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1 **Graphite Nanoplatelets Filled Silicone Composites with Novel Electrical and Dielectric**  
2 **Properties**

3  
4 *Renaud Metz<sup>1,2</sup>, Christophe Blanc<sup>1</sup>, Guillaume Prévost<sup>1</sup>, Mehrdad Hassanzadeh<sup>3</sup>*

5  
6 *<sup>1</sup>Laboratoire Charles Coulomb UMR 5221 CNRS-Université de Montpellier, Place Eugène*  
7 *Bataillon, Bâtiment 11, Montpellier, France*

8  
9 *<sup>2</sup>Université Claude Bernard - Lyon 1, Villeurbanne, France*

10  
11 *<sup>3</sup>Schneider Electric, 37 Quai Merlin, 38000 Grenoble, France*

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16  
17 Address correspondence to E-mail: Renaud.metz@gmail.com

18  
19 **Abstract**

20 In the design of medium and low voltage equipment such as cable accessories, generator, motor  
21 end windings or bushings, issues with electrical field enhancement occur at interfaces between  
22 insulators and conductors, resulting in accelerated material ageing. The purpose of this paper is  
23 to present a novel dielectric composite material which has the properties to mitigate this local  
24 amplification. It is a functional dielectric which resistivity decreases by several orders with  
25 electric field from  $10^{14}$  to  $10^9 \Omega\text{m}$  up to  $1 \text{ kVmm}^{-1}$  while the dielectric constant decreases from  
26 15 to 12 in the  $10^{-2} - 10^6 \text{ Hz}$  range. This novel material is made with graphite nanoplatelets.  
27 It may be used as a resistive or capacitive field grading material in electrical applications.

28  
29 **1 Introduction**

30 The increasing energy demand with the concomitant decrease of the size of the electric devices  
31 and the penetration of renewable energy sources such as wind farms and solar power systems  
32 in the distribution network, imply additional electric stress on voltage insulating materials [1–  
33 10]. Providing an efficient and safe insulation is therefore a challenge. As a matter of fact,  
34 intense electric fields can generate localized partial discharges, resulting in accelerated aging

1 or even dielectric breakdown. Electrical system design is therefore optimized to prevent or limit  
2 any intensification of the electric field at “triple points” or “triple junctions” (where three  
3 materials with different permittivity meet) [1-2]. A classical way to highlight the triple points  
4 problem consists to consider the essential components of a cable: a conductor, an insulator and  
5 a ground shield. At cable termination where the shield has been removed, the electric field  
6 concentrated in the insulation is spread out (**Fig. 1. A**). A concentration of voltage equipotential  
7 lines is observed at the triple point where the interfaces between the shield, the insulator and  
8 the air meet. In **Fig. 1. B**, the triple point has been coated with a material that has a high enough  
9 dielectric constant to redistribute AC fields, i.e. make the voltage equipotential lines scatter.  
10 The optimized length and thickness of the coating depend on the specific design as such as the  
11 geometry and the detailed dielectric properties of the layers. Such a solution does grade the  
12 distribution of the potential as depicted in Fig.1.B. There also exist capacitive field grading  
13 materials that have nonlinear dielectric constant that increases with the field. These solutions  
14 do not work in DC. In order to get a coating which works under DC as well as AC and imSurge  
15 conditions, it is advantageous to use a material that possesses a nonlinear resistivity which  
16 decreases with the field. In **Fig. 2**, an overview of the different methods that are used or  
17 proposed to control the field in practice is depicted. At first and for most electrical or electronic  
18 equipment, geometric field grading (**Fig. 2.1.**) is used. It means that the design of the equipment  
19 is optimized in order to decrease the local field enhancement. The metal parts are usually bent  
20 and/or the thickness of the insulator is locally increased. This is the first choice of treatment.  
21 To decrease further the field, processing of field grading materials is carried out (**Fig.2.2.**).  
22 Those composites are made by adding to polymers inorganic filler with a specific permittivity  
23 (**Fig.2.3.**) or resistivity (**Fig.2.4.**). There is also an approach in which the insulating body is  
24 made up of a staggered arrangement of one or several concentric cylindrical layers of insulating  
25 material and layers of conducting materials. The conducting layers are insulated, with floating  
26 potential (**Fig.2 5**). For each method, the preferential AC/DC or overvoltage conditions of  
27 operation are reported. It appears that only the linear resistive field grading solution works  
28 under DC conditions but not against overvoltage (surge) that are likely to occur in the mains  
29 supply. For this, nonlinear field grading materials are necessary (**Fig.2 6**). Contrary to nonlinear  
30 capacitive field grading materials (**Fig.2 7**). The unique solution which might be used under  
31 AC, DC and surge conditions is nonlinear resistive field grading (**Fig.2. 8**). This work aims at  
32 presenting the interest of such a new nonlinear resistive field grading composite material made  
33 of graphite nanoplatelets randomly dispersed in a polymer and at evaluating its performances  
34 for medium voltage applications.

1  
2 Fillers known to transfer their non-linear electric properties to the matrix of a composite mainly  
3 consist of ZnO microvaristors and/or other metallic oxides, [12-20] doped silicon carbide [21-  
4 26] or carbonaceous particles [27-32]. Among carbon fillers, nano-sheets have driven attention  
5 because nonlinear composites may be obtained at a low filling ratio ( $< 5$  vol.%). A pioneering  
6 work was based on the study of nanocomposites made of monolayers of graphene oxide (GO)  
7 previously slightly thermally reduced [33-34]. The switching field  $E_s$ , above which there is a  
8 departure from Ohmic behavior ( $\rho \propto E^{-\alpha}$ ,  $\alpha > 1$ , for  $E > E_s$ ) was modulated not only by the  
9 nanosheet volume fraction used but also by the GO reduction rate [35,37]. The non-linear  
10 effects were then attributed to the numerous surface oxide groups of the nanosheets at the origin  
11 of barrier voltages.

12 Recently, Gaska *et al.* prepared nanocomposites from graphite nanoplatelets (GnP) dispersed  
13 and oriented by extrusion in low-density polyethylene [36,37]. A nonlinear behavior was  
14 observed at very high fields  $\sim 20\text{MVm}^{-1}$  ( $20\text{kVmm}^{-1}$ ). This result was not expected since these  
15 fillers do not exhibit surface oxide groups comparable to the ones which decorate the surface  
16 of GO, neither in quality nor in density. Recently we retrieved this result with graphite  
17 nanoplatelets dispersed in a silicone matrix [38].

18 In this paper, after briefly recalling the electrical behavior of these new composites, we report  
19 a detailed characterization of their properties. In particular, we show that they reveal a fair  
20 dielectric constant increase at small filler loadings concomitant to a decrease of the resistivity  
21 with the electric field. We report the detailed electrical characteristics of the composites and  
22 consider their use for resistive and capacitive field grading. We then discuss the possible origins  
23 of the global non-linear electrical behavior.

24

## 25 **2 Materials and method**

26 *Raw materials:* The silicone matrix used in this study is the Bluestar RTV141 resin. It is a room  
27 temperature vulcanizing silicone, reticulated by poly-addition. The graphite nanoplatelets  
28 (GnP) fillers were purchased from XG Sciences in powder form. The grade M25 was carried

1 out in this work. According to the supplier, the mean diameter of these platelets as primary  
2 particles is around 25 $\mu$ m and their mean thickness around 6nm, corresponding to about 20  
3 layers of graphene monolayers stacked on top of each other's. Our analysis by optical  
4 microscopy and secondary electron microscopy show that the nanoplatelets are not isolated  
5 from one another. They tend to gather together into disordered clusters made of entangled  
6 platelets, some dimensions of which are significantly larger than several microns. Furthermore,  
7 primary nanoplatelets form strongly bonded aggregates. Large shear forces are required to  
8 break the latter and to obtain individual nanoplatelets. Such shear forces were not carried out  
9 during the processing of our composites despite the use of a speed mixer, *i.e.* a bladeless mixer  
10 which combines dual asymmetric centrifugal mixing technology. Large micronic aggregates up  
11 to 100  $\mu$ m are still observed in the final materials.

12 *Composite Fabrication:* To prepare the composites, a master batch filled with 5 wt.% of GnP  
13 was first prepared by inserting the fillers progressively in the silicone resin and manually mixing  
14 for homogenizing. The GnP fillers were then dispersed in the matrix by dual asymmetric  
15 centrifugal mixing using a Flacteck Speedmixer from Hauschild. The composites were prepared  
16 by inserting this master batch into the right amount of neat resin, and by mixing it with the help  
17 of the speed mixer. The dispersion was performed under primary vacuum ( $\sim$  400 Pa) to  
18 simultaneously degas the composite. The hardener was then added to the mixture and dispersed  
19 by the same technique. The final blend was poured in a steel open mold of 1 mm thick  
20 previously heated at  $T = 150^{\circ}\text{C}$ . To ensure a full polymerization, the samples are heated during  
21 1 hour at  $150^{\circ}\text{C}$  under 150 bars and 2 hours at  $90^{\circ}\text{C}$  during 30 minutes under 150 bars.  
22 Specimens of 110mm x 77mm x 1mm dimensions were prepared for electrical characterization  
23 by compression molding at 15MPa and then curing at  $150^{\circ}\text{C}$  during 1hour (**Fig. 3**).

24 *Composite characterization:* The chemical bonding of the composite surfaces was examined  
25 by an Attenuated Total Reflection (ATR) Fourier-transformed infrared (FT-IR) spectroscopy  
26 (Perkin Elmer, USA) in the wavelength range of 400-4000  $\text{cm}^{-1}$ .

1 In the range 0-1kV, the procedure for determining the volume resistivity is based on the current  
2 absorption-resorption method according to ASTM D 257-14 [39]. A guarded cell linked to a  
3 high voltage DC power supply and picoammeter (Keithley electrometer 6517B) is used. A  
4 guard ring configuration was used for the measurements in order to exclusively evaluate volume  
5 conductivity. In this configuration, surface currents are diverted directly to ground and are thus  
6 not measured. Polarization and depolarization of a duration of 1 hour are carried out for the neat  
7 polymer matrix and of 30 minutes for the GnP-based composites (after a first polarization at  
8 1kVmm<sup>-1</sup>). Volume resistivity is calculated with the following relation:  $\rho = \frac{RA}{h}$  where  $\rho$  is the  
9 volume resistivity in  $\Omega\text{m}$ , R the measured volume resistance, in  $\Omega$ , A the effective area of the  
10 guarded electrode, in m<sup>2</sup> and h the average thickness of the specimen. In the case of the  
11 measuring cell, the diameter of the electrode was 54 mm.

12 We have also measured the behavior of the sample at high field in AC (50Hz). A  $\frac{\pi}{2}$  phase shift  
13 between current and voltage was observed, indicating a mainly capacitive behavior at this  
14 frequency. The dielectric permittivity  $\epsilon_r$  (real part) was extracted from the data.

15 The dielectric measurements were performed on a Broadband Dielectric Spectrometer,  
16 Novocontrol alpha analyzer, using an applied ac voltage of 1V, over a frequency range from  
17 10<sup>-2</sup> Hz to 1MHz Gold electrodes on both sides of the samples were previously deposited by  
18 sputtering with a thickness of ~ 20 nm).

19

## 20 **3 Results**

### 21 **3.1 FT-IR Spectroscopy**

22 **Fig. 4** shows the attenuated total reflection Fourier-transformed infrared spectra of the  
23 neat silicone rubber and the 4 wt.% filled silicone after full reticulation at 150°C. The main  
24 peaks are Si-CH<sub>3</sub> at 1260 cm<sup>-1</sup> and 1400 cm<sup>-1</sup>, together with CH<sub>3</sub> peaks near 2900 cm<sup>-1</sup> for side  
25 chains of silicone [40]. Both peaks around 1000-1100 cm<sup>-1</sup> have been attributed to Si-O-Si and  
26 the peaks near 800 cm<sup>-1</sup> to (CH<sub>3</sub>)<sub>2</sub>-Si-O groups. The spectra are very similar and suggest that

1 the silicone rubber was not modified by the presence of the graphite nanoplatelets. This suggests  
2 that the nanoplatelets do not take part to the chemical covalent chains of the silicone network.

### 3 4 **3.2 Resistivity versus DC electric field**

5 **Fig. 5** shows the change of resistivity of the GnP based composite as a function of the  
6 electrical field for an increasing volume fraction of fillers. It is interesting to note that the  
7 resistivity extends over a large range of values ( $10^9$ - $10^{16}$   $\Omega\text{m}$ ). The pristine silicone resin and  
8 low filled composites (1-3 wt. %) are insulators with a resistivity in the  $10^{16}$ -  $10^{14}$   $\Omega\text{m}$  range  
9 and a slight rise of resistivity is observed at high electric fields. Surprisingly, these composite  
10 materials exhibit a higher resistivity than that of the pristine silicone matrix. This is not intuitive  
11 since the graphite nanoplatelets are conductive (through and in-plane resistivities:  $10^{-2}$  and  $10^{-$   
12  $7$   $\Omega\text{m}^{-1}$ , respectively) [36]. Adding such fillers in an insulating matrix should *a priori* lead to an  
13 increase of the conductivity of the composites. However, such a macroscopic behavior has  
14 already been reported [33,42] and attributed to ionic transport disturbed by the nanoplatelets  
15 network [33], trapping of charge carriers in deep traps [41] or thought as an electronic Coulomb  
16 blockade phenomenon [42]. In contrast, the electrical behavior significantly changes for filler  
17 concentrations above 4 wt. % and is typical of that of percolated composites with  $\rho =$   
18  $\rho_f (f - f_c)^t$ , where  $\rho_f$  is the resistivity of the conductive filler,  $f$  and  $f_c$  are the actual and  
19 critical filler volume fraction respectively and  $t$  is the critical exponent of resistivity.

20  
21 **Fig. 6** compares the conductivity of the most loaded sample (5 wt.%) with the data from  
22 References [33-35]. The graphite nanoplatelets composite materials exhibit a switching field  
23  $\sim 3 \times 10^4 \text{Vm}^{-1}$  which is two orders of magnitude lower than slightly thermally reduced  
24 graphene oxide (GO)-based nanocomposites for which  $E_s \sim 10^6 \text{Vm}^{-1}$  ( $1\text{kVmm}^{-1}$ ). The GO was  
25 thermally reduced at  $120^\circ\text{C}$  for 12 h in dry air to obtain nonlinear properties. (As received GO-  
26 Silicone at 3 wt. is reported: such nanocomposite remains insulating even at the highest electric

1 field :  $6.3 \cdot 10^{12} \Omega \cdot m$  at 6 kV/mm [35]). Above this breakdown field, the resistivity behaves  
 2 nonlinearly with a nonlinear coefficient  $\alpha = \log\left(\frac{\rho_1}{\rho_2}\right) / \log\left(\frac{E_1}{E_2}\right) \sim 3$ , lower than  $\alpha \sim 10$  for  
 3 slightly reduced GO-based nanocomposites. **Fig. 6** also reports the conductivity of the GnP-  
 4 based extruded composite studied in the References [36-37]. The extrusion of the loaded low-  
 5 density polyethylene results in the alignment of the GnP fillers. The electric conductivity has  
 6 been measured perpendicularly to this direction. It is about 6 orders of magnitude lower than  
 7 the parallel one. The nonlinear coefficient  $\alpha \sim 4$  suggests that the orientation of the GnP does  
 8 not influence the nonlinearity; only the switching field ( $\sim 2 \times 10^7 \text{ Vm}^{-1}$ ) is affected. A  
 9 correlation between the nanoplatelets and the nonlinear property is however tricky since the  
 10 matrix is a low-density polyethylene thermoplastic instead of the polydimethylsiloxane  
 11 thermoset used in the present work.

12

### 13 **3.3 Permittivity versus frequency**

14 Beyond the nonlinear dependency of the conductivity with high electric fields, the  
 15 effective use of a GnP-based composite as field grading material depends also on its losses.  
 16 Indeed, if ohmic heating or dielectric losses become large, thermal runaway and subsequent  
 17 breakdown may occur, limiting the use of this field grading material.

18 In the linear regime, the macroscopic Maxwell's curl equation for the magnetic vector  
 19 field,  $\mathbf{H}(\mathbf{r}, t)$ , in a non-magnetic material is:

$$20 \quad \nabla \times \mathbf{H}(\mathbf{r}, t) = \frac{\partial \mathbf{D}(\mathbf{r}, t)}{\partial t} + \mathbf{J}_F$$

21 where  $\mathbf{J}_F$  is the free current density ( $\mathbf{J}_F = \sigma \mathbf{E}(\mathbf{r}, t)$ ) and  $\mathbf{D}$  is the electric displacement  
 22 field  $\mathbf{D} = \epsilon_0 \epsilon \mathbf{E}(\mathbf{r}, t)$  where  $\epsilon_0$  is the vacuum permittivity,  $\epsilon$  is the relative permittivity of the  
 23 medium and  $\sigma$  its conductivity.

24 This gives:



$$\nabla \times \mathbf{H}(\mathbf{r}, t) = \varepsilon_0 \frac{\partial \varepsilon \mathbf{E}(\mathbf{r}, t)}{\partial t} + \sigma \mathbf{E}(\mathbf{r}, t)$$

With time-harmonic vector fields of angular frequency  $\omega$  ( $\mathbf{H}(\mathbf{r}, t) = \mathbf{H}(\mathbf{r})e^{j\omega t}$  and  $\mathbf{E}(\mathbf{r}, t) = \mathbf{E}(\mathbf{r})e^{j\omega t}$ ), one gets:

$$\nabla \times \mathbf{H}(\mathbf{r}) = j\omega\varepsilon_0\varepsilon'_r\mathbf{E}(\mathbf{r}) + (\varepsilon_0\varepsilon''_r + \sigma(\omega))\mathbf{E}(\mathbf{r})$$

where  $\varepsilon'_r$  and  $\varepsilon''_r$  are, respectively, the relative real and imaginary part of the permittivity ( $\mathbf{H}(\mathbf{r})$  et  $\mathbf{E}(\mathbf{r})$  are complex fields which may include a phase between them). The latter is the linear answer of the material to the applied electric field, meaning that it depends only on the frequency. Finally, the conductivity  $\sigma(\omega) = \sigma_{DC}$  is assumed to be constant for the frequency range of interest.

Assuming that there are neither other loss mechanisms, nor mutual influence of the loss mechanisms, the complex relative dielectric permittivity can then be redefined as:

$$\varepsilon_r^* = \varepsilon'_r - j \left( \varepsilon''_r + \frac{\sigma_{DC}}{\omega\varepsilon_0} \right)$$

The dissipation or loss tangent:

$$\tan \delta_{total} = \tan \delta_{conductive} + \tan \delta_{dielectric} = \frac{\varepsilon''_r + \frac{\sigma_{DC}}{\omega\varepsilon_0}}{\varepsilon'_r}$$

therefore, characterizes the total electrical dissipation.

A dielectric spectrum of a composite (45 wt.% GnP) is shown in **Fig. 7**. The dielectric constant decreases from 15 to 12 in the  $10^{-2} - 10^6$  Hz range but is much higher than the neat polymer. This is significant considering the relative low filler fraction and the fact that GO-based nanocomposites have a typical permittivity of  $\sim 8$  [33]. This high permittivity was already noted in GNPs nanocomposites aimed for electromagnetic interference (EMI) shielding applications (see [43]). It allows GnP-based composites to be used as capacitive field grading material. Meanwhile, the loss factor increases only moderately from  $210^{-2}$  to  $510^{-2}$  (**Fig. 7**) which indicates a low DC conductivity, though an order of magnitude higher than for GO-based nanocomposites.

For AC stress grading applications, the relevant function is the dependence of the permittivity  $\varepsilon'_r$  with the field. The permittivity (AC,  $f = 50\text{Hz}$ ) of the specimens as a function of the electric field has been extracted from the electrical characteristics. **Fig.8** shows a rise of the permittivity

1 above 3 wt.% which suggests a percolation threshold. It is also worth noting that the percolation  
2 is perceptible as it is for DC-resistivity.

3

#### 4 **4 Discussion**

5 The origin of the nonlinear resistivity of the GNP composite is not straightforward. First let us  
6 note that a two-phase composite made of a polymer insulating host loaded with conductive  
7 fillers has to be above the percolation threshold to show a strong nonlinear resistivity behavior.  
8 Indeed, at low volume concentration, the conductivity of such a composite is mainly the result  
9 of transport processes occurring within the polymer matrix. It is only above the percolation,  
10 where the fillers are in close contact, that efficient conductive paths might appear. **Fig. 9** shows  
11 a transmitted light micrograph of the specimen loaded with 5 wt.% of graphite nanoplatelets. A  
12 multiscale microstructure is observed with the presence of micronic aggregates of nanoplatelets  
13 which may coexist with isolated primary nanoplatelets present in the grey background. Due to  
14 the large aspect ratio of GNP, percolation is therefore achieved at low filling fractions by  
15 aggregates-aggregates junctions involving or not isolated nanoplatelets. The origin of the  
16 electric change of the composites, observed above the critical filler volume fraction of about 3  
17 vol.% (see **Fig. 5**), is then associated to a percolated microstructure. This might also explain  
18 why the switching field observed in our systems is two decades lower than the switching field  
19 observed in graphite nanoplatelets (GnP) in extruded low-density polyethylene [36,37].  
20 Although the fillers content was similar (~1 and ~5%), the nanoplatelets were more dispersed  
21 in this system and, above all, strongly oriented by the extrusion **Fig. 10** illustrates the  
22 microstructures of an extruded and a randomly oriented nanocomposite when the concentration  
23 of the filler-loading increases. When the nanoplatelets are aligned (**Fig. 10 a**), the electrical  
24 conduction path remains blocked by layers of polymer matrix even at a large filler content.  
25 These layers restrict the rise of current with the increase of applied electric field  $E$ . Since the  
26 resistivity of the carbon filler is lower, a great part of applied voltage is transferred to the matrix

1 layer according to the voltage division rule. By contrast, a percolated microstructure forms  
2 rather easily with randomly oriented nanoplatelets (**Fig. 10 b**). The different microstructures  
3 explain the critical change in electrical resistivity with the field for the specimens of our study  
4 and the lack of percolation behavior in the case of extruded nanocomposites.

5 Percolation is necessary but not sufficient to provide an efficient nonlinear behavior in a two-  
6 phase composite. Two main mechanisms can be at the origin of nonlinear phenomena [44].  
7 When conductive fillers remain separated by a thin layer of insulating polymer, the process of  
8 charge carrier transport can be controlled by tunneling/hopping [21]. This is the case of silicon  
9 carbide fillers for which the non-linearities stem from the contacts between particles [44]. On  
10 the other hand, the nonlinear behavior can be due to an intrinsic property of the particles as  
11 observed for ZnO microvaristors [44] or graphene oxide fillers [33]. The latter case is  
12 interesting since these fillers are also high aspect ratio carbonaceous particles Individual  
13 graphene oxide sheets are close-to-insulating because of the extensive presence of saturated  $sp^3$   
14 bonds and a high density of electronegative oxygen atoms bonded to carbon which give rise to  
15 an energy gap in the electron density of states ( $\sim 2-10 \text{ eV}$  [45]). However, chemical or thermal  
16 reduction results in a pronounced increase of conductivity ( $\sim 3$  orders). Partially reduced,  
17 individual graphene oxide sheets are characterized by a nonlinear current-voltage  $I(V)$  behavior  
18 [46] due to their heterogeneous microstructure. The 2D-sheets are made of  $sp^2$  carbon clusters  
19 separated by amorphous and highly disordered  $sp^3$  bonded regions This disrupted structure  
20 forms electrostatic barriers between the conductive  $sp^2$  clusters and limit the charge transport  
21 inside the partially reduced GO individual sheets for an  $sp^2$  fraction below 0.6, *i.e.* below 20  
22 at.% oxygen [46]. The charge transport in individual partially reduced GO is space-charge-  
23 limited, the injected carriers in the individual sheet altering the local electric field created by  
24 the electrode potentials [47]. The electrons are indeed blocked by the energy barriers at low  
25 electric field and become capable of tunneling through them when the local electric field  
26 exceeds a specific local switching field which depends on the  $sp^2$  clusters size, itself controlled

1 by the reduction rate of the GO sheet. The nonlinearity decreases as the reduction of the GO  
2 progresses [45,47] as a consequence of the increase of the  $sp^2$  cluster size. At a  $sp^2$  fraction of  
3 about 60% the sheets lose their nonlinearity behavior [46]. When such individual GO sheets  
4 are dispersed in a polymer matrix (at and above percolation) the composite conductivity is  
5 thought to be dictated by the motion of charge carriers within the sheets. The contacts between  
6 sheets do add only weak additional resistance, since conductivity within thin GO films have  
7 been shown to be not limited by junctions between the sheets [45].

8 In the case of GnP, some surface groups are present but they are mainly localized on the edge  
9 of the nanoplatelets. Moreover, their thickness is one order thicker than the GO sheets (11 nm  
10 [33]), and surface oxide groups such as carbonyl groups [36,45, 47-48] are far less abundant.  
11 The linear resistivity through and in-plane are  $10^{-2}$  and  $10^{-7}$   $\Omega\text{m}$  respectively [36], suggesting a  
12 large amount of delocalized  $\pi$  electrons available. The mechanisms invoked for GO sheets are  
13 therefore not relevant here for the GnP/silicone composites. It is therefore very likely that  
14 contacts between GnP aggregates or contact between aggregate and isolated primary of the  
15 multiscale organization possess a distribution of characteristic voltages above which the  
16 electrons can tunnel through.

17

## 18 **5 Conclusions**

19 We have examined the electrical behavior of graphite nanoplatelets filled silicone composites.  
20 They are found to possess nonlinear resistive field grading behavior with a resistivity-  
21 concentration dependence typical of percolated composites. For filler concentration below the  
22 percolation threshold, the resistivity of composites is found higher than pristine silicone matrix.  
23 GnP-Polymer interface barriers then hinder the charge movement of impurities ions within the  
24 host matrix. At about 4 wt.% of nanofillers, a field-dependent conductivity variation of 6 orders  
25 of magnitude is observed. GnP composites show similar properties than GO-based  
26 nanocomposites but the transition is less sharp and the switching field 2 orders of magnitude

1 lower. The nonlinear properties are interpreted as the result of a percolated or density (closed  
2 neighbors) microstructure made of the coexistence of aggregates and single nanoplatelets where  
3 the inter-platelet junction resistances are responsible of the macroscopic nonlinear behavior.  
4 After percolation threshold, further increase in the volume fraction does not result in any  
5 distinct change of the resistivity which agrees well with the behavior of composites filled with  
6 percolated semi-conductive fillers. At low field, composites of graphite nanoplatelets exhibit  
7 one order higher resistivity compared to the pristine polymer matrix, a significant dielectric  
8 constant of about 13 at 50 Hz associated to a loss factor of only 0.01. All these characteristics  
9 render the GnPs/silicone composites quite suitable materials for field grading materials.

10

11

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18

## 19 **Declaration**

### 20 **Conflict of interest**

21 The authors declare no conflict of interest.

22

23

## 24 **References**

25 1. T. Christen, L. Donzel, G. Greuter, Nonlinear Resistive Electric Field Grading Part 1: Theory  
26 and Simulation. IEEE Electrical Insulation Magazine 26(6), 47-59 (2010). doi:  
27 10.1109/MEI.2010.5599979

28

- 1 2. C. Liu, Y. Zheng, B. Zhang, X. Zheng, S. Hu, K. Han, Review of Nonlinear Conductivity  
2 Theory. Research of Modified Composite Materials IEEE Access 7, 50536-50548 (2019). doi:  
3 10.1109/ACCESS.2019.2906662  
4
- 5 3. G. Mazzanti, J. Castellon, G. Chen, J.C. Fothergill, M. Fu, N. Hozumi, J.H. Lee, L. Li, T.  
6 Marsinotto, F. Fauseth, P. Morshuis, C. Reed, I. Troia, A. Tzimas, K. Wu, The Insulation of  
7 HVDC Extruded Cable System Joints. Part 1: Review of Materials, Design and Testing  
8 Procedures IEEE Transactions on Dielectrics and Electrical Insulation 26(3), 964-972 (2019).  
9 doi: 10.1109/TDEI.2019.007916  
10
- 11 4. H. Ye, T. Fechner, X. Lei, Y. Luo, M. Zhou, Z. Han, H. Wang, Q. Zhuang, R. Xu, D. Li,  
12 Review on HVDC cable terminations. IET journals, The institution of Engineering and  
13 Technology - High Voltage 3(2), 79-89 (2018). doi: 10.1049/hve.2017.0144  
14
- 15 5. H. Hourdequin, L. Laudebat, M. Locatelli, P. Bidan, Contribution à la conception de  
16 structures de packaging pour les modules de puissance très haute tension : contraintes sur les  
17 isolants. Symposium de génie électrique : EF-EPF-MGE-2016, 7-9 Juin 2016, Grenoble, France  
18
- 19 6. C. Li, C. Lin, J. Hu, L. Weidong, Q. Li, B. Zhang, S. He, Y. Yang, F. Liu, J. He, Novel  
20 HVDC Spacers by Adaptively Controlling Surface Charges-Part I: Charge Transport and  
21 Control Strategy. IEEE Transactions on Dielectrics and Electrical Insulation 25(4), 1238 - 1247  
22 (2018). doi: 10.1109/TDEI.2018.007054  
23
- 24 7. A. Naeini, E. Cherney, S. Jayaram, Modified Stress Grading System for a 13.8 kV Inverter-  
25 Fed Rotating Machine. IEEE Transactions on Dielectrics and Electrical Insulation 26(4),1261-  
26 1266 (2019). doi: 10.1109/TDEI.2019.007991  
27
- 28 8. C. Staubach, T. Hildinger, A. Staubach, Comprehensive electrical and thermal analysis of  
29 the stress grading system of a large hydro generator. IEEE Electrical Insulation Magazine  
30 34(1):37-42 (2018). doi: 10.1109/MEI.2018.8246120  
31
- 32 9. U. Patel, Jayaram S (2012) Impact of poor power quality on stress grading system of cable  
33 termination, Annual Report Conference on Electrical Insulation and Dielectric Phenomena, 14-  
34 17 Oct 2012. doi : 101109/CEIDP20126378820  
35
- 36 10. X. Zhu, Y. Wang, Y. Zhang, J. Wu, Y. Yin, Harmonics in SiC/Alkyd Resin Composites  
37 with Different SiC Particle Sizes under Different Temperatures. IEEE Transactions on  
38 Dielectrics and Electrical Insulation 26(4):1350-1357 (2019). doi: 10.1109/TDEI.2019.008055  
39
- 40 11. A. Can-Ortiz, L. Laudebat, Z. Valdez-Nava and S. Diaham, Nonlinear Electrical  
41 Conduction in Polymer Composites for Field Grading in High-Voltage Applications: A Review,  
42 Polymers 13, 1370, 1-58 (2021). doi.org/10.3390/polym13091370  
43
- 44 12. S. Blatt, V. Hinrichsen, Mathematical Model for Numerical Simulation of Current  
45 Density in Microvaristor Filled Insulation Materials. IEEE Transactions on Dielectrics and  
46 electrical Insulation 12(2):1161-1170 (2015). doi: 10.1109/TDEI.2014.004740  
47
- 48 13. D. Weida, C. Richter, M. Clemens, Design of ZnO Microvaristor Material Stress-cone For  
49 Cable Accessories. IEEE Transactions on Dielectrics and Electrical Insulation 18(4),1262-1267  
50 (2011). doi: 10.1109/TDEI.2011.5976125  
51

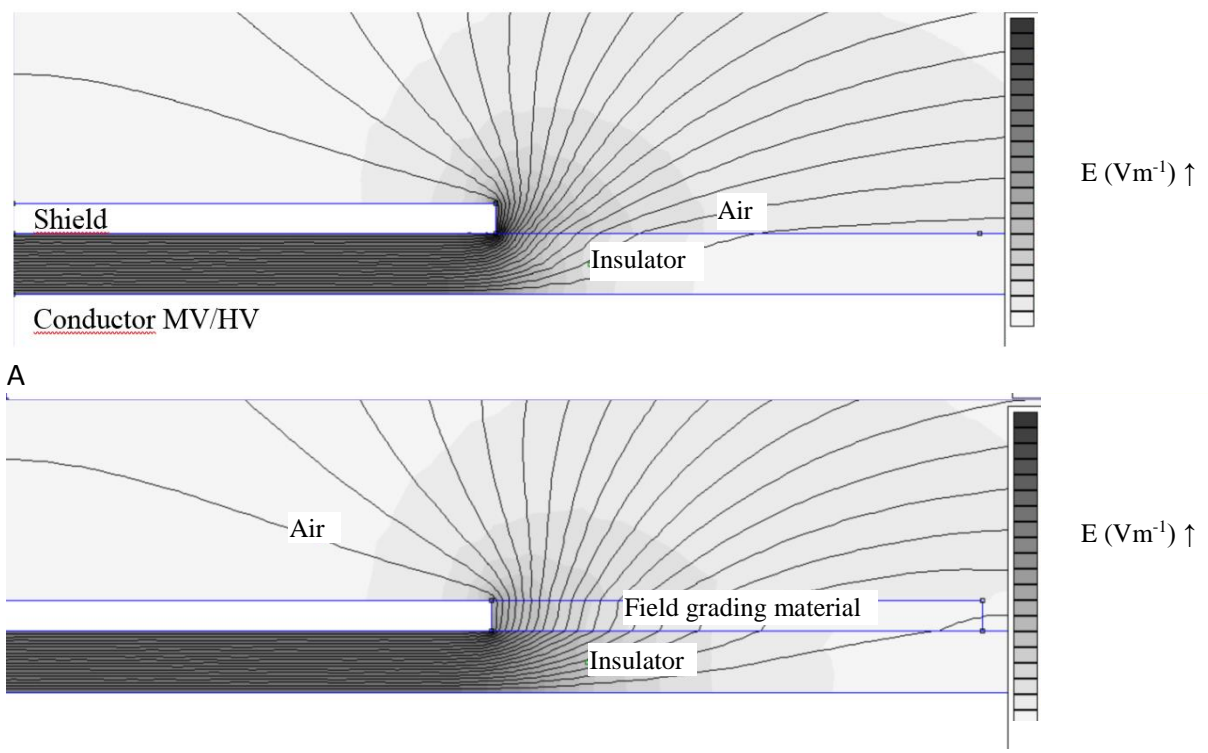
- 1 14. R. Abd-Rahman, A. Haddad, N. Harid, H. Griffiths, Stress Control on Polymeric Outdoor  
2 Insulators Using Zinc Oxide Microvaristor Composites. *IEEE Transactions on Dielectrics and*  
3 *Electrical Insulation* 19(2):705-713 (2012). doi:10.1109/TDEI.2012.6180266  
4
- 5 15. H. Ahmad, A. Haddad, H. Griffiths, S. Robson, T. Nishimura, N. Tsukamoto, Electrical  
6 characterisation of ZnO microvaristor materials and compounds. *IEEE Conference on*  
7 *Electrical Insulation and Dielectric Phenomena (CEIDP):688-692 (2015)*  
8 10.1109/CEIDP.2015.7352035  
9
- 10 16. L. Donzel, M. Montenegro-Uratsun, M. Hagemeister, P. Rukwid, ZnO stress grading tape  
11 for stator windings for electrical machines located at higher altitudes. *Cigré 2016 D1-107: 1-12*  
12 (2016)  
13
- 14 17. X. Zhao, X. Yang, J. Hu, H. Yang, Q. Li, J. He, Grading of Electric Field Distribution of  
15 AC Polymeric Outdoor Insulators Using Field Grading Material. *IEEE Transactions on*  
16 *Dielectrics and Electrical Insulation* 26(4), 1253-1260 (2019). doi: 10.1109/TDEI.2019.007989  
17
- 18 18. X. Yang, J. Hu, J. He, Adjusting nonlinear characteristics of ZnO-silicone rubber  
19 composites by controlling filler's shape and size. *IEEE International Conference on Dielectrics*  
20 *(ICD) 1, 313-317 (2016)*. doi:10.1109/ICD.2016.7547607  
21
- 22 19. B.R.Varlow, J. Robertson, K.P. Donnelly, Nonlinear fillers in electrical insulating materials.  
23 *IET Science, Measurement & Technology* 1(2):96-102 (2007). doi:10.1049/iet-smt:20060007  
24
- 25 20. Z. Li, Z. Yang, Y. Xing, W. Zhu, J. Su, X. Kong, J. Jiang, B. Du, Improving the Electric  
26 Field Distribution in Stress Cone of HTS DC Cable Terminals by Nonlinear Conductive  
27 Epoxy/ZnO Composites. *IEEE Transactions on Applied Superconductivity* 29(2), 7000305  
28 (2009). doi: 10.1109/TASC.2018.2889357  
29
- 30 21. X.Wang, J.K. Nelson, L.S.Schadler, H. Hillborg, Mechanisms Leading to Nonlinear  
31 Electrical Response of a Nano p-SiC/Silicone Rubber Composite. *IEEE Transactions on*  
32 *Dielectrics and Electrical Insulation* 17(6),1687-1696 (2010). doi:  
33 10.1109/TDEI.2010.5658218  
34
- 35 22. E. Mårtensson, U. Gäfvert, A three-dimensional network model describing a non-linear  
36 composite material. *Journal of Physics D: Applied Physics* 37(1), 112-119 (2004). doi:  
37 10.1088/0022-3727/37/1/019  
38
- 39 23. F. Wang, P. Zhang, M. Gao, X. Zhao, J. Gao, Research on the Non-linear Conductivity  
40 Characteristics of Nano-SiC Silicone Rubber Composites. *Annual Report Conference on*  
41 *Electrical Insulation and Dielectric Phenomena, 535-538 (2013)*. doi :  
42 10.1109/CEIDP.2013.6748326  
43
- 44 24. A. Merouchi, E. David, F. Baudoin, D. Mary, I. Fofana, Optimization of the Electrical  
45 Properties of Epoxy- SiC Composites for Stress-Grading Application. *IEEE Conference on*  
46 *Electrical Insulation and Dielectric Phenomena (CEIDP) 713-716 (2015)*. doi:  
47 10.1109/CEIDP.2015.7352140  
48
- 49 25. B.X. Du, Z.L. Li, Z.R. Yang, Field-dependent Conductivity and Space Charge Behavior of  
50 Silicone Rubber/SiC Composites. *IEEE Transactions on Dielectrics and Electrical Insulation*  
51 23(5), 3108-3116 (2016) doi: 10.1109/TDEI.2016.005768

- 1  
2 26. B.X. Du, Z.R. Yang, Z.L. Li, J. Li, IEEE Transactions on Dielectrics and Electrical  
3 Insulation 24(3):1340-1348 (2017). doi: 10.1109/TDEI.2017.006137  
4  
5 27. L.S. Schadler, X. Wang, J.K. Nelson, H. Hillborg, Dielectric Polymer Nanocomposites J  
6 Keith Nelson Editor 259 (2010). doi: 10.1007/978-1-4419-1591-7  
7  
8 28. L.X. He, S.C. Tjong, Zener tunneling in conductive graphite/epoxy composites:  
9 Dielectric breakdown aspects. Express Polymer Letters 7(4), 375-382 (2013). doi:  
10 10.3144/expresspolymlett.2013.34  
11  
12 29. Q. Liu, X. Yao, X. Zhou, Z. Qin, Z. Liu, Varistor effect in Ag-graphene/epoxy resin  
13 nanocomposites. Scripta Materialia 66(2), 113-116 (2012)  
14 doi:10.1016/j.scriptamat.2011.10.016  
15  
16 30. Y. Yuan, Z. Qu, Q. Wang, E. Cheng, X. Sun, The Nonlinear I–V Behavior of Graphene  
17 Nanoplatelets/Epoxy Resin Composites Obtained by Different Processing Methods. Journal of  
18 Inorganic and Organometallic Polymers and Materials 29, 1198 (2019) doi:10.1007/s10904-  
19 019-01083-6  
20  
21 31. H. Lin, W. Lu, G. Chen, Nonlinear DC conduction behavior in epoxy resin/graphite  
22 nanosheets composites. Physica B: Condensed Matter 400(1), 229-236 (2007).  
23 doi:10.1016/j.physb.2007.07.015  
24  
25 32. Y. Yuan, Q. Wang, Z. Qu, Nonlinear DC Conduction Behavior in Graphene  
26 Nanoplatelets/Epoxy Resin Composites. IOP Conference Series: Materials Science and  
27 Engineering 301(1), 012015 (2018). doi:10.1088/1757-899X/301/1/012015  
28  
29 33. Z. Wang, J.K. Nelson, H. Hillborg, S. Zhao, L.S. Schadler, Graphene Oxide Filled  
30 Nanocomposite with Novel Electrical and Dielectric Properties. Advanced Materials 24(23),  
31 3134-3137 (2012). doi: 10.1002/adma.201200827  
32  
33 34. Z. Wang, J.K. Nelson, H. Hillborg, S. Zhao, L.S. Schadler, Nonlinear Conductivity and  
34 Dielectric Response of Graphene Oxide Filled Silicone Rubber Nanocomposites. Annual  
35 Report Conference on Electrical Insulation and Dielectric Phenomena 40-43 (2012). doi:  
36 10.1109/CEIDP.2012.6378717  
37  
38 35. W. Li, U.W. Gedde, H. Hillborg, Structure and Electrical Properties of Silicone Rubber  
39 filled with thermally Reduced Graphene Oxide. IEEE Transactions on Dielectrics and Electrical  
40 Insulation 23(2),1156-1163 (2016). doi: 10.1109/TDEI.2015.005485  
41  
42 36. K. Gaska, X. Xu, R. Kádár, B. Ganjipour, A.Yurgens, S. Gubanski, Influence of  
43 manufacturing process on electrical properties of LDPE-GnP nanocomposites. Proceedings of  
44 the Nordic Insulation Symposium 25 (2017)  
45  
46 37. G. Xu, S. Gubanski, R. Kádár, Electrical, Mechanical, and Thermal Properties of LDPE  
47 Graphene Nanoplatelets Composites Produced by Means of Melt Extrusion Process. Polymers  
48 9(1):1-12 (2017). doi:10.3390/polym9010011  
49  
50

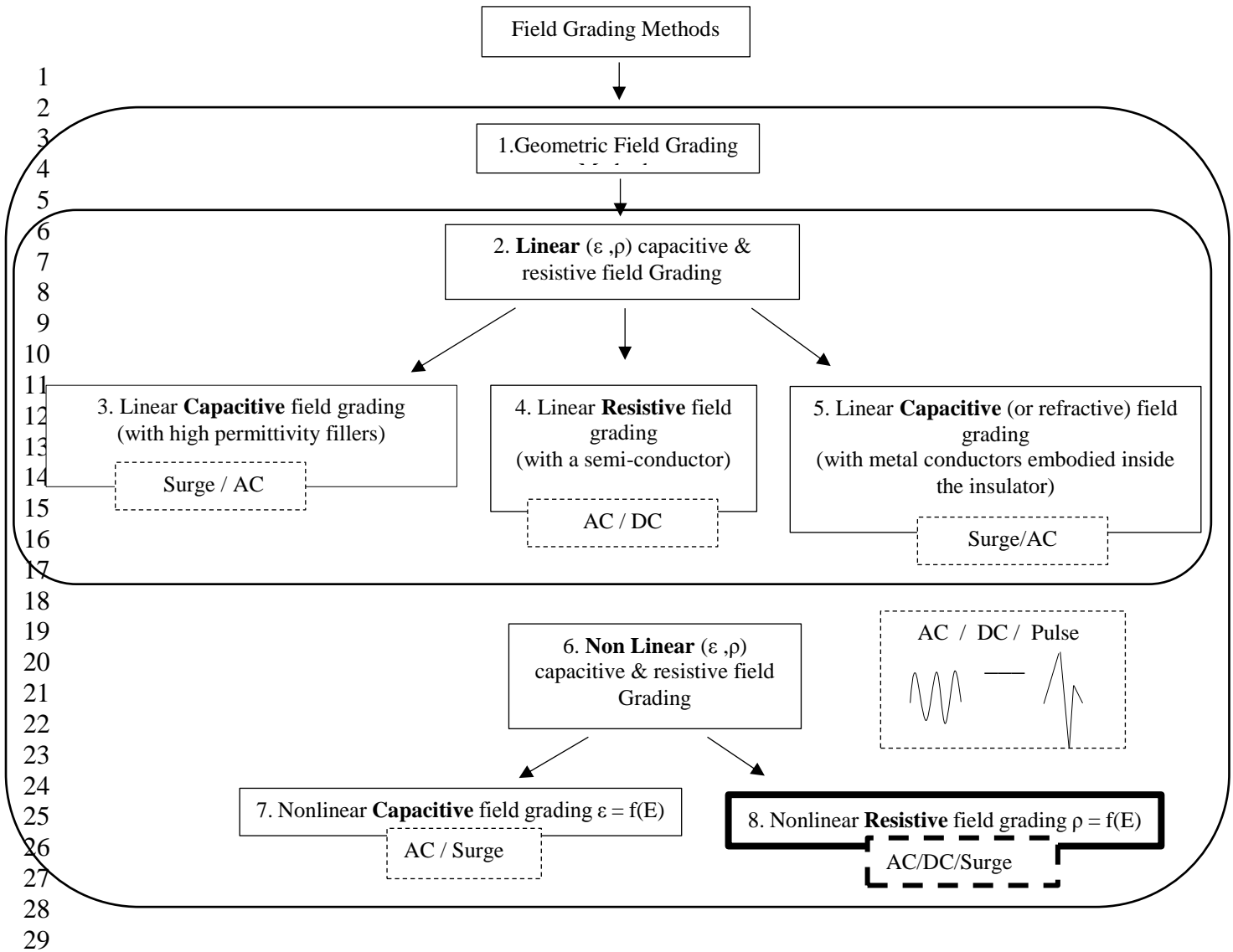


- 1 38. R. Metz, C. Blanc, S. Dominguez, S. Tahir, R. Leparc, M. Hassanzadeh, Nonlinear field  
2 dependent conductivity dielectrics made of graphite nanoplatelets filled composites, *Materials*  
3 *Letters* 292:129611 (2021). doi:10.1016/j.matlet.2021.129611  
4  
5  
6 39 ASTM D257-14 Standard Test Methods for DC Resistance or Conductance of Insulating  
7 Materials, ASTM International, Subcommittee : D0912, West Conshohocken, PA (2014)  
8  
9 40. H. Takao, M. Okoshi and N. Inoue, Swelling and modification of silicone surface by F2  
10 laser irradiation, *Appl. Phys. A, Materials Science & Processing*, 79, 1571-1574 (2004)  
11  
12 41. M. Wåhlander, F. Nilsson, R.L. Andersson, A. Carlmark, H. Hillborg, E. Malmström,  
13 Reduced and Surface-Modified Graphene Oxide with Nonlinear Resistivity. *Macromolecular*  
14 *Rapid Communications* 38(16), 1700291 (2017). doi: 10.1002/marc.201700291  
15  
16 42. S. Diahm, E. Pizzutilo, L. Da Gama Fernandes Vieira, Z. Valdez Nava, J.Y. Chane  
17 Ching, E. Flahaut, D. Fabiani, Novel Electrical Conduction Properties Obtained in Few-Layer  
18 Graphene/Epoxy Nanocomposites. *IEEE International conference on Nanotechnology* 27-30,  
19 472-475 (2015). doi : 10.1109/NANO.2015.7388640  
20  
21 43. A. H. Kumar, M. B. Ahamed, K. Deshmukh, M. S. Sirajuddeen, Morphology, Dielectric  
22 and EMI Shielding Characteristics of Graphene Nanoplatelets, Montmorillonite Nanoclay and  
23 Titanium Dioxide Nanoparticles Reinforced Polyvinylidene fluoride Nanocomposites. *Polym.*  
24 *Mater.* 31, 2003-2016 (2021). doi:10.1007/s10904-020-01869-z  
25  
26 44. L. Donzel, F. Greuter, T. Christen, Nonlinear Resistive Electric Field Grading Part 2:  
27 Materials and Applications. *IEEE Electrical Insulation Magazine* 27 (2), 18-29 (2011). doi:  
28 10.1109/MEI.2011.5739419  
29  
30 45. C. Gómez-Navarro, R.T. Weitz, A.M. Bittner, M. Scolari, A. Mews, M. Burghard and K.  
31 Kern , Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide  
32 Sheets. *Nano Letters* 7 (11), 3499–3503 (2007). doi : 10.1021/nl072090c  
33  
34 46. C. Mattevi, G. Eda, S. Agnoli, S. Miller, K.A. Mkhoyan, O. Celik, D. Mastrogiovanni, G.  
35 Granozzi, E. Garfunkel, M. Chhowalla, Evolution of Electrical, Chemical, and Structural  
36 Properties of Transparent and Conducting Chemically Derived Graphene Thin Films. *Adv*  
37 *Funct Mater* 19, 2577–2583 (2009). doi: 10.1002/adfm.200900166  
38  
39 47. I. Jung, D. Dikin, R. Piner, R. Ruoff, Tunable Electrical Conductivity of Individual  
40 Graphene Oxide Sheets Reduced at “Low” Temperatures. *Nano Lett* (12), 4283-4287 (2008).  
41 doi: 10.1021/nl8019938  
42  
43 48. B. Ghavami, A. Rastkar-Ebrahimzadeh, Varistor characteristics of a nano-device  
44 containing graphene and oxidised graphene: verification by DFT + NEGF. *Molecular Physics*  
45 113(23), 1-7 (2015). doi:10.1080/00268976.2015.1053549  
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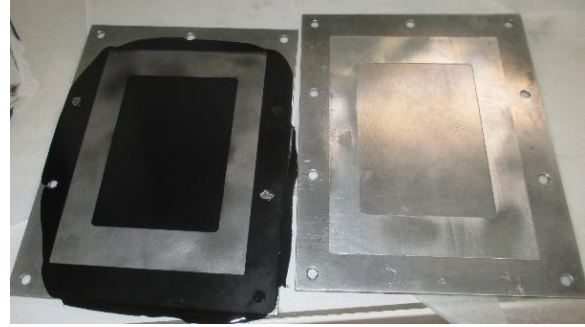
**Fig.1.** (A) Equipotential lines and electric field intensity near a shielded cable termination. Electric field may reach critical values near the end of the shield as depicted by grey scale. B. A layer of nonlinear material coats the termination of the cable: the equipotential lines are scattered, leading to a field reduction in the vicinity of the shield/insulator/air.



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30 **Fig.2.** Schematic overview of some electric stress grading strategies to overcome flashovers  
31 and breakdown under AC, DC and imSurge conditions.



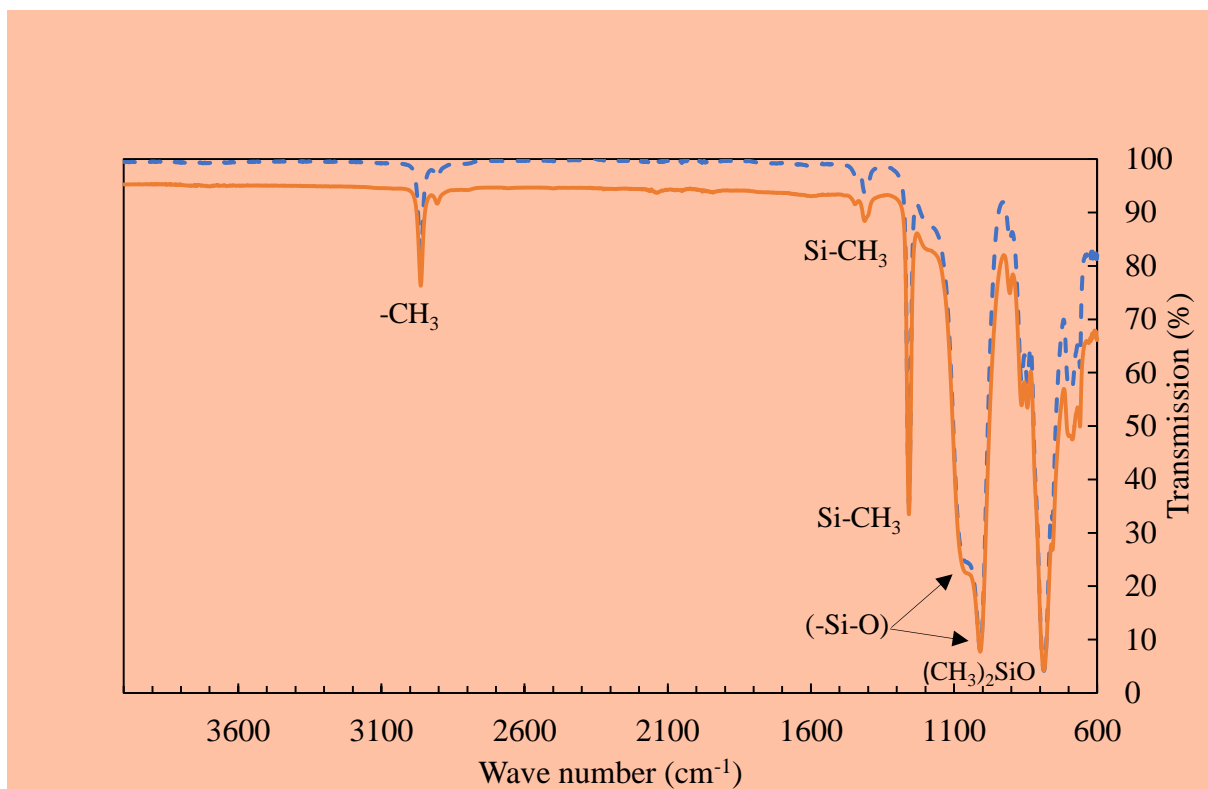
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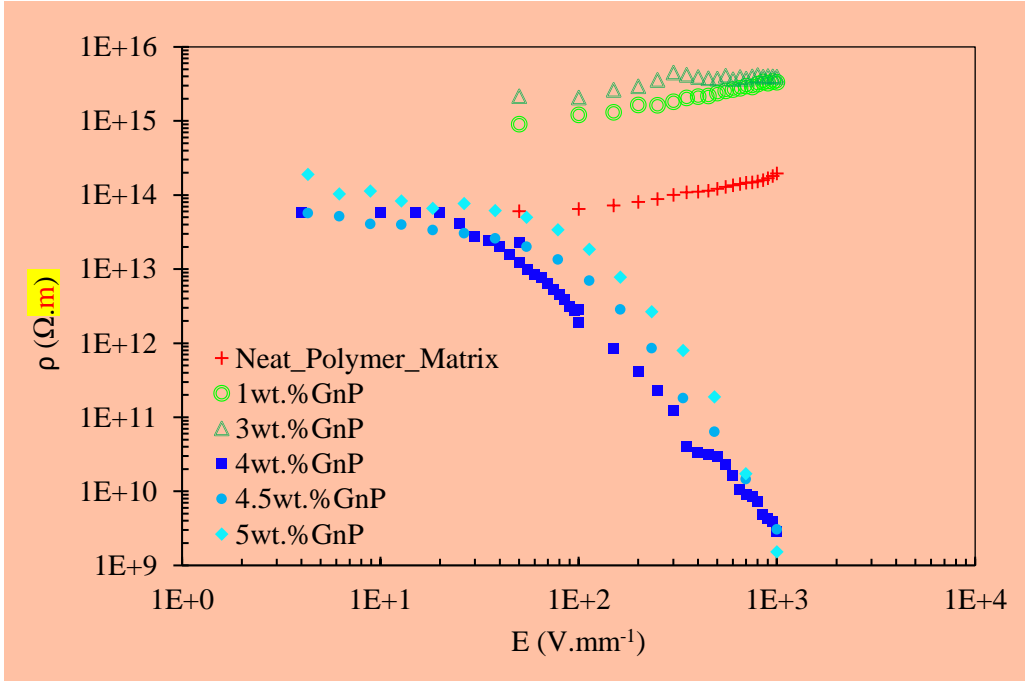
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**Fig. 3.** (A) Electric heated platens for polymer composite plates production. (B) Resulting specimen after 150°C during 1 hour.



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 2 **Fig. 4.** ATR FT-IR spectra (Attenuated Total Reflection Fourier-transformed infrared) of the  
 3 neat silicone (dash line) and 4 wt.% filled graphite nanoplatelets (hatched curve).

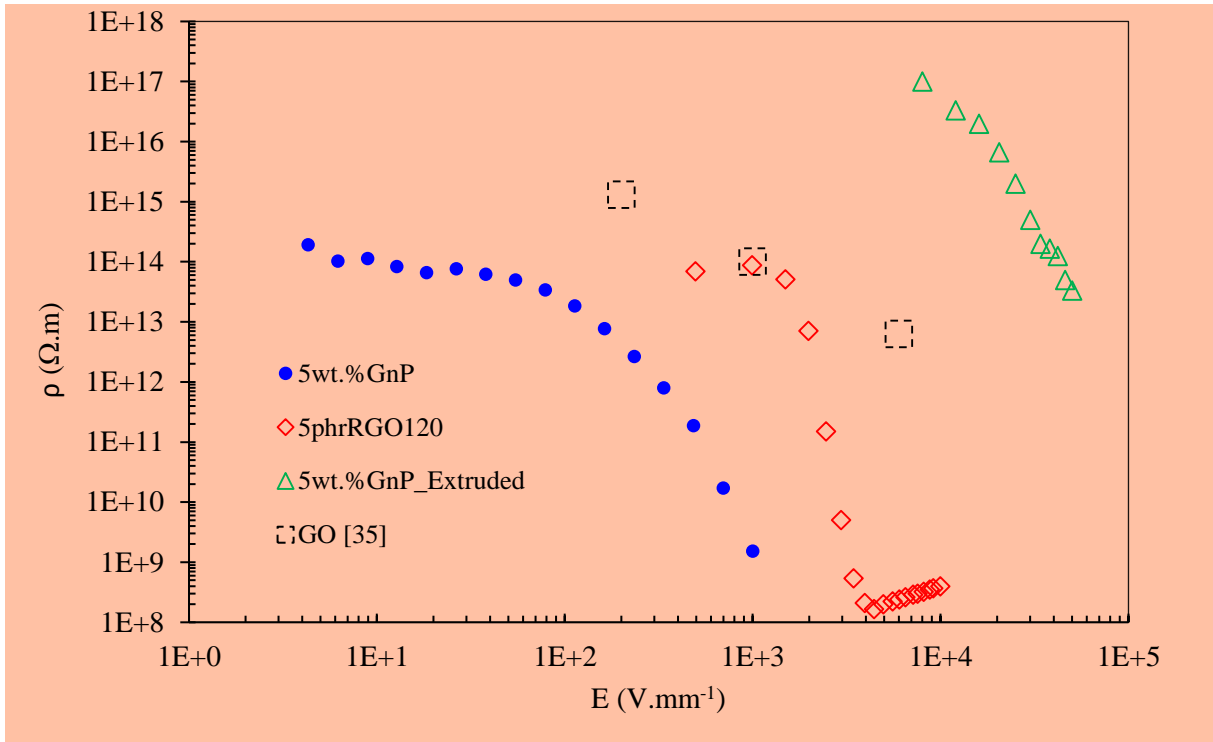
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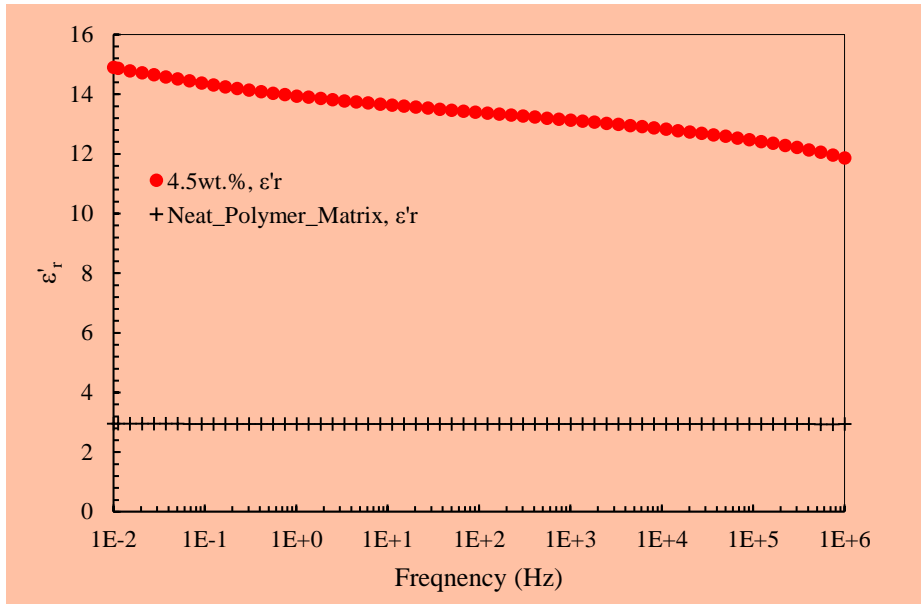
**Fig. 5** Plot of resistivity with respect to field strength for GnP\_based silicone composites with different loading of graphite nanoplatelets

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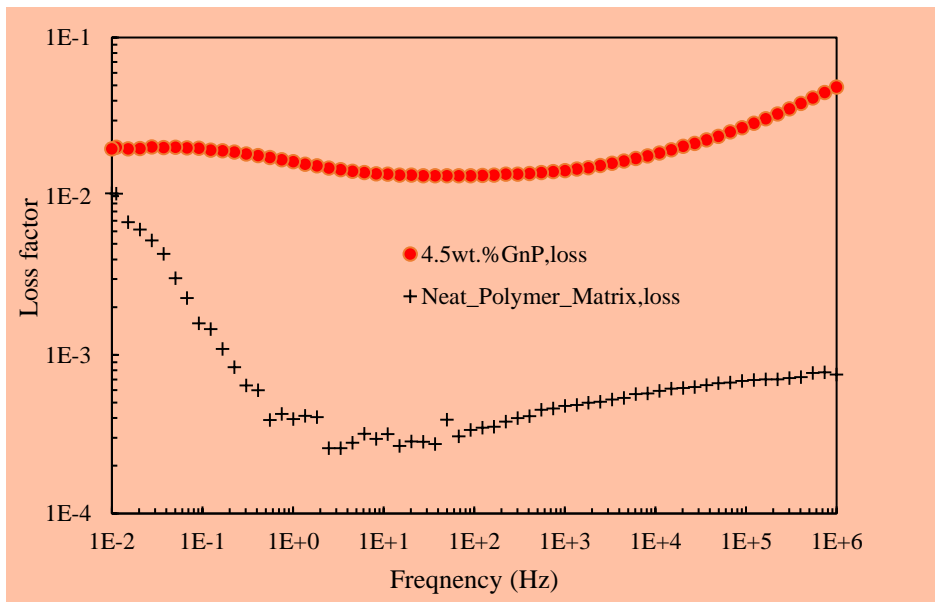


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**Fig. 6** Typical resistivity-field dependency of a GnP-based composite (5 wt.% GnP in silicone) compared with two series of samples from the literature: slightly thermally reduced graphene oxide at 120°C (empty diamonds) [32], GO/silicone composite filled at 3 wt.% [35] and GnP/polyethylene composite in a direction perpendicular to the extrusion direction at high field (empty triangles) [35]



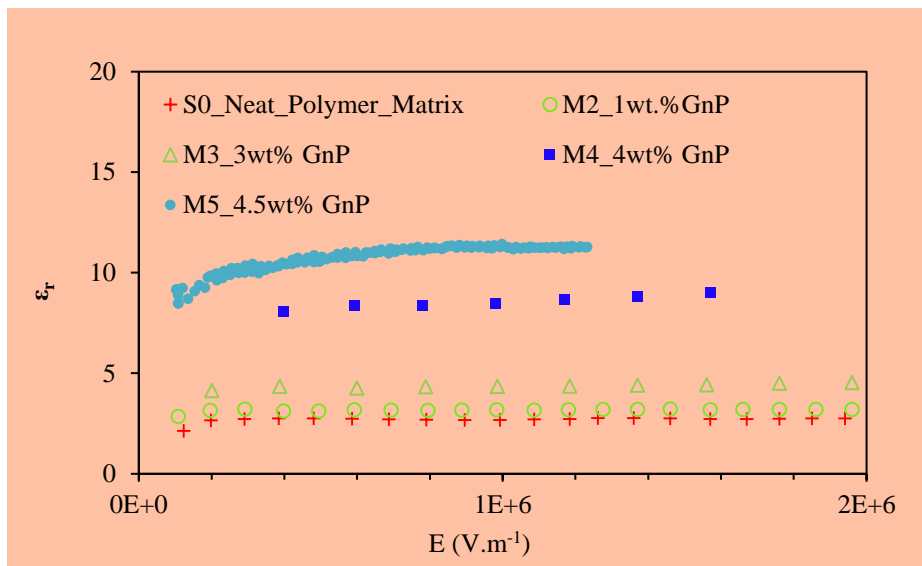
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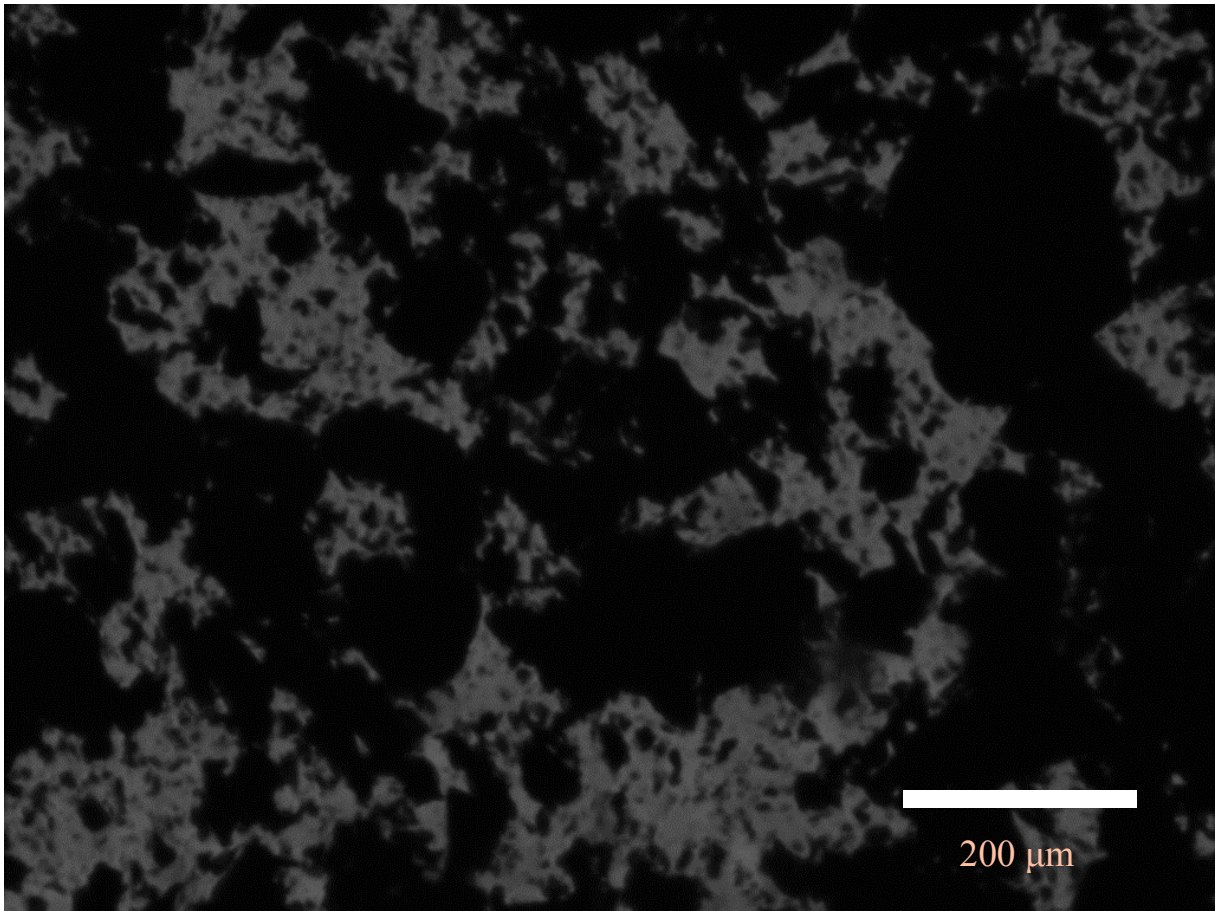
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**Fig. 7** Relative permittivity and dissipation factor ( $\tan \delta$ ) spectrum at room temperature for the pure PDMS matrix and a 4.5 wt.% GnP /silicone nanocomposite



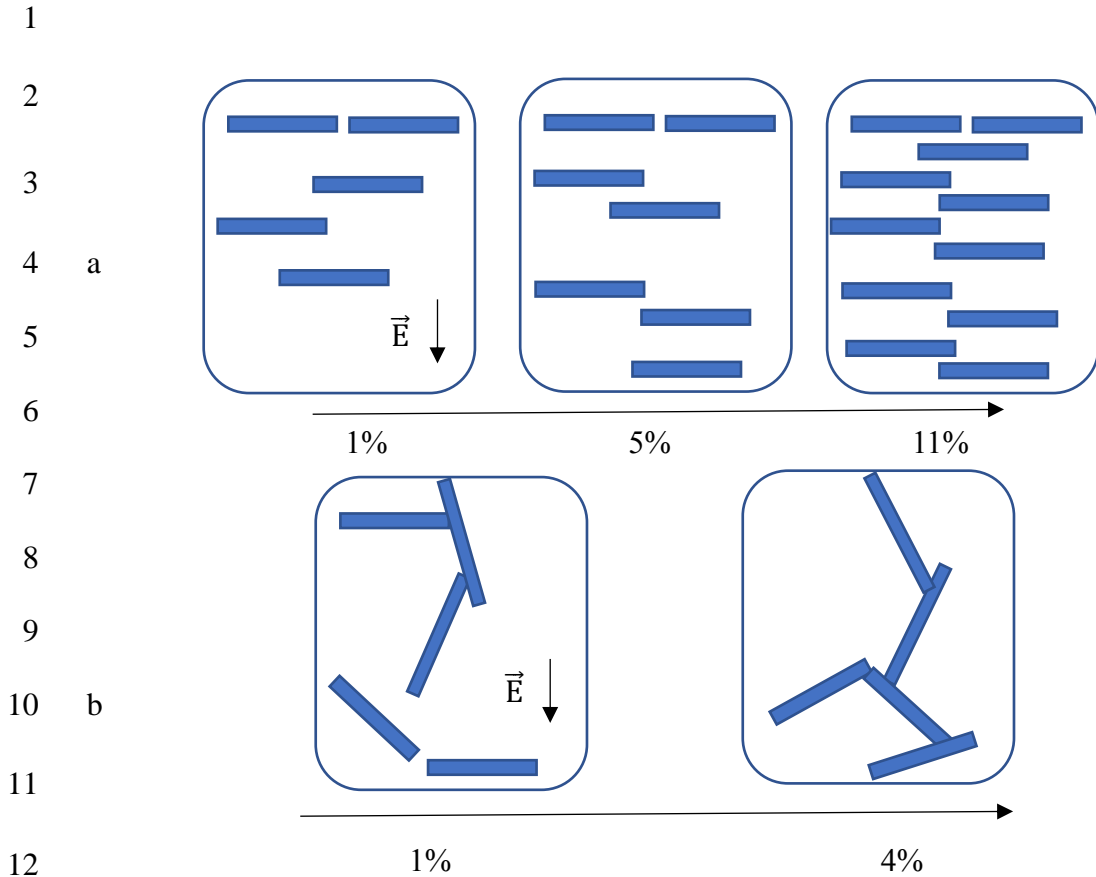


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 2 **Fig. 8.** Plot of the permittivity with respect to field strength for GnP based silicone composites  
 3 with different loading of graphite nanoplatelets. (50 Hz)



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**Fig. 9** Optical microscopy of the specimen with 5 wt.% of fillers. A multiscale microstructure with micronic aggregates is observed in a grey background filled of isolated primary nanoplatelets



**Fig. 10** Sketch of expected microstructure as a function of the volume concentration of the fillers for (A) extruded nanocomposites with nanoplatelets aligned in the direction of the extrusion flow and for (B) randomly oriented nanocomposites. (Electrical measurements are carried out perpendicular to the parallel filler alignment as depicted by the electric field vector  $\vec{E}$ )