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Additive impact on space charge of XLPE-based insulators subjected to radio-chemical aging

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***Abstract*— This work investigates the development of space charge distribution through by means of the pulsed-electroacoustic method on differently-filled XLPE tapes subjected to radiochemical aging. The contribution of these different fillers on the space charge distribution and its evolution with aging is highlighted and linked with the physical-chemical properties (e.g. oxidation degree) of these materials.**

Keywords—XLPE, space charge, additives, antioxidants, polymeric insulation, PEA method

I. Introduction

Crosslinked polyethylene (XLPE) is widely used as electrical insulation for a wide range of applications, e.g., cables and accessories. Up to now, many different XLPE-based polymeric compounds are available. The use of a specific compound mainly depends on application purposes.
As known, depending on the applied voltage, it is possible to define three cable groups: low-voltage (LV), medium-voltage (MV) and high-voltage (HV) cables. In the recent decades, the possibility to deliver energy through HVDC links has deepen the Research on innovative insulating materials, aiming at reducing the material DC conductivity and space charge accumulation [1-2]. It has been found that highly pure polymeric compounds are needed in order to ensure acceptable reliability of the final cable system, since impurities i.e., by-products, volatiles, contaminants and some additives, can act as trapping centers of accumulated charges, which cause significant electric field distortions [2-4].

One of the most common insulating materials for HV applications is polyethylene crosslinked through dicumyl peroxide (DCP). This material, after the final degassing process in the manufacturing chain, is characterized by a very high purity which brings to reduced space charge accumulation. Besides this, a low quantity of additives, mainly antioxidants, are needed inside the polymeric compound in order to guarantee a good application life of these cable systems (usually 40 years). The concentration of these additives is kept to reasonably low values since they may introduce, as previously mentioned, chemical traps for charges.

Under these circumstances, a lot of research has been focusing on the study of space charge accumulation inside materials for HV applications, primarily through pulsed electroacoustic (PEA) and thermal-step methods [2-5]. On the contrary, few works focus on the space charge behavior on LV cable systems, mainly due to the fact that the low applied voltage cannot lead to space charge-related insulation failures (as it occurs in the case of HV systems). Nevertheless, the use of space charge measurements can provide some significant information on charge accumulation and trap characteristics inside the insulating material. As a matter of fact, these properties can evolve during aging, underlining possible microstructural modifications which are related to aging e.g., oxidation processes and degradation phenomena. In addition, since the LV insulation materials are characterized by high concentration of additives and fillers [6-9], it is possible to believe that these molecules can affect the space charge behavior and modify the neat polymer response with aging (e.g., delaying oxidation through antioxidants).

Therefore, this paper aims at investigating the space charge properties of polyethylene crosslinked through silanes (widely used for low voltage applications due to its low cost) with different additives. Moreover, the evolution of these properties with aging is reported and discussed.
This research is part of the H2020 Euratom TeaM Cables Project which aims at providing nuclear power plants (NPPs) operators with a novel methodology for efficient and reliable NPP cable ageing management.

II. Ease of Use

A. Specimens

In order to investigate the additive impact on the space charge, the XLPE-based materials here analyzed are characterized by a growing complexity in fillers, e.g., antioxidants and flame retardants.
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 for a better electrode-specimen contact. Materials compositions are reported in Table 1. Name of additives cannot be disclosed due to confidentiality reasons.

TABLE I. Specification and Chemical Composition of Samples

Sample number	Sample composition
#1	Silane crosslinked polyethylene matrix (XLPE)
#2	Silane crosslinked polyethylene matrix (XLPE) + 50phr flame retardants (ATH) + both antioxidants

B. Accelerated aging

To simulate typical aging environments inside NPPs, accelerated aging has been performed. Three different dose rates, namely high, medium and low, corresponding to 400 Gy/h, 77 Gy/h and 7 Gy/h respectively, have been chosen to perform aging on tapes. Radio-chemical aging have been performed in the Panoza (medium and low dose rate) and Roza (high dose rate) facilities at UJV Rez, Czech Republic, through a ^{60}Co γ-ray source.

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Aging conditions are summarized in Table 2.

TABLE II. ACCELERATED AGING CONDITIONS

Aging type	Aging properties		
	Dose rate (Gy/h)	Sampling time (h)	Max. absorbed dose (kGy)
Low	7	3456	81
Medium	77	864	333
High	400	167	334

C. Space charge measurements

Space charge measurements have been performed through the Pulsed Electro-Acoustic (PEA) method. In the PEA method the sample is subjected to two coexistent applied voltages: a DC voltage V_0 and a pulsed voltage $V_p(t)$. The applied DC voltage inject charges inside the specimen, while the pulsed voltage causes an acoustic pressure wave due to its interaction with charged particles. This wave is finally transduced into a voltage signal by a piezoelectric sensor. The trend of this signal in time is then related to the charge distribution in space by known parameters, such as the sound velocity on the specimen, its thickness, and the applied electric field [10 - 11].

In this work the applied DC electric field was set equal to 10 kV/mm at room temperature, in a shielded environment. The volt on phase lasted 10000 s while the volt off phase lasted 3500 s.

The value of total absolute stored charge density in the bulk at a chosen depolarization time is given by (1) [9-10]:

$$q_s(E, t_d) = \frac{1}{l}\int_0^l |q(x, E, t_d)|dx \qquad (1)$$

where l is insulation thickness and t_d is the depolarization time, $q(x,E,t_d)$ is the space charge profile detected at time t_d.

The maximum value of q_s, namely Q_{max}, can be calculated at the beginning of depolarization once the poling electrode charge has been dissipated, let say at about t_d=5s.

The apparent trap-controlled mobility approximate equation is again reported in [9 - 10] and given by:

$$\mu(T) = \frac{E}{Q_{max}{}^2(T)} \cdot \frac{dQ(T)}{dT} \qquad (2)$$

where ε is the dielectric permittivity of the considered medium and $dq(t)/dt$ is the slope of the depolarization curve at time t.

Finally, the trap depth is derived by the approximated formula from [10-11]:

$$\Delta U = kT \ln\left(\mu \frac{kT}{\nu e R^2}\right) \qquad (3)$$

where ΔU_i is the difference between two energy levels (trap depth), ν is the attempt frequency, k is the Boltzmann constant, T is temperature, μ is the trap mobility, R is the mean distance between localized states ($5 \cdot 10^{-7}$ m), e is the electron charge ($1.6 \cdot 10^{-19}$ C).

III. RESULTS AND DISCUSSION

A. Stored charge

The total absolute stored charge density for the two considered materials and aging environments as a function of the total absorbed dose is reported in Figure 1. In all the analyzed conditions, it is possible to notice a different quantity of accumulated charge density depending on the aging severity the samples are subjected to.

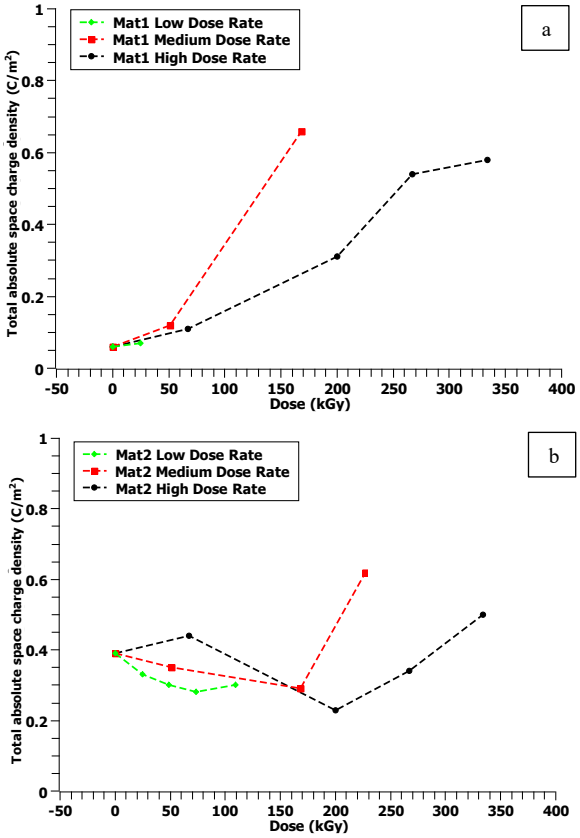

Fig. 1. Total absolute stored charge density. (a) PE neat material (b) Stabilized PE + Flame retardants.

For the neat PE material (Figure 1.a), the initial stored charge density is very low (~0.05 C/m^2), probably due to the very low concentration of trap charge sites in the base polymer. This value reaches a significant high value (~0.7 C/m^2) at high absorbed doses. However, the trend over aging is similar among the different analyzed conditions. Indeed, the total space charge density tendency is characterized by an initial increase followed by a stabilization of the value for high absorbed doses. However, due to the different aging severities and periods, the trend curves stop at different points of the just described trend. Only the high dose rate aging exhibits the complete trend, whose value stabilizes at ~0.6 C/m^2. As a result, softer aging conditions depict a steeper increase of the property probably due to the contribution of the aging time, which is significantly higher in this case (Tab.2). For example, the increasing branch of the medium dose rate aging reaches ~0.6 C/m^2 at the half of the absorbed dose relevant to high dose rate.

These behaviors can be explained by the aging effects on trap sites. Indeed, aging may cause the deepening and the increase of the number of the polymer traps (related e.g., to oxidation process), leading to a higher accumulated charge density.

Focusing on the filled PE material (Figure 1.b), one can notice that the initial value of accumulated charge density value is significantly higher than in the previous case, starting at ~ 0.4 C/m^2. This could be likely imputed to the introduction

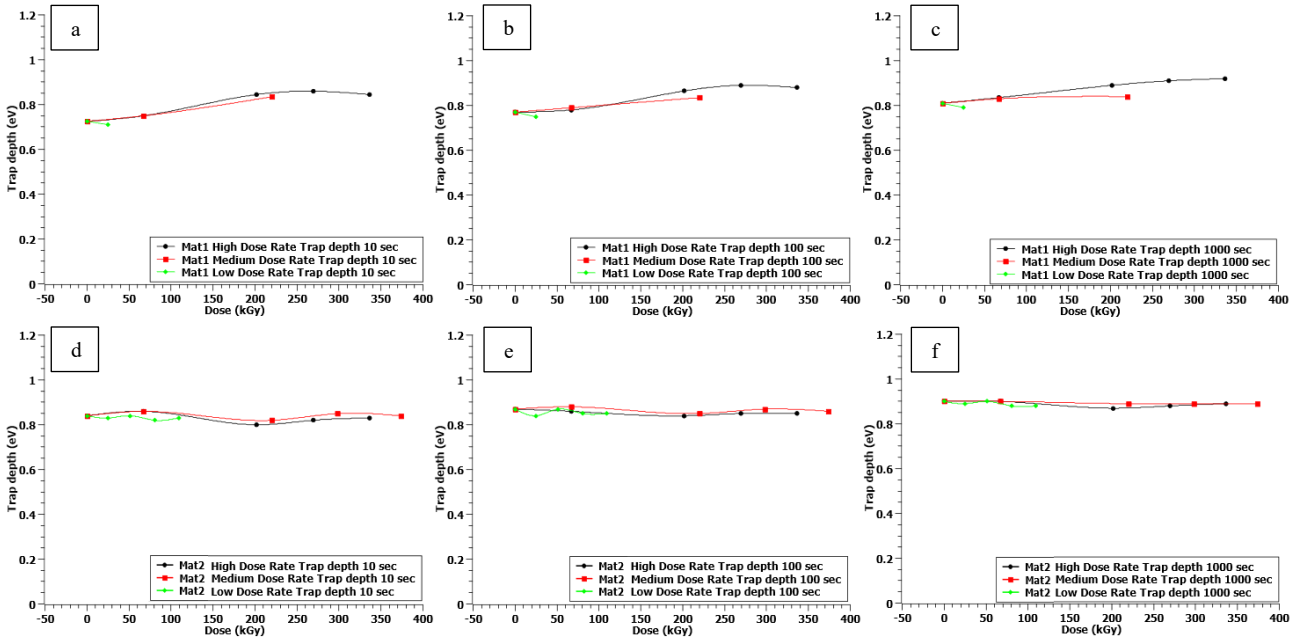

Fig. 2. Trap depth values for the different materials and aging conditions considered. (a) Material 1 – 10 sec after volt off, (b) Material 1 – 100 sec after volt off, (c) Material 1 – 1000 sec after volt off, (d) Material 2 – 10 sec after volt off, (e) Material 2 – 100 sec after volt off, (f) Material 2 – 1000 sec after volt off

of additives and fillers in significant concentration (~ 33% w/w), which can store charges acting as chemical deep traps. With aging, the total charge density values depict an initial decrease, followed by a stabilization and a final raise. Also in this case, lowering the aging severity causes a shift of the trending curve towards lower absorbed doses. The initial decay of the value could be linked to the impact of radiation on the analyzed specimens. Indeed, it is known [11–14] that radiation can lead to two main effects on additives: consuming and reducing the antioxidants into smaller molecules and destroying ATH clusters. The former phenomenon can result into lower concentration of charge store sites, leading to the reduction of the total charge density value. Then, the charge density values are kept almost constant, probably due to the balance between the reduction of the abovementioned charge store sites and the introduction of new ones, related to oxidation process occurring during aging. Finally, after the complete running out of antioxidant molecules, aging stresses lead to the increase of oxidized species which correspond to the increase of charge density as it can be seen in Figure 1.b.

B. Trap depth

Figure 2 reports the trend of trap depths obtained from the mobility calculated at 10 s, 100 s and 1000 s after *volt off* for the analyzed materials and aging conditions. Due to the experimental setup used, it is possible to record only traps with energy >0.5eV, whose depth and distribution are not constant throughout the polymer volume. As known, after volt off, traps release charges with sufficient mobility: initially traps with lower depth are discharged, deeper traps follow. Hence, registering the values of trap depths at three different sampling times would allow the definition of a rough distribution of the trap depths inside the material. By doing so, we can acquire shallow, medium and deep trap properties referring to the 10 s, 100 s and 1000 s response after volt off, respectively.

Focusing on the neat PE material, we can notice that, for all the aging conditions analyzed, traps increase their depth by ~ 0.1 eV during the first aging periods. After this initial increase, the trap depth values reach a plateau in the case of 10 and 100 s after volt off, while it slowly continues increasing in the case of 1000 s (deeper traps). This suggests that aging brings to the even arising of deep trap distribution. However, while the shallower traps created by aging rapidly reach their maximum depth with time, deeper traps still increase their depth value. This is expected due to the degradation processes taking place during radio-chemical aging, which mainly causes radical and oxidized species formation. The presence of oxidized species (e.g., oxidized polymer chains) and free radicals brings to the arise of new chemical traps, which are characterized by significant depths (chemical deep traps), leading to a higher value of accumulated charge density on aged samples (Figure 1). Hence, it would be possible to claim that as we increase the aging period, we are introducing deeper and deeper traps inside the polymeric compound (Figure 2.c). Regarding the different dose rates, it can be pointed out that for 10 s measurements (Figure 2.a) very little changes can be appreciated, suggesting an invariance of the related trap depths with aging severity. On the contrary, deeper trap trends (Figure 2.b,c) depict a dependence on the impacting dose rates. This could be considered as a confirmation that radiation mainly changes the deep trap characteristics due to the introduction of chemical deep traps.

Focusing on the filled material (Figure 2.d,e,f), the trend of trap depth with aging is remarkably different. The unaged material exhibits deeper traps (~ 0.85 – 0.9 eV) than those seen for the unaged base PE (~ 0.75 – 0.8 eV). This proves that the presence of fillers and additives can also impact the trap properties, evenly raising the distribution of deep traps.

Hence, additives themselves can be considered as a trap site for accumulation of charges. In particular, the high concentration of ATH and its chemical properties can be considered as the main cause of the trap depths for unaged specimens. On the one hand, ATH -OH bonds are found to be deep trap charge sites [16]; on the other hand, the variation of trap depth is nearly negligible with aging. As a matter of fact, ATH molecules are inorganic species, hence they are not subject to significant degradation mechanisms due to aging. Nonetheless, as claimed in the previous section, radiation can destroy the ATH agglomeration into clusters, but it does not change the chemical properties of these molecules. Consequently, the trap depths caused by ATH cannot change with aging, claiming a relationship between the stabilization of the trap depth (Figure 2.d,e,f), and ATH properties.

Furthermore, the raising of new species given by radio-chemical aging, often associated with the introduction of new traps, do not cause sufficient increasing of the trap depth in comparison to the one related to the unaged material. In other words, this behavior can be related to the fact that ATH trap depth properties overwhelm the trap depth modification caused by the degradation products (e.g., oxidized polymer chains). Indeed, this latter are demonstrated to cause a maximum trap depth ~ 0.8 eV (Figure 2.a,b,c), which is lower than the one related to the ATH molecules.

IV. Conclusions

In this article, the effect of additives and fillers on space charge behavior inside XLPE has been investigated through the PEA method and discussed. The use of XLPE materials characterized by different additives and fillers (antioxidant and flame retardants) allowed the definition of the role of these molecules on the trapped charges inside the specimens.

Materials have been subjected to accelerated aging in order to evaluate the response of antioxidant degradation products and new radicals on the accumulated charge density. Moreover, the use of different dose rates allowed the definition of the role of the aging severity on the material space charge behavior. It has been demonstrated that aging causes the increase of both accumulated charge density and traps with different depths in the base XLPE material. This has been imputed to the increase of radical and oxidized species created by the radio-chemical aging conditions analyzed. Finally, aging severity contributes to the kinetics of degradation. In particular, it has been found that the higher the dose rate, the faster the increase of the space charge properties (both accumulated charge density and trap depth).

Additionally, it has been demonstrated that additives can influence the response of these materials with aging, affecting both the accumulated charge density and the trap depths due to additive chemical properties. The presence of ATH brings to the increase of both the accumulated charge density and trap depths. It has been concluded that, in the case of filled polymers, the contribution of ATH on trap depths overwhelms the one given by degradation products, so that the trap depths resulted to be constant with aging and, consequently, independent on both aging duration and severity.

Future work on this topic will include the analyses of space charge patterns and behaviors on XLPE materials with different kind and concentration of additives and correlation with other physical-chemical characterization techniques (e.g., quantitative FTIR).

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