Effects of Graphene Coatings on hindering Space Charge injection in Epoxy Resin

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Abstract- **The reliability of epoxy resins (and dielectrics in general) employed for HVDC applications is significantly affected by space charge accumulation in the insulating material. Several methods have been tested to limit the injection and accumulation of space charge. In this work, planar specimens featuring graphene coatings were tested. Measurements of space charge accumulation, conductivity and permittivity at different temperatures (from 30°C to 60°C) and fields (from 30 kV/mm to 50 kV/mm) were carried out on epoxy specimens with and without coatings. Results show accumulation of space charge for low fields and temperatures in the reference specimens, while a reduction can be noticed with a layer of graphene coating. On the other hand, at higher fields or temperatures, the effect is reversed.**

Keywords—Space Charge, Graphene, Epoxy

I. INTRODUCTION

The accumulation of space charge in electrical insulation has been recognized to be a major aging factor in DC insulation[1-3]. Small amount of accumulated space charge can distort the Laplacian electric field, and this will in turn influence the degradation rate and life expectancy of the insulating material. Due to the power law, which describes the aging rate under electrical stress, even a moderate increase of electrical field inside the insulation can significantly accelerate the local degradation mechanism driven by electrical stress. Indeed, the relationship between aging rate K, the electrical stress, E, and the so-called voltage endurance coefficient, n, can be described by the inverse power life model (IPM), defined by (1) [4]:

$$K(E) = K_D \left(\frac{E}{E_D}\right)^n \qquad (1)$$

where E_D is design field and K_D the corresponding aging rate constant. If, e.g., the electric field inside insulation locally becomes 20% higher than E_D, and considering a life of 30 years at failure probability 1% for a design field of 40 kV/mm, and $n = 15$, the increase of electric field will bring to life reduction of 90%, that is from 30 to 3 years.

Hence, accumulation of space charge can be the main accelerated degradation process in DC insulation. If, in addition, voltage polarity inversions phenomena are present (as it may happen in transmission assets), the accumulation of heterocharge (that is, charge having the opposite sign as that of the near electrode) can bring to further abnormal field distribution, causing significant field enhancement at the interface insulation-electrode, which can affect apparatus reliability and life [5].

Any material which has to be used as DC insulation has to be characterized to be space charge free at the operating field and temperature. Innovative techniques such as nanostructuration or coating of interfaces can help increasing field and/or temperature above which space charge accumulation becomes large enough to affect field profile and/or accelerate local degradation mechanisms [6] following different approaches.

Since space charge accumulation is fundamentally the result of a localized unbalance between charge injection and extraction rates occurring above a certain threshold field, this work is an attempt at entirely preventing charge injection in the first place, through the very same field distortion that charge accumulation is introducing.

The threshold field of space charge accumulation identified by a bend from the linear ohmic relationship between the stored charge density and field (Fig. 1), usually experimentally derived from the space charge profile measurements.

The consequence of the application of a field higher than such threshold, and the following injection of -for example- homocharge (that is, charge having the same sign as that of the
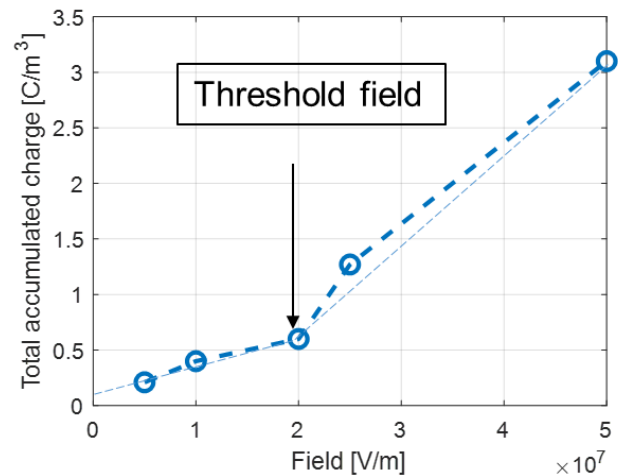

Fig. 1. Example of accumulated space charge for the same material under different applied fields. A threshold field is highlighted around 20 kV/mm from the change in slope of trending lines.
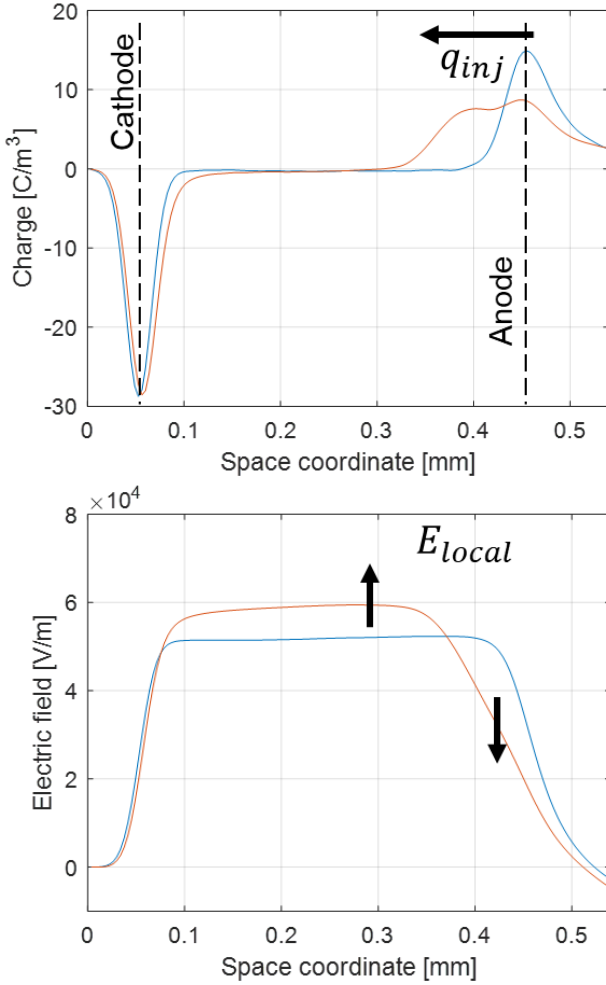
Fig. 2. Charge (top) and field (bottom) distribution in case of no charge injection (blue line) or mild homocharge injection near the anode (red line).

Sample code	Top side coating	Bottom side coating
D.E.R 332	NO	NO
D.E.R 332 + 1C	YES	NO
D.E.R 332 + 2C	YES	YES

Layers of graphene were deposited on an epoxy resin, and its effect was investigated by means of space charge accumulation, conductivity and permittivity measurements at different temperatures (from 30°C to 60°C) and fields (from 30 kV/mm to 50 kV/mm), before and after introducing coatings.

II. MATERIALS AND METHODS

For this paper, flat specimens of D.E.R. 332 (Sigma-Aldrich) were produced, using Poly(propylene-glycol)-bis(2-aminopropyl ether as hardener, and coatings on either one or both of the planar faces of samples were obtained by means of spray deposition of graphene nanoplates by Nanesa Srl. A list of samples used in this work is given in Table I.

Space charge measurements are carried out with Pulsed Electro-Acoustic (PEA) method. The space charge measurements are conducted on thermally pre-treated samples (72 hours at 60° C in vacuum). Tests were performed at 30°C, 60°C and 90°C, in a controlled environment, with fields ranging from 20 to 40 kV/mm, in order to explore both the low and high field characteristics of space charge accumulation.

Conductivity was determined by averaging the current measured at steady state conditions, after 24-72 hours of voltage application. Gold electrodes and a guard ring were sputtered on the samples, and they were stored short-circuited for several hours at 60 °C to remove charge possibly injected during sputtering.

Measurements were performed by a dielectric analyzer (Alpha-A, Novocontrol Technologies) by employing AC voltage of 3 kVrms, at temperatures ranging from -20°C to 60°C, with a sputtered sample diameter of 20 mm. Tests have been performed under 4 different temperatures in order to investigate temperature modification over electrical relaxation.

III. RESULTS AND DISCUSSION

Results show accumulation of space charge (Fig. 3) for lower fields and temperatures in the reference specimens, while a reduction of the accumulated charge can be noticed when a layer of graphene is coating the interface between the dielectric and one or both of the electrodes, respectively named wit suffix "+1C" or "+2C".

This is proof that the concept discussed above is a valid one, as also shown by charge patterns in Fig. 4. On the other hand, at higher temperatures, the effect is reversed.

Graphene layers seem to introduce substantial heterocharge accumulation, likely due to ionic species present in the bulk which migrate fast towards opposite electrodes, thanks to their larger mobility at high temperatures. This heterocharge cannot be neutralized at the electrode due to the presence of graphene

near electrode) near the anode is shown in Fig. 2. As can be seen, when the penetration of charge is reduced, the resulting field distribution is strongly reduced near the injecting electrode, while mildly increased it in other locations.

It is possible that the resulting field near the injecting electrode becomes lower than the threshold field, preventing further charge injection.

Those accumulated homocharges are however usually able to migrate in the bulk of the material, so that their effect of local field reduction is mitigated (Fig. 2), eventually allowing further charge injection. It is worth noting that charge migration can become significant if trap depth in the insulation bulk is low.

This work investigates the possibility of introducing a layer between electrodes and the dielectric able to accumulate charges in deep traps, so that once those are injected, they will be characterized by very little mobility, rendering the described field reduction almost permanent.

The chosen material is graphene, which can be deposited with thin coatings, and is characterized by deep trap distributions.
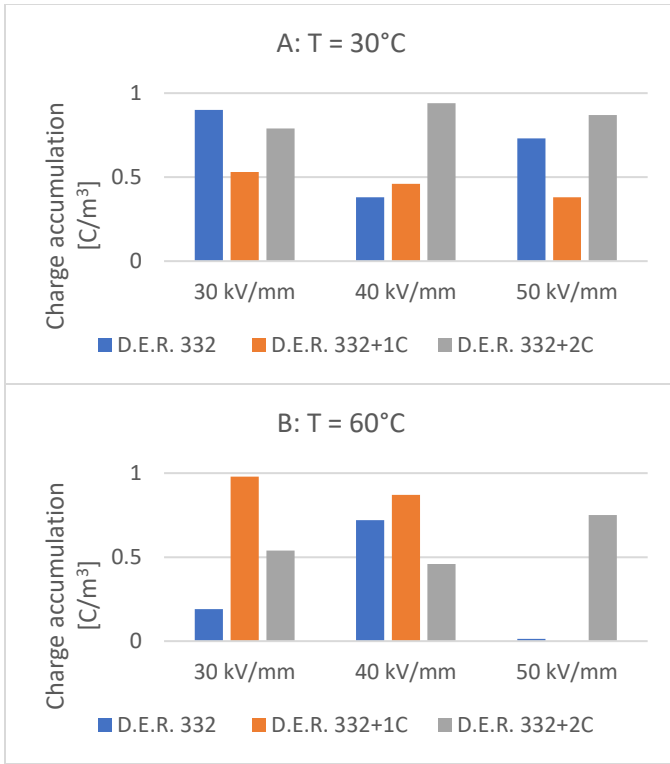
A: T = 30°C

B: T = 60°C

Fig. 3. Charge accumulated in different specimens stressed with different fields and under different temperatures.
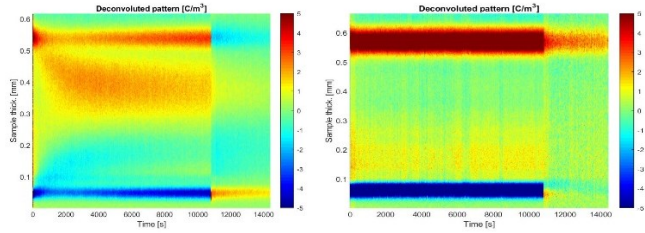

Fig. 4. Space charge profiles for specimens tested at 30°C with 30 kV/mm, when no coating is present (left) and when the side facing the anode is coated with graphene (right).
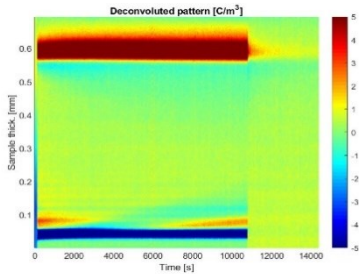

Fig. 5. Space charge profiles for specimens tested at 60°C with 30 kV/mm, when both sides of the specimen are coated with graphene.

coating which inhibits opposite charge injection. Coating of both interfaces results in the worsening of such effect (Fig. 5).

Conductivity measurements (Table II) show a strong decrease of conduction current upon the introduction of graphene coatings, both for the tests at 30°C and 60°C. It must be also noticed from tests at higher temperature that the neat

Conditions	Conductivity [S/m]	
	D.E.R. 332	D.E.R. 332 + 1C
30kV/mm, 30°C	$1.3 \cdot 10^{-13}$	$1 \cdot 10^{-14}$
30kV/mm, 60°C	$1 \cdot 10^{-11}$	$2.5 \cdot 10^{-14}$

resin is characterized by a much higher temperature coefficient of conductivity.

Fig. 6 reports the trend of complex permittivity as a function of frequency for the neat and the coated epoxy at four different temperatures. In both the analysed conditions the temperature increase causes the raise of the real part of permittivity, as expected. On the contrary, the dielectric losses decrease at high frequencies while they invert their trend at lower frequencies, suggesting an enhanced low-frequency dielectric response (e.g. interfacial polarization and conduction) [7]. In particular, at high frequencies, it is possible to define a peak, related to β relaxation, which shifts towards higher frequencies as we increase the testing temperature, as expected.

Focusing on the real part of permittivity, the presence of graphene coating leads to the increase of the considered electric property. Moreover, the graphene layer causes the increase of the dielectric losses, particularly at high frequencies (~104 Hz). This frequency region, which is linked to the dipolar polarization, relates the peak to the graphene itself, due to its dipolar properties. It has been reported in previous works [8] that graphene nanoparticles can give raise to a new peak at frequencies >106 Hz, which has been related to the induced dipoles created by the nanofiller. In the present work, the analyzed frequency region is limited to 104 Hz, allowing the analysis of the increasing branch of the peak only. The presence of graphene-related peak causes the overwhelming of the ~103 Hz peak already discussed for the base epoxy, due to the lower magnitude of this latter peak.

At 60 °C, it is possible to notice an abrupt increase of ε' which can reach up to 25. This trend has been related to electrode polarization (EP) phenomenon. Briefly reporting, EP arises when the ionic species reach the metallic electrodes and accumulate in thin layers next to the sample surface forming a so-called space-charge region [9, 10]. The presence of these ions may be mainly related to the manufacturing process the specimens have been subjected to before testing. It is known that, during the epoxy curing phase, some unreacted monomers and hardener can give rise to ionic species in the final polymeric compound. These latter may lead the electrical response once they are subjected to an external AC field [11], as it can be noticed from Fig. 6. It is worth recalling at this point that the considered epoxy owns a Tg~75 °C, whose onset is ~ 60°C. It is known that polymers, operating at temperatures close to Tg, depict an enhanced chain mobility, leading to an easier movement of ions and radicals throughout the insulation causing higher conductivity (as seen in Table I) and permittivity values (Fig. 6). It is evident that, the kinetics of these radicals is catalyzed by temperature, and it can bring to the so-called Quasi-DC conduction [12, 13]. In both the conditions considered, the presence of Q-DC conduction at high temperatures is confirmed by the trends of ε'', which exhibit a slope ~ -1. In particular, the
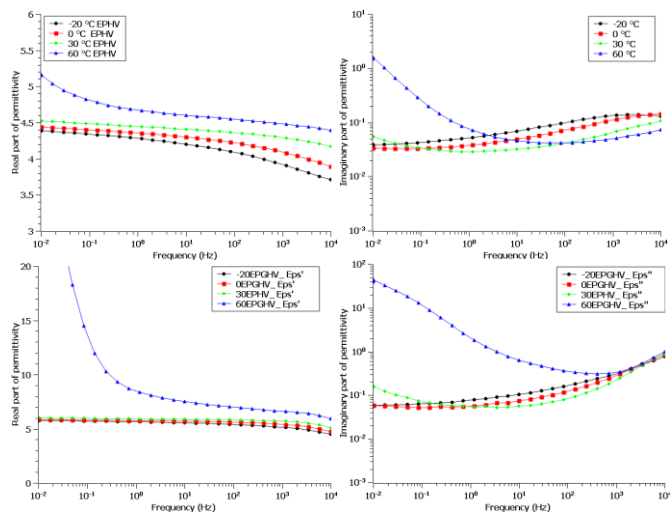
Fig. 6. Trend of real (left column) and imaginary (right column) parts of permittivity, as a function of frequency for a neat (top row) and coated (bottom row) specimen, at four different temperatures.

introduction of graphene coating and related species can enhance the Q-DC conduction, leading to very high dielectric losses (ε'' > 30) in addition to the abovementioned EP.

V. CONCLUSIONS

This paper indicates that the introduction of a thin layer capable of trapping homocharge and consequently prevent further charge injection, hence its accumulation in the bulk of the material, is feasible on dielectrics.

However, issues arise from the usage of graphene on the tested epoxy resin at high temperatures, due to the buildup of heterocharge, arising from the increased mobility of ionic species inside the resin, at those temperatures. The presence of a blocking layer is preventing their extraction, and heterocharge formation is observed.

In conclusion, it is very likely that in the presence of a different dielectric, the same coating material and technique can be confirmed to be a valid one, also for higher temperatures and fields.

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