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Adding nanofillers in polymeric insulating materials: so far so good? The case of polypropylene for DC cables

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Abstract— **This paper has the purpose to point at the weaknesses implicit in nanostructuration of insulating polymers for cable insulation, with reference to polypropylene and nanosilica. It also tries to single out which types of properties would be more or less affected by nanofiller introduction, and if in a positive or negative way, depending on nanofiller functionalization process. It is shown, for example, that nanofiller might increase, rather than decrease, space charge and conduction current, as an effect of functionalization, and that a decrease of space charge is not necessarily correlated to an increase of life.**

Keywords — Nanodielectrics, Polymeric cable insulation, HVDC, space charge, DC breakdown strength, conductivity

I. Introduction

A European project, GRIDABLE (Polymer Nanocomposite Insulation Material Enabling Integration of Renewables and DC Storage Technologies in the AC Energy Grid), which was launched under the HORIZON 2020, has (among others) the purpose to investigate nanostructured polypropylene, PP, as insulating materials for DC cables, as well as manufacturing large scale prototypes. Proper dispersion and removal of moisture content from the chosen filler (SiO_2) were properly addressed using different types of functionalization. The purpose of this investigation is to screen several material combinations and focus on those more promising for DC application. While in literature most of papers indicate that dielectric nanostructuration is a tool able to improve insulating material performance almost from any point of view [1-5], other work provides the evidence that dealing with nanoparticle may be an issue, regarding in particular electrical properties [6-11]. Indeed, water molecules or ionic species linked to nanoparticle surfaces (difficult to eliminate even with dedicate treatments) may worsen rather than improving electrical properties [6, 9-11]. In addition, the aspect ratio has to be taken into account. The larger the aspect ratio, the better some properties (e.g. mechanical strength, partial discharge resistance), but water/ionic species are more difficult to be eliminated [9, 11, 12]. This paper presents and discusses results of nanostructuration of PP-based materials for DC cable insulation, referring mainly to electrical property measurements.

II. Experimental procedures and results

Several base polymers were considered, with compounds including PP of various manufacturers and rehological-mechanical characteristics, an elastomer and an HDPE, also from different manufacturers. In this paper we focus on one of them, PP, which is compared with two XLPE compounds for DC applications, XLPE-A and XLPE-B. Based on preliminary space charge measurement tests, performed by PEA (pulsed electroacoustic) technique, [13, 14], it was clear that some treatments were much better than others, in terms of space charge amount and mobility, so that this paper focuses on a few bad and good cases, in relation to the space charge behavior, and 1% nanofiller content.

Silica nanoparticles, with a weight percentage of 1%, subjected to four functionalization treatments, here named T1 to T4, were examined. T1 and T4 were modified by dry processing using a non-polar silane as a modifying agent and trifluoroacetic acid or ammonia as catalyst, while T2 and T3 were modified by a solution method through a polar silane, dried for 48h in a vacuum oven at 80 °C. Table 1 summarizes the various material combinations considered in this paper. Results from tests carried out on the current state-of-the-art materials for HVDC application, namely XLPE, were also considered (using XLPE compounds obtained from two different sources). The tested specimens consisted of press-molded slabs 0.4 mm thick (on average).

Table 2 summarizes the value of space charge amplitude at the beginning of depolarization and equivalent mobility, after a polarization period of 3 hours under a poling field of 50 kV/mm and temperature of 20 °C. Also, conductivity after 24 h polarization at 50 kV/mm and 20 °C, and dielectric strength (ES_0) measured at room temperature (20 °C), are displayed (the latter obtained by ramp-voltage tests in oil, using cylindrical rods with 6.4 mm of diameter with edges rounded to 0.8 mm radius (ASTM D3755) as electrodes. A few accelerated life tests were also performed (at room temperature), to highlight any correlation with space charge, both at 0.8 ES_0. Note that the values of dielectric strength and life test field provided in Tables and figures are obtained under the rough approximation of uniform field between electrodes.

Table 1. Summary of the material characteristics analyzed in the paper. Example of reading: PPT41: base material PP, functionalization treatment 4, percent nanofiller 1.

Material code	Contents		
	Elastomer	Random copolymer	Polyethylene

PP	40%	55%	5%
PPT11	39.6%	54.45%	4.95%
PPT21	39.6%	54.45%	4.95%
PPT31	39.6%	54.45%	4.95%
PPT41	39.6%	54.45%	4.95%

Both space charge and charging-discharging current measurements were performed at different fields and temperatures. This allowed the space charge amplitude vs electric field characteristics to be plotted for the tested materials, according to [14-16], and the temperature coefficient of conductivity to be estimated, α, derived from:

$$\gamma(T) = \gamma_0 \, exp\left(-\frac{\alpha}{T}\right) \tag{1}$$

where γ_0 stands for conductivity at 0 °C and α is the activation energy (temperature coefficient). The charge amplitude from space charge measurements is estimated as [15, 16]:

$$q(E,t) = \frac{1}{L}\int_0^L |q_p(E,x,t)|dx \tag{2}$$

where 0 and L denote the electrodes positions and $q_p(E,x,t)$ is the space charge profile for a given poling field E. Mobility is then calculated by:

$$\mu(t) = \frac{\varepsilon}{q^2(t)} \frac{dq(t)}{dt} \tag{3}$$

where $q(t)$ is the charge density that can be calculated at any depolarization time, $dq(t)/dt$ is the slope of the depolarization curve at time t, ε is the permittivity of the specimens tested. Once the apparent trap-controlled mobility is known, the distribution of trap depth could be estimated. An approximate method to obtain the trap depth distribution, $\Delta U(t)$, is described in [15].

Figure 1 shows an example of polarization/depolarization space charge patterns from unfilled and nanofilled materials, that is PP, PPT21 and PPT31, the second worsening and the third improving the space charge behavior compared to the base material, at 50 kV/mm and 60 °C.

According to the space charge measurement at room temperature (20 ºC), adding nanofiller to the base PP material, even with a 1% content, may result in reduced space charge accumulation. As an example, PPT21 in Fig. 2 has a reduced space charge accumulation of 0.26 C/m^3, from from 2.9 C/m^3 of the neat material). Increasing the temperature, e.g. at 60 ºC, the opposite may also occur. In this condition, space charge accumulation of material PPT21 increases from 0.46 C/m^3 (neat PP) to 1.31 C/m^3.
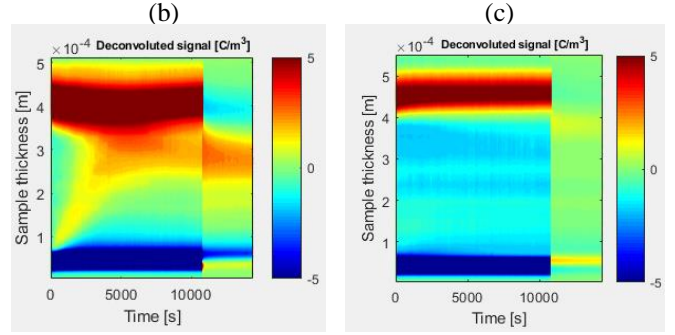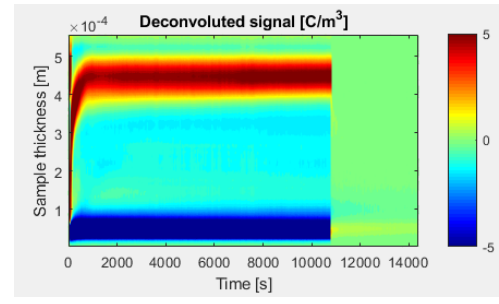

(a)

(b)

(c)

Fig. 1. Example of space charge patterns at 60 ºC (a) base material, PP; (b) PPT21, worsening the space charge behavior; (c) PPT31, improving the space charge behavior.
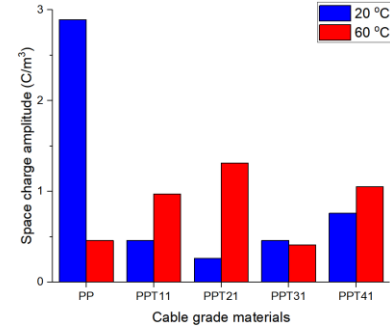

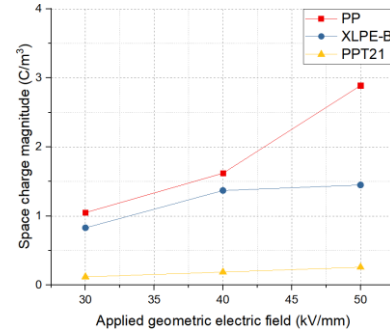Fig. 2. Effect of nanofiller on space charge behavior at 20 and 60 °C.

Fig. 3. Example of space charge magnitude vs applied (geometric) electric field characteristic at 20 °C, nanofilled material vs XLPE and PP material.

As a general consideration, based on Table 2 and Figs. 1-3, it can be noted that nanostructuration may improve or worsen electrical properties with respect to the base material, depending on various factors, from type of functionalization treatment to temperature. While some properties can be improved for DC application, e.g. decreasing space charge content and conductivity, others can be worsened, e.g. the temperature coefficient α and life.

Table 2. Values of space charge amplitude (3 s after the beginning of depolarization, eq. (2)), equivalent mobility (eq. (3)), after polarization at 50 kV/mm and temperature 20 °C, conductivity after 24 h polarization at 50 kV/mm and 20 °C, dielectric strength ES_0 at room temperature (20 °C), life test at 80% ES_0 and temperature coefficient α (eq. (1)). Space charge and conductivity are mean values, while dielectric strength and life tests data are relevant to 63.2% cumulative probability for a two-parameter Weibull distribution.

Material code	Electrical properties					
	Space charge amplitude (C/m³)	Equivalent mobility (m² V⁻¹ s⁻¹)	Conductivity (S/m)	Dielectric strength (kV/mm)	Life test – Time (minutes)	α (°C⁻¹)
XLPE-A	1.24	1E-13	6.36E-16	433	0.1	0.06
XLPE-B	1.45	1.75E-13	7.78E-15	418.9	5.8	0.07
PP	2.89	2E-14	1.64E-15	394	250.1	0.06
PPT11	0.46	3E-13	1.29E-16	497.1	7	0.1
PPT21	0.26	1E-13	4.81E-17	488.1	17.3	0.07
PPT31	0.46	5E-13	1.45E-15	475.1	1.5	0.13
PPT41	0.76	4E-13	2.93E-17	419.9	0.04	0.06

Correlation between space charge and dielectric strength or conductivity was investigated. Fig. 4 shows those two correlation plots. In the case of space charge and dielectric strength, the correlation and determination coefficients are acceptable (i.e. $r = -0.84$, $R^2 = 0.7$), but for conductivity those are reduced to only $r = -0.39$, $R^2 = 0.15$, mostly due to the presence of an outlier (XPE-B). Censoring it results in marginally better correlation ($r = -0.42$, $R^2 = 0.17$).
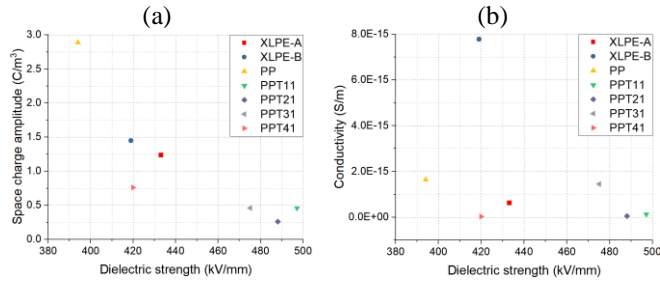

Fig. 4. (a): Correlation plot space charge amplitude vs dielectric strength, E_{S0}, for materials of Table 2 at 20 °C ($r = 0.84$). (b): conductivity vs dielectric strength, E_{S0}, for materials of Table 2 at 20 °C ($r = 0.42$).

Further, correlation between dielectric life and space charge or conductivity was also studied. Fig. 5 shows two correlation plots of life with space charge and conductivity. Generally speaking, correlation for this case is rather poor. This can be associated with the fact that life tests are conducted under different fields, corresponding to 0.8 times the breakdown field of each material (which in turn is characterized by a different dielectric strength). Life and space charge accumulation produce a correlation with $r = -0.47$, $R^2 = 0.23$, while life and conductivity are characterized by $r = -0.44$, $R^2 = 0.2$. Hence, those coefficients do not suggest that the action of nanostructuration can reflect into longer life, and, indeed, results showed worsening of life in some cases.

In order to better understand the obtained results, SEM imaging was also carried out for the tested materials, to highlight any morphological structure causing such apparently uncorrelated results. Fig. 6 contributes to explain how different functionalization affect the final structure of the polymer, eventually modifying its electrical (and possibly mechanical) properties. It is reasonably possible that inhomogeneous structures such as those shown in Fig. 6b, e contributes to decrease the life of a material, introducing undesired regions where both mechanical and electrical stress might be enhanced. For the same reason, but on a minor scale, materials such as T2,

T3 pictured in Fig. 6c, d do not perform as well as the neat material. The issue of agglomeration of nanoparticles (possibly represented by some of the white parts of Fig. 6, among elastomeric domains) is not fully resolved, and this is preventing the material from performing to its full potential.
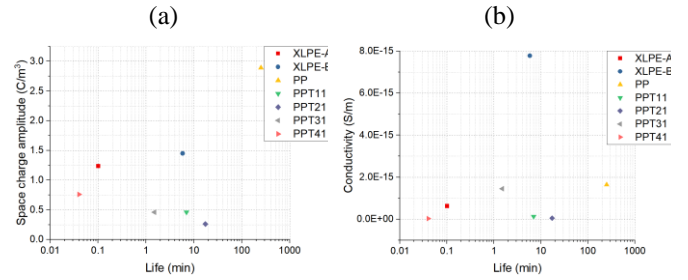

Fig. 5. (a): Correlation plot space charge amplitude vs life, for materials of Table 2 at 20 °C. (b): conductivity vs life, for materials of Table 2 at 20 °C.
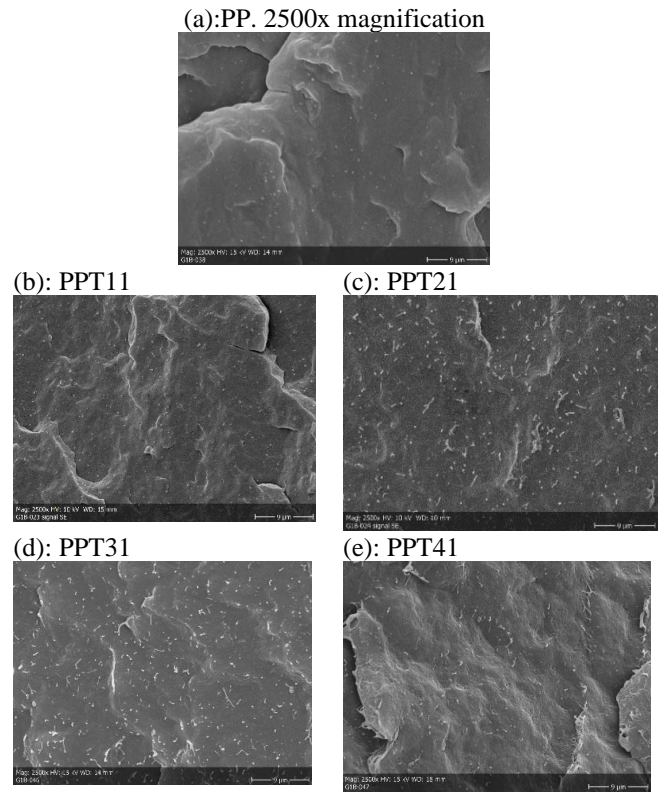

Fig. 6. Different functionalization effect on the final structure of the polymer.

III. DISCUSSION

There is evidence from the experimental results that the choice of base materials and functionalization process can influence significantly electrical properties, such as space charge, conductivity and its temperature coefficient, dielectric strength and life. Functionalization can play a role regarding electrical properties which are very sensitive to trap density and depth, as well as ionic species (as space charge and conductivity), but it may be less influential, or influential in a negative way, on short and long-term breakdown. It can be recalled, in addition, that electrical properties can be drastically influenced by nanoparticle aspect ratio, as also electric tree and

corona resistance [5, 7, 8, 12]. The effect on α can be negative, in the sense that increasing α cable feasibility (at high voltage and current) is worsened [17], while that on conductivity can be positive or negative, because it has been shown that, depending on the functionalization treatment and the type of compound, conductivity can vary of orders of magnitude (see Table 2). Nanofilled materials considered above tend to display the same or lower values of conductivity than the base material, which reflects positively on Partial Discharge Inception Voltage, PDIV, but larger values of α, which is negative for cable design and feasibility. Indeed, as seen for other properties, functionalization in particular can dramatically affect results, introducing very subtle differences with the treatment T3, and useful improvements for the others, with particular advantages for the treatment T4.

As said, nanostructuration can modify electrical properties certainly, but not always in the desired way, since the simple act of adding fillers to a matrix can and will induce a modification of chemical, physical and morphological properties. The final performance of a material will be then given by the combined effect of fillers to introduce new trapping sites in the insulation, reducing the overall charge storage, while on the other hand leaving the polymerization undisturbed, and the final structure as well dispersed and homogenous as in the base material.

IV. CONCLUSIONS

As shown, adding SiO_2 nanoparticles in a base polymer (PP compounds in this paper) may be effective to improve, but also to worsen, the electrical properties of the base polymer, depending on functionalization and other parameters, as temperature. For example, adding nanoparticles to PP decreases space charge amplitude at 20°C, but it tends to increase space charge at higher temperature, while varying significanty conduction current. Additionally, although nano-filled materials may provide better dielectric strength compared to the base polymer, this may not reflect into better voltage endurance (life). This will hold also for mechanical properties, as it will be shown in a next paper. Such results can be due to profound chemical, physical and morphological changes to the microscopic structure of the polymer, induced by the fillers. For example, the burden of agglomeration and of functionalization by-products is a well-known issue of nanostructured materials, but further work is currently in progress in order to improve this aspect and eventually fully exploit the high potential of those polymers. Hence, the main message of this paper would be to be cautious thinking of nanostructuration as THE solution to improve overall electrical properties of polymeric insulating materials.

V. ACKNOWLEDGMENT

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