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Impact of additives and fillers on space charge behavior of polyethylene insulation: investigation and modeling

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***Abstract*- Diagnostic measurements on electrically insulating materials are a compulsory step to assure an acceptable service life of the electrical equipment. In particular, this paper focuses on the consequences of the implementation of several concentrations of antioxidants (Irganox® 1076 and Irganox® PS802) inside Si-XLPE matrices. Thermally Stimulated Depolarization Current (TSDC) measurements were carried out on pure and filled samples to obtain information about the space charge behavior and trap distribution of the specimens. Postprocessing based on Randal-Wilkins model highlighted additive impact on Si-XLPE properties. Similar trap depth and different trap density values were found in samples with different concentrations of the same additive, suggesting a close correlation between the energy levels of localized states and the used antioxidants.**

Keywords: space charge, trap distribution, TSDC, XLPE, antioxidants, additives.

I. Introduction

Polymer insulating materials are more and more often used in modern electrical systems, thus pushing researchers to search how to extend their lifetimes and enhance their performance. Among them, crosslinked polyethylene (XLPE) is broadly used as electrical insulating material, in particular in HV cables [1]. Nonetheless, pure XLPE, due to its short lifetime, needs to be stabilized by means of additives. In particular, antioxidants manage to preserve the molecules from undergoing chemical reactions which may severely degrade the material [2]. Nonetheless, these additives may have an impact on the electrical properties of the base insulating material, acting as traps for electrons and holes. Therefore, they may significantly modify charge transport leading to space charge accumulation. This inhomogeneous charge distribution might consistently distort the local electric field, thus exceeding dielectric strength value and/or promoting further charge injection, if very close to the electrodes. The most important characteristic of traps is their distribution, i.e., their density (measured in $eV^{-1}m^{-3}$) as a function of their depth (measured in eV). This property may be investigated by means of thermally stimulated depolarization currents (TSDC), a non-destructive consolidated method whose outputs are strongly correlated with trap distribution [3].
The aim of this paper is to quantify and assess the trap distribution inside materials with different additives, in order to highlight the contribution of these species and their impact on the investigated property.

II. Experimental setup and data processing

A. Materials

The analyzed materials are reported in Table 1. They are based on the same Silane crosslinked polyethylene (Si-XLPE) matrix and characterized by an increasing concentration of two types of additives, namely a primary (Irganox® 1076) and secondary (Irganox® PS802) antioxidant. Samples were produced in the form of plaques with thickness ~0.5 mm [4]. Samples were metallized through plasma cold sputtering in order to ensure appropriate contact between cell electrodes and tested material. Metallization was performed on both surfaces of the specimen, according to ASTM D257-14.

Table 1
Antioxidant Content in the Studied Specimens.

Material	Additive	Concentration (phr)
XLPE	-	-
	Irganox® 1076	0.3
		0.6
		1
	Irganox® PS802	0.3
		0.6

B. Thermally stimulated direct current (TSDC) measurements

TSDC measurements allow the investigation of some of the most important space charge characteristics, such as trap depth and density. TSDC is characterized by four different steps:

1. First, the specimen is heated till the set temperature (T_1=70°C) is reached and the voltage is set to a value corresponding to the desired electric field E=1 kV/mm.
2. The temperature and the voltage are kept constant until the conduction current is reached.
3. The sample is cooled down to temperature T_2= -50 °C under volt-on conditions. Due to the abrupt decrease of temperature, the charges coming from the applied electric field are expected to be blocked inside traps.
4. Finally, the voltage is turned off and temperature is increased to a maximum value of T_3=100°C, releasing trapped charges. This gives rise to a current which can be measured and whose trend with respect to temperature can convey information about the trap distribution.

Apart from step 2, all temperature variations occur at a specific heating rate, β=3°C/min. Keithley 2290E-5 and Keysight B2981A, were used as HVDC source and picoamperometer, respectively. The thermal setup included a liquid N_2-based temperature control system with an accuracy of 0.1°C (Novocontrol Novocool) and the load cell was a Novocontrol BDS1200 HV sample cell equipped with a Pt100 temperature probe. Finally, a diode-based circuit and a 1 MΩ series resistor were used as protection for the picoamperometer. Some limits may arise from the limited electric field (1 kV/mm), as usually much higher values were applied in other articles [5,6].

C. Data analysis

TSDC plots consist of the current measured in step 4 as a function of temperature. After dividing the current by the surface area of the three-electrode configuration intermediate circle, the plots can be interpreted by means of Randal-Wilkins model [5,7]. Fitting curves are obtained by:

$$J(T) = A \cdot e^{-\frac{E_g}{kT}-\frac{\nu}{\beta}\int_{T_0}^{T} e^{-\frac{E_g}{kT'}}dT'} \quad (1)$$

where J is the current density, A is a constant, E_g the trap depth, k the Boltzmann constant, T the temperature, ν the attempt to escape frequency, β the heating rate. However, in the low-temperature tail, the integral can be neglected (initial rise method), and equation 1 becomes:

$$J(T) = A \cdot e^{\left(-\frac{E_g}{kT}\right)} \quad (2)$$

which may be associated to an Arrhenius-like equation.

Thus, by plotting ln(J) versus 1/T, we obtain an almost straight line, whose slope is the trap depth divided by the Boltzmann constant.

A software developed in [8] managed to plot the trap density of all values of trap depth from 0 to 1.5 eV and it was used in this work. However, the parameter describing the distances between molecules was changed from 5 μm to 500 nm, as found in [9]. The trap distributions will have their peak exactly at the value E_g found according to (2) by using the right attempt-to-escape frequency value that can be derived from:

$$\nu = \frac{\beta E_g}{kT_M^2} \cdot e^{\left(\frac{E_g}{kT_M}\right)} \quad (3)$$

where T_M is the temperature corresponding to the peak of the current.

Finally, the values of trap volume density may be obtained integrating the trap distribution peak referred to the given E_g:

$$n_T = \int_{E_{g,min}}^{E_{g,max}} \rho(E_g) dE_g \quad (4)$$

where n_T is the trap volume density, $\rho(E_g)$ is the trap density, $E_{g,min}$ and $E_{g,max}$ are the lowest and highest values of E_g for the peak.

III. RESULTS

A. Depolarization currents

The depolarization currents coming from Step 4 are shown in Figures 1 and 2 for XLPE material with primary and secondary antioxidants, respectively. As expected, the peak intensity grows with increasing additive concentration for both fillers. This is in accordance with the fact that higher content of antioxidants would increase the number of traps and, consequently, the number of charges in them. This results into a significant rise of the depolarization current in the last step of TSDC. Moreover, the current peak slightly shifts towards lower values of temperature as the concentration of additives grows (Figures 1 and 2).

B. Trap distribution and volume density

Figures 3 and 4 plot the trap density values as a function of the trap depth for the investigated samples.

Pure Si-XLPE material exhibits a trap depth of 1.05 eV (Figures 5a and 6a), similar to values found in literature [10,11].

Filled samples display different trap distribution. With reference to Irganox® PS802-filled materials, it is found that the characteristic trap depth value, coming from Figure 3, is very similar to the pure sample one, ranging from 1.01 eV to 1.07 eV (Figure 5(a)). On the contrary, Irganox® 1076-filled

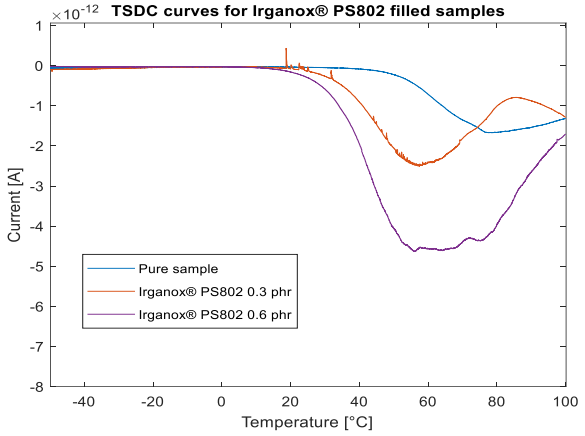

Figure 1 TSDC curves of Irganox® PS802 filled samples

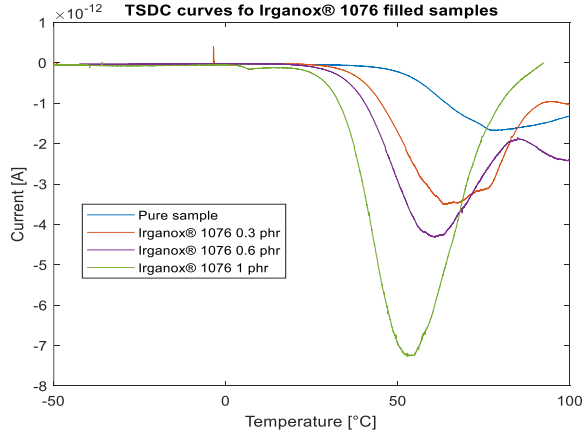

Figure 2 TSDC curves of Irganox® 1076 filled samples

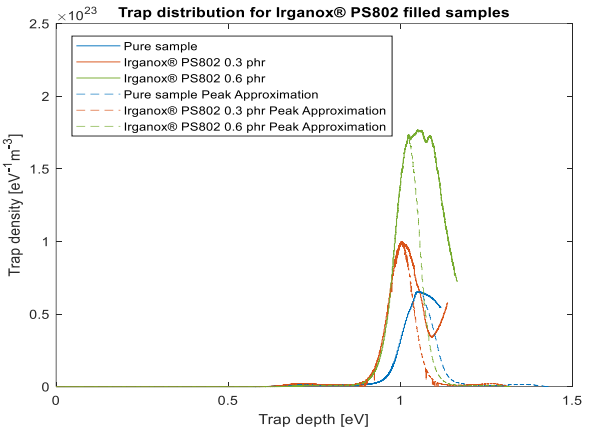

Figure 3 Trap distribution of Irganox® PS802 filled samples

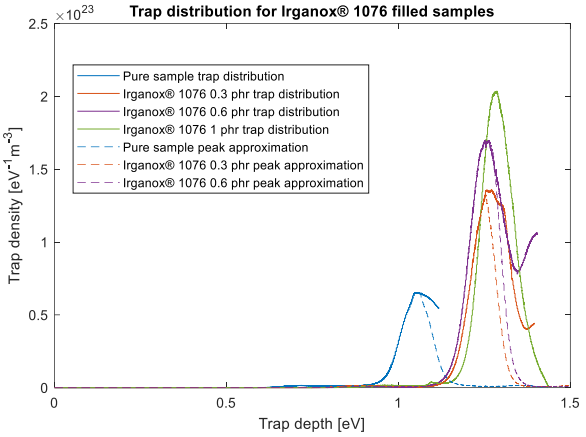

Figure 4 Trap distribution of Irganox® 1076 filled samples

specimens have quite bigger trap depths, going from 1.26 eV to 1.29 eV, as represented in Figure 6(a). Obtained values are reported in Table 2.

TABLE 2
TRAP DEPTHS OF FILLED SAMPLES

Additive	Trap depth (eV)
Pure	1.05
Irganox ® 1076	1.26-1.29
Irganox ® PS802	1.01-1.07

It is also worth noting that higher concentrations of antioxidants lead to an increase of trap density, as plotted in Figures 5(b) and 6(b). Moreover, the plots, related to the same additive type, show very similar values of trap depths also with different concentration.

Finally, the multipeak behavior of trap density (Figures 3 and 4) was simplified by considering just one peak with a gaussian trend. Equation (4) was applied to each one of them. Then, Figures 7 and 8 report the values of trap volume density as a function of the different content for the two antioxidants considered. It is found that both materials with Irganox® PS802 and those with Irganox ®1076 follow a linear increasing trend of the property.

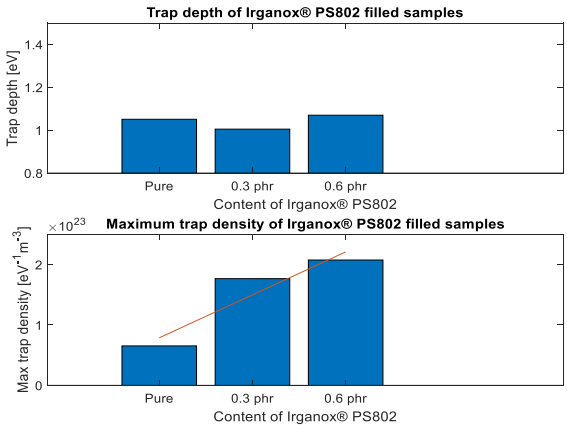

Figure 5 (a) Trap depth and (b) maximum trap density of Irganox® PS802 filled samples

IV. DISCUSSION

From the results reported in the previous section, it is found that presence of antioxidants introduces new traps, whose depths may exceed the one of PE. With reference to Irganox® PS802-filled materials, results highlight that the characteristic trap depth is very similar to the neat PE value (Table 2). Hence, the trap depth of the additive is either equal to or lower than the Si-XLPE value. Nonetheless, the monotonic increase of trap density with antioxidant content (Figure 6(b)) confirms the former hypothesis. Regarding Irganox® 1076, its trap depth value results to be higher than the PE one (Table 2). A possible explanation for that may be sought in the chemical properties of the two antioxidants. In particular, Irganox® PS802 is characterized by one thioether and two ester groups, while Irganox® 1076 by a phenol and an ester group. The electron affinity of these molecules may differ and, recalling that this property is strictly related to the trap depth [12], this would result into different trap depth values, as confirmed by Figures 5(a) and 6(a). Therefore, it may be concluded that the electron affinity of Irganox® 1076 is higher than Irganox® PS802 value. It seems reasonable to suppose that the introduction of a higher concentration of fillers rises the surface-volume ratio, thus strengthening chemical bonds and increasing the amount of

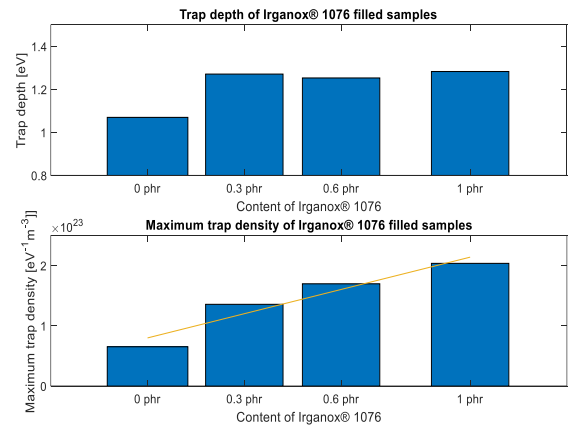

Figure 6(a) Trap depth and (b) maximum trap density of Irganox® 1076 filled samples

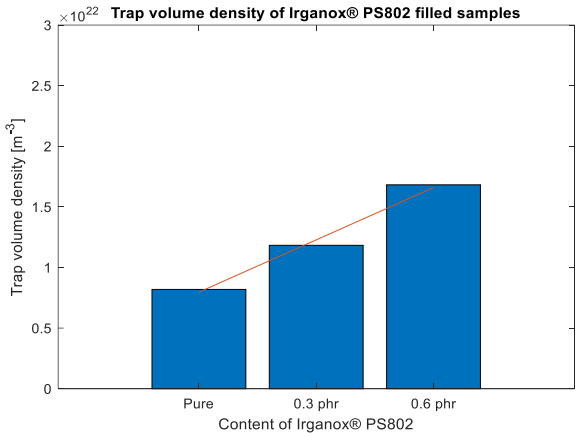

Figure 7 Trap volume density of Irganox® PS802 filled samples

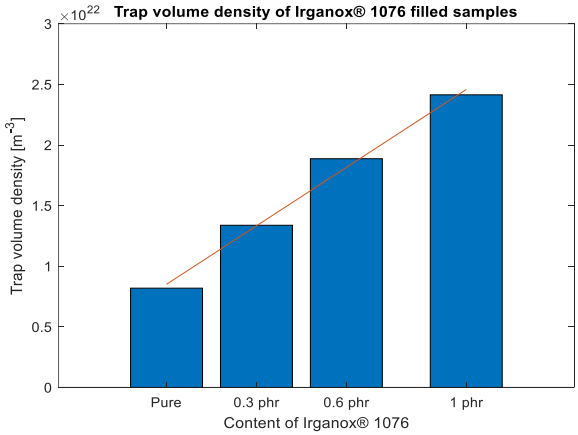

Figure 8 Trap volume density of Irganox® 1076 filled samples

trapped charge along with trap and volume density (Figures 5-8). This is in accordance with Lewis's theory [13], which states that interfaces are a key factor for any insulating material chemical structures and, as a consequence, of their macroscopic properties.

V. CONCLUSIONS

In this paper, a series of TSDC measurements on several Si-XLPE samples were described. Results were then analyzed by means of a postprocessing software properly developed. This study showed that higher antioxidant phr values introduced higher values of trap density, but kept the trap depth constant, assessing the trap depth of the considered additives. Eventually, the data analysis proved that the increase of additive content does not modify the trap depth, which resulted to be the one of the additive, but just the trap density and volume density. This conclusion is of great interest suggesting the suitability of the TSDC technique for the assessment of the additive concentrations and space charge property of insulating materials.

Further development will include the analysis of the impact of other additives (e.g., flame retardants) on Si-XLPE, and the investigation of the changes of additive space charge property with aging.

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