Filler impact analysis on aging of crosslinked polyethylene for nuclear applications through dielectric spectroscopy

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***Abstract*- This paper investigates the evolution of electrical properties with aging for two XLPE based materials having different chemical compositions. It is shown that aging and material composition can significantly affect the electrical response, suggesting the suitability of dielectric spectroscopy for polymer diagnostics. Furthermore, the dielectric response is correlated with the evolution of mechanical properties, in particular elongation at break (EaB), in order to evaluate the possible scaling-up of the current cable qualification standard.**

I. INTRODUCTION

In each nuclear power plant (NPP) thousands of kilometers of low voltage (LV) cables are installed, whose application can spread from power transmission to instrumentation and control (I&C) of signals.

Nowadays, qualification of low voltage cables is based on the IEC/IEEE 62582-3 standard [1,2] and achieved sometimes by means of destructive techniques, in particular tensile stress tests. For LV cables in service, indeed, one of the criteria to assess the end-of-life is the reduction of elongation-at-break (EaB) to 50% of its initial value.

Old NPPs built during 70s and 80s are now reaching their end of design life (usually 40 years) [2]. Since NPP utilities are trying to extend the life of nuclear plants up to other 40 years, qualification of LV cables is a key problem since on-field tests of mechanical properties of LV cables can be very complicate for most applications.

In this framework, the new European H2020 TeaM Cables Project aims at providing NPP operators with a novel methodology for efficient and reliable NPP cable aging management by, among other, developing methodologies for nondestructive testing techniques (NDTs).

Among the possible NDTs, electrical measurements and, dielectric spectroscopy in particular, are now becoming more and more important and considered as a valid alternative to traditional tests.

This paper analyzes the correlation between the dielectric measurements and the traditional mechanical properties, above all elongation-at-break of insulating materials; in order to evaluate the possible correspondence between these two quantities and to set a criterion for cable qualification based on electrical nondestructive techniques. Electrical and mechanical response of different-filled crosslinked polyethylene (XLPE) and their evolution with aging are reported. Moreover, correlation between these two set of tests is presented and discussed.

II. EXPERIMENTAL SETUP

A. *Specimens*

The analyzed material is cross-linked polyethylene (XLPE), widely used as insulating material for low-voltage cables, with different amount and kinds of additives.

XLPE specimens are obtained in form of tapes with thickness of ~500μm. Due to the roughness of the surface, 3x3 cm samples have been metallized with gold through cold-sputtering. Materials compositions are reported in Tab.1.

TABLE I
SPECIFICATION AND CHEMICAL COMPOSITION OF SAMPLES

Sample number	Sample composition
#1	Crosslinked matrix alone
#2	Crosslinked matrix + 1phr primary antioxidant
#3	Crosslinked matrix + 1phr secondary antioxidant
#4	Crosslinked matrix + both antioxidants
#5	Crosslinked matrix + 25phr flame retardants
#6	Crosslinked matrix + 50phr flame retardants
#7	Crosslinked matrix + 50phr flame retardants + both antioxidants

For the sake of brevity, only the study on compositions #1 and #7 are here reported, since they present, respectively, the lowest and highest amount of fillers of the available materials.

B. *Accelerated aging*

In order to reproduce the typical environmental stresses inside a nuclear power plant, specimens have been aged by the means of both high temperature and gamma radiation.

Aging has been performed inside the Panoza facility at UJV (Rez Czech Republic) through a ^{60}Co γ-irradiation source. The dose rate set for the aging is 70 Gy/h at 50°C. Specimens were aged for 200 days and sampling made every about 40 days. The maximum absorbed dose is 374 kGy.

C. Electrical measurements

Electrical response of samples as a function of frequency is investigated by means of the dielectric spectroscopy technique.

Dielectric spectroscopy allows the evaluation of the complex permittivity with frequency. Dielectric spectra were obtained through a Novocontrol Alpha Dielectric Analyzer v2.2 with applied voltage of 3 V_{rms} at room temperature. The frequency range analyzed was 10^{-2}-10^{6} Hz.

D. Mechanical measurements

Tensile strength and elongation at break are two common indicators reflecting the mechanical strength of the insulating material, according to [3].

Tensile tests have been performed using Instron 5500K8810/4505H2190 machine with 100 N load cell and pneumatic grips. The dumbbell shape samples (type 2, EN-ISO 37:2005) for tensile were used. Grip distance was 50 mm and cross-head test speed 50mm/min. Elongation was detected by cross-head motion without extensometer (nominal elongation at break). Five sample from each material were tested.

Samples have been conditioned at least 24 hours before testing at preferred atmosphere (23 ± 2) °C and (50 ± 10) % R.H. Finally, EaB values have been calculated and reported.

III. Results

A. Dielectric spectroscopy results

Figures 1 and 2 present, respectively, the complex permittivity trend as a function of frequency and aging time for the two different material compositions (#1 and #7) considered. As expected, for both the analyzed materials, the complex permittivity increases with the increase of aging period. However, behaviors of these trends are deeply different.

The imaginary part of permittivity for material #1 (Fig. 1.b) displays a quite flat behavior with frequency, which is typical of very low-filled PE materials. Moreover, after an initial steep increase for the first aging, the increase of ε'' with aging is quite constant.

Focusing on the high frequencies range, one can notice very small differences between plots relevant to 4th and 5th aging period, which suggests that the material may not bare any further aging process, reaching a sort of saturation for dielectric losses.

At low frequencies, ε'' trend is similar to the one discussed for the high frequencies except for the last aging periods considered (4th and 5th). Here, complex permittivity increases, reducing the frequencies, with a slope of -1. This behavior is well known in literature [4], and it is related to conduction phenomena. Together with these, the raise of the imaginary part of permittivity can be imputable to the interfacial polarization peak which likely occurs at lower frequencies (10^{-3} Hz), outside the range here analyzed.

Figure 2.b shows the imaginary part of permittivity for material #7. In this case, the dielectric losses are extremely lower than material #1 and do not significantly vary with the aging period (up to 4th). Further aging causes a significant increase of ε'' suggesting an advanced degradation of the polymer, as discussed in the following.

The trend of ε'' at high frequencies is quite flat and its increase follows the aging period. On the contrary, at lower frequencies, the different lines are almost overlapped: this area is ruled by the interfacial polarization peak occurring at lower frequencies (probably 10^{-4}-10^{-5} Hz).

B. Tensile stress results

Results coming from EaB evaluation are reported in Fig.3. The material #1 seems to have greater initial EaB value compared to material #7, being almost twice higher. However, during aging, EaB of material #1 decreases with faster rate than EaB of material #7 as the dose increases.

This is in accordance with the assumption that the antioxidants added in material #7 would hinder the degradation induced by irradiation. When the results are compared at dose of 145 kGy, the decrease in EaB of material #1 is very remarkable (326% from the initial), while in the case of material #7 the decrease has been more moderate (74% from the initial). When aging overcome the dose of 200 kGy, material #7 shows EaB lower than 50% and at 300 kGy the EaB has diminished to less than 10%.

IV. Discussion

As showed and widely known in literature [5-8], aging can significantly change the physical-chemical properties of organic species, including polymers.

This process yields to the formation of higher dipolar oxygen-bonded chains, whose electrical response (dipolar polarization) is placed in the highest frequency range here considered. For this reason, this frequency range is usually reported as sensitive to degradation [6-8]. Among the high frequencies of the analyzed spectra, 100 kHz showed in literature to be representative of this frequency range and highly related to both the dipolar polarization and the aging of the polymer [4,5,7].

Fig. 4 shows the plot of the imaginary part of permittivity at 100 kHz as a function of the total absorbed dose for the two tested materials. Here again, the behavior of the two materials is deeply different. Material #1, in particular, presents a larger increase of the ε'' with higher dose. This is imputable to the fact that the composition #1 does not contain any stabilizer (in addition to the ones coming from the manufacturing process). Therefore, environmental stressors, irradiation dose and temperature in this case, can easily impact on the polymer and yield to stronger and homogenous degradation.

On the other hand, material #7 shows a much slower increase of ε'' with aging. This behavior can be referred to the huge amount of additives and stabilizers which are present inside the composition #7, in particular, primary and secondary antioxidants which prevent oxidation of the polymer and consequently most of the degradation process results inhibited.

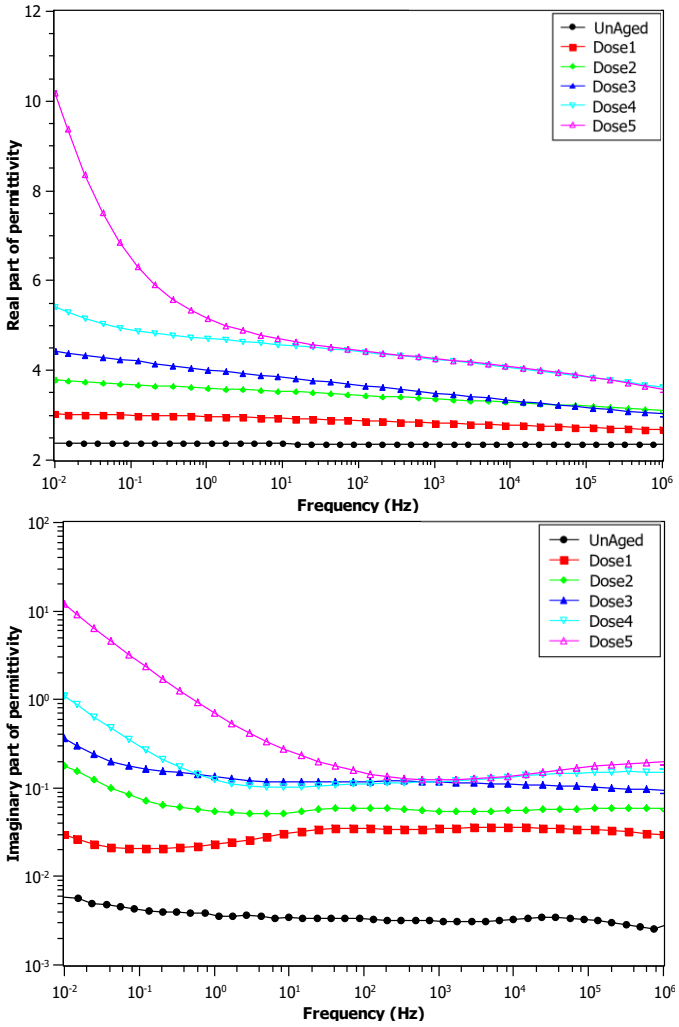

Fig. 1. Real (a) and imaginary (b) part of permittivity of material #1 as a function of frequency for five different aging period considered

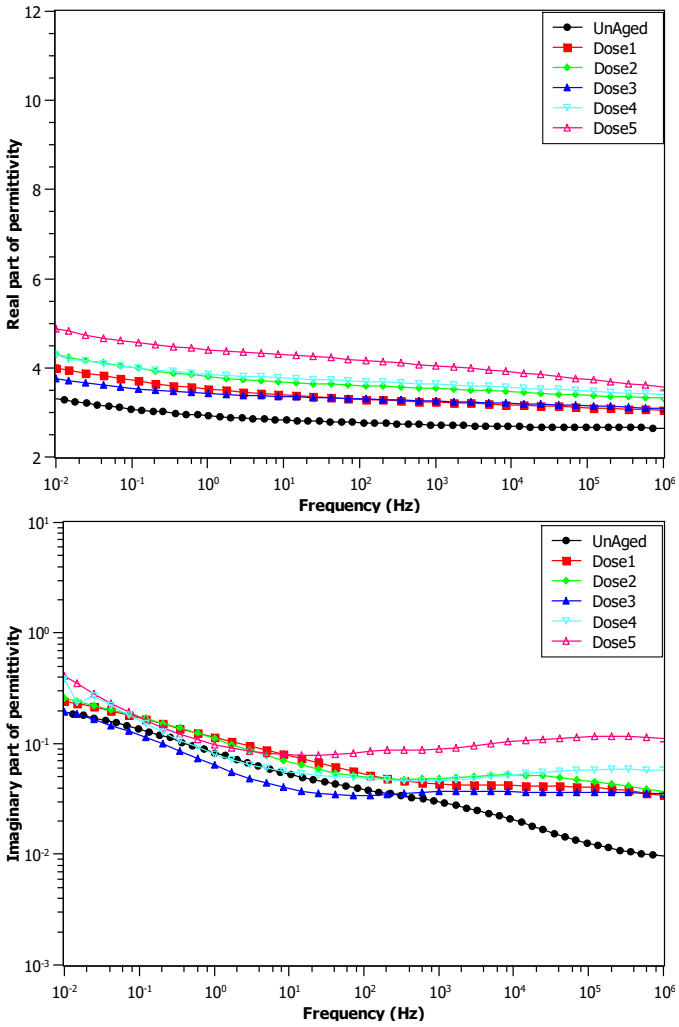

Fig. 2. Real (a) and imaginary (b) part of permittivity of material #7 as a function of frequency for five different aging period considered

Nevertheless, it is worth commenting that degradation process can occur also due to the presence of environmental stressors which may not lead to oxidized species but can affect the structure of the polymer (e.g. chain breaking and crosslink formation) leading to different physical and electrical response of the material, as shown. The inhibition of the degradation process can be linked also to the ε'' trend at 100 kHz (Fig. 4) for material #7. Here, the ε'' values remain almost constant from the first aging period up to the 4th, while further aging causes an abrupt increase of ε'' suggesting an enhanced degradation of the polymer, as confirmed by the mechanical tests (Fig.3).

Previous studies [8] showed that during aging the primary antioxidant can move from the inner part of the polymer to the outer part changing its shape into needles (polymorphism of the antioxidant). Oxidation, indeed, occurs primarily in the outer layers of the polymer due to the interaction of the surface with the environment; this activates the antioxidants which act like an oxygen-proof layer, localizing the degradation only in the outer layer of the polymer.

This phenomenon, often reported in literature as diffusion limited oxidation (DLO) [9], yields to an inhomogeneous degradation, due to the fact that oxygen is not able to reach the inner part of the specimen. Moreover, superficial cracks are created on the polymer and may significantly affect the mechanical properties of the sample, particularly EaB, which can reach very low values, in these cases (Fig. 3).

Figure 5 reports the cross-plot of the imaginary part of permittivity vs. the EaB values obtained through the tensile mechanical stress. As showed, quite good correlation is obtained for material #1 (full circle), which follows an exponential decay of the mechanical property corresponding to the increase of the ε'' value. On the contrary, material #7 (empty circle) shows good correlation between the two parameters only after the first aging period. A possible explanation is that during the first aging period, the aforementioned polymorphism and movement of antioxidants towards the surface can significantly vary the dielectric response of the material without changing the mechanical behavior.

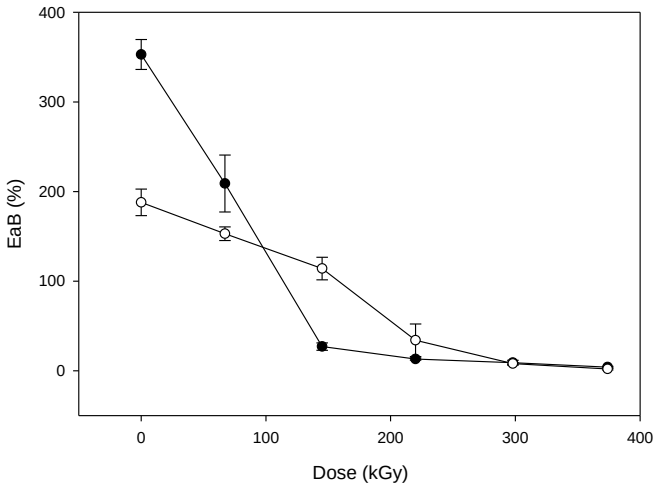

Fig. 3. Plot of the Elongation at Break (EaB) as a function of dose for material n.1 (full circle) and material n.7 (empty circle).

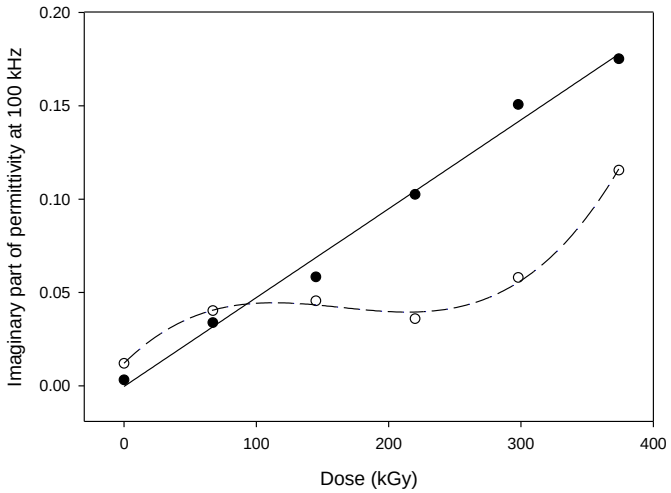

Fig. 4. Cross-plot of the imaginary part of permittivity at 100 kHz as a function of dose for material n.1 (full circle - linear fitting) and material n.7 (empty circle – 3rd grade polynomial fitting).

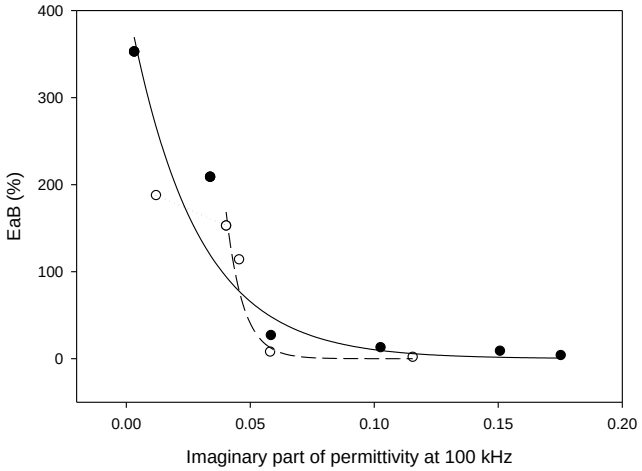

Fig. 5. Cross-plot of the imaginary part of permittivity versus EaB for material n.1 (full circle) and material n.7 (empty circle).

V. Conclusions

This paper investigated the evolution of dielectric and mechanical response of differently filled XLPEs during aging. It has been shown that aging and material composition can significantly affect the electrical response, suggesting the suitability of the dielectric spectroscopy for polymer diagnostics.

Moreover, dielectric losses have been correlated with the mechanical properties (above all EaB), in order to evaluate the possibility to up-scale the available qualification standards. It has been shown that only if oxidation, and in general degradation, is homogenous throughout the sample thickness, the two parameters are strictly related throughout all the aging process. Indeed, electric permittivity is a bulk property while EaB is related also to local degradation.

The presence of particular additives during the first aging period, moreover, could modify dielectric response without varying the mechanical properties, in the same way, leading to a weaker correlation between the two parameters. This correlation trend needs to be confirmed by further aging tests ongoing on these cables.

Further research will include chemical characterization on the same materials in order to deeply investigate aging development and try to correlate the obtained dielectric spectra with the micro-scale chemical modification of the polymer caused by aging.

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