

POLYMER NANODIELECTRICS WITH ANTIOXIDANT GRAFTED NANOSILICA: THE EFFECT OF INTERFACES ON DC ELECTRICAL PERFORMANCE

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ABSTRACT

Antioxidants are placed in the amorphous phase inside semicrystalline polymers, where they can easily diffuse towards the polymer bulk. This movement could lead to the creation of new interfaces on the polymer surface, made up of antioxidant crystals, possibly causing additional space charge accumulation. In this article, a new methodology to integrate antioxidants into the main polymer matrix by grafting them on nanoparticle surface is presented and tested. This methodology reduced the movement of additives, without losing the oxidative prevention effect of antioxidant molecules. Space charge behavior of the obtained materials is reported and discussed.

KEYWORDS

Space charge, antioxidant, nanodielectrics, antioxidant diffusion, insulation, PEA method.

INTRODUCTION

High voltage DC (HVDC) links play a significant role in the global power grid today, and they will continue growing their importance in the near future given the possibility to deliver higher power throughout longer distances.

As the voltage of HVDC links increases, the development of new insulating materials is becoming more and more challenging for the Electrical Engineering research field [1]–[4]. The need of introducing additives, in industrial-grade cable insulations, has found to be source of anisotropy factors (e.g. new interfaces) inside the polymer insulation [5]–[7]. Interfaces can trigger different phenomena i.e., partial discharges and space charge accumulation, worsening the electrical performance of the resulting material. While the former can be considered as a secondary problem due to the very low repetition rate of the event, the latter may become a significant issue in the case of very high voltages, due to possible electric field distortions. For this reason, the quantity of additives is usually limited inside HVDC insulations which are, consequently, characterized by very high purity.

Moreover, nano filled dielectrics (nanodielectrics) are now considered as a promising technology for modern HVDC cable systems. Nanoparticles are usually added inside the insulating material to improve some of the electrical and physical properties of the base material and, consequently, to overcome current material limitations (e.g. thermal conductivity). Nowadays, the implementation procedures of these particles are well established, and particles can result to be evenly distributed in the polymer thickness.

Besides the request of high purity materials, antioxidants need to be placed inside the insulation in order to

guarantee an acceptable application life of the designed cable. These additives are usually placed in the amorphous phase inside semi-crystalline polymers (e.g. polyethylene). Due to this, they can easily move towards the polymer bulk due to diffusion phenomena. If their concentration is sufficiently high, they can turn themselves into crystals, upon reaching the outer surface of the insulation [8], [9]. Here, they can create a superficial layer characterized by higher conductivity, due to formation of possible percolation network. In this way, an additional interface is created on the polymer surface, which can cause electric field distortions, particularly during the initial application life period of the cable system (as the antioxidants concentration is higher).

Another issue caused by such additives lays on the fact that, due to the chemical kinetics of these additives, oxidative degradation remains blocked on the outer surface of the insulation, leading to non-homogenous degradation throughout the polymer thickness and, consequently, to possible electric field distortions [10], [11].

For this reason, innovative ways for the implementation of antioxidants inside the polymer are, nowadays, becoming more and more common [12], [13]. In this article, a new methodology to integrate antioxidants into the main polymer matrix by the means of nanoparticles is presented and tested. It consists of the grafting of antioxidant molecules on nanoparticle surface, reducing diffusion phenomena as nanofiller movement inside the insulation bulk is very limited. Therefore, the interfacial phenomena are diminished; furthermore, the antioxidant protection effect has been found, in our previous work [12], to be kept to sufficiently high values, acceptable for field applications. In this article, space charge (SC) properties of these materials are investigated through the PEA system. This technique would allow the validation of the good DC performance of the resulting material and the effective reduction of space charge accumulation due to the decrease of interfaces caused by the reduced mobility of antioxidant molecules.

MATERIALS AND METHODS

Materials

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 h 2. the modified silica was put into vacuum oven for another 24 h 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 h. 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 h 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 grafted on silica surface. A schematic of the multilayer structure and the species involved is reported in Figure 1.

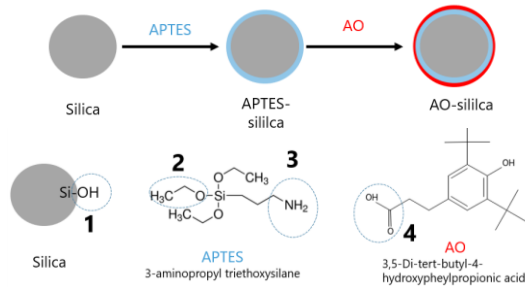


Figure 1. (a) Grafted nanoparticles scheme. (b) Chemical species involved.

B. Specimens manufacturing

Four different types of samples were produced in total. Along with a pure polyethylene reference sample (base polymer), three other specimens loaded with different type of fillers. Materials and their composition are briefly reported in Tab.1.

Table 1. Description of materials.

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

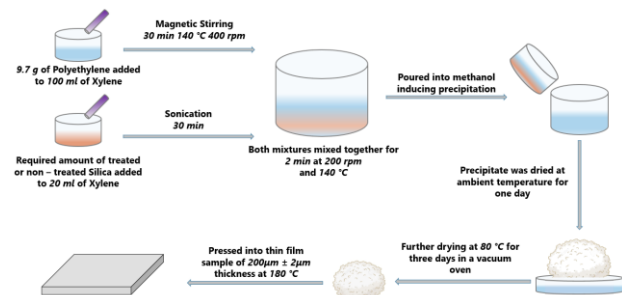


Figure 2. Nanoparticles implementation schematic.

Initially, 9.7 g of polyethylene (PE) was mixed with 100 ml of xylene and heated at 140 °C for 30 min while stirring at 200 rpm. Appropriate amount of treated, non-treated nano-silica or antioxidant was dispersed in 20 ml of xylene and sonicated for 30 min. The dispersion was then added to the polyethylene-xylene mixture and stirred for 2 min at 300 rpm to prevent re-agglomeration. Finally, the mixture was poured into methanol to precipitate. The precipitate was then filtered and left to dry at room temperature for one

day. It was then dried for three days in a vacuum oven at 80 °C to eliminate any remaining solvent traces. The resulting polymer nanocomposites were first pressed into thin sheets at 180 °C; then re-pressed into film samples, quenched in water at 20 °C to obtain samples with a thickness of 200μm ± 2μm. A schematic of the above mentioned process is reported in Figure 2.

Space charge measurement setup

Space charge measurements were performed through the Pulsed Electro-Acoustic (PEA) method, whose schematic is reported in Figure 3.

Two coexistent voltages: a DC voltage V_0 and a pulsed voltage $V_p(t)$ are applied to the sample under test. The applied DC voltage injects charges inside the specimen, while the pulsed voltage causes an acoustic pressure wave due to its interaction with charged particles. The piezoelectric sensor, at the bottom of the cell, transduces the acoustic wave into a voltage signal. Knowing the sound velocity in the specimen, it is possible to obtain the charge distribution in space [1], [14].

In this work the applied DC electric field was set equal to 20 kV/mm at room temperature, in a shielded environment. The volt on phase lasted 10000 s while the volt off phase lasted 3500 s.

The value of total absolute stored charge density in the bulk at a chosen depolarization time is given by (1) [9-10]:

$$q_s(E, t_d) = \frac{1}{l} \int_0^l |q(x, E, t_d)| dx \quad (1)$$

where l is insulation thickness and t_d is the depolarization time, $q(x, E, t_d)$ is the space charge profile detected at time t_d . The maximum value of q_s , namely Q_{max} , can be calculated at the beginning of depolarization once the poling electrode charge has been dissipated, say at about $t_d = 5s$.

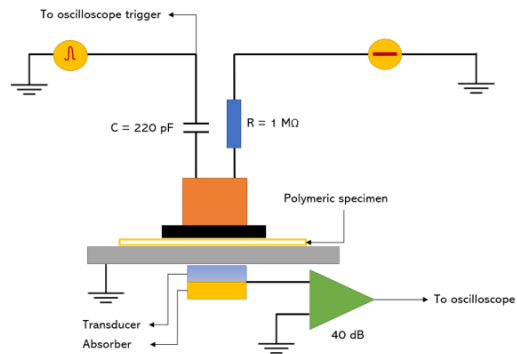


Figure 3. Schematic of the PEA measurement setup.

Degassing treatment

As already reported in literature [2], [5] and in the introduction, polymer space charge characteristics are dependent on species, acting as trap sites (e.g., impurities), inside the material under test. During the manufacturing process, some additives are added inside the compound to catalyze or activate particular reactions e.g., crosslinking. This process typically leads to the storage of additional undesired species e.g., non-reacted molecules and moisture, which may worsen polymer electric property. For this reason, a degassing treatment is usually suggested to remove these components.

The degassing procedure usually implies the application of a medium-high temperature for some days to the material. The process is typically performed under vacuum, where possible, to enhance the extraction of external species. In this article, the degassing procedure consisted of placing

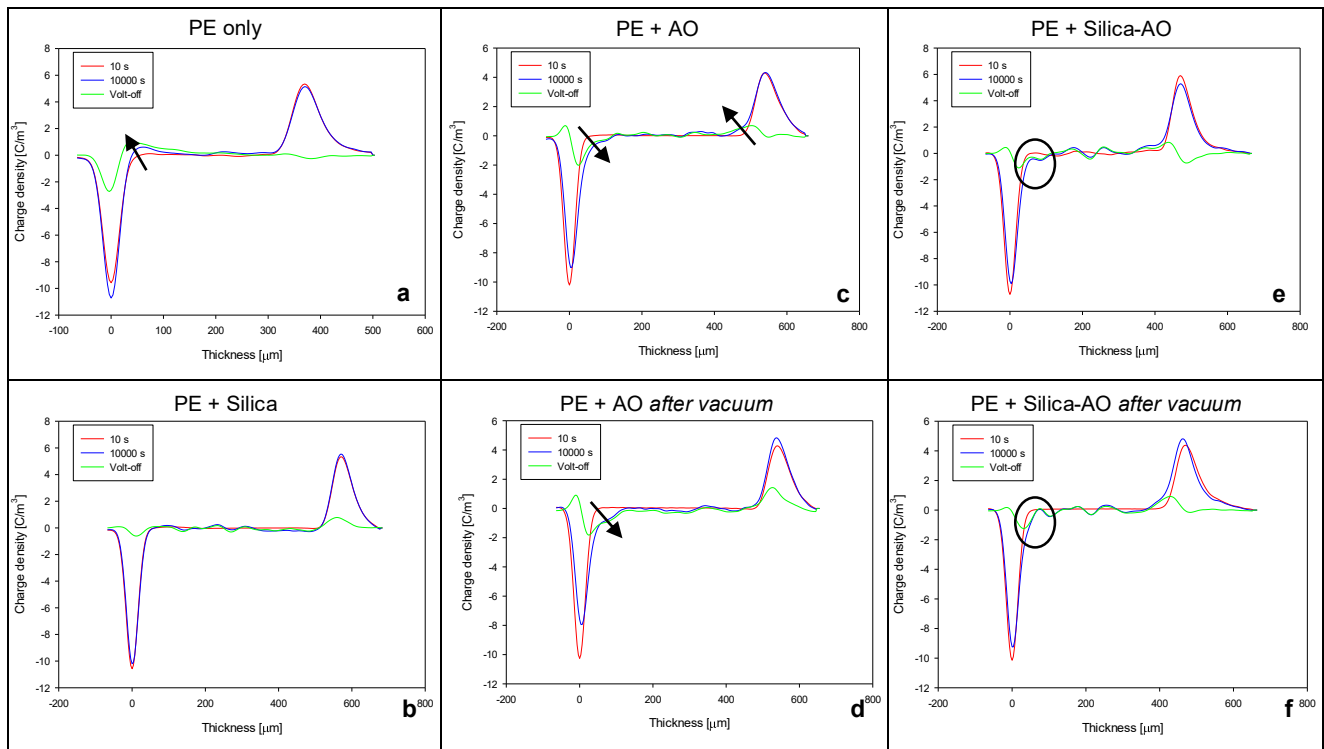


Figure 4. Charge density profile for the different materials considered.

the materials inside a vacuum oven at 80 °C for 48 hours, applied only to the filled materials. Space charge measurements have been performed before and after the treatment on filled samples in order to evaluate any modification of the charge accumulation and displacement by the degassing process.

RESULTS

Space charge (SC) profiles

In this section, space charge profiles for the investigated materials are reported and discussed.

It has been chosen to report the charge density profiles immediately after *volt on* (10 s), at the end of poling phase (10 000s) and at *volt off*. The first two density profiles allow the definition of the stored space charge in the polymer bulk during the application of the DC electric field, while the *volt off* profile permits the evaluation of the trapped charge inside the polymer.

The obtained space charge profiles are reported in

Figure 4. During the *volt on* the pure PE material showed to accumulate, close to the cathode, a significant amount of heterocharge, which increases with time. Finally, the charge is kept also in *volt off* phase, suggesting that a considerable quantity of charge is kept into deep traps.

The introduction of silica nanoparticles appears to be beneficial for the polymer matrix (

Figure 4.b). In this case basically no charge accumulation is registered on the profile. Very little fluctuations in the bulk of the material can be related to the resolution of the instrumentation.

Considering the PE+AO material, one can notice the presence of homocharges next to both electrodes and, again, little fluctuations in the bulk. After vacuum, the positive charge from the anode disappeared, while the negative charge from the cathode considerably increased, as if a bigger concentration of trap sites were placed next to the negative electrode.

Different reasoning has to be done for the PE+AO-Silica. In this case, bigger fluctuations are registered in the bulk of the material. Charges close to the electrodes are very little as in the case of PE + Silica material. However, the degassing process showed to improve the space charge

behavior, resulting into a more stable profile, and further reduced space charge accumulation.

Total absolute space charge density

Figure 5 reports the values of the total absolute space charge density for the different considered materials. The plain polyethylene exhibits the highest space charge density ($\sim 0.35 \text{ C/m}^3$), due to the accumulation of heterocharge, as it will be discussed in the following section.

The introduction of Silica nanoparticles brings significant reduction to this property, down to $\sim 0.15 \text{ C/m}^3$. This suggests a reduced number of stored charges due to the presence of nanofillers, which could facilitate the movement of charges through the polymer bulk.

Similarly, the presence of antioxidant molecules also brings

a reduction in total absolute space charge density with respect to plain PE (~0.3 C/m³). This again could be assigned to the easier movement of the charges inside the polymer. Basically, the same result is obtained in the case of grafted antioxidant (PE+Silica-AO), suggesting that the charge accumulation could be ruled by the antioxidant in the amorphous phase and grafted on the silica surface) depict almost equal values of the property ~0.25 C/m³. This is possibly assigned to the removal of trap sites e.g., volatile species and water (implied into the manufacturing phase). It is worth noting that the obtained value is still higher than the one referred to the PE+Silica material, but it is sufficiently low to guarantee a reduced SC accumulation as requested for HV applications whilst ensuring the required protection against oxidation.

molecule properties rather than the nanofiller ones. However, it is worth noting that, despite a higher concentration of external species, the concentration of SC is unchanged.

Once degassed, AO-filled samples reduce their SC density value. In particular, materials containing antioxidants (both in the amorphous phase and grafted on the silica surface) depict almost equal values of the property ~0.25 C/m³. This is possibly assigned to the removal of trap sites e.g., volatile species and water (implied into the manufacturing phase). It is worth noting that the obtained value is still higher than the one referred to the PE+Silica material, but it is sufficiently low to guarantee a reduced SC accumulation as requested for HV applications whilst ensuring the required protection against oxidation.

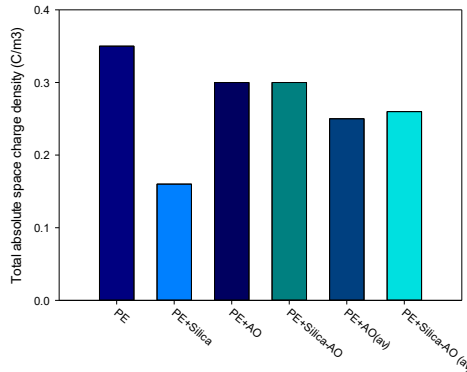


Figure 5. Total absolute space charge density values for the different analyzed materials. (av stands for after vacuum).

DISCUSSION

The addition of antioxidant molecules into the insulating materials is a mandatory step to ensure a sufficiently long service time of extruded power cables and other electrical equipment. Pure polymers do not provide adequate protection against environmental stresses, which could cause unexpected and extremely fast system failure. Nonetheless, additives, such as antioxidants, are known to act as trap sites, increasing the accumulation of space charge in the polymer bulk. Luckily, these species are highly efficient, if a very small concentration is added to the insulation material, it limits space charge growth. It is common procedure to add these additives at the end of the manufacturing process for the stabilization of the produced insulating material. Chemical analyses, presented in various works [8], [15], proved that this method is efficient in terms of protection of the polymer from oxidation. For traditional semicrystalline polymers, antioxidant molecules are placed in the amorphous region, where they are free to move towards the polymer thickness through diffusion phenomena and stop on the polymer surface (where oxidation occurs). This free movement can cause the creation of little interfaces which can modify the polymer space charge profile [2], [5], as seen in

Figure 4.c, d, where charges accumulate next to the electrodes. This phenomenon is intensified during aging, when the reaction of the superficial antioxidant molecules with oxygen hinders the permeation of the oxygen in the polymer bulk. This could result into a non-homogenous degradation of the insulating material, usually reported as diffusion limited oxidation (DLO), bringing to the creation of additional localized interfaces, as already reported in literature [3]. Major part of phenol antioxidants, as the one considered in this paper, melts between 40 and 70°C.

Hence the most common degassing treatments, usually done by the manufacturers to remove e.g., crosslinking by-products, bring to the melting of these species and to an easier diffusion in the polymer bulk. It has been found in [8] that antioxidants can agglomerate in form of crystals on the polymer surface during the vacuum treatment (

Figure 6 [8]), creating additional interfaces on the polymer surface. These interfaces could enhance the space charge accumulation and for this reason they can be associated to the increase of homocharge next to the cathode after vacuum for PE+AO (

Figure 4.d).

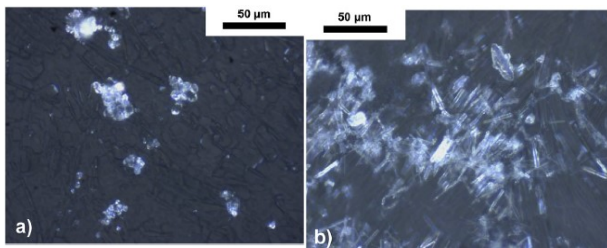


Figure 6. Micrographs of antioxidant crystals on the polymer surface. a) before and b) after vacuum treatment [8].

Also nanoparticles might diffuse through the polymer bulk [16]. Nonetheless, their movement is way more restricted than in the case of free additive molecules due to the presence of numerous bonds and entanglements between the nanoparticles and the polymeric matrix. Up to now, silica nanoparticles are being added inside the polymer due to the widely reported benefits such fillers bring to the insulating materials e.g., higher electric strength and enhanced thermal and mechanical properties [1], [17], [18]. As for space charge properties, nanosilica particles allow the reduction of total absolute space charge density (Figure 5) and the removal of the charge packets close to the cathode from the plain PE (

Figure 4.b), suggesting an easier charge extraction. Despite its good properties, this material does not ensure sufficient long application time due to the lack of antioxidant molecules.

Grafting the antioxidant molecules on the nanosilica surface represents an innovative way to overcome this issue. Once grafted, antioxidant molecules exhibit the same lower diffusion rate as the nanoparticles. This allows, on the one hand, the preventing of formation of antioxidant crystals and on the other hand, it guarantees a homogenous oxidative degradation throughout the polymer thickness, inhibiting possible DLO effects. This occurs because, during aging, oxygen is able to migrate inside the polymer not being hindered by the antioxidant molecules on the surface. Moreover, the performance of the grafted antioxidants in blocking the oxidation process is reported to be good in our previous work [12], showing a quite high oxidation induction time value.

The space charge performance of the proposed material showed to be satisfactory, depicting almost the same total absolute space charge density as PE+AO (Figure 5). Though, its space charge profile is significantly different (

Figure 4.e). The accumulation of charges close to the electrodes is significantly reduced while little fluctuations are observed in the bulk of the material. Hence, as for the PE+Silica material, the presence of fillers appears to facilitate the movement of charges, leading to a limited space charge accumulation.

The degassing process in this material (PE+AO-Silica) resulted to be beneficial, leading to a decrease of the total absolute space charge density while negligible variations are observed in the charge density profiles (

Figure 4). In particular, no additional interface-related charge accumulation is recorded (

Figure 4) close to the electrodes. This is likely assigned to the negligible AO grafted molecule diffusion rate, which prevents the formation of the antioxidant crystals (trap sites) during the degassing process.

CONCLUSIONS

This article explained an innovative way to implement needed additives i.e., antioxidants, inside polymeric insulating materials. Space charge characteristics of the produced materials, along with reference AO-filled ones, were presented and discussed.

PEA measurements reported that antioxidants, as charge trap sites, cause significant space charge accumulation, particularly homocharges close to the electrodes. The introduction of Silica nanoparticles caused the decrease of space charge accumulation in addition to their known enhancement of electrical and thermal properties to the polymeric matrix.

Grafting of the antioxidant molecules on nanoparticle surfaces allowed on the one hand to provide to the polymer matrix protection against oxidation and, on the other hand, to reduce the mobility of AO molecules, without worsening their antioxidant effect. The limited mobility of AOs proved to prevent possible interface-related charge accumulation and diffusion limited oxidation phenomenon.

It was demonstrated that the proposed material exhibits better space charge characteristics than reference material (PE+AO), thanks to the presence of nanoparticles which assisted the charge movement. The degassing treatment

was used to remove any volatile product and it showed to be beneficial for the filled samples, leading to the removal of undesired products and, consequently, to a reduction of space charge density.

Future work on this topic will include the analysis of the material DC performance with aging, in order to evaluate its stability over time.

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