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Additive effect on dielectric spectrum of crosslinked polyethylene used in nuclear power plant cables

Simone Vincenzo Suraci
*Dept. of Electrical
Electronic & Inform.
Eng. University of
Bologna*
Bologna, Italy
simone.suraci@unibo.it

Davide Fabiani
*Dept. of Electrical
Electronic & Inform.
Eng. University of
Bologna*
Bologna, Italy
davide.fabiani@unibo.it

Chuanyang Li
*Dept. of Electrical
Electronic & Inform.
Eng. University of
Bologna*
Bologna, Italy
chuanyang.li@unibo.it

Abstract— This article deals with the modification on electric behavior of crosslinked polyethylene (XLPE) for nuclear applications due to the effect of additives and fillers. Material responses were investigated through dielectric spectroscopy which appeared to be very sensitive to the change in filler composition. It is shown that the addition of antioxidants and fire-retardant fillers provides a modification on the imaginary and real parts of permittivity spectra with respect to the base material. Furthermore, the influence of degassing treatment and the resulting crosslinking by-products removal on dielectric spectra are here investigated.

Keywords – XLPE, dielectric spectroscopy, nuclear dielectrics, polyethylene, additives, antioxidants, flame retardants.

I. INTRODUCTION

Low-voltage electric cables are extensively used throughout nuclear power plants (NPPs) for power transmission, control of equipment and instrumentation, communication of signals and data. Most of the NPP commissioned in '70s and '80s are now reaching end-of-life but decommission costs are pushing NPP regulator to ask for life extension of NPPs up to 60 (possibly even 80) years [1, 2]. Since electric cables are one of the long-life equipment that have not considered for replacement during the design life of a NPP, usually 40 years, evaluating degradation condition and predicting residual life are very critical issues. Moreover, as new reactors are being constructed and many others are in planning for the next future, appropriate cable choice and use of effective condition monitoring (CM) techniques to assess cable condition from commissioning, can be very useful at a later time for an effective cable lifetime management [1-4].

This is the scope of a new EU Project called TeaM CABLES which aims at providing NPP operators with a novel methodology for efficient and reliable NPP cable ageing management by developing cable ageing models and algorithms, which are based on multi-scale studies and can be tailored to cover variations in fillers, additives and degrees of crosslinking.

As known, the design on nuclear cables can differ depending on the applied voltage and on the specific application (control, power or instrumentation). In any case the most sensitive part in terms of aging is the electrical insulation which surrounds the conductor. Insulation is made by using polymeric blend which can be filled of different kinds and concentration of fillers.

The materials chosen for analysis inside the TeaM CABLES project are the most commonly used in NPPs:

- Crosslinked Polyethylene (XLPE)
- Ethylene propylene diene terpolymer (EVA-EPDM)

In this paper, the electrical response of different-filled crosslinked polyethylene (XLPE) is investigated through dielectric spectroscopy technique.

Furthermore, as known [5], crosslinking process can lead to the formation of the so-called crosslinking by-products which can affect the electrical response of the material; for this reason, a degassing procedure was performed and its influence on the dielectric spectra is analyzed and commented with relation to the filler electrical response.

II. EXPERIMENTAL SETUP

A. Materials

This paper investigates the fillers impact on the physical-chemical properties of XLPE. Seven different samples made with a growing formulation complexity: are analyzed, see Table 1.

The additives here considered are antioxidants and fire retardants, required in order to prevent or slow down degradation of the polymer insulation [6]. In particular, two classes of antioxidants (AO) species are used here: free-radical scavengers, usually called *primary antioxidants*, and peroxide scavengers, also called *secondary antioxidants*.

TABLE I. SPECIFICATION AND CHEMICAL COMPOSITION OF SAMPLES

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

The former are commercially available as phenol-based compounds which can react with chain-propagating radicals, e.g. peroxy, alkoxy, resulting in a chain terminating reaction. This kind of chemical compounds are quite polar species due to the presence of a distinguishing -OH group.

The latter are available in form of thioethers, which are able to decompose hydroperoxides (ROOH) into nonreactive products. On the contrary, this kind of antioxidant is quite non-polar.

Flame retardants are very commonly and copiously used as additives for insulation for nuclear application due to safety reasons. Their action can result in an endothermic reaction which forms an inert residue and water which dilutes the smoke.

This kind of additives can be both organic or inorganic, in this paper, inorganic aluminum hydroxide (ATH) is used as a flame-retardant additive in XLPE [6].

B. Measurements

Dielectric response of specimens was analyzed in the range of 10^{-2} - 10^6 Hz through a NovoControl Alpha Dielectric Analyzer V2.2 with applied voltage of 3 V_{rms} at room temperature. Due to roughness of the surface, specimens have been metallized through cold plasma-sputtering in order to obtain a homogenous contact between the electrodes and the analyzed material.

C. Degassing treatment

Crosslinked polyethylene specimens were obtained through a chemical crosslinking process. As known, this method brings to a quite high concentration of chemical species, called crosslinking by-products, which are usually highly polar [2]. In order to get rid of these species, specimens have been degassed under vacuum at 70 °C for 72 hours. After this process, electrical response of specimens has been tested again through dielectric spectroscopy technique to evaluate crosslinking by-products contribution on dielectric response.

III. RESULTS AND DISCUSSION

Real and imaginary parts of permittivity are reported in Figs. 1 and 2 for the untreated and the degassed samples, respectively.

In both cases, different concentration and type of additives can bring to noticeable variation in the dielectric spectra, in particular for the real part of permittivity. The reason of this behavior can be related to the chemical composition of additives and their dipolar properties, as discussed below.

Moreover, ϵ' increases linearly in the low-frequency range with reducing frequency, that can be imputed to electrode polarization effect as reported in literature [7]. This phenomenon can be explained through the presence of dissolved free ions inside the polymer which tend to move towards the electrode/sample interface, leading to the development of ionic double layers. Electrode polarization (EP) depends microscopically upon the electrode surface topography and area, as well as upon the surface chemistry (reactive surface groups or atoms).

Fig. 1.a shows that the real permittivity slightly changes for antioxidants-filled XLPE (sample n. 2,3,4) with respect to non-filled XLPE (sample 1), probably due to the very little variation in material composition.

Though, the presence of species which are external from main matrix brings to the presence of dissolved free ions which results in a tiny raise in the lowest frequencies range. Referring to sample 4, it is worth noting that the combination of both antioxidants causes the enhancement of EP phenomenon with larger variation of ϵ' values at low-frequency.

Additives can cause formation of interfaces inside the polymer blend, this leads the imaginary part of permittivity (Fig. 1.b) to behave raising its value as the antioxidants concentration raises. As a result, sample 4 loss factor is an order of magnitude higher than the reference XLPE.

Focusing on the flame-retardants filled specimens (sample 5 and 6), one can notice an increase of real part of permittivity in the whole spectrum (Fig.2.a) due to the presence of polar ATH species with respect to the reference XLPE (sample1).

However, doubling the concentration of ATH does not cause appreciable variation of ϵ' values in the high-middle frequencies range; on the contrary, it causes a wider increase of ϵ' in the low frequency range due to a larger electrode polarization phenomenon with respect to the 25% filled specimen.

Referring to the imaginary part of permittivity (Fig. 1.b), larger concentration of fillers results in higher losses due to the interfacial polarization phenomena that occur in the polymer. However, ϵ'' values of the flame-retardants filled polymers do not significantly vary with respect to the antioxidants filled XLPE (sample 4), this behavior, quite singular, can be imputed to the presence of crosslinking by-products which remain trapped inside the polymer blend during the process of chemical crosslinking [5]. These species are usually highly polar and can affect the whole dielectric spectra bandwidth due to their ability to interact with interfaces inside the polymer blend.

In order to get rid of by-products that can cover the effect of the additives, a degassing treatment under vacuum was performed on the same samples.

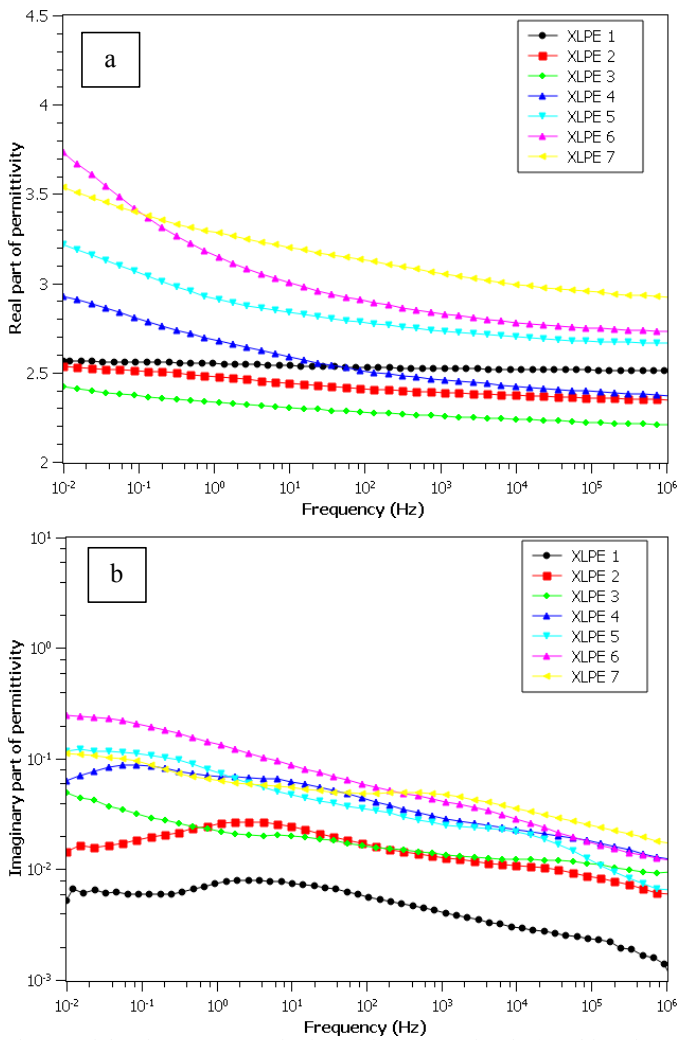


Fig. 1. Dielectric spectra as a function of frequency of real (a) and imaginary (b) part of permittivity. Measurements performed at room temperature on untreated specimens.

The same process has been performed also in nitrogen, but the treatment appeared as ineffective since negligible variation can be noticed in the resulted dielectric spectra.

Figs. 2.a and 2.b show the behavior of real and imaginary parts of permittivity, respectively, after degassing. These results show clearly that degassing procedure significantly changes the dielectric response of the investigated materials. In particular, the real part of permittivity (Fig. 1.a) decreases with respect to untreated specimens. This can be associated with the removal of crosslinking byproducts which are, as stated above, highly polar species and whose presence can result in the raise of ϵ' .

This treatment highlights a sharp separation between the antioxidants-filled and ATH-filled XLPEs. So that the former do not significantly vary their ϵ' with respect to the neat sample, while the latter keep their initial ϵ' value (Figs. 1.a and 1.b).

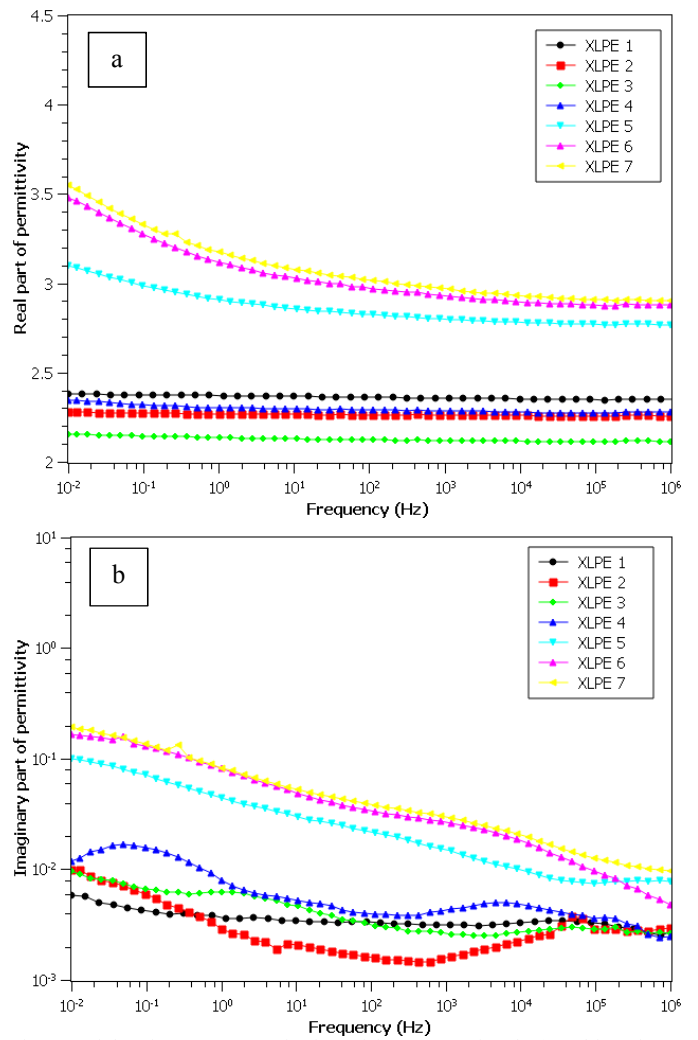


Fig. 2. Dielectric spectra as a function of frequency of real (a) and imaginary (b) part of permittivity. Measurements performed at room temperature on degassed specimens.

Moreover, the degassing process causes the reduction of the low-frequencies raise of ϵ' and consequently of the electrode polarization effect, confirming an efficient extraction of the polar crosslinking by-product species. On the contrary, dielectric response of ATH-filled samples is not significantly affected, keeping the same dielectric response due to the very high concentration of fillers which results in the already discussed raise of the real part of permittivity due to the electrode polarization.

Also the imaginary part of permittivity (Fig. 2.b) shows two populations in the dielectric response spectra, one relevant to the AO-filled samples and the other to the ATH-filled materials. The degassing treatment causes a significant decrease of ϵ'' for the neat and AO-filled samples, in addition to the removal of some polarization peaks that appeared in the 1-10 Hz range (Fig. 1.b), likely imputed to interfacial polarization created by crosslinking by-products.

After the treatment, dielectric losses do not significantly change with the raising of additives (samples 1-4), nevertheless one can notice two different polarization peaks in sample 4 which can be imputed to the presence of the two different kind of additives inside the blend. In particular, the peak in the high frequency range is similar to the one that appears in the imaginary part of permittivity of sample 2 while the low-frequency one can be related to the thioether-filled specimen.

Additionally, the highly filled materials (samples 5,6,7) show larger dielectric losses than the other materials. The huge amount of additives can cause an agglomeration of these species which can lead to strong interfacial phenomena and causes high losses particularly in the very low-frequency range.

IV. CONCLUSIONS

This paper investigates the change in physical-chemical properties of crosslinked polyethylene due to the effect of additives through dielectric spectroscopy technique.

Additives appeared to remarkably change electrical response of XLPE; in fact, also very low additive concentration proved to have a noticeable impact on dielectric spectroscopy.

Moreover, crosslinking by-product effect on dielectric response was investigated. These species demonstrated to have very high influence due to their dipolar properties. Degassing treatment caused the removal of these highly polar species and the lowering of dielectric losses in all the materials here considered, so that the effect of the additives could be singled out more precisely.

These results constitute the base for studying the effect of temperature and radiation aging on insulating materials used for NPP low-voltage cables. Indeed, non-destructive electrical

techniques like e.g. dielectric spectroscopy can be used to assess insulation aging once the effect of material chemical composition has been singled out on the dielectric spectrum.

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