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Assessment of the chemical and electrical properties of nano structured polyethylene with antioxidant-grafted nanosilica

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Abstract- In this work five different kind of PE-based materials are presented and characterized: neat PE, PE with nano-silica particles, PE with AO in the amorphous phase, PE with AO-grafted nano-silica particles and the combination of the two latter. Initially, the chemical properties of the materials have been characterized by means of Oxidation Induction Time (OIT) and Fourier Transform InfraRed Spectroscopy (FTIR), in order to investigate their oxidability performances and their resulting chemical composition, respectively. Moreover, electrical performance of these materials has been analyzed through dielectric spectroscopy measurements in order to keep into account the actual suitability of the resulting material for electrical applications. In conclusion, materials with AO-grafted nanoparticles resulted to be convenient in terms of both chemical and electrical property evolution over time.

I. INTRODUCTION

Antioxidants (AOs) have been widely used in the last decades as additives of polymeric materials to guarantee an acceptable shelf and operational life of these materials [1]. Commercial AO chemical compounds, usually phenols derivatives, are only soluble, in semi-crystalline polymers like polyethylene (PE), in the amorphous phase [1]. This leads to the free mobility of these molecules inside the polymeric matrix. Due to diffusion phenomena, which can be enhanced during aging, AOs tend to migrate from the bulk to the surface of the material accumulating and turning themselves into crystals [1, 2]. This phenomenon has been widely shown in literature [2, 3] to lead to the creation of interfaces which can deeply influence, usually worsening, the electrical properties of the insulation matter.

For this reason, researchers have been focusing on the possibility of improving on the one hand the AOs effectiveness, on the other hand the polymer properties aiming at reducing the amount of actual AOs dispersed in the polymer and the abovementioned interface-related phenomena. On the contrary, very few studies [4, 5] analyzed the possibility of incorporating the needed AOs molecules through different kind of fillers

which are not able to move through the amorphous part i.e. nanofillers.

Indeed, the opportunity to embed nanofillers with peculiar electrical properties inside the polymer matrix could open a wide range of development for dielectric materials.

In this work a new methodology to integrate AO to the main polymer matrix by means of nanoparticles is presented. In particular, grafting the AO molecules to the surface of nanoparticles i.e. nanosilica, showed to be convenient in terms of oxidability performances of PE [4]. Hence, the chemical and electrical properties of the new material are here investigated and discussed.

II. MATERIALS AND METHODS

A. Preparation AO-grafted nanoparticles

The antioxidant grafted silica is produced through the following steps: 1. the silica was firstly mixed with 3-aminopropyl triethoxysilane and catalyst (trifluoroacetic acid and water) in a sealed jar at room temperature for 24 hours. 2. the modified silica was put into vacuum oven for another 24 hours at 80 °C in order to remove unreacted residuals. 3. the obtained 3-aminopropyl triethoxysilane modified silica was mixed with 3,5-Di-tert-butyl-4-hydroxyphenylpropionic acid in a glass flask in a toluene solvent environment. The modification was carried on at 70 °C for 24 hours. 4. after the modification, the silica was washed by toluene many times to remove unreacted chemicals. 5. the washed silica was kept into the fumed hood for another 24 hours to evaporate the toluene, then the final studied silica is obtained. After that, the quantity of the silica was tested by using thermogravimetric measurement. The results showed that per 1 gram of silica, there is 15% of 3,5-Di-tert-butyl-4-hydroxyphenylpropionic acid is grafted on silica surface.

B. Specimens manufacturing

Five different types of samples were produced in total. Along with a pure polyethylene reference sample (base

polymer), three other samples loaded with different type of fillers and one with a combination of two fillers were produced. Materials and their composition are briefly reported in Tab.1.

TABLE I. MATERIALS

Material name	Material properties and fillers
LDPE	Neat LDPE
LDPE+silica	LDPE + 3 wt.% nanosilica
LDPE+AO	LDPE + 3 wt.% antioxidant
LDPE+AOgraftedsilica	LDPE + 3 wt.% of silica nanoparticles grafted with AO
LDPE+AOgraftedsilica+AO	LDPE + 1.5 wt.% of silica nanoparticles grafted with AO + 1.5 wt.% antioxidant

Initially, 9.7 g of polyethylene (PE) was added to 100 ml of xylene and heated at 140 °C for 30 min, whilst stirring at 200 rpm. The required amount of treated, non-treated nanosilica or antioxidant was dispersed in 20 ml of xylene and sonicated for 30 min. This was then poured into the polyethylene-xylene mixture and magnetically stirred for another 2 min at 300 rpm to avoid re-agglomeration. The polyethylene, xylene and silica nanoparticle mixture was then removed from heat and poured into methanol inducing precipitation. The resulting precipitate was dried at room temperature for one day after filtration. It was then further dried in a vacuum oven at 80 °C for three days to remove any traces of solvent. The obtained polymer nanocomposite was pressed at 180 °C into sheets, then was further processed and re-pressed into film samples (quenched in water, 20 °C) of $200\mu\text{m} \pm 2\mu\text{m}$ thickness.

C. FTIR measurements

Fourier Transform Infra-red spectroscopy has been performed through a Bruker Alpha in ATR mode for all the materials here analyzed. Spectra with wavenumbers between $4000\text{--}400\text{ cm}^{-1}$ has been recorded with a 16-scan acquisition and 4 cm^{-1} spectral resolution.

D. Oxidation induction time (OIT) measurements

Oxidation induction time (OIT) has been investigated through a TA Instruments STD SQ600 capable of simultaneously perform thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses. Due to the actual experimental setup in place of pure oxygen, pure air has been insufflated inside the oven chamber. Hence, the values reported here refer to air induction to oxidation (OIT*). As for OIT, the OIT* tests are quantitative measurements of the oxidability of the polymer matter. The higher the OIT*, the lower the oxidized grade of the polymer. Isotherm in air has been set at 230°C.

D. Dielectric spectroscopy

Electrical properties, in particular the complex permittivity as a function of the frequency, have been studied through the dielectric spectroscopy technique obtained by the means of a Novocontrol Alpha Dielectric analyzer.

The complex permittivity is defined as:

$$\hat{\epsilon} = \epsilon' - j\epsilon''$$

Where ϵ' is the real part of permittivity defined as the dielectric constant of the material, and ϵ'' is the imaginary part of permittivity related to the material dielectric losses [2, 5, 6].

The instrumentation has been set through the following parameters:

- Applied voltage 3 V_{rms} ;
- Frequency range: $10^{-2}\text{--}10^6\text{ Hz}$;
- Room temperature ($\sim 20\text{ }^\circ\text{C}$).

III. RESULTS

A. FTIR results

Figure 1 displays the FTIR spectra for the five materials here analyzed. FTIR has been performed in ATR mode so that the spectra refer only to the surface of the specimens.

It has to be recalled some known wave numbers related to the species which are present in the investigated materials [7]:

- 1472 cm^{-1} CH_2 stretching (crystalline phase);
- 1733 cm^{-1} C=O stretching (from phenol-based AO);
- 1101 cm^{-1} Si-O-Si symmetric stretching;
- 469 cm^{-1} Si-O-Si bending.

As expected, in all the specimens in which the nanosilica is present, the Si-O-Si related wavenumber appear on the spectra. The silica-related peak heights decrease with the decrease of the concentration of silica nanoparticles, as expected. Moreover, it is worth commenting that, if the silica is grafted with the AO molecule, the intensity of the peak again decreases probably due to the grafting manufacturing on one head of the silica molecule.

Contextually, the presence of phenol-based AO molecules results in the increase of the characteristic C=O peak at 1733 cm^{-1} . This peak is present in all the AO-filled specimens but in the case of AO grafted silica, this peak is way lower than in the case of the AO dispersed molecules probably due to the resulting different structure of the molecule itself after grafting.

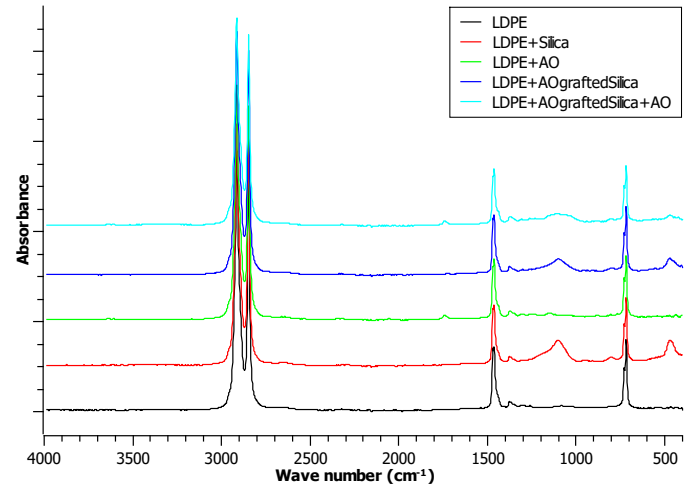


Fig. 1. FTIR spectra as a function of the different filler type and concentration.

B. Oxidation induction time (OIT) results

Figure 2 reports the values of oxidation induction time measurements for the analyzed specimens. Unfortunately, due to instrumentation limitation the experiment could be performed only for 45 minutes (30 mins under air). It is worth noting that all the AO-filled configurations showed the highest recordable value of OIT ($> 30\text{ mins}$).

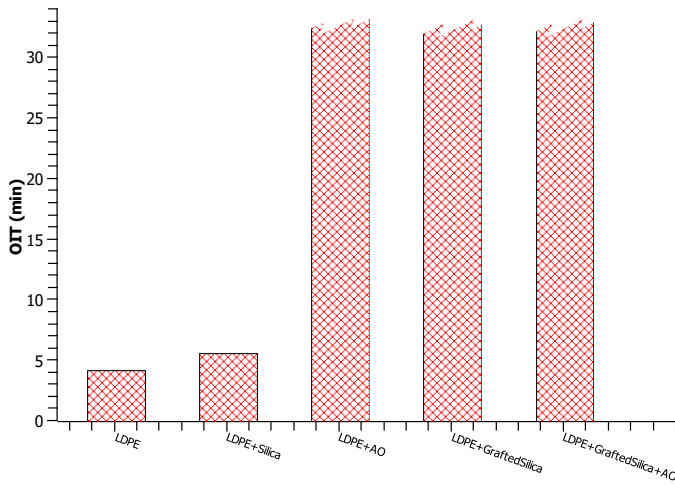


Fig. 2. OIT values as a function of the different filler type and concentration.

The addition of silica nanoparticles produces a little increase of the OIT value (around 7 mins), this phenomenon has been already presented in literature [4] and it is probably imputable to the decrease of the oxidable polymer matter.

The presence of AO molecules (both grafted and non-grafted) results into a significant increase of the OIT value (above the maximum recordable) and consequently into a good protection from oxidation for the polymeric material. So that, it is possible to claim that the presence of AOs molecules in all the configurations considered provide sufficient protection against oxidation (avoiding problems of interfaces).

C. Dielectric spectroscopy results

In order to investigate the electrical response of these materials, dielectric spectroscopy has been performed and experimental results are reported in Figure 3.

The base LDPE material shows a peculiar 2.3 dielectric permittivity (Fig.3.a) together with significant low losses (between 10^{-4} - 10^{-3}) (Fig.3.b). The addition of the AO molecules results into a slightly increase of both the parts of complex permittivity. In both cases no significant peak is registered, as expected, due to a very simple and plain configuration of the material.

Moving to the nanosilica-filled materials, one can observe a peak around 5 Hz (interfacial polarization region), likely imputable to the nanosilica particles interfaces.

The increase of the complex permittivity is more significant on the material filled only with nanosilica. The real part of permittivity, indeed, increases by up to 0.7, while the dielectric losses up to two order of magnitude.

The grafting and the addition of external AOs to the nanosilica-filled materials brings to the decrease of the complex permittivity in comparison of the nanosilica-only filled only material. Possible reasons for that will be presented in the following section.

IV. DISCUSSION

It has been shown that AO molecules are necessary for the stability of the insulating material over its application time. Indeed, the base PE material does not provide sufficient

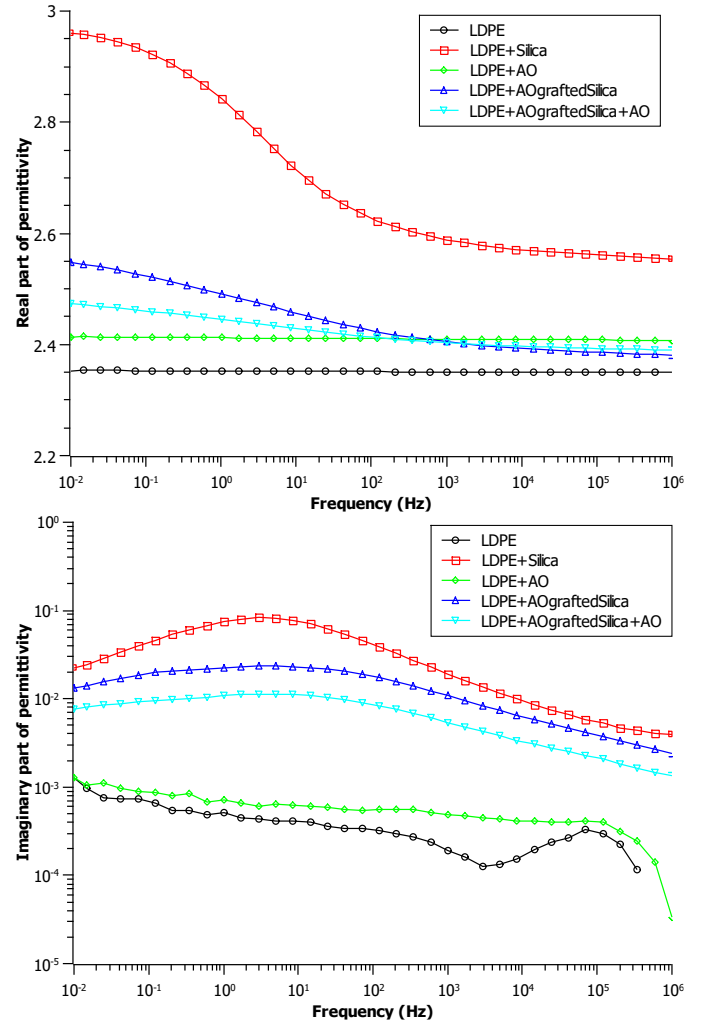


Fig. 3. Real and imaginary part of permittivity as a function of the different filler type and concentration.

protection from oxidation, as reported by OIT measurements (Fig.2), even though it shows the lowest dielectric losses (Fig.3).

The addition of silica nanoparticles slightly increases the protection from oxidation; however, this protection is not sufficient since the OIT values are relatively low and not adequate for a long-term application of the insulation matter. Focusing on the electrical properties of this material (Fig.3), one can see a significant increase of the complex permittivity, particularly the imaginary part up to two orders of magnitude. The huge increase of the dielectric losses is probably linked to the agglomeration of silica nanoparticles. As a matter of fact, the unmodified silica has high surface activity due to strong silanol group interactions. The nanoparticles in such a high concentration can agglomerate resulting in very big clusters which own big interfaces electrically responding in the frequency region considered.

The introduction of AO molecules to the base LDPE material resulted to be the most advisable configuration among the materials analyzed in this article. Indeed, the presence of AO molecules, whose FTIR response can be seen in the C=O

wavenumber (Fig. 1), caused an increase of the OIT value and consequently an efficient protection of the insulation polymer. This, together with a very little increase of the dielectric losses, suggesting a good suitability for these materials for also HV systems.

On the other side, the presence of AO molecules dissolved inside the amorphous region results into their free mobility through the polymer matrix. This phenomenon, widely reported in literature, can be on the one side very convenient for the protection against oxidation, while, on the other side, it can impact negatively on the electrical properties.

Indeed, the AO free mobility allows AO molecules to move towards the polymer reaching the external layer where the polymer is in contact with the environmental oxygen, resulting in a successful protection from degradation. On the other side, the movement of these molecules could cause the formation of new interfaces due to the arrangement of these ones into crystals or due to their reaction with the external oxygen. Indeed, AOs reacting with oxygen constrain the degradation to the external layer of the insulation, resulting in a non-homogenous degradation through the polymer thickness [6]. Both the abovementioned phenomena bring to the increase of the interfacial polarization-related losses. In addition, under harsh aging conditions, AO molecules can evaporate resulting in their physical loss and, consequently, in a decrease of effective oxidation protection.

A possible scenario for overcoming these limitations related to AO free molecules could be the grafting the AO particles to the silica nanoparticles. This configuration results into a high protection from oxidation, as confirmed by OIT measurements (Fig.2), and comparable to the conventional AO-filled LDPE. AO molecules would not migrate through the material since they will be stuck to the nanosilica particles, causing on the one side a homogenous degradation (if the nanoparticles are well distributed) and avoiding the formation of new interfaces. As it can be seen in Fig. 3, electrical properties show a decrease of the dielectric losses in comparison to the nanosilica-filled material, this is probably imputable to the reduction of the actual effective silica interfaces due to the superficial modification during the grafting process.

Indeed, grafting an organic moiety on one nanoparticles surface can result in reducing the surface activity, thus providing better compatibility with polymer. However, agglomeration is still possible, as it can be seen from the presence of interfacial polarization losses (Fig.3) but it is reduced. As a matter of fact, on the external nanoparticles layers there are some sites still remaining hydrophilic which can form hydrogen bond result in silica cluster. Anyway, the number of these sites is much lower than in untreated silica.

In conclusion, grafting antioxidant on nanoparticles showed to have a good protection from oxidation, allow the overcoming of the AO molecules limitations with aging and keep the dielectric losses to low values. Indeed, it is possible to believe that, with aging, the grafted AO could not further enhance the interfacial losses as it usually happens instead for the AO free molecules [2].

Finally, the combination of AO molecules together with the grafted nanosilica-filled LDPE shows not to provide significant performance improvements in terms of both oxidative protection and lowering of the dielectric losses.

V. CONCLUSIONS

In this work five different configuration of AO-filled PE are presented and investigated. The availability of different formulation of materials allowed the impact of the additives in terms of both thermal and electrical properties to be evaluated. In particular, a new methodology to incorporate the essential AO molecules inside PE is presented in this work. The AO-grafted nano-filled material showed to obtain a significant protection against oxidation, getting rid of the limitations of the AO free molecules dispersed in the polymer amorphous phase. In fact, the creation of interfaces could provoke the enhancement of the dielectric losses, causing a non-optimal configuration for electrical application of PE. In conclusion, it has been shown that the grafting of AO molecules on the surface of nanoparticles could be fruitful in terms of both chemical and electrical stability of the material over time. This work could be considered as a first step for the establishment of a new composite material based on PE with higher durability and stability overtime for electrical application as insulator.

Future work on this topic will include the investigation of the conductivity and space charge properties of the proposed material and its endurance with aging.

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