Electrical Analyses of Gamma Radiation-Induced Aging on EPDM-Based Insulation Systems

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Abstract- This paper deals with the investigation of the insulating properties of EPDM materials subjected to radiation aging with two non-destructive techniques: electrical (dielectric spectroscopy) and chemical (FTIR). Flat samples of EPDM were subjected to accelerated aging at 860 Gy/h for 664 h with four withdrawals at room temperature. The dielectric spectroscopy results indicate that the tan δ at 100 kHz coherently follows the aging evolution of the materials and it is suggested to be a suitable aging marker. The spectra of FTIR results suggest that EPDM undergoes chain scission and oxidation after radiation ageing. These results confirm the suitability of the electrical nondestructive technique for aging evaluation.

I. Introduction

Ethylene propylene diene monomer (EPDM) is extensively utilized in cable insulation applications owing to its superior resistance to moisture, heat, and oxidation [1]. In nuclear power plants (NPPs), this material is frequently used as wire insulator or in joints, including cable power transmission in the reactor containment [2], [3].

In contrast to conventional power plants, polymer materials used in NPPs are subjected not only to typical thermal and mechanical stresses but also to unavoidable radiation stresses. Cables operating under nominal conditions are exposed to low gamma (γ) radiation doses, whereas, under accident conditions, they encounter high doses of both gamma and beta radiation. Radiation aging breaks and ionizes chemical bonds in the insulation, depleting its insulating properties and increasing the risk of cable insulation failure [4].

Numerous studies have been conducted to address the issue of radiation-induced degradation in EPDM [2], [5], [6], [7], [8]. In those works, different condition monitoring (CM) techniques have been employed to evaluate the performance of insulation, including mechanical methods (indenter modulus, elongation at break (EaB)), electrical measurements (dielectric spectroscopy, DC conductivity measurements and pulsed electro-acoustic (PEA) analysis), and chemical tests (Fourier transform infrared spectroscopy (FTIR), thermal gravimetric analysis (TGA), and nuclear magnetic resonance (NMR) measurements) analyses. Many radiation ageing investigations on EPDM conventionally use EaB testing, for insulation aging evaluation. Nevertheless, the obvious limitations of EaB testing are that the sample must be removed and sent to a laboratory for testing and the test process is destructive.

This paper investigates the insulation properties of EPDM following radiation aging through two distinct nondestructive approaches: dielectric spectroscopy for electrical properties and FTIR for chemical characterization. The research aims to identify the intrinsic relationships among these properties.

II. Materials and Methods

A. Materials

Materials under tests are EPDM sheets provided by MIXER S.p.A. in Bagnacavallo, Italy. Sheets were manufactured from precursors by compression molding at 180°C for 10 minutes.

The accelerated aging procedure was carried out at the ROZA facility (UJV Řež, Czech Republic) through a ^{60}Co gamma radiation source at room temperature. The dose rate was 860Gy/h and the aging time ranged from ~70h to ~664h. Four withdrawals were performed in total with periods as reported in Tab.1. Figure 1 reports the different materials as received after the withdrawal steps. In general, it is evident a tendency of the material to become darker with aging, likely due to oxidation.

TABLE I
Withdrawals of Radiation-aged Samples

Withdrawal #	1	2	3	4	5
Aging time (h)	0	68	236	501	664
Dose (kGy)	0	58	203	431	571

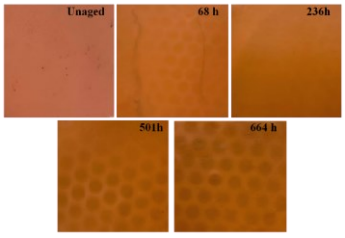

Fig. 1. Unaged and radiation-aged EPDM samples

B. Dielectric spectroscopy

In this work, dielectric spectra were recorded using the Novocontrol Alpha Dielectric Analyzer v2.2 under room temperature. The applied voltage was 3 V_{rms} and the frequency ranged from 10^6 to 0.1 Hz, allowing the investigation of both low frequency dipolar polarization and high frequency interfacial polarization.

For the sake of this work, from the measurements, the real part of permittivity and dissipation factor tan δ are reported and discussed

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C. *Fourier Transform Infrared Spectroscopy (FTIR)*

Due to the thickness of samples, the attenuated total reflectance (ATR) technique of FTIR spectroscopy was used to detect types of chemical bonds (functional groups) in EPDM structures caused by radiation aging. FTIR spectra were recorded using Perkin Elmer Spectrum Two FT-IR Spectrometer equipped with a diamond/ZnSe crystal. An average of 16 scans was collected for each spectrum in the 400–4000 cm^{-1} range with a resolution of 4 cm^{-1}. A background spectrum was measured at first and automatically subtracted from each scan. The results of absorbance were normalized at 2849 cm^{-1} peak, corresponding to the CH_2 symmetric stretching mode and is mostly unaffected by aging [7].

III. RESULTS

A. *Dielectric spectroscopy results*

Fig. 2 shows the dielectric spectra results of EPDM aged at 860 Gy/h for the different withdrawal times. In particular, the real part of permittivity (ε') and tan δ (dissipation factor) are illustrated in Fig. 2 (a) and (b). Results indicate that ε' remains relatively stable (~2.5) across the frequency range examined. During the first aging period, the dielectric constant is reduced probably due to the removal of some polar species e.g., antioxidants. Further aging causes the monotonic raise of the electrical property with aging time.

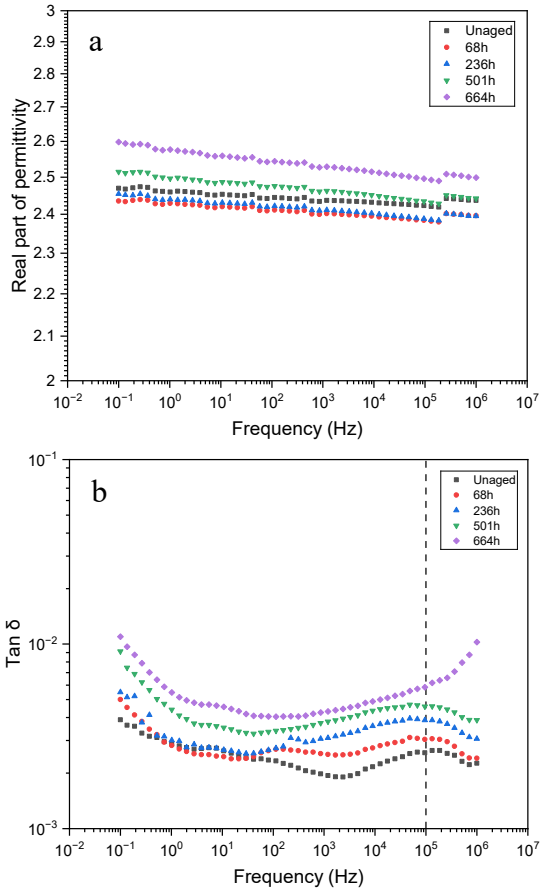

Fig. 2. (a) Real part of permittivity and (b) tan δ as a function of frequencies and aging time

The curves of tan δ (Fig. 2.b) show two peaks: one occurring at frequencies at ~100 kHz and another one at frequencies lower than 0.1 Hz and outside the range of the measurement. During the first two aging periods, the trend of the low frequency dielectric response is almost overlapped, suggesting that the modifications in interfacial structures are very limited. Further aging causes the increase of the property in the considered region claiming a structural modification, possibly linked to chain scission and rearrangement along with the arising of free radicals.

For frequencies higher than 100 Hz, one can notice a monotonic growth of the electrical property. This phenomenon may be generally related to the dipolar polarization, whose frequency ranges from 10^3 to 10^9 Hz [9].

In Figure 2(b), the peak of dielectric loss appears at 10^5 Hz, accompanied by a relaxation peak possibly classified as β-relaxation and linkable to the arising of dipolar species such as oxidized species. This is in accordance with previous studies on other materials e.g., XLPE, EVA-EPDM, where the values of tan δ at 100 kHz proposed to be suitable aging marker [9-11]. As a confirmation, a monotonic increase of the property may be recorded for the considered accelerated aging and Fig. 3 shows the trend of tan δ as function of aging time and dose.

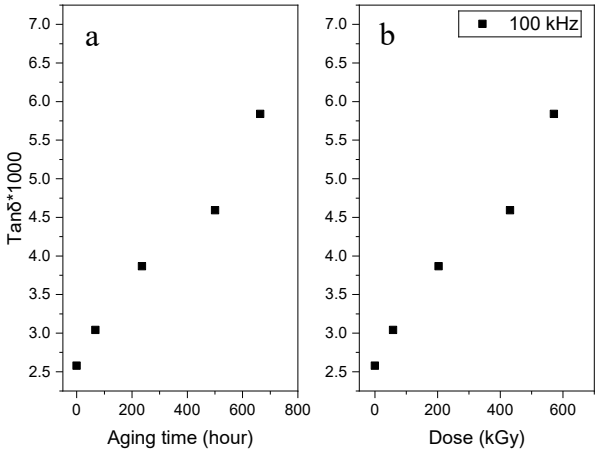

Fig. 3. Tan δ at 100 kHz variates with aging time and dose

B. *FTIR results*

Fig. 4 reports the whole view of FTIR spectra after normalizing at 2849 cm^{-1} peak (the CH_2 symmetric stretching mode). Compared to the unaged spectrum, there is an overall increasing trend in the absorbance peak and area values after irradiation aging.

Specifically, the IR absorption in the 3600–3000 cm^{-1} region is primarily responsible for the presence of hydroxyl (-OH) and hydroperoxide (-OOH) groups [5], [7], [12]. The increase in peak intensity at this absorption band suggests the formation of OH groups by the oxidation reaction [5].An increase in this region between unaged and radiation-aged is clearly observed in the detailed spectrum results plot (Fig. 5). This indicates that during the initial aging period the changes are higher than the ones reported from the second period on.

The peaks at 2849 cm^{-1} and 2920 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of methylene

groups (-CH_2), respectively [13-15]. It is difficult to discern the changes solely from the peak values. However, the spectra show that the region of the aged samples is significantly broader than that of the unaged one. Therefore, the areas under the curves of peaks (2945-2830 cm^{-1}) are compared.

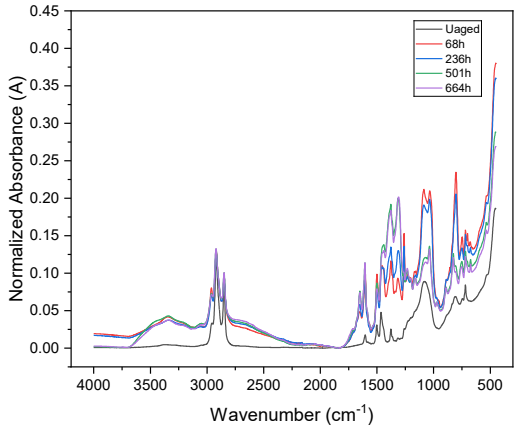

Fig. 4. Overall view of FTIR spectra

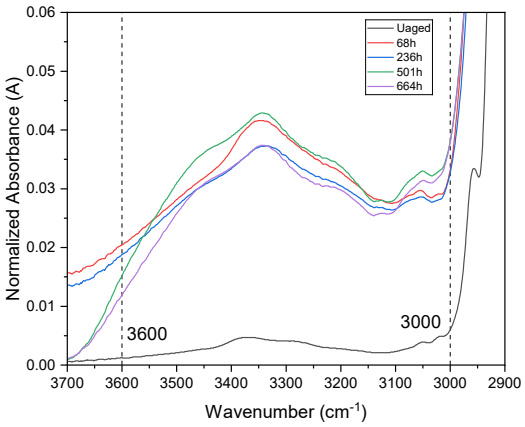

Fig. 5. Spectra of 3600-3000 cm^{-1} bands

As shown in Fig. 6 (a) and (b), the bands areas of radiation-aged EPDM are significantly higher than that of the virgin sample. Still, the differences among the aged materials are less pronounced, although there is an overall increasing trend. The increase of this absorption band indicates the modification of the C-H structure of the polymer probably related to the initial chain scission and following recombination.

It is also worth noting the spectrum in the range of 1760-1690 cm^{-1} where is assigned to the carbonyl groups (C=O) [7]. The area of this absorption band is an indicator of the degree of oxidative degradation of the polymer [13]. Here, the carbonyl index (*CI*) is represented by the new peak 1720 cm^{-1} over reference peak 2849 cm^{-1}. As illustrated in the Fig. 7 (a) and (b), after 68 hours of radiation aging, the *CI* value of the samples is 4.5 times higher than that of the unaged samples. The *CI* increases with aging time, indicating oxidative reactions occurring in the polymer due to radiation exposure.

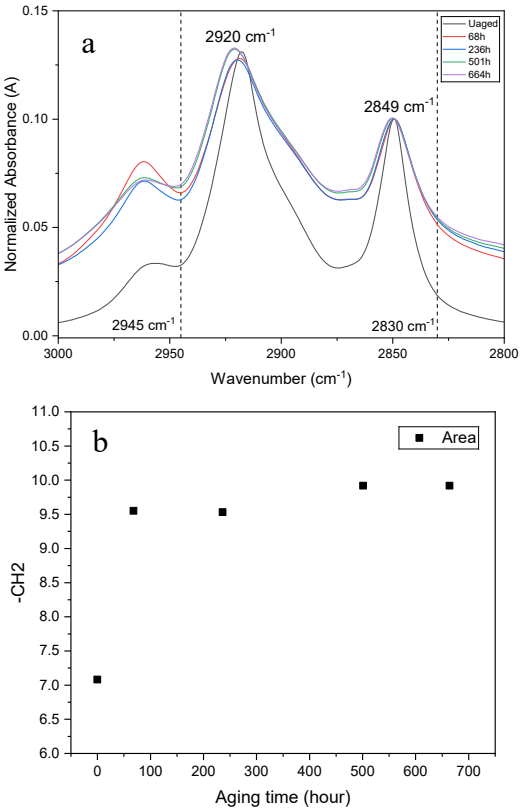

Fig. 6. (a) Spectra of 2945-2830 cm^{-1} bands and (b) the bands area variation of -CH_2

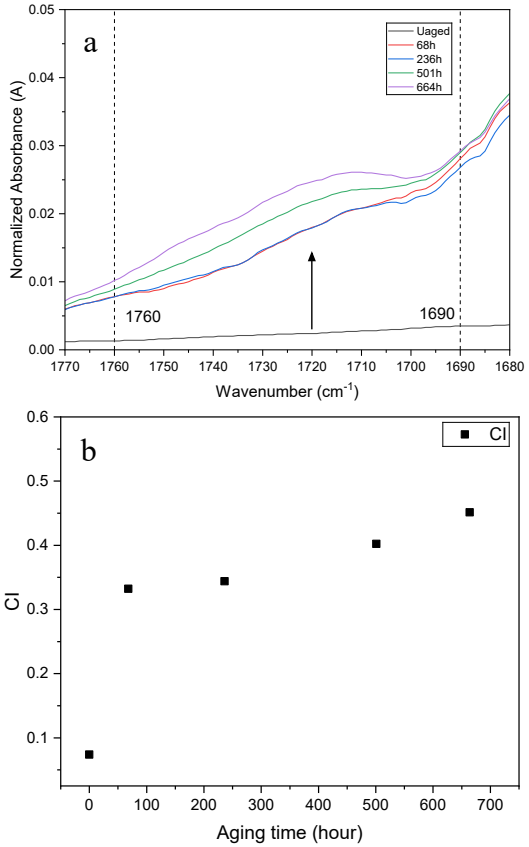

Fig. 7. (a) Spectra of 1760-1690 cm^{-1} bands and (b) the *CI* variation

IV. Discussion

The two main ageing mechanisms of EPDM polymers under γ-irradiation conditions are cross-linking and chain scission. During the ageing, these two processes occur simultaneously. The chain scission is stabilized in oxidizing environment since alkyl radicals formed during the ageing process strongly react with oxygen[8]. In particular, radicals generated from the scission of C–H and C–C bonds can combine with oxygen dissolved in the polymer, initiating chain reactions.

With reference to the tested EPDM, the FTIR results indicate that radiation leads to the formation of oxidation products, specifically carbonyl groups. As radiation aging time and dose increase, the occurrence of reactions also rises, resulting in a higher quantity of oxidation products.

Comparinfg Fig. 6(b) and Fig. 7(b) reveals that both EPDMs experienced drastic changes in the initial stage of radiation aging (0-68h). This may be attributed to the chain scission of macromolecules and oxidative reactions involving free radicals. After 68h, however, the area of the -CH_2 irradiation zone tends to stabilize, indicating that chain scission events are either equilibrated or hindered. The slight increase of *CI* thereafter suggests that the oxidation reaction continues with lower rate. The possible reason for this phenomenon may lie in the fact that during the early stages of irradiation aging the main degradation mechanism are hydrolysis of the polymer (as seen in Fig. 5) and structural modifications (Fig. 6) rather than oxidation reactions.

Both hydroxyl and carbonyl groups are strongly polar species, for this reason they respond to the external electric field in the dipolar polarization area of the dielectric spectrum. Being these species clearly related to aging, it may be possible to correlate the aging level of the polymer with the value of tanδ, confirming what already reported in literature [10] regarding the validity of this parameter for nondestructive polymer aging investigation.

V. Conclusions

This paper investigated the radiation aging of EPDM insulating materials at room temperature from two perspectives: electrical and chemical properties. The results showed that the radiation at 860 Gy/h dose rate significantly affected the polymer properties. The following conclusions can be drawn.

a) The first aging period of EPDM aging causes the biggest modifications of the polymer properties. In particular, the parameter related to chain scission (area related to -CH_2) and the carbonyl and hydroxyl concentration show an initial large increase of the property, suggesting that copious chain scission and oxidation events occur.
b) Further aging brings to the stabilization of the chain scission parameter, while carbonyl and hydroxyl groups continue to increase with a slower pace.
c) The buildup of oxidation species is also recorded by tanδ tests which show a monotonic increase of the property in the dipolar polarization region, validating its possible use for polymer nondestructive aging evaluation.

Future research will investigate radiation aging at lower dose rates and the combined effects of thermal and radiation aging, aiming at finding a unique end-of-life point related to the nondestructive dielectric spectroscopy tests for EPDM-based insulation systems.

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