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Investigation of thermal degradation of LDPE-based materials through electrical measurements

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Abstract — Influence of temperature on low-density polyethylene (LDPE) has been analyzed in this paper. Commercial LDPE films with different thickness were stressed at high temperature (110 °C) and characterized using different test methods such as: impedance spectroscopy, tensile testing and chemical measurements. Thermal treatment has been carried out both in air and under vacuum in order to single out the oxidation contribution on polymer degradation. As a result of these tests we obtained a good correlation between mechanical and electrical properties, which could lead to developing a nondestructive technique (NDT) for polymer diagnostics.

Keywords—LDPE, oxidation, degradation, chain modification, thermal ageing, dielectric spectroscopy.

I. INTRODUCTION

Polymeric materials are widely used in industrial and domestic life for widely different applications: from common ICT instrumentation to electrical insulation systems. This huge field of application of polymers increased academia and industrial interest, which brought to the underlining of new features and possible applications of these materials.

Polymers are widely appreciated 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. However, any polymeric material gradually degrades during its life application particularly under the effect of radiation and temperature, which can be extremely severe in nuclear energy applications. As known, degradation mechanisms in polymers are mainly related to structural modification, additives consumption and, above all, oxidation [1].

The nuclear energy companies interested in polymer-as-insulation brought to the necessity to evaluate polymer health and exercise conditions. Nowadays, insulation end-life point in nuclear applications is set by standards through destructive tensile stress measurements [2-4].

This paper deals with thermal degradation of low density polyethylene (LDPE), traditionally used as a precursor of many

other PEs used as insulation in nuclear power plants (NPPs). Aim of this paper is, on the one hand, to find a correlation among chemical, physical and electric modifications of polymers; on the other hand, to propose new nondestructive techniques (NDTs) drawing a parallelism between actual standard destructive techniques (above all tensile stress) and nondestructive electrical measurements, such as impedance spectroscopy studied in this paper [5-6].

The polymer here investigated was thermally aged both in air and under vacuum in order to separate oxidation contribution in the degradation development. Both destructive and nondestructive tests were performed and finally NDT results were compared and correlated to those obtained with conventional condition monitoring (CM) techniques [5-6].

II. EASE OF USE

A. Specimens

LDPE made directly from commercial pellets, thus with no additional additives, other than anti-oxidants, was used for tests described in this paper. The nature and amount of anti-oxidants cannot be disclosed being an industrial secret..

LDPE plates specimens were prepared through hot pressing the tape obtained by pellets. Plates were finally divided into 3x3 cm samples with thickness of 165-250 μm .

B. Thermal aging

Polymer was aged in oven at 110 °C (about 15°C less than melting temperature T_m) both in air and under vacuum, this latter to isolate oxidation contribution in degradation process. The maximum ageing time was 700 h in the case of air treatment (500h in the under vacuum case) and specimens were removed for analysis every 100h.

C. Measurements

Dielectric properties of thermally aged LDPE plates have been investigated through a NovoControl Alpha Dielectric Analyzer with applied voltage of 3 V_{rms} in the frequency range between 10^{-2} and 10^6 Hz.

Information about mechanical properties, e.g. Young modulus and elongation-at-break, were obtained using tensile tests made with a LBG Universal Testing Machine with 100 N load cell. Specimens were prepared cutting small dog bone-like pieces of polymer and tested with extension rate at 50 mm min⁻¹ as requested by standards [7]. At least four tensile tests were made for each aging time because of data dispersion.

Finally, chemical tests carried out on specimens are briefly reported in Tab. 1.

TABLE I. PERFORMED CHEMICAL TESTS

| Chemical test | Element investigated |
|--|--|
| Fourier Transform Infrared Spectroscopy (FTIR) | Carbonyl and carboxyl groups |
| Gel fraction | Crosslinking grade |
| Differential scanning calorimetry (DSC) | Fusion enthalpy, Crystallinity |
| Oxidation Induction Time (OIT) | Oxidation level / Antioxidants consumption |

OIT, OIT_p and DSC analysis were achieved through a TA Instruments STD SQ600 capable to perform simultaneously DSC and TGA measurements.

The oxidation induction time test allows the evaluation of antioxidant consumption and in general, the polymer oxidation level. Referring to the test method [8], samples were cut into small pieces, put in a sample pan and finally thermally treated inside the STD instrumentation. Thermal handling consists of a fast heating in an inert atmosphere (in this study nitrogen) until a predetermined temperature is reached; once heat flux is stabilized, the inert gas should have been replaced by oxygen. In this work, atmospheric air has been used in place of pure oxygen for reasons of tests simplification. The obtained thermographs show a positive slope next to the temperature at which exothermal reactions, for example oxidation ones, occur. Atmosphere switching time is defined as t_1 while the time in which the slope in the thermograph occurs is t_2 . Oxidation induction time can be expressed as:

$$OIT = t_2 - t_1$$

For the sake of brevity, we reported only electrical, mechanical and OIT tests which showed the best correlation between degradation time and polymer properties change.

III. EXPERIMENTAL RESULTS

A. Dielectric spectroscopy

Figures 1 and 2 show, respectively, dielectric spectroscopy spectra of both real (ϵ') and imaginary (ϵ'') part of permittivity as a function of frequency and at different aging times for both air and under vacuum tests.

Focusing on the real part of permittivity ϵ' , it can be noticed that small variations show up with the change of frequencies so that ϵ' can be considered pretty constant in the entire analyzed

spectra. Otherwise, it is worth noting that permittivity trends do not exactly follow, as expected, a raise with aging time. This peculiar behavior is discussed in the next section.

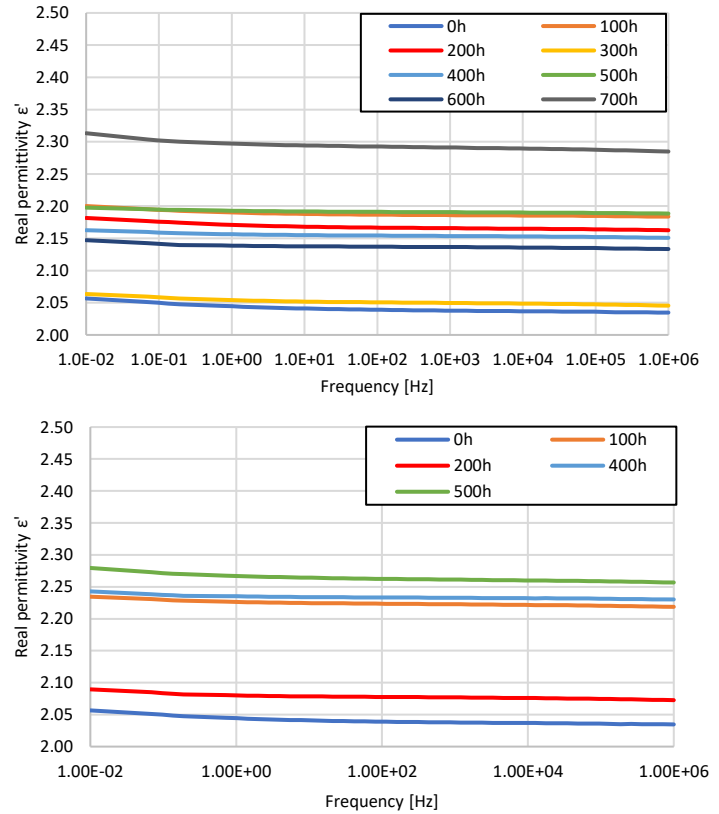


Fig. 1 Dielectric spectra as a function of frequency of real part of permittivity and different aging times. Aging made in air (a) and under vacuum (b).

Figure 2 shows the trends of the imaginary part of permittivity for the investigated ageing treatments. Imaginary permittivity has been used as a marker to qualify condition of dielectrics [6], as it is very sensitive to aging. Here again trends do not follow the hypothetical raise of ϵ'' with aging times. However, it is worth noting the different behavior between under-vacuum and air treatments at low frequencies. In fact, it shows up that there are bigger variations of ϵ'' under vacuum than in air, as a function of aging time in the low frequencies range. Comparison between numerical values is briefly reported in Tab.2.

TABLE II. IMMAGINARY PART OF PERMITTIVITY VALUES AT 10⁻² Hz

| Ageing time | ϵ'' values |
|----------------|----------------------|
| 500 h (air) | $2.27 \cdot 10^{-3}$ |
| 500 h (vacuum) | $6.46 \cdot 10^{-3}$ |

Otherwise, it can be noticed that the entire spectrum reported in Fig. 2.b shows larger variations with aging times, than Fig. 2.a spectrum.

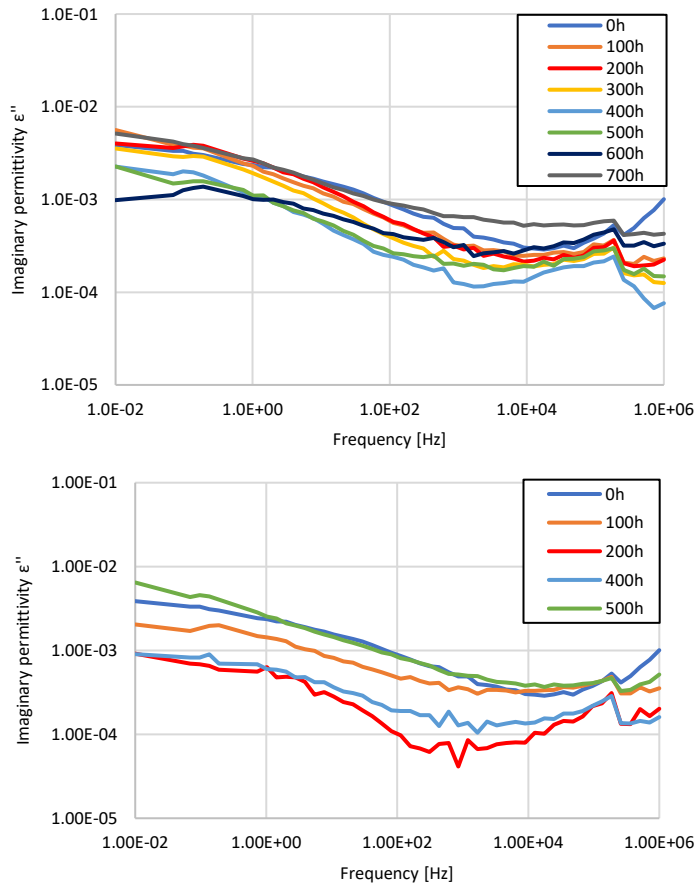


Fig. 2. Imaginary part of permittivity dielectric spectra as a function of frequency and different aging times. Aging made in air (a) and under vacuum (b).

B. Tensile tests

Tensile stress tests allowed trends of elongation at break (EaB), stress-at-break and Young modulus to be evaluated as a function of aging time and kinds of treatments. For the sake of brevity, in this paper only the Young modulus trend is reported (Fig. 3) as it showed the best correlation between electrical and chemical-physical properties.

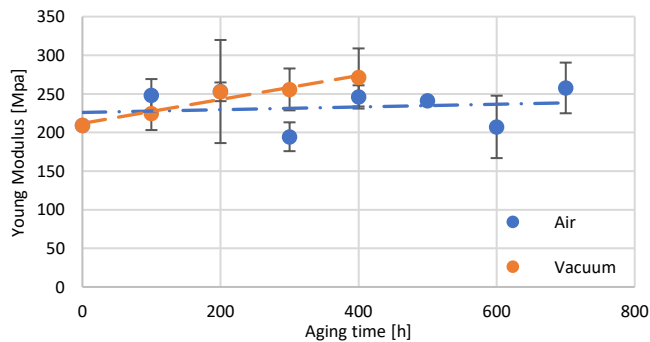


Fig. 3. Young modulus as a function of aging times. Interpolation made through linear trendline.

It can be noticed that for both thermal treatments, Young modulus grows slightly with aging times. In particular, modulus increase under vacuum could be associated likely to stronger morphological modifications, such as crosslinking, which raises polymer stiffness and, as a consequence, the Young modulus. Results not reported here show that elongation-at-break is not significantly affected during the aging times here considered.

C. Chemical tests

Differential scanning calorimetry (DSC) tests allowed the evaluation of crystallinity degree of polymer for different aging times. Table III shows the crystallinity values of the unaged sample (0 h) and 500 h aged sample for both treatments. It can be observed that crystallinity raises with aging time but it does not show important differences between the two kinds of treatments. These little variations can be imputed to non-homogenous sample characteristics.

TABLE III. DSC TESTS

| Ageing time | Crystallinity [%] |
|----------------|-------------------|
| 0 h | 48.5 % |
| 500 h (air) | 53.9% |
| 500 h (vacuum) | 52% |

Figure 4 shows three thermographs reporting the heat flow as a function of time. As described in the previous section, these thermographs allow the evaluation of oxidation induction time of the tested polymer. Numerical values are reported in Table IV. Focusing on the 500h-aged samples, big differences appear in the two treatments. Specimens aged in air, in fact, gets an OIT value much smaller than the ones treated under vacuum, underlining a higher antioxidants consumption in the case of air treatment. On the other hand, very small antioxidants consumption can be noticed in the case of vacuum aging, where OIT value is comparable to that obtained on the unaged sample.

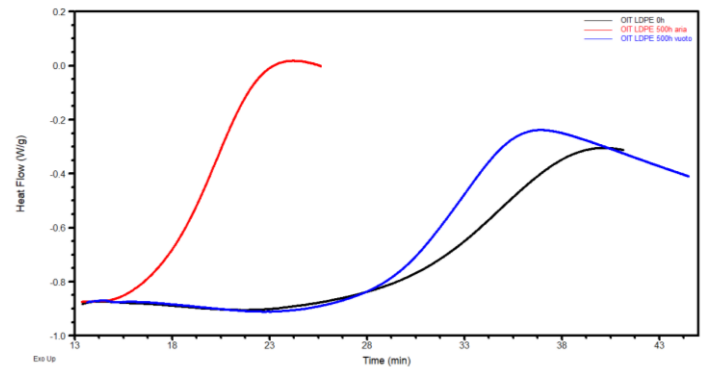


Fig. 4. Oxidation induction time thermographs for unaged sample (black), 500h-aged in air (red) and under vacuum (blue).

TABLE IV. OXIDATION INDUCTION TIME TESTS

| Ageing time | OIT [min] |
|----------------|-----------|
| 0 h | 16.11 |
| 500 h (air) | 4.35 |
| 500 h (vacuum) | 13.7 |

IV. DISCUSSION

As reported in literature [1, 5-6] oxidation, with morphological modifications and additives consumption, brings to the modification of ϵ'' values (Fig. 2). These phenomena have different, sometimes even opposite, response on ϵ'' spectra of the analyzed material.

As it can be seen in Fig. 2, the imaginary permittivity shows a sort of positive parabolic trend with aging times, underlining the presence of two opposite phenomena that occur during thermal aging. Initial decrease of ϵ'' until 300h-treatment (400h in the case of in air treatment) can be imputed to crosslinking structural modifications which make polymer chains less mobile under the electric field, in the frequency range here considered and at room temperature. Crosslinking effects are evidenced also by mechanical tests reported in Fig. 3, which show a continuous raise of Young Modulus. These behaviors are more prominent in the vacuum aging, as expected, because of the lack of oxygen and, obviously, of oxidation reactions.

On the contrary, raises of ϵ'' values appear after 400h treatment in both treatment cases. These ones can be attributed to radical formation which is associated, in particular, with antioxidants response inside the polymer.

Referring to [9] a possible explanation of the interactions between antioxidants and polymer chain reactions is proposed. Seguchi et al., in fact, state that the effect of antioxidants is the depression of initial radical formation in polymer chains produced by thermal treatment. Moreover, the decrease of antioxidants inside polymer is due to evaporation during thermal ageing, especially at high temperatures.

This theory can be applied to interpret ϵ'' trends showed in Fig. 2. After an initial decrease for both aging, one can notice a more pronounced raise of ϵ'' in the case of vacuum aging than in air, which however remains lower than the reference unaged material even at 500h of aging. For in-air aging the behavior is similar but for times $> 500h$ ϵ'' is larger. This phenomenon can be imputed to the effectiveness of antioxidants which inhibits radical formations, keeping low the value of ϵ'' for the aging times here considered. In air aging, due to larger radical formation, antioxidant inhibition ability can saturate particularly at long aging times, thus allowing oxidation reactions to occur, resulting into a steep increase of ϵ'' . This behavior was observed in one specimen out of 3, after about 400h of aging (results not reported here for the sake of brevity). A further confirmation of these speculations comes from OIT measurements, which show a huge difference in antioxidants consumption between the two

treatments, indicating that much longer aging times are necessary to incept oxidation reaction on most of the samples here considered.

V. CONCLUSIONS

Investigation of thermal degradation of LDPE-based materials through electrical, mechanical and chemical measurements have been carried out in this paper. In particular, electrical measurements have been correlated to various polymer degradation mechanisms, settling the ability of the imaginary part of permittivity to represent polymer modifications and additives consumption.

Vacuum aging showed a larger crosslinking contribution which has been reflected in higher low frequencies ϵ'' values, while in-air aging brought to radical / oxidation inhibition made by antioxidants, as reflected in OIT and mechanical measurements.

Finally, a good correlation between NDT electrical and standard measurements has been showed and discussed. Further measurements will be necessary on different kinds of polymers in order to explore the applicability of the electrical technique as a universal polymer diagnostic method.

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