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Investigation on thermal degradation phenomena on low density polyethylene (LDPE) through dielectric spectroscopy

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Abstract — Investigation of thermal degradation of low-density polyethylene (LDPE) has been carried out in this paper. LDPE plaques made directly from commercial pellets has been thermally stressed at high temperature (110°C) and characterized through both chemical and electrical measurements. In particular, oxidation and morphological changes contributions inside polymer have been correlated to modification of the imaginary part of dielectric constant. This comparison could put the basis in developing specific nondestructive techniques (NDT) for polymer diagnostics based on electrical measurements.

Keywords — LDPE, oxidation, FTIR, degradation, thermal aging, dielectric spectroscopy, crosslinking, chain-scission.

I. INTRODUCTION

In the last decades much interest has been focused on polymer research and development. This trend is led by the roughly unlimited applications that polymeric blends can have (e.g. from everyday life to high technology devices). Low-density polyethylene (LDPE) composites, in particular, are commonly used in industry because of their characteristics such as light-weightiness together with good mechanical properties other than their excellent features as electrical insulation. This latter is one of the most important application in polymer science, and the one analyzed in this paper. As known, any polymeric material gradually degrades during its life application mainly because of high temperature gradients or severe radiation rates. These stresses are predominant inside a nuclear power plant (NPP) where cable insulation made of different kinds of polymeric blends can reach their end-of-life point before the one fixed during the design phase.

For this reason, many nuclear energy companies are interested in developing a condition monitoring technique that could evaluate online cable insulation health, through nondestructive techniques which are, nowadays, quite uncommon (such as electrical ones). At the moment, in fact,

traditional condition monitoring techniques are destructive but well standardized (e.g. tensile stress method).

Degradation inside insulation is caused by different kinds of mechanisms, such as: structural modification, additives consumption and, above all, oxidation [1-3]. This latter is the core of this paper due to its predominant contribution inside polymer degradation.

This paper deals with thermal degradation of low density polyethylene (LDPE), traditionally used as a precursor of many other PEs used as, but not limited to, insulation in nuclear power plants (NPPs). Main aims of this paper are:

1. to find a correlation among chemical, physical and electric modifications of polymers;
2. to propose new nondestructive techniques (NDTs) comparing actual standard destructive approach with nondestructive electrical ones, such as dielectric spectroscopy performed in this paper [2,4,5].

The polymer here investigated was thermally aged both *in air* and *under vacuum* in order to induce and prevent oxidation inside the insulation respectively. Both electrical (nondestructive) and chemical (destructive) tests have been carried out in order to evaluate polymer degradation conditions inside the polymer chain. Finally, tests results were discussed in order to compare conventional condition monitoring (CM) techniques [6,7] with electrical, thus nondestructive, ones.

II. EXPERIMENTAL SETUP

A. Specimens

LDPE plaques made directly from commercial pellets, thus with no extra additives are investigated in this paper. The kind and amount of additives and antioxidants inside pellets cannot be disclosed because of industrial secrecy. The device used for press molding is a press machine with monitor of temperature

and pressure. Plates obtained by this process were finally cut into 3x3 cm samples with thickness of 165-260 μm .

B. Thermal aging

Specimens were thermally aged in oven at 110°C (about 15°C less than melting temperature T_m) both *in air* and *under vacuum*, in order to split the possible oxidation contribution in the degradation process. The maximum aging time was 700 h and every 100 h specimens were removed for analysis.

C. Measurements

A NovoControl Alpha Dielectric Analyzer with applied voltage of 3 V_{rms} was used to investigate dielectric properties in the frequency range between 10⁻² and 10⁶ Hz. Here, the dielectric constant (both real and imaginary part) trend as a function of frequency is reported as it manifested the best correlation with chemical-physical modification inside the polymer.

In order to evaluate the presence and amount of oxidative groups and to quantify the grade of oxidation, FTIR and oxidation induction time (OIT) measurements were carried out.

To perform the former analysis, an Alpha FT-IT spectrometer from Bruker with ALPHA's Platinum ATR-single reflection diamond ATR module (Spectral range: 7500 cm⁻¹ – 375 cm⁻¹; spectral resolution: < 3 cm⁻¹) was used.

Oxidation induction time was evaluated through a TA Instruments STD SQ600 device capable to perform simultaneously DSC and TGA measurements. Due to actual experimental setup, air has been used as second gas in place of pure oxygen (as requested by standards [7]), so that numerical values of OIT* here reported are referred to air induction to oxidation. OIT* tests are quantitative measurements of oxidisability level of the polymer, in general, the lower the OIT the lower the oxidisability grade.

Gel fraction measurements were performed as requested by standards [8] in Xylene in order to evaluate crosslinking grade.

III. RESULTS

A. Dielectric results

Fig. 1.a and 1.b report the real part of permittivity for both aging conditions. ϵ' values have little variation with aging times and its trend is pretty constant throughout the frequency spectra. Moreover, it is worth noting that the ϵ' does not increase, as expected, with increasing of aging time, this peculiar behavior will be discussed in the next section.

Fig. 2 shows the imaginary part of permittivity trend as a function of frequency for *in air* (Fig. 2.a) and *under vacuum* (Fig. 2.b) treatment. It can be observed that ϵ'' raise is not monotonous with increasing aging times. The trend is quite different for the two aging treatments, showing bigger variations with aging times *under vacuum* than *in air* and a different behavior in the range between 10²-10⁴ Hz. In general, longer aging times *under vacuum*, cause bigger variations on ϵ'' values than in air. This can be imputed to different degradation phenomena that can happen inside the polymer under different aging conditions as discussed in the following section.

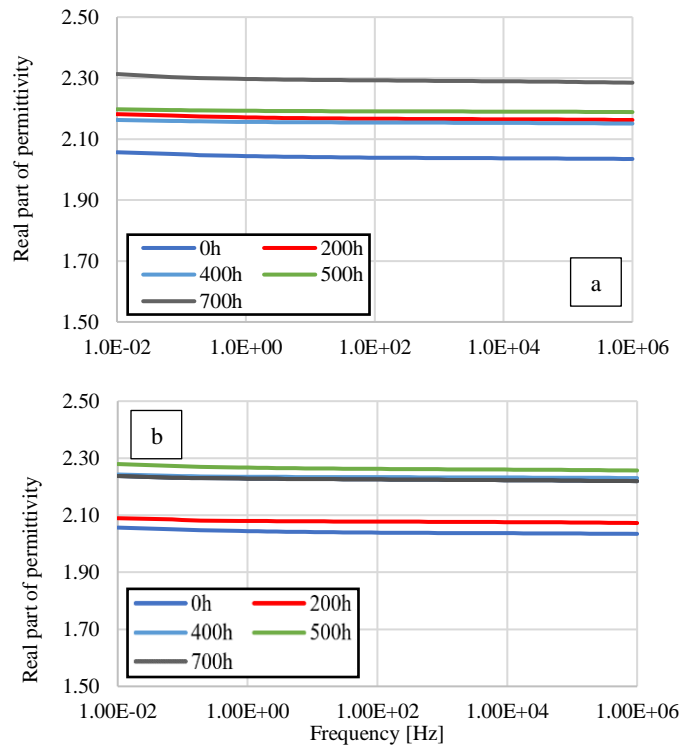


Fig. 1. Real part of dielectric permittivity (a) in air and (b) under vacuum plotted as a function of frequency (logarithmic scale) for different aging times.

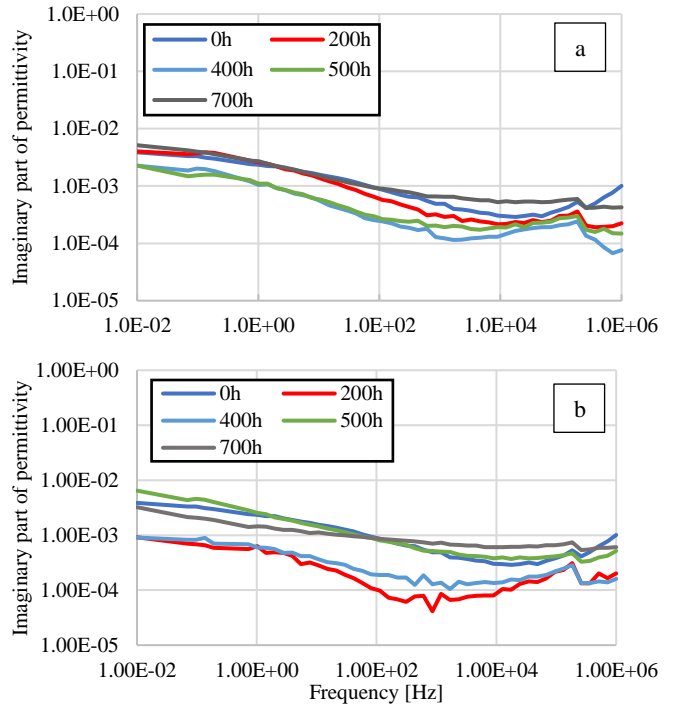


Fig. 2. Imaginary part of dielectric permittivity (a) in air and (b) under vacuum plotted as a function of frequency (logarithmic scale) for different aging times.

B. FTIR analysis

FTIR spectra (Fig. 3) show unchanged trend for the first 600h aging time for both aging treatments. The intense peaks at

2925, 2850, 1460 and 725 cm^{-1} are assigned to the ($-\text{CH}_2-$) methylene group inside polyethylene.

Further aging *in air* brings to the reveal of new peaks with wave number of 1700-1800 and 1200-1300 cm^{-1} which are attributed to carbonyl and carboxyl compounds. As known [9], these groups are related to oxidation inside the polymer as they are characterized by oxygen molecules inside their chemical structure. On the other hand, 800 h aging *under vacuum* shows very little peaks related to oxidative groups due to antioxidants consumption caused by thermal treatment with longer aging times.

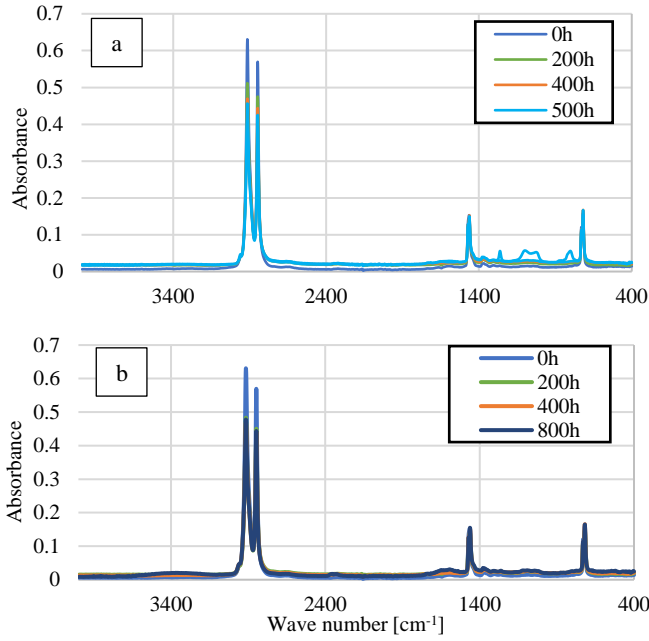


Fig. 3. FTIR analysis of thermally aged LDPE (a) in air and (b) under vacuum.

C. OIT measurements

Fig. 4 shows OIT measurements as a function of aging time in air and under vacuum. It can be noticed that, as expected, *in air* aging causes bigger reduction of OIT values than the one made by the *under vacuum* treatment. This can be imputed to higher antioxidant consumption during *in air* aging together with oxygen reactions which bring to oxidative functional groups as confirmed by FTIR spectra (Fig. 3.a) at aging time longer than 700h.

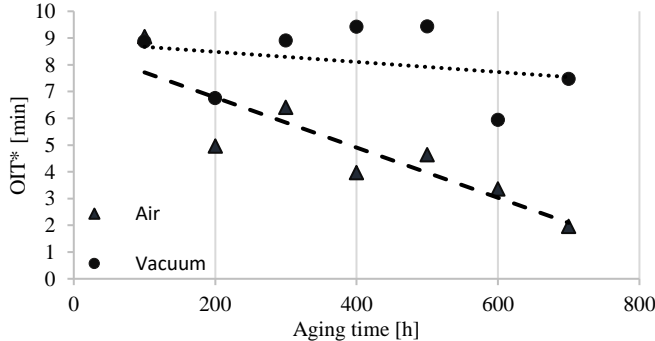


Fig. 4. OIT* measurements as a function of aging time in air (triangle) and under vacuum (circle)

D. Gel-fraction measurements

Gel-fraction measurements allow the evaluation of crosslinking grade inside the polymeric insulation. Experimental results are reported in Fig. 5 as a function of aging time and parameters.

It is worth noting that *in air* crosslinking grade increases mainly in the first 400h-aging, further aging causes lower variations.

Crosslinking grade does not significantly change during the whole *under vacuum* aging. As known in literature [10] the crosslinking grade depends, among other parameters, both on the concentration and the efficiency of antioxidants. Antioxidants, in fact, are used both to avoid oxidation reactions and as stabilizers inside the polymer chain. The *under vacuum* treatment does not cause big antioxidants consumption and, consequently, the gel fraction does not significantly change during aging.

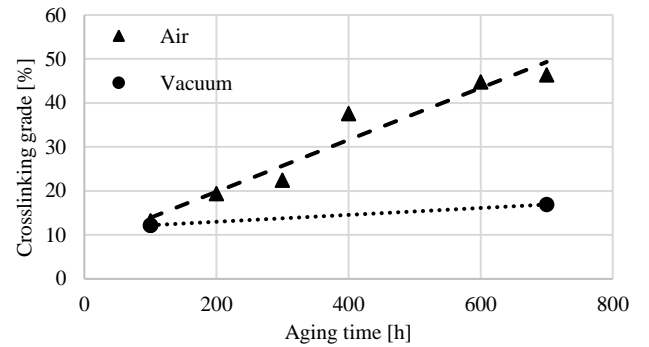


Fig. 5. Gel-fraction measurements as a function of aging time in air (triangle) and under vacuum (circle)

Although there are no chemical crosslinking agents, aging treatment can cause chain-scission phenomena together with some recombination of chemical bonds between broken chains which can bring to embrittlement of the polymer and the raise of the crosslinking grade.

IV. DISCUSSION

Chain scission, crosslinking, additives consumption and, above all, oxidation are known in literature [1,2,9] to be the main degradation phenomena inside insulation. Depending on the kind and intensity of the degradation the insulation polymer can have different electrical response as a function of frequency [2,4]. In particular, ϵ'' has been used as a marker to qualify condition and losses inside dielectrics as it is very sensitive to aging.

Fig. 2 show a peculiar trend of ϵ'' , its initial decrease with aging times is likely attributed to crosslinking structural modification and additives consumption as confirmed by OIT (Fig. 4) and gel-fraction measurements (Fig. 5), where they show bigger variations in the first aging times.

Longer aging times cause raises of ϵ'' , this can be imputed to dipolar radical formation inside the polymer. In fact, once additives and, in particular antioxidants, decrease their concentration inside the polymer, as confirmed by the decrease of OIT values, oxygen molecules are able to bond with radicals made by thermal treatment bringing to strong dipolar molecules that cause bigger electrical responses and higher ϵ'' values.

This behavior can be observed in both aging treatments. OIT measurements show almost the same induction time for the first aging periods, this is likely due to the same level of antioxidants extraction made by the thermal treatment. Longer aging cause higher antioxidants consumption *in air* than *under vacuum* due to the presence of oxygen. However, crosslinking raise *under vacuum* can be likely imputed both to antioxidants extraction and to the recombination of radicals and chains made by thermal treatment which make the polymer stiffer (Fig. 5) and. This embrittlement, together with the presence of antioxidants, causes higher ϵ'' values in the low frequencies range, as reported in literature [2,4].

However, after the running out of antioxidants inside the insulation material, oxygen is free to bond with radicals and one can notice a steep increase, up to two orders of magnitudes, of the imaginary part of permittivity in the whole frequency range due to oxidative dipolar groups and radical recombination (Fig. 6). Further confirmation of oxidative groups can be seen in FTIR spectra (Fig. 7).

These results confirm the good correlation between the imaginary part of permittivity and the physical-chemical (e.g. oxidation) modifications inside the polymeric insulation

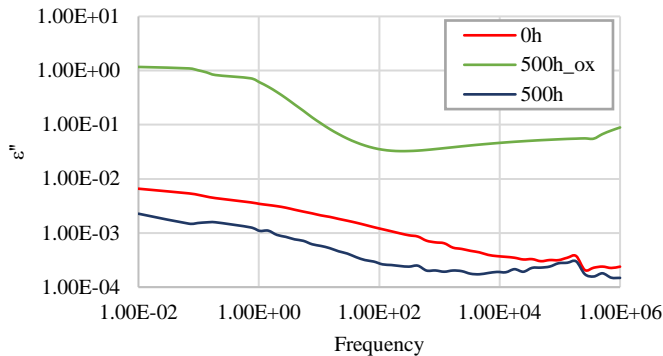


Fig. 6. Imaginary part of permittivity as a function of frequency for a specimen with (blue) and without (green) additives.

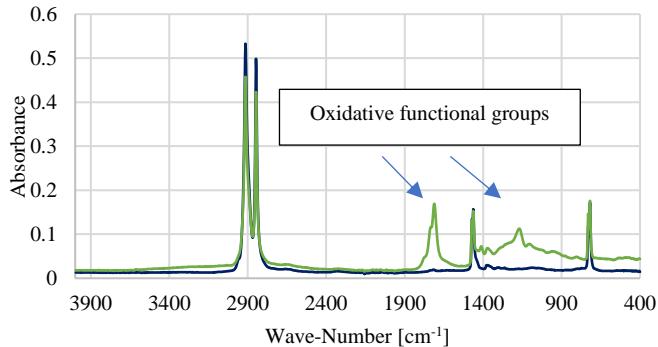


Fig. 7. FTIR spectrum for a specimen with (blue) and without (green) additives.

V. CONCLUSIONS

Investigation of thermal degradation of LDPE-based materials through electrical, and chemical measurements has been performed in this paper. In particular, electrical measurements have been correlated to degradation mechanisms inside the polymer insulation comparing those ones with chemical analyses. As a result, we obtained a good correlation between the imaginary part of permittivity trend as a function of frequency with various degradation phenomena e.g. oxidation grade, additives consumption and crosslinking.

Finally, electrical measurements showed a good correlation with standard techniques settling the ability of the imaginary part of permittivity to represent polymer modifications and additives consumptions.

Further investigations will be the analysis of different kinds of antioxidants and the use of different kinds of polymer characterization tests.

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