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Quantitative investigation and modelling of the electrical response of XLPE insulation with different filler content

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Abstract – *In this article, electrical properties of XLPE-based materials with different additives are reported. In particular, it is shown that additives can deeply influence, among others, the complex permittivity of the analyzed material, putting the basis for a modelling approach which correlates the variation of the dielectric properties with the additive concentrations and characteristics.*

I. INTRODUCTION

Nowadays, the use of polymers as insulating material is a well-established technology. In order to permit these materials to last over their application time (usually between 40 and 60 years) and to ensure their protection against degradation stressors, a variety of additives are added to the base insulating polymer [1], [2].

While for high voltage (HV) systems high purity materials are usually needed to guarantee good operational performances, inside low-voltage (LV) systems the electric fields are so low that it is possible to fill the base polymer with all the required additives (e.g. plasticizers, antioxidants, flame retardants). In particular, it has been estimated that LV cables usually own up to 60% of fillers, reducing their effective insulating material concentration [3].

It is evident that high concentration of additives can have an impact on both the physical-chemical and, consequently, on the electrical properties of the base material. Lots of works [1], [4] show how these fillers effect the chemical properties of the material (e.g. Oxidation Induction Time, Ester index, crystallinity), but very few works focus on the electrical implication that these additives can have on e.g. dielectric losses [5], [6].

If the analyzed polymer is used as insulating material for cables, electrical properties are the ones to focus on in order to avoid any unexpected cable crisis and electrical breakdown. For this reason, correlating the change of electrical properties with the kind and concentration of additives can be important for the evaluation of the suitability of a polymeric compound to fulfill a given application.

In particular, it has been demonstrated that additives can influence the dielectric spectra of the base material. Thus, dielectric spectroscopy is suggested to be used as a monitoring technique for the evaluation of the changes in electrical properties due to additives [7]. Moreover, these latter may

significantly influence the response of the material to aging. As an example, antioxidants (AOs) are usually put inside the polymer in order to delay or avoid degradation oxidative reactions by environmental stressors.

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 aging management, through, among others, developing a new multiscale modelling approach, to study polymer radiation aging.

Aim of this article is, on the one hand, to evaluate the dielectric response of XLPE materials with different additives. On the other hand, it aims at building a preliminary modelling approach which correlates the dielectric response of the investigated materials with different kinds and concentrations of additives and fillers.

II. MATERIALS AND METHODS

A. Specimens

Sample specimens have been produced by Nexans starting from the same silane crosslinked polyethylene (XLPE) matrix. Different kinds and concentrations of additives i.e. antioxidants and flame retardants are investigated in this work. Additives properties of the materials under test are briefly reported in Tab.1.

TABLE I. COMPOSITION OF SPECIMENS

Filler type	Filler amount (phr)
Primary antioxidant (Irganox 1076)	0, 0.3, 0.6, 1, 3
Secondary antioxidant (Irganox PS802)	0, 0.3, 0.6, 1
Flame retardant (ATH)	0, 25, 50

B. Dielectric spectroscopy measurements

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

Dielectric spectroscopy allows the evaluation of the complex permittivity as a function of frequency.

Dielectric spectra are obtained through a Novocontrol Alpha Dielectric Analyzer v2.2 with applied voltage of 3 V_{rms} at room temperature. The frequency range analyzed is 10¹-10⁶ Hz.

C. Modelling approach

Several works [5]–[8] show that a representative frequency among the highest frequency region here investigated may be 10^5 Hz. It has been demonstrated that this frequency is both linked to the oxidized polymer chains and, consequently, to aging, and to the dipolar molecules inside the polymeric material, e.g. antioxidants and other additives.

It is predictable that the increase of the dielectric properties in the dipolar polarization area and the concentration of additives follows, for low concentrations, a linear or exponential law. As the concentration of additives increases, reaching a given threshold value, the variation of the dielectric property with additive concentration is more and more reduced. Finally, it reaches a stabilization phase during which the increase of concentration does not lead to any modification of the considered property. This because high concentrations of additives or fillers may cause the agglomeration of these species whose dielectric response shall be shifted towards lower frequencies due to the formation of interfaces (interfacial polarization) [9]. When this happens, the 10^5 Hz value does not increase so that a flex and a stabilization (or plateau) of the electrical property with additive concentration is expected. As a result, the described curve owns a S-like shape. Therefore, this trend may be linked to a Boltzmann sigmoidal law, defined as follows:

$$y = A_2 + \frac{A_1 - A_2}{1 + e^{-\frac{x - x_0}{dx}}} \quad (1)$$

where: A_1 and A_2 are, respectively, the initial and final value of the dielectric property
 x_0 is the value halfway between the A_1 and A_2
 dx describes the steepness of the curve.

III. RESULTS AND DISCUSSION

A. AO Dielectric spectroscopy results and discussion

Figure 1 depicts the trend of the imaginary part of permittivity as a function of frequency for the two analyzed antioxidants. In both cases, the increase of the concentration of these additives causes the raise of the dielectric losses, as expected.

It is important to recall that the frequency to which a molecule electrically respond is related to the characteristic relaxation time of that molecule. As known, the relaxation frequency is related to both the polarity and the size of the molecule [9]; usually, the smaller the molecule the higher the characteristic frequency. Due to the fact that the investigated AOs molecules are, in steady-state situation, not bonded with any other molecule and they are not considered as big molecules due to their chemical formula, it is possible to claim that their dielectric response is only led by the dipolar polarization, whose characteristic frequency region is around 10^9 - 10^4 Hz [9]. Therefore, it can be claimed that the analyzed frequencies

represent only the lower frequency part of the dipolar polarization region.

However, since the dielectric spectra is made by a convolution of peaks, a peak occurring in some frequency region may cause an increase of the baseline throughout a wide range of frequencies. This phenomenon is clearly seen in Fig. 1 and it is applicable to both the considered AOs.

Focusing on primary antioxidant behavior (Fig. 1.a), one can notice that no significant peak appears in the spectrum, so that the trend with frequency could be considered as almost flat. This is expected since the analyzed additives i.e. Irganox 1076 and PS802 are usually placed in the amorphous phase of the polymer matrix and, without aging stressors, do not bond with any external molecule.

It is possible to analyze that the increase of the dielectric losses with the concentration of AO is not linear. Indeed, it shows bigger variation with low concentrations of AO (between 0 and 0.6 phr) while higher concentrations (up to 3phr) cause reduced changes in the dielectric losses trend.

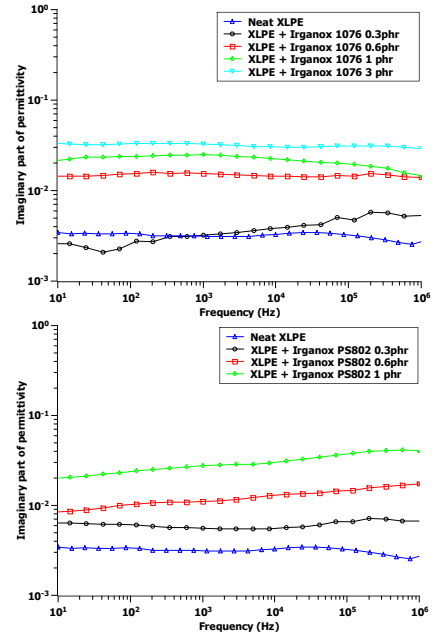


Fig. 1. Imaginary part of permittivity as a function of frequency for the different materials analyzed. (a) primary antioxidant (b) secondary antioxidant.

Referring to the secondary AO dielectric spectrum (Fig.1.b), one can notice a peak occurring at around 10^6 Hz, which is not present in the case of the primary AO (Fig.1.a). This peak is probably related to the thioether-based molecule and its dielectric response, since the secondary AO is a bigger molecule compared to the Irganox 1076. Hence, it responds at lower frequencies and consequently in the frequency region analyzed. Even in this case, the dielectric losses raise with the increase of the AO concentration. In the highest frequency region, the increase could be considered as linear since the spectra are approximately equally shifted one each other. Lower frequency regions show non-linear increase of the spectra due to the fact that they are outside the dipolar polarization area so that this behavior could be related to other kinds of phenomena

e.g. response of interfaces, which anyway increase as the concentration of additive raise.

B. Dielectric spectroscopy results of ATH-filled materials

Figure 2 reports the trend of the imaginary part of permittivity as a function of different amounts of ATH fillers. Unfortunately, only two ATH concentrations are available, so that the modelling approach could be considered as not completely reliable.

Even in this case, the imaginary part of permittivity increases with the concentration of fillers. In particular, the dielectric response of the ATH-filled polymers is led by a huge interfacial polarization peak occurring at lower frequencies (likely around 10^{-3} Hz), whose lower branch can be seen in Figure 2. It is worth commenting that doubling the concentration of ATH fillers does not significantly impact on the dielectric spectra. A reason to this behavior can be found in the fact that ATH fillers, thanks to their -OH molecules, easily bond each other through hydrogen bonds turning themselves into clusters. These latter have their dielectric response placed in the very low frequency region, due to the arise of bigger interfaces. As a result, at high frequencies, the contribution of the dipolar polarization is reduced due to its convolution with the bigger interfacial polarization peak.

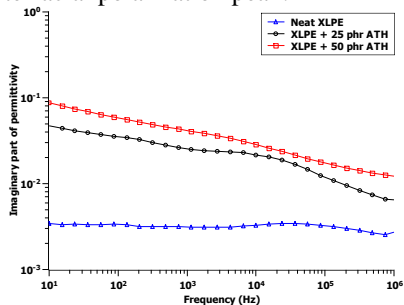


Fig. 2. Imaginary part of permittivity as a function of frequency for the ATH-filled materials analyzed.

C. Modelling results

It has been discussed that the frequency region, in which the additive electric response is placed, is the highest frequency region investigated. Figure 3 shows the trend of the dielectric losses at 10^5 Hz as a function of the nominal concentration of AOs inside the analyzed polymer. In both the conditions analyzed, the fitting has been performed through (1).

This behavior may be clearly seen in the case of Irganox 1076 (Fig.3.a) thanks to the higher phr concentration (up to 3 phr), while it is derived in the case of Irganox PS802 in Fig.3.b (dashed line). Here, the maximum concentration of thioether-based AO is up to 1 phr and correlation can be recorded only in the initial exponential branch of the curve. Focusing on the trend of the ATH-filled materials (Figure 4), it is evident that the number of points is not enough to obtain a reliable fitting (dashed curve). Anyway, it is worth indicating that the two experimental data points, related to 25 and 50 phr of ATH filler, are placed in the right-hand side of the curve. Similar to what has been discussed for the antioxidant molecules, the right branch of the curve is related to the higher concentration of additives and, consequently, it may be linked to the interfaces given by filler agglomeration.

In conclusion, the values of the characteristic variables together with the fitting factor R^2 of the presented sigmodal trends are reported in Tab.2.

TABLE II. MODELLING VARIABLES

Filler type	A_1	A_2	x_0	dx	R^2
Primary antioxidant (Irganox 1076)	-0.005	0.03	0.62	0.45	0.98
Secondary antioxidant (Irganox PS802)	0	0.1	1.19	0.35	0.99
Flame retardant (ATH)	0.002	0.02	21.2	4.9	1

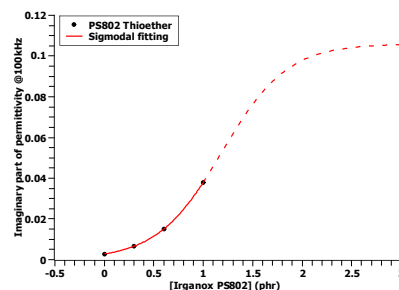
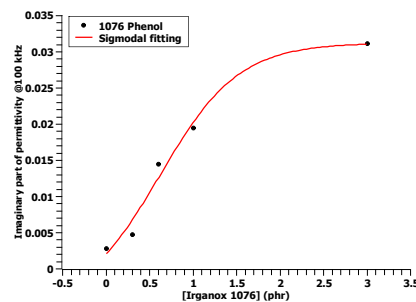


Fig. 3. Imaginary part of permittivity at 100 kHz as a function of the concentration of considered antioxidants. (a) Primary antioxidant (b) Secondary antioxidant. Sigmodal fitting.

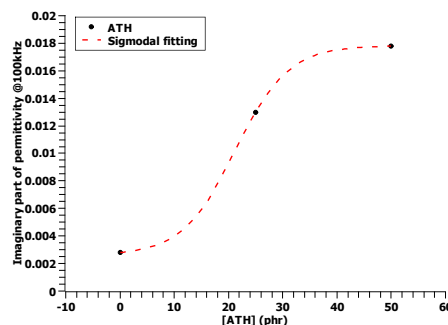


Fig. 4. Imaginary part of permittivity at 100 kHz as a function of the concentration of considered flame retardants (ATH). Sigmodal fitting.

D. Discussion on modelling of the electrical properties

In the previous section, it has been shown that different additives can show a similar trend of the dielectric response with additive concentration.

The trend, which has been estimated to follow a sigmodal law, mainly differences in the highest asymptotical value reached by the dielectric property and in the maximum concentration until which the dependence between the two parameters (additive concentration and electrical property) follows an exponential law (threshold value).

It can be demonstrated that both these parameters are dependent on the capability of the additive to be mixed inside the polymer matrix [10]. In particular, the starting point of the flattening phase showed to correspond to the saturation point of the additive into the polymer matrix. Bigger additive concentration leads to agglomeration, and, consequently, to the non-variation of the electrical property related to dipolar polarization.

As discussed, Irganox 1076 phenol-based antioxidant (Fig. 3.a) shows, at relatively high concentration a stabilization of its dielectric response. This behavior has been already shown in our previous work [5] and it is related to the agglomeration of the AO molecule into crystal on the surface [11]. As a matter of fact, phenol molecules are dispersed in the amorphous phase of the polymeric matrix, which allows them to freely move towards the polymer bulk and finally reach the surface due to diffusion phenomena. It has been demonstrated by Xu et al. [11] that the maximum soluble concentration of the Irganox 1076 into the silane XLPE is about 1 phr. As a consequence, further concentration of AO would result into agglomeration of the molecules and formation of crystals on the material surface. The same threshold value showed to possibly be derived through the presented modelling approach (Fig. 3).

As stated above, the dielectric response of these crystals is mainly placed in the lower frequency region due to interfaces. However, it has been demonstrated [5], that also the higher frequency region dielectric response can vary but less significantly (Fig. 1.a and 2.a).

Irganox PS802 is characterized by a larger molecule based on thioether bonds. The dielectric response of these molecules perfectly follows the initial exponential behavior of the proposed modelling. For this kind of molecules, no evidence on the effective solubility inside the polymer matrix has been reported. Nevertheless, the modelling fitting (Fig.3.b) suggests that likely no agglomeration occurred with the concentrations analyzed (up to 1 phr).

Finally, with respect to the ATH-filled molecules no further discussion can be done due to the very few available data. The lowest concentration (25 phr) roughly corresponds to the starting of flattening phase (threshold value). Indeed, doubling the ATH concentration results into a little increase of the dielectric property at high frequencies (Fig.2), hence it does not follow a quantitative rise. This suggests and confirms the agglomeration of the ATH molecules and their dielectric response shifting towards lower frequencies.

IV. CONCLUSIONS

In this article, the study of the variation of the dielectric response of differently filled materials is reported and discussed.

Results show that the electrical response is deeply influenced by the additive characteristics and amounts inside the polymer matrix. Specifically, the choosing of particular frequencies of the dielectric response allows a good correlation between the additive amount and the electrical property considered to be built.

It is shown that the presence of high dipolar molecules, e.g. antioxidants and ATH here analyzed, can have an effect on the dielectric spectroscopy at around 10^5 Hz due to the dipolar polarization phenomenon characterizing these additives. Also, the presence of these molecules in high concentrations showed to cause two main effects: a non-properly dispersion in the polymeric matrix (leading to their migration to the surface) and/or their aggregation. Both phenomena produce the creation of interfaces, whose electrical response results to be placed in lower frequencies e.g. 0.1 Hz (interfacial polarization), which are not here investigated.

Future work on this topic will include quantitative chemical analyses e.g. FTIR and OIT measurements, together with a broadening of the analyzed dielectric spectra frequencies.

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