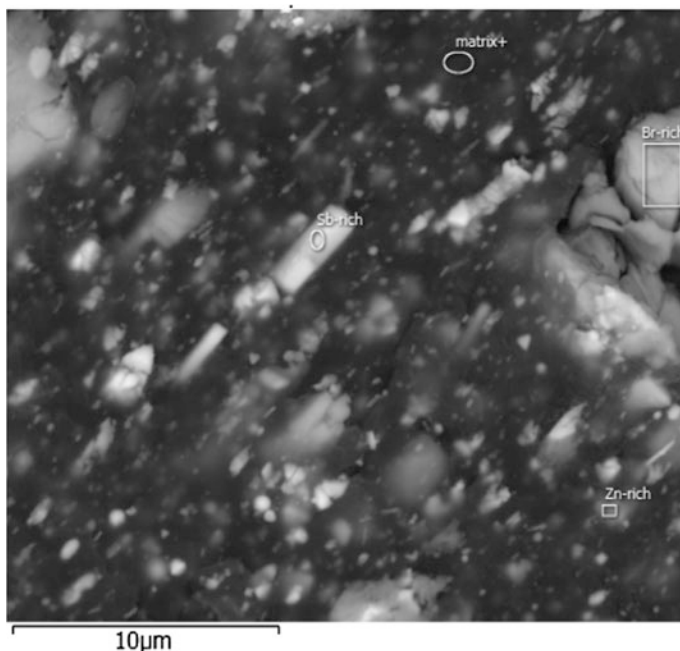
Fig. 1 SEM image (5000×) of the cross-section of pristine XLPE insulation material

Table 1 Composition of the commercial, filled, cross-linked polyethylene

Identified component (probable function)	Weight percentage (%)
XLPE (polymer base)	56–60
Brominated components (e.g. DBDE, flame retardant)	~15
Sb_2O_3 + ZnS (flame retardant and colorant)	<20
pTMQ (antioxidant)	<3
Others	2–6

supporting the identification and weight percentage calculation of these components are not provided here, but will be published separately. DBDE and Sb_2O_3 are likely included to function as flame retardants [4], ZnS as white pigment [4] and polymerized 1,2-dihydro-2,2,4-trimethylquinoline as antioxidant [5].

Characterization Results

EGA data taken on pristine and aged XLPE materials (aging condition: 540 Gy/h for 25 days at 90 °C) are shown in Fig. 2. Antioxidant fragments start to come out of the samples near the program starting temperature of 220 °C, fragments of
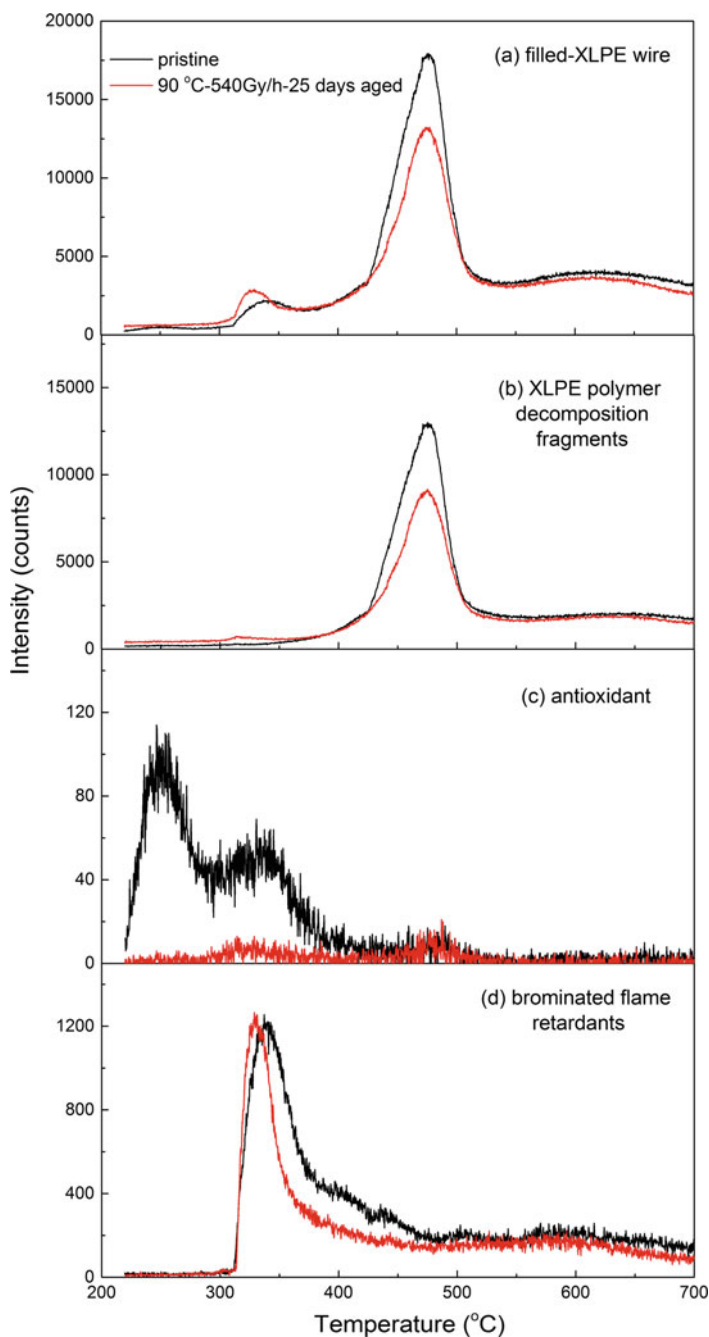
Fig. 2 EGA data for **a** pristine and aged XLPE wire; **b** the fragments of the decomposition of the XLPE polymer chains; **c** the fragments of the decompositions of the antioxidant; and **d** the fragments of the decomposition of flame retardant decabromodiphenyl ether (DBDE). Note that the antioxidant curve shown in **c** is obtained by summing the mass intensity given by the different fragments of pTMQ; similarly the flame retardant curve shown in **d** is obtained by summing the mass intensity given by DBDE and its fragments

brominated flame retardant DBDE start to come out at about 300 °C, and XLPE polymer decomposition fragments start to come out at about 300 °C. Figure 2a shows a significant decrease in the intensity of the aged material compared with that of the pristine material, which is mainly caused by the intensity decline in the decomposition fragments of the XLPE polymer matrix, as shown in Fig. 2b. Figure 2c shows a significant decrease of the antioxidant in the aged material in comparison with the pristine XLPE.

OIT results for pristine, 90 °C thermally-only aged, and simultaneously 90 °C thermal and 450 Gy/h gamma radiation aged filled-XLPE materials are shown in Fig. 3. OIT of pristine material is 45.2 min. When the material is aged thermally at 90 °C for 20 days, the OIT decreases to 40.1 min, dropping by approximately 11%. When the material is simultaneously aged thermally at 90 °C and by gamma radiation at 450 Gy/h for 20 days, the OIT decreases to 11.8 min, dropping by approximately 74%.

DSC cooling and re-heating curves of pristine, thermally only aged (aging conditions: 90 °C for 10 and 25 days), and simultaneously thermal and gamma radiation aged materials (aging conditions: 540 Gy/h at 90 °C for 10 and 25 days) are displayed in Fig. 4 and 5. It is shown in the cooling curve of pristine material that three exothermic signals are observed, with their maxima at 93.4, 102.6 and 115.9 °C. Figure 4a shows the cooling curves of pristine and thermally only aged materials, no significant difference is observed. Similar observations are made for their re-heating curves as in Fig. 4b. Figure 5a shows the cooling curves of pristine and simultaneously thermal and gamma radiation aged materials, it is observed that the peaks initially at 102.6 and 115.9 °C shift to lower temperatures, and the magnitude of the peak at 93.4 °C declines. Similar observations are made for re-heating curves as in Fig. 5b, in which the peaks shift to lower temperatures and the curve between the temperature range of about 100–120 °C gets flatter compared with pristine XLPE.

Fig. 3 OIT of filled-XLPE aged at 90 °C for various durations (5, 10, 15 and 20 days), at the dose rates of 0 and 450 Gy/h. The uncertainty is less than 2 min
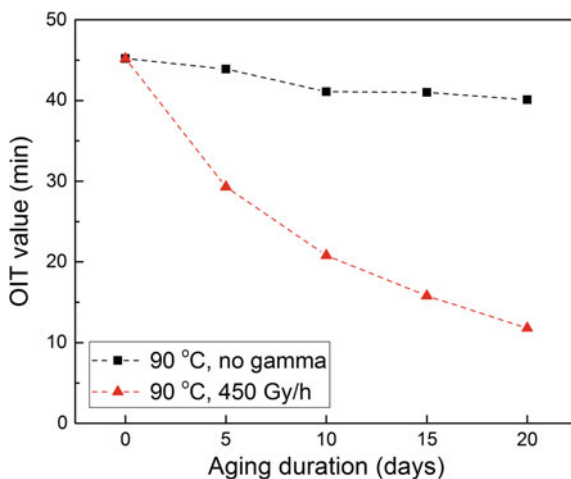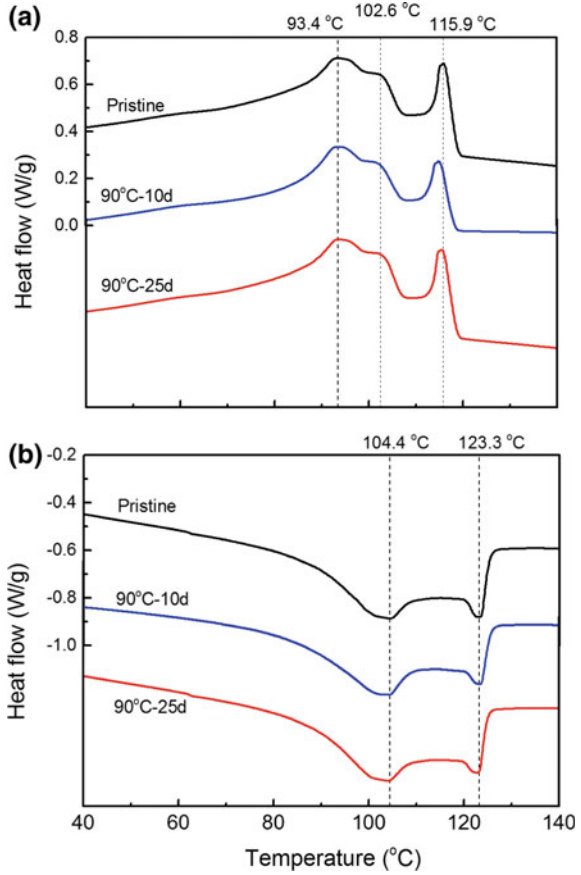
Fig. 4 Cooling (**a**) and
re-heating (**b**) DSC curves of
XLPE insulation materials
that were thermally-only aged
at 90 °C for durations of 10
and 25 days

The loss tangent of pristine and differently aged XLPE cable material over the frequency range of 10^5–10^6 Hz is exhibited in Fig. 6. At the frequency of 10^6 Hz, the loss tangent is 4.4×10^{-4} for pristine material, increasing to 7.4×10^{-4} (an increase of 68.2%) when the material is exposed to aging for 10 days, and to 1.2×10^{-3} (an increase of 172.7%) at exposure for 25 days. When no gamma radiation is present in the aging process at 90 °C for 25 days, the loss tangent is observed to decrease from 4.4×10^{-4} to 3.88×10^{-4} (a decline of 11.8%).

Interpretation

GC-MS and OIT results indicate that the aging process consumes antioxidants in the material. As has been discussed in section 1.4.1, the XLPE material appears to include pTMQ as an antioxidant. The melting temperature of pTMQ ranges from

Fig. 5 Cooling (**a**) and re-heating (**b**) DSC curves of XLPE insulation materials aged at 90 °C for durations of 10 and 25 days at the dose rate of 540 Gy/h
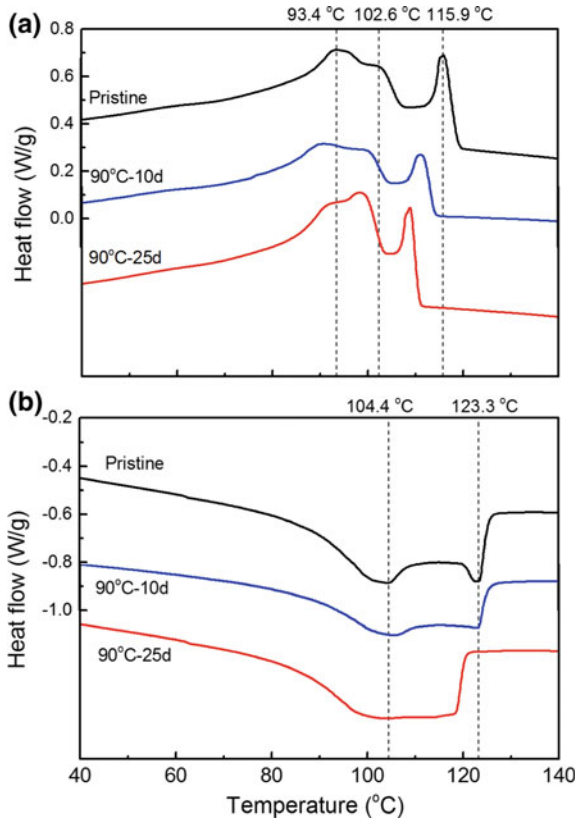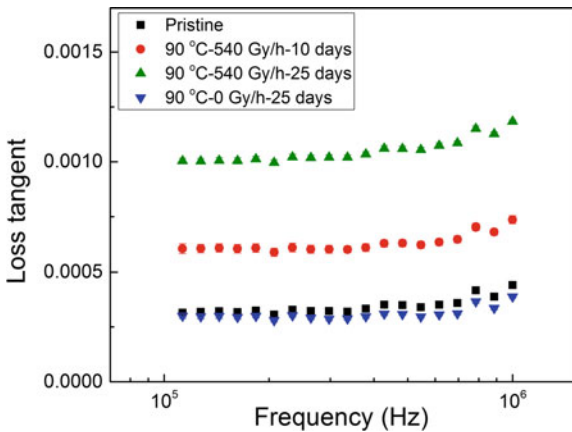

Fig. 6 Loss tangent of four sets of differently aged XLPE materials. (Note that the uncertainty is calculated by standard deviation of 5 measurements for each sample, the error bars are in the plot but too small to be seen.)

72 to 94 °C [6]. When the XLPE material studied here is thermally-only aged at 90 °C, loss of pTMQ antioxidant takes place. When the material is simultaneously aged by gamma radiation at 90 °C, thermal decomposition, evaporation or sublime take place, on the one hand, and, on the other, the gamma radiation breaks the polymer bonds and generates free radicals, which consume the antioxidants by chemical reaction. This explains why the OIT value decreases about seven times quicker when gamma radiation is present in the aging process. Compared with the DSC curves of pristine material, no significant change is observed for those of 90 °C thermally-only aged materials, indicating that when the material is thermally-only aged at 90 °C for 25 days or less, no significant changes take place in the polymer structures. When gamma radiation is involved in the aging process, however, the recrystallization peaks in the cooling curves and melting peaks in the re-heating curves shift to lower temperatures, indicating that the crystals formed during the cooling process are weaker. It is very likely that gamma radiation breaks the crystals to some extent and introduces defects, free radicals and chain branching in the crystals, making the crystals smaller and/or less perfect and hence melt at lower temperatures. When the material is thermally-only aged at 90 °C, a decrease in loss tangent is observed. When the material is simultaneously aged by thermal and gamma radiation, there is an increase in its loss tangent. Free radicals contribute to the conductivity of the material. When the material is at elevated temperature, there is a competing process between the generation and consumption of the free radicals. When no gamma radiation is involved in the aging process, the process of free radicals consumption by reacting with the antioxidant dominates over the free radicals generation process. When gamma radiation is involved in the aging process, the process of free radicals generation dominates leading to a larger number of defects and may account for the elevation in observed dielectric loss as the material ages. Dielectric loss is therefore promising as a reliable nondestructive indicator of the aging severity for the commercial XLPE cable insulation materials studied here.

Conclusions

The studied commercial XLPE cable insulation material is a composite with XLPE as polymer matrix and various fillers including antioxidant [polymerized 1,2-dihydro-2,2,4-trimethylquinoline (pTMQ)], flame retardants [decabro-modiphenyl ether (DBDE) and Sb_2O_3], and white pigment (ZnS). The level of antioxidants decreases with aging by volatilization and chemical reaction with free radicals. When thermally aged at 90 °C for 25 days or less, no significant changes are caused in the polymer structure. When gamma radiation is present in the aging process, gamma radiation causes damage to the crystals and introduces defects, free radicals and chain-branching in the crystals, which causes the crystals to melt at lower temperatures. Consumption of free radicals dominates over their generation when the material is thermally aged, while the generation of free radicals dominates over their consumption when the material is exposed to gamma radiation. Dielectric

loss tangent is proved to be sensitive to the aging severity for the studied commercial XLPE cable insulation material and may hold promise as a nondestructive indicator of such. A paper including more characterization results of a larger sample set aged at a broader range of aging conditions is in preparation, which will give a clearer picture of the aging mechanisms taking place in irradiated XLPE, and further examine dielectric loss as a suitable nondestructive indicator of XLPE aging due to gamma radiation exposure.

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