Insulating Properties of Graphene Oxide

D.G. Mitrakas, M.G. Danikas *

Department of Electrical and Computer Engineering,
Power Systems Laboratory,
Democritus University of Thrace, Xanthi, Greece

Abstract

Many researchers concentrated recently their efforts on the investigation of the physical properties of graphene, such as its electrical and thermal conductivity and its strength. Its flexibility and transparency opened new possibilities regarding numerous applications, such as electronics, energy storage devices, polymers and electrodes. Relatively little was reported w.r.t. the insulating properties of graphene oxide. It is the purpose of the present paper to investigate whether graphene oxide can be suitable as insulating material for high voltage applications.

Keywords

Graphene oxide, insulating properties, insulation lifetime, enclosed cavities

Introduction

Graphene concentrated the lights of publicity and the scientific interest of numerous researchers around the globe for its physical properties, such as the very high electrical and thermal conductivity and its strength. Its transparency and its flexibility opened new roads for many applications, such as, among others, composite polymers, transparent electrodes and storage energy devices. A. Geim and K. Novoselov received the Nobel prize in physics for "groundbreaking experiments regarding the two-dimensional material graphene" [1].

Properties of Graphene

A graphene film is –at the moment– the thinnest known material, the gases cannot penetrate it, and it has higher mechanical strength than stainless steel. Its properties open new inroads regarding novel applications. At room temperature, its thermal conductivity is very high, higher than that of diamond, and of the order of 5000 W m^{-1} K^{-1}. Graphene is almost transparent, absorbing only 2.3% of light. It is an excellent electrical conductor, having a high charge mobility of 200000 cm^2 V^{-1} s^{-1}. Such properties were recorded with very thin graphene samples of the highest quality and of small surface. It was also reported that graphene properties (such as electronic properties, thermal conductivity, hardness and elasticity) may change with the sample thickness [2].

Possible Applications of Graphene

Many industrial applications were proposed, such as energy storage devices, transistors, electrodes, composite polymers, nanocomposites, sensors etc. The quantity and morphology of graphene for each of the above applications may vary, depending on the application itself. For example, sensors or transparent electrodes require thin graphene films, whereas batteries, super-capacitors and synthetic polymers require quantities of nano-films or graphene platelets. Graphene dispersion in the matrices of the base polymer should be as good as possible.

Graphene Oxide as Insulating Material

The reply to the question whether graphene oxide is a good insulating material, is not easy to be given since the chemical structure of graphene oxide is sensitive to the temperature. The electrical conductivity of graphene oxide can be studied with the aid of dielectric spectroscopy [3]. Dielectric spectroscopy records the change of dielectric properties of a material with the frequency and the temperature. It gives indications as to the insulating properties of the material, taking into account the relaxation phenomena. The latter change the dielectric behavior of the material and allow the storage of more electric energy in the volume of the material.

It is evident that the conductivity of graphene oxide increase is a function of temperature and of frequency (Fig. 1a). The frequency spectrum is in the range of 0.1 Hz up to 10^6 Hz and the range of temperature is in the range of -40^0 C – 30^0 C. The slope of the conductivity curve with frequency decreases as the temperature increases. The dielectric constant takes low values and presents a rather small dependency on frequency at low temperatures. However, this changes at higher temperatures (Fig. 1b) (note the same ranges of frequency and temperature for Figs. 1a and 1b) [4].

Fig 2a shows the conductivity in the temperature range 40^0 C – 90^0 C. It shows a stepwise increase at lower frequencies and reaches a plateau value at higher frequencies. Fig. 2b shows a decrease of dielectric constant with frequency increase for the same temperature range as in Fig. 2a [4].

Fig. 3a shows conductivity changes from 100^0 C to 150^0 C. The conductivity plateau value appears also at higher temperatures. The transition from plateau value to the exponential increase moves to higher temperatures as the temperature increases. It is to be noted that conductivity increases dramatically as the temperature increases above 100^0 C. Fig. 3b shows that the dielectric constant changes significantly as the frequency decreases [4].

Fig. 4 shows conductivity as a function of temperature at the frequency of 0.1 Hz. One may see three transitions from -40^0 C to 150^0 C. Two transitions from the region of insulating material to the region of semiconduction at about 10^0 C and 100^0 C and one transition from the region of semiconduction to the region of insulating material at 90^0 C. At room temperature electrical conductivity has semiconductive characteristics but at lower temperatures has insulating characteristics. Fig. 5 shows the variation of the dielectric constant with temperature at various frequencies [4].

It should be noted that graphene oxide is hydrophilic material and it is very sensitive to humidity variations. Its resistance is 10^8 Ω for relative humidity of 15% but it becomes ten times smaller when the relative humidity is 95%. The relationship of its resistance with humidity, renders the aforementioned material ideal as humidity sensor [5].

Graphene oxide can be selected to be added to polymer matrices because of its high mechanical strength and its high thermal conductivity. Pure graphene oxide is thermally unstable. The decomposition of graphene oxide nanosheets (GOn) is not valid for nanocomposites GO/PVDF because of the strong interactions between its constituents. Fig. 6 shows that the permittivity of such a nano-composite (GO/PVDF) with concentrations above 1 wt% is higher than that of pure PVDF.

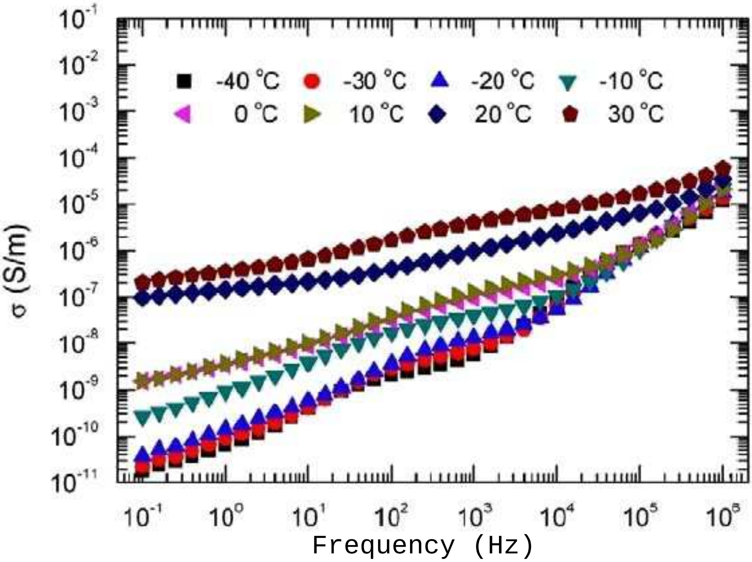


Fig. 1a Conductivity of graphene oxide with frequency and temperature

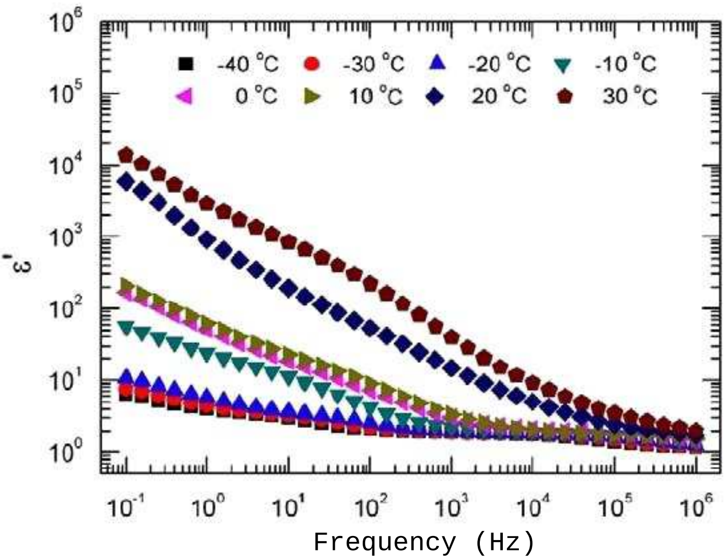


Fig. 1b Dielectric constant of graphene oxide with frequency and temperature

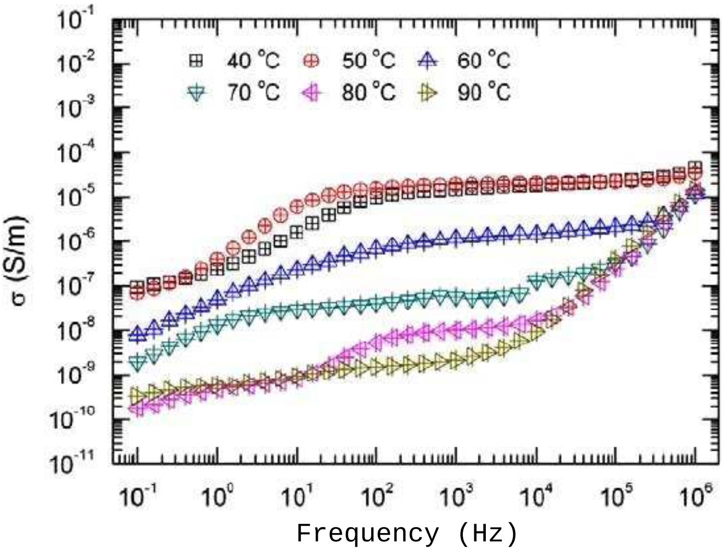


Fig. 2a Conductivity of graphene oxide with frequency and temperature

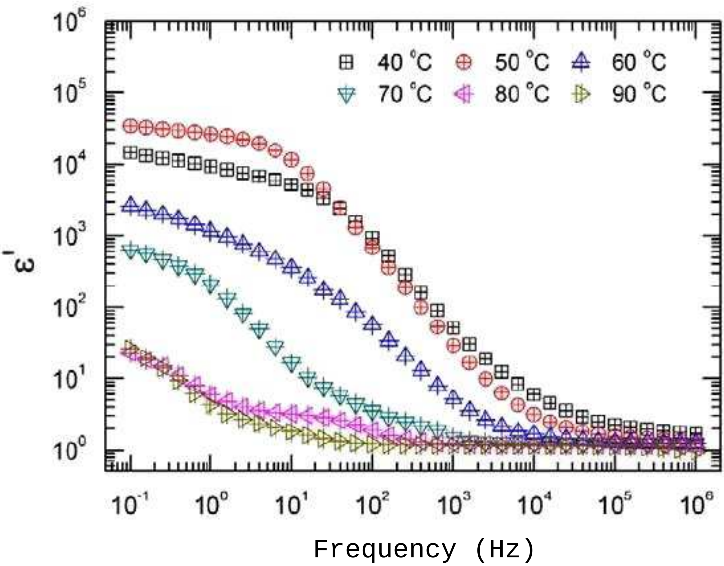


Fig. 2b Dielectric constant of graphene oxide with frequency and temperature

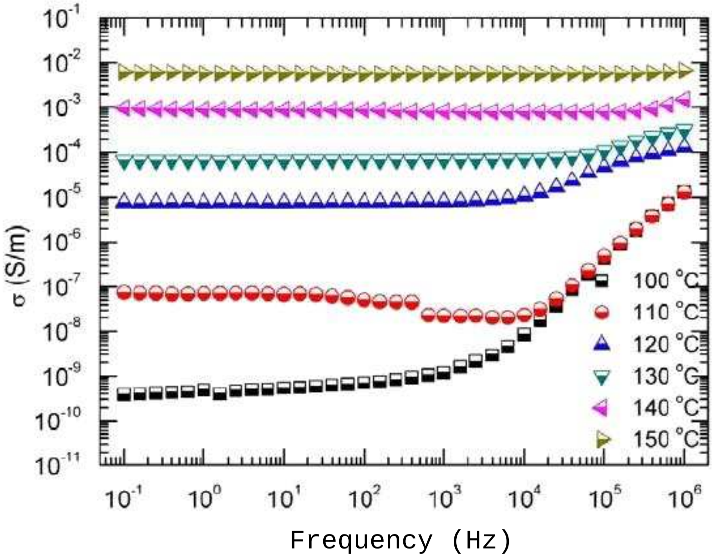


Fig. 3a Conductivity of graphene oxide with frequency and temperature

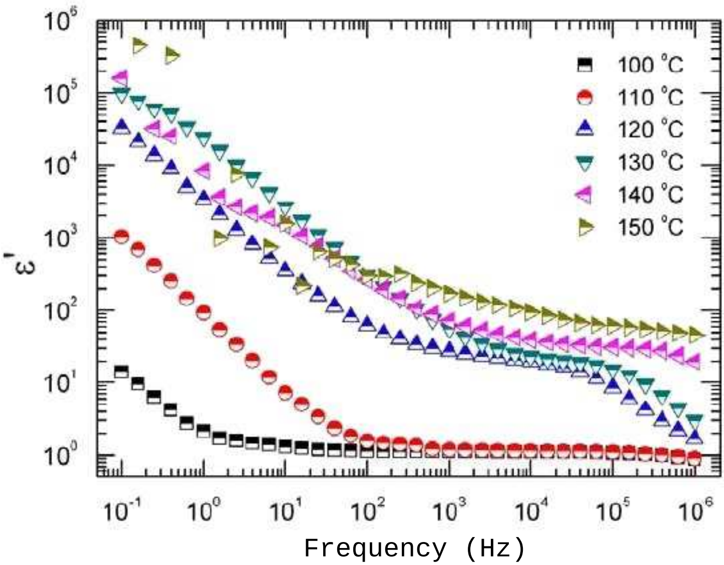
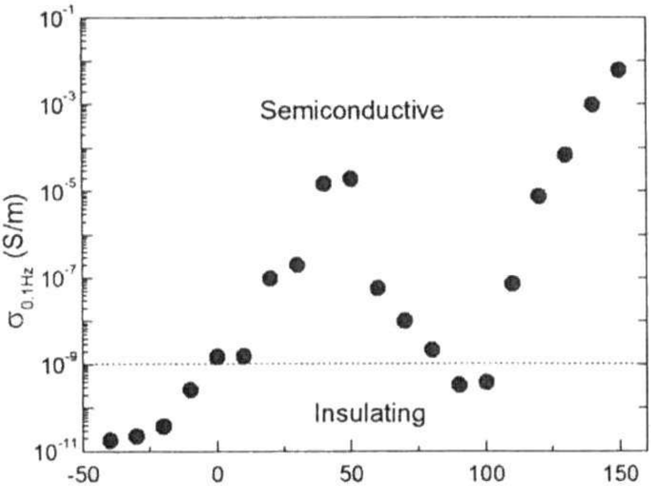
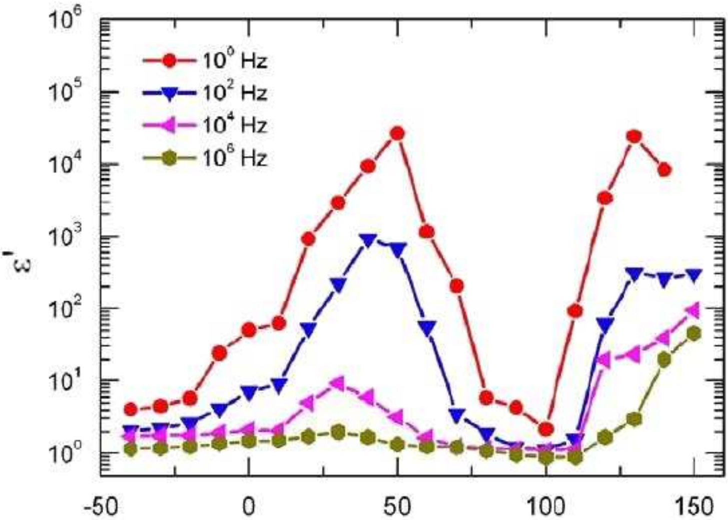


Fig. 3b Dielectric constant of graphene oxide with frequency and temperature



Temperature (⁰C)

Fig. 4 Conductivity of graphene oxide with temperature at frequency 0.1 Hz



Temperature (⁰C)

Fig. 5 Dielectric constant of graphene oxide

However, for concentrations GOn lower than 0.5 wt%, permittivity is lower than that of pure PVDF. Fig. 7 shows that the presence of GOn in various concentrations does not result in a change of electrical conductivity of the nanocomposite in relation to the pure PVDF at higher frequencies, whereas small differences (increase of conductivity) are observed as the frequency decreases [6].

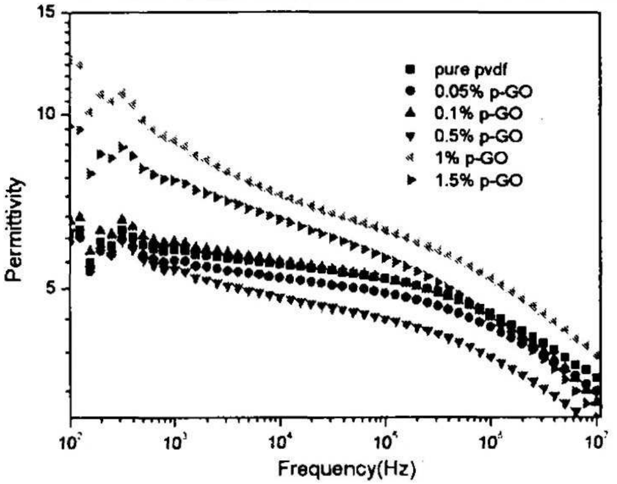


Fig. 6 Dielectric constant of Gon/PVDF

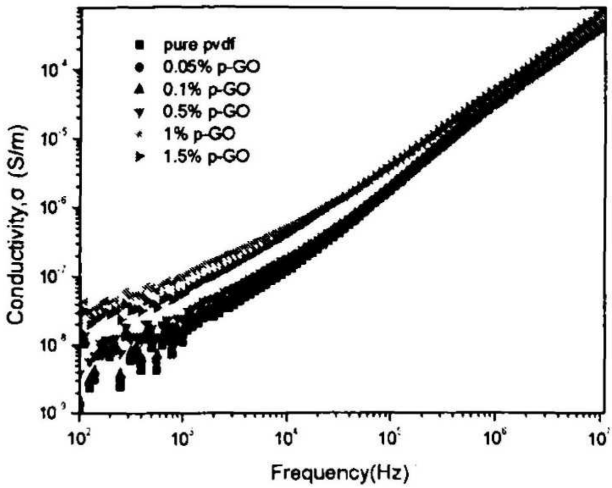


Fig. 7 Conductivity of GOn/PVDF

Graphene oxide in combination with silicon oxide may be used as thin coatings in XLPE. As evaluation index of such a combination the OIT (oxidative induction time) was used, an evaluation which is taken during accelerated ageing at 120⁰ C. Fig. 8 shows OIT values as a function of time for the pure polymer, the combination XLPE- SiO_2 as well as for the combination XLPE-GO-SiO_2.

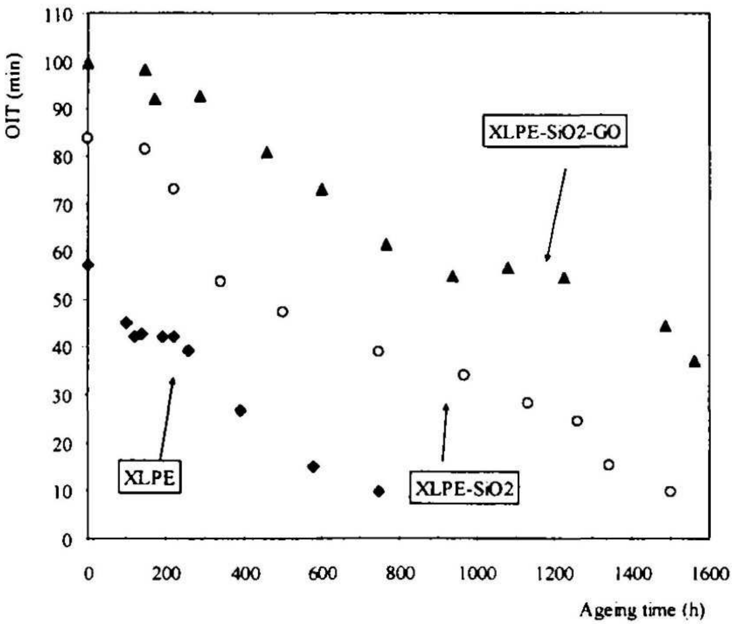


Fig. 8 Values of OIT with time

It is evident that such coatings contribute to the increase of resistance in the thermal oxidation. The presence of 0.5 wt% GO gives even more higher values of OIT. All coatings seem to increase the surface resistivity but the coating with GO is the better one. The presence of GO contributes to the hindrance of oxygen and of oxidation of the polymer. Moreover, the change in coating structure are adequate in improving the thermal stability of XLPE [7].

Work done with epoxy resin with graphene oxide up to 0.5 wt% showed that there is no difference between pure epoxy resin and the one with GO regarding the dielectric behavior. The addition of GO does not render any better the epoxy resin (Fig. 9) whereas there is a marked difference with epoxy resin nanocomposite after thermal treatment (Fig. 10) [8].

In general, for relatively low and higher voltages, it can be said that GO cannot be used as insulating material because for practical atmospheric conditions above 40^0 C, it does not show insulating behavior except for the temperature range between 90^0 C and 100^0 C and also below 10^0 C. Such temperature ranges, however, are very specific and do not generally satisfy ordinary industrial applications, especially in the high voltage industry. In very low voltages, i.e. in electronics applications, GO has in general a semiconducting character and as such is investigated in the scientific bibliography. In some specific cases, such as in very low humidity or in very low temperature, GO has an insulating behavior, which can have particular applications.

Cavity Considerations and Graphene Oxide

It is known that the electric field E_C inside an enclosed cavity in an insulating material of dielectric constant ε_r is given by the equation

$$E_C = 3\ \varepsilon_r\ E\ /\ (2\ \varepsilon_r + 1) \qquad (1)$$

where, E is the applied electric field to the insulating material.

It is also know that, assuming a uniform electric field E applied to the insulating material, the expected lifetime L is given by the equation

$$L = k\ (E\ d)^{-n} \qquad (2)$$

with k and n constants depending on the material and the quality of its construction, and d the thickness of the material.

Combining Equations (1) and (2), we have that

$$L = k\ [E_C\ d(2\varepsilon_r + 1)\ /\ 3\varepsilon_r]^{-n} \qquad (3)$$

which gives a relation between the lifetime of the material in terms of the thickness of the material.

Based on Fig. 11, and considering that in a sample the cavity has a radius R, the applied field to the sample is E, E_C is the field inside the cavity, d is the overall thickness of the sample and α as in Fig. 11, and having in mind that d = 2α + 2R, Equation (3) becomes]

$$L = k\ [2\ E_C\ (\alpha + R) * (2\varepsilon_r + 1)\ /\ 3\varepsilon_r]^{-n} \qquad (4)$$

Consequently we have a relation between the lifetime L and the radius R of the spherical cavity.

In the case of graphene oxide (GO), for temperature t = 90⁰ C and from Fig. 2b, the dielectric constant is given as $\varepsilon_r = 2$, f = 50 Hz, with insulation thickness d = 0.1 mm, k = 4, n = 10, we finally get the curve of Fig. 12. This shows the change in lifetime in hours w.r.t. the electric field E_c inside the cavity in GO.

It is evident from Fig. 12, that as the electric field becomes larger, lifetime becomes shorter with a given cavity size.

In the case of GO, for power frequency, and various temperatures T = –10⁰ C (from Fig. 1b we have $\varepsilon_r = 9$), T = 0⁰ C (from Fig. 1b $\varepsilon_r = 15$), T = 10⁰ C (from Fig. 1b, $\varepsilon_r = 21$), T = 90⁰ C (from Fig. 2b $\varepsilon_r = 2$), T = 100⁰ C (from Fig. 3b, $\varepsilon_r = 1.8$), we have correspondingly the lines L1, L2, L3, L4 and L5 in Fig. 13.

Fig. 13 shows the lifetimes in hours at various temperatures and in function of various electric field values inside the cavity in GO. We observe that lifetime changes w.r.t. temperature and therefore w.r.t. the dielectric constant of the material. Smaller dielectric constant means smaller lifetime.

From Equation (4), for a constant electric field value $E_c = 0.12$ kV/mm, k = 4, α = 1 mm, $\varepsilon_r = 2$, n = 10 and for different values of cavity radius, we find that the corresponding lifetime is

<u>Tab. 1</u>

R (mm)	L (hours)
0.2	6308812
0.1	15060285
0.05	23980986
0.01	35362772
0.005	37162029
0.001	38674015
0.0001	39023459

Cavities decrease the lifetime of insulation. By increasing the cavity radius R, lifetime decreases. As the cavity radius goes at about 0.001 mm and smaller, the difference in lifetimes becomes small or in other words, cavities of such magnitudes do not significantly decrease the lifetime of GO. It must be noted that the above Tab. 1 is rather qualitative rather than quantitative. It is evident from the above results that the electric behavior of GO depends on the temperature. In regions between 90⁰ C –100⁰ C as well as below 10⁰ C, GO presents insulating behavior. In normal applications, however, under normal atmospheric conditions, its insulating behavior is lost.

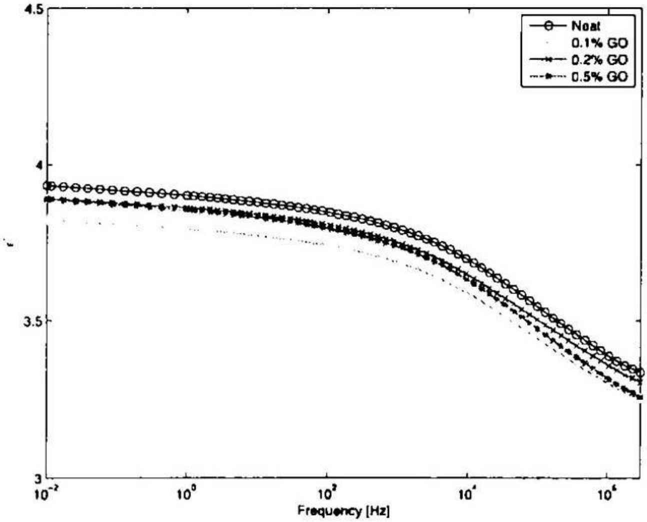


Fig. 9 Dielectric constant epoxy nanocomposite with GO at 20^{0} C

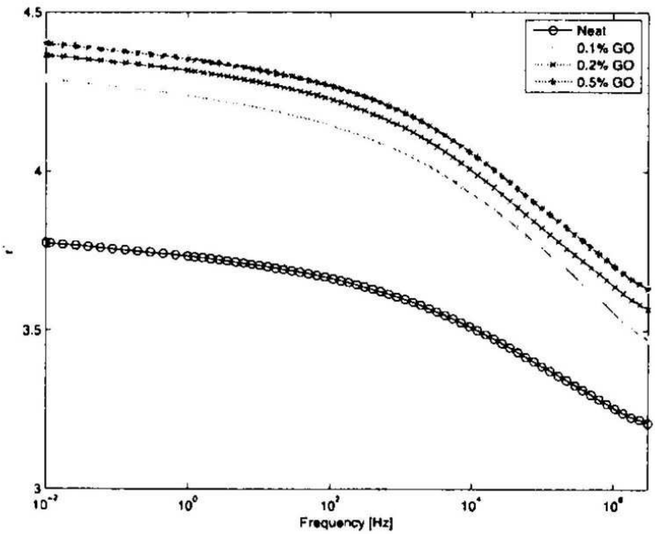


Fig. 10 Dielectric constant of epoxy nanocomposite with GO after thermal treatment

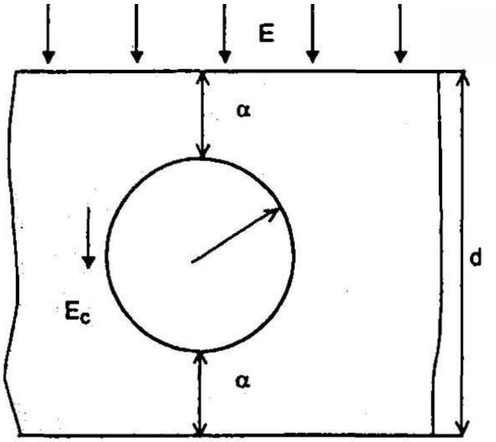


Fig. 11 Enclosed cavity in a solid dielectric

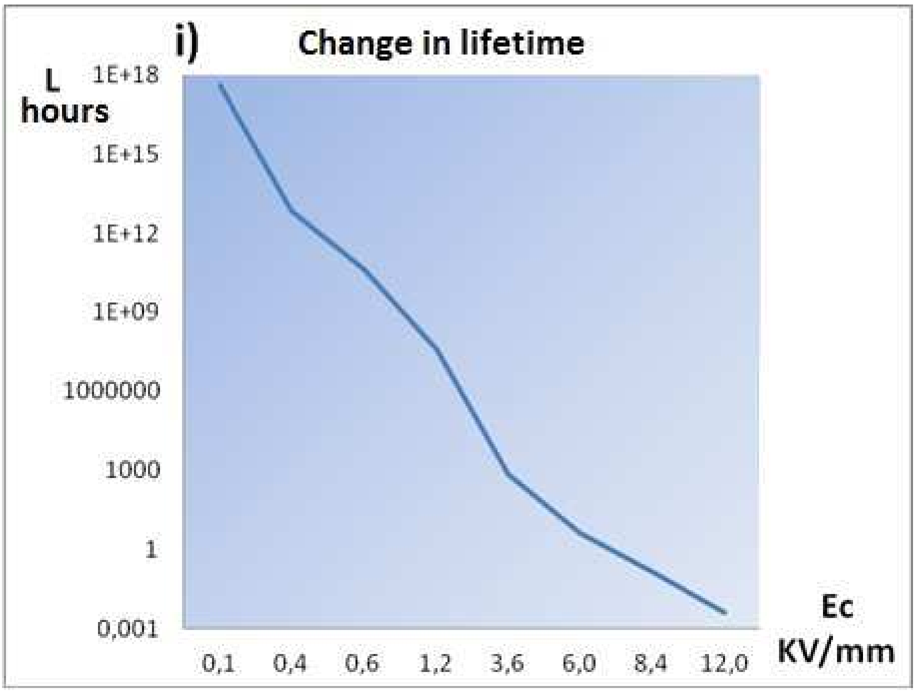


Fig. 12 Change in lifetime in (hours) with the electric field E_C in (KV/mm)

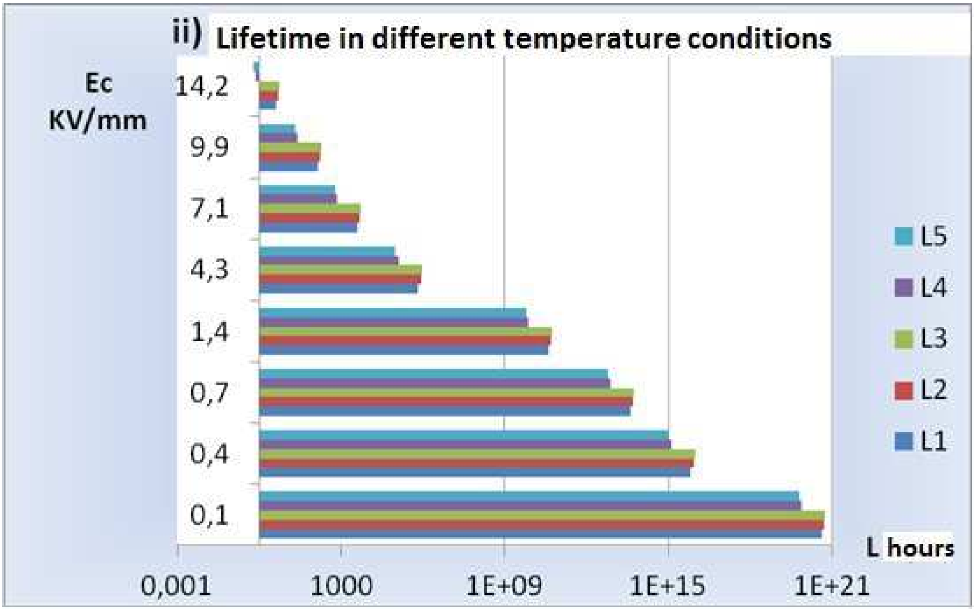


Fig. 13 Change in lifetime in (hours) with the electric field E_C in (KV/mm) and with different temperature conditions

Conclusion

Graphene is an excellent novel material for a variety of applications. However, graphene oxide is not suitable for high voltage applications since its insulating properties are confined to a small temperature range.

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* About The Authors

D.G. Mitrakas, received his degree from Democritus University of Thrace, Department of Electrical and Computer Engineering in May 2014. Since then, he is a self-employed electrical engineer with a particular interest in power systems applications.

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