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# A contribution from dielectric analysis to the study of the formation of multi-wall carbon nanotubes percolated networks in epoxy resin under an electric field

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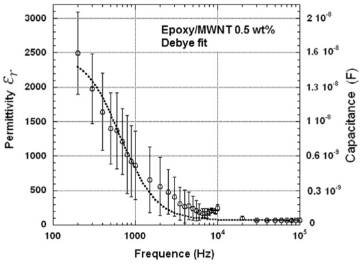
## HIGHLIGHTS

- We report the formation of percolating networks of MWNTs under AC electric field.
- MWNT/epoxy dielectric properties were measured by impedance spectroscopy.
- Lower percolation thresholds were obtained for composites with aligned CNTs.
- Application of AC electric field helps the debundling of CNTs.
- CNT/Epoxy with percolated networks presents interfacial and hopping polarizations.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The formation of percolation networks in epoxy matrix nanocomposites reinforced with multi-wall carbon nanotubes (MWNT) during the curing process, at different MWNT contents, was studied by using a parallel plate cell subjected to a 300 V/cm AC electric field at 1 kHz. The percolation was verified by the electrical current output measured during and after the resin curing. The behavior of electric dipoles was characterized by impedance spectroscopy and followed the Debye first order dispersion model, by which an average relaxation time of $6.0 \times 10^{-4}$ s and a cut-off frequency of 1.7 kHz were experimentally found. By applying the theory of percolation, a critical probability, $p_c$, equal to 0.038 vol% and an exponent of conductivity of 2.0 were found. Both aligned and random samples showed dipole relaxation times typical of interfacial and/or charge-hopping polarization, while the permittivity exhibited an exponential decrease with frequency. This behavior can be related to the increased ability to trap electrical charges due to the formation of the carbon nanotubes network. Optical and electron microscopies confirm the theoretical prediction that the application of an electric field during cure helps the process of MWNT debundling in epoxy resin.

## 1. Introduction

Carbon nanotubes (CNTs) are cylindrical structures with very high aspect ratio and surface area, having unique transport and mechanical properties [1,2]. CNTs can present conducting or

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semiconducting properties [3,4], which allows a wide range of applications in electronic materials, such as polymer matrix nanocomposites with electromagnetic shielding (EMI) and electrostatic discharge (ESD) properties, presenting bulk conductivities between $10^{-9}$ S/m and $10^{-1}$ S/m [5,6].

The electrical conductivity in polymer/CNT nanocomposites is generally explained by nanotube network formation, allowing the percolation of electric currents through the material. Even at low concentrations (<1 wt%), CNTs can increase the conductivity of epoxy matrices up to ESD levels [7,8]. However, to achieve high electrical conductivities at low CNT contents and better capability to shield electromagnetic waves, the alignment of CNTs is important [9–11].

Several experimental studies [12–15] show that AC or DC electric fields can help alignment and separation of nanotubes dispersed in polymer matrices, since these particles may be polarized and could be able to rotate or to translate in the presence of an electric field. The observed polarization can be attributed to the delocalized vibration of $\pi$ electrons of the $sp^2$ carbon atoms and should increase the process of repulsion between two parallel CNTs [16]. An outstanding review on this topic has been recently published [17].

Most of the alignment methods are based on AC external electric fields that can induce a dipole moment on metallic CNTs [18], which tend to align parallel to the field [19]. For a more comprehensive understanding of the process, and to know how the electric field influences charge migration and electric dipole reorientation in the nanocomposites, the measurement of the dielectric properties, such as permittivity, dielectric constant, and relaxation time, is essential. Another important factor is related to the cut-off frequency, which indicates the frequency at which the induced dipoles still respond to AC electric fields stimuli. At higher frequencies the alternating field is much faster than the speed of interfacial charges thus undermining the process of polarization and the possibility of jumping or tunneling of charges between sites [13,14]. Moreover, AC fields can promote, in addition to the nanotube alignment, a better dispersion of CNTs in the matrix, when compared to DC fields [10,12]. This is also a relevant issue, as one of the major technological obstacles for using CNTs is to debundle them, which is a serious limitation for making nanocomposites, nanocircuits and nanotransistors.

Yet many other factors influence the electron conductivity of the nanocomposites, including the polymer crosslinking process, which is directly linked to the matrix stiffness, and the interaction between the nanotubes and the matrix [8,19–21].

Nevertheless, there is a gap in the literature about the determination of the dielectric parameters (permittivity, relaxation time, cut-off frequency) for aligned multi-walled carbon nanotubes (MWNT) networks in epoxy nanocomposites over a wide frequency range. Thus, in this work, epoxy/MWNT systems were submitted to sinusoidal AC electric fields, during the curing process, to induce the alignment of nanotubes and to evaluate the influence of the crosslinking degree and CNT content on the formation of carbon nanotube networks. The systems were further characterized by electrical measurements (AC and DC electrical conductivity, electric hysteresis, electric permittivity, relaxation time of dipoles and capacitance) and morphological analyses (optical, transmission and scanning electron microscopies). The percolation threshold of the systems was determined according to the classical theory of percolation.

## 2. Experimental

### 2.1. Materials

The carbon nanotubes (MWCNT - CVD), used in this work were produced by Bayer Baytubes® and have a purity of 95%. Their diameters range from 5 to 20 nm and lengths of 1–10 μm. The polymer matrix consisted of bisphenol-A-based epoxy resin (Araldite GY 251) with an amine-based hardener (Aradur HY 956), obtained from Huntsman Advanced Materials. The solvent used was analytical grade acetone (Cinetica Quimica-Brazil).

### 2.2. Preparation of nanocomposites

Initially, the MWNT were dispersed in acetone by sonication (Sonics 750 W) and magnetic stirring, for 30 min at a power of 166 W. The epoxy resin was then added, followed by sonication and magnetic stirring for 40 min at a power of 250 W. The removal of solvent was carried out by heating the system under vacuum for 2 h. The samples were then cooled down to room temperature and the curing agent was added, at a 5:1 (w/w) epoxy:hardener ratio, and the system homogenized for 5 min.

The epoxy/MWNT dispersion was transferred to a polytetrafluoroethylene circular cell (6 mm thick) with two aluminum electrodes with an area of 45.4 cm$^2$. Samples introduced into the cell were subjected to sinusoidal electric fields with a frequency of 1 kHz, during the curing process.

### 2.3. Characterization

The electrical properties investigated in this work were: AC bulk conductivity during the curing process, DC conductivity (after curing), electrical permittivity (relaxation time of induced dipoles), and electrical capacitance.

Fig. 1 shows the experimental scheme used to determine the AC bulk electrical conductivity of the sample during the curing process (4 h). A sinusoidal generator with adjustable amplitude and frequency linked to an amplifier power (gain of 50 V/V and bandwidth of 200 kHz) was used to provide the electric field. The acquisition of the electric current was performed by using a True RMS ET-2907 Multimeter (Minipa) attached to a PC computer.

The DC electric conductivity was carried out through a DC voltage generator and an ammeter (Minipa). The measurements of voltage and electric current were made with sputtered gold electrodes (26 mm$^2$) in epoxy/MWNT systems with thickness of 1 mm, using three different samples for each composition. The permittivity values were obtained through phase analysis between voltage and current with the support of a Tectronics 2024B oscilloscope. DC conductivity and permittivity measurements were carried out at room temperature after 48 h of the curing process.

Characterization and comparison of clusters morphology were made by transmission optical microscopy (TOM) using an OLYMPUS CX31 microscope. Transmission electron microscopy

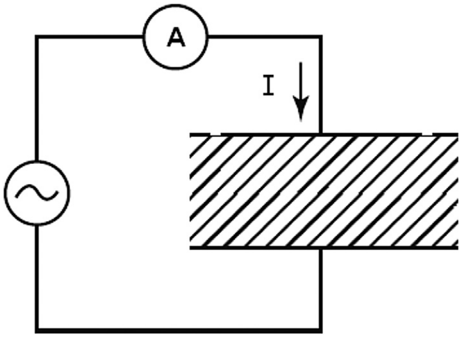

**Fig. 1.** Experimental scheme used to determine the AC electrical conductivity during the curing of epoxy/MWNT systems.

(TEM) analyses were carried out in a JEOL – JEM 1200ExII (120 kV) equipment in samples previously obtained with an ultramicrotome. Morphological characterization of the fractured surface of the samples was carried out on a Zeiss DSM 940A scanning electron microscope (SEM) at 15 kV.

Determination of gel-time of the epoxy system was performed following ASTM D 2471-99 standard. The temperature increase during the exothermic reaction, characteristic of the cure process, was also monitored.

## 3. Results and discussion

### 3.1. Formation of percolation networks

Fig. 2 shows the electric conductivity behavior of the nanocomposites during the curing process. During this period the systems were subjected to a 300 V/cm sinusoidal electric field with frequency of 1 kHz.

For the epoxy system without the addition of nanotubes it is observed that the electrical conductivity decreases gradually with time. This behavior is attributed to the crosslinking formation, reducing the concentration of potential charge carriers (unreacted amine and epoxy molecules) in the thermosetting polymer [12]. In contrast, in samples with MWNT it is observed an increase in electrical conductivity at the beginning of the process. This behavior suggests the rapid formation of aligned paths that promote the electric percolation through the material. The formation of these paths is related to the polarization and orientation of metallic CNT, due to the applied external electric field [12,19].

When the cure process advances, the electric conductivity reaches a maximum value and then starts to decrease. This is associated with the curing process that can disrupt the nanotube network [12]. Comparing the curves of temperature increase and electric conductivity in function of reaction time for a sample with 0.5 wt% MWNT (Fig. 3) it is evidenced a link between the gel-time and the decrease in electrical conductivity around 1500 and 2000 s.

In order to better understand this behavior it should be pointed out that during the alignment process, the CNT vibrate in response to external electric field, while the viscosity is low enough to permit mobility, facilitating electron tunneling between neighboring nanotubes. During this process some paths are formed on a permanent way due to the action of attractive forces (van der Waals). On the other hand, there are paths in which the distances between the nanoparticles are larger, but there is still the possibility of electron tunneling. However, when the resin reaches a high curing degree the CNTs can be separated from each other by the crosslink formation, causing loss of contact between neighboring CNTs and preventing the percolation process.

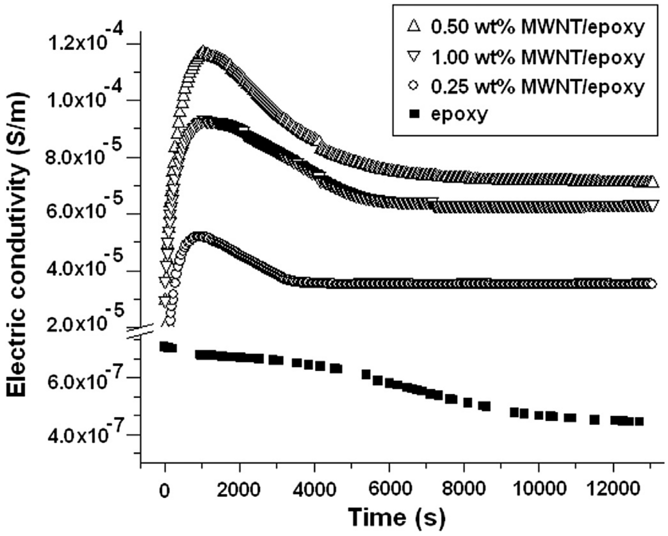

**Fig. 2.** Electric conductivity behavior of epoxy/MWNT nanocomposites during the curing process at a 300 V/cm sinusoidal electric field and frequency of 1 kHz, at room temperature, for different MWNT contents.

It is also worthy to note that the addition of CNTs resulted in a clear increase of the electric conductivity values, i.e. about two orders of magnitude, compared to the neat resin. However, this increase does not strictly follow the CNT content. For example, although the electric conductivity of specimens with 0.5 wt% was approximately twice that for samples with 0.25 wt%, specimens with 1.0 wt% CNTs presented slightly lower values compared to those with 0.5 wt%. A similar behavior, in certain other instances, has been also reported by other researchers [10,22–24], and several reasons can explain this phenomenon. The first, and probably the most important, are the strong van der Waals forces acting between CNTs. According to the simulations based on models of molecular dynamics (MD) using Lennard-Jones (LJ) potential, the energy interaction between two metallic nanotubes in contact (in parallel position) is around 40 $k_BT$/nm [25,26] and, in general, ropes of carbon nanotubes have around 10–20 nanotubes. Therefore, concentration of CNTs and dispersion state are strongly connected. The higher the concentration, the smaller the distance between CNTs, and agglomeration takes place. Second, if we assume a simplified view of the dispersion, where one can employ Stokes–Einstein relation to calculate the diffusion coefficient (D) [27] of one CNT in the system during the dispersion process in the resin, so

$$D = k_BT/6\pi r\eta \quad (1)$$

where $k_B$ is the Boltzmann's constant, T is the temperature, η is the dynamic viscosity, and r is the radius of a spherical particle (considering spherical CNT clusters [28]). Thus, it is possible to state that dispersion is inversely proportional to the viscosity of the media, and adding CNTs to epoxy resin undoubtedly increases the viscosity of the system [29]. Concluding, above a certain concentration limit (in this case located between 0.5 and 1.0 wt%), the difficulty to disperse the CNTs and their re-agglomeration can lower the number of paths to electrons to percolate through the system. Nevertheless, it must be stressed that this ‘concentration limit’ is far beyond the percolation threshold, which will be discussed in the next session.

Fig. 4 shows optical micrographs of a sample with 0.5 wt% MWNT after curing. It can be observed an orientation trend of the carbon nanotube clusters due to the electric field action during the cure process (Fig. 4a). However, when no electric field was applied during the cure (Fig. 4b) there were no trends of cluster orientation. It is also noticed the presence of CNT agglomerates in both cases. However, it is very clear that these are much smaller when the AC field is applied, evidencing an effective enhancement on the dispersion during the alignment process. Transmission electron micrographs (TEM) of an epoxy/0.5 wt% MWNT composite, after complete curing, show that the MWNTs dispersed around the clusters tend to align in parallel to the applied field (Fig. 5a). On the other hand, in agreement with the optical microscopy images, a totally random distribution is observed for a sample cured in the absence of AC field (Fig. 5b).

Fig. 6 shows a scanning electron micrograph (SEM) of a nanotube cluster. It is observed that most of the MWNT detach from the epoxy matrix by a pull-out mechanism, evidencing a relatively low nanotube/matrix interaction.

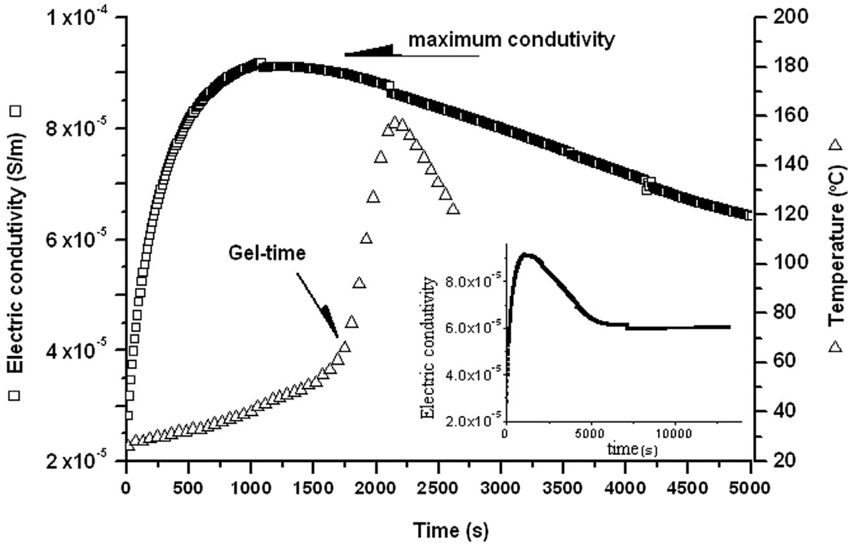

**Fig. 3.** Relationship between the temperature and the decrease in electrical conductivity during the curing process for a sample with 0.5 wt% MWNT.

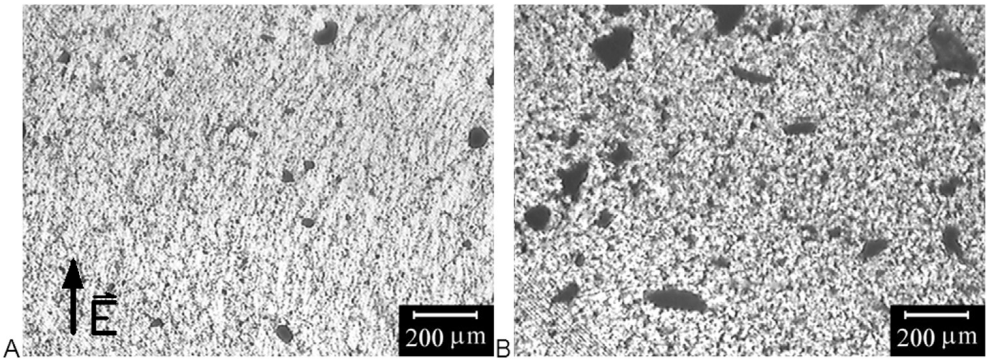

**Fig. 4.** Optical micrographs of a sample with 0.5 wt% MWNT after curing. (A) Orientation of carbon nanotube clusters due to the electric field action during the cure process. (B) No trends of cluster orientation are observed in the absence of electric field during the cure.

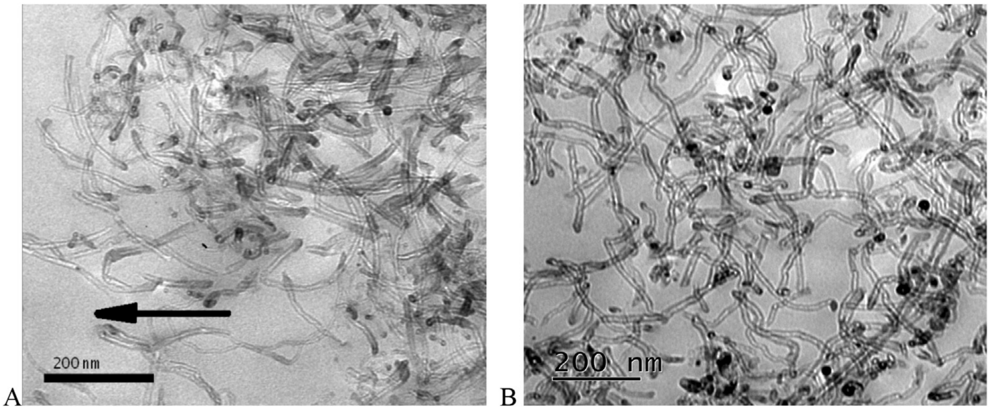

**Fig. 5.** TEM images of 0.5 wt% MWNT/epoxy nanocomposites: (A) sample cured under an AC electric field, showing the tendency to alignment of the MWNTs dispersed around the clusters near from electrodes due the influence of the field; (B) sample cured in the absence of electric field.

### *3.2. Determination of percolation threshold*

The electrical behavior of epoxy matrix nanocomposites with different contents of randomly dispersed MWNT is presented in Fig. 7. Composites with lower MWNT contents (0.05 and 0.10 wt%) showed also lower conductivity values, around $10^{-8}$ S/m. Much higher conductivity values are reached with 0.25 and 0.50 wt% MWNT, in the order of $10^{-4}$ and $10^{-3}$ S/m, respectively. This behavior can be explained by using the concepts of percolation theory [30]. According to the theory, the DC conductivity of the

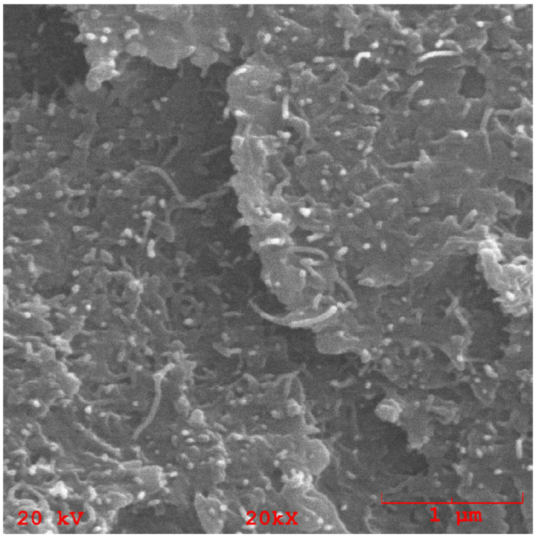

**Fig. 6.** Scanning electron micrograph of a fractured surface of an epoxy/0.5 wt% MWNT nanocomposite.

material is proportional to the volume fraction of the component responsible for electrical conduction, in this case the CNTs, obeying the following relationship:

$$\sigma\alpha(\rho - \rho_c)^{\mu} \qquad (2)$$

where σ is the DC conductivity, p is the volume fraction of CNTs, $p_c$ is the critical volume fraction and μ is the conductivity exponent. The conductivity exponent μ is related to the geometry of the system and usually takes values around 1.3 and 2 for two-dimensional and three-dimensional systems, respectively and $\mu > 2$ if system is anisotropic [30]. According to the experimental data and curve fit it was possible to determine the values for the critical concentration and the conductivity exponent, (0.038 ± 0.007) vol% and 2.1 ± 0.1, respectively. The value 0.038 vol% (~0.07 wt%) is relatively near from the percolation threshold found in the work of Sandler et al. [31] which was between 0.0225 wt% and 0.04 wt%. In another work, values in the order of 0.0025 wt% were found for oriented MWNT [32], but in that case the length and diameter of the aligned nanotubes were three times larger than those used in this work. More recently, higher values for the percolation threshold have been reported, ranging from 0.02 to 0.5 wt% [8,10]. The values found for the critical concentration must be associated with the dispersion process, limited length of the nanotubes and their average diameter, as well as the dispersion state of MWNT in the polymer matrix, requiring smaller or larger volume fractions to form the electric percolation path.

### 3.3. *Electric permittivity*

The variation in the real component of permittivity and the capacitance behavior over the frequency range, 200 Hz to 100 kHz, for composites containing 0.5 wt% MWNT randomly distributed in the epoxy matrix is presented in Fig. 8. The real component, often called the relative permittivity, is responsible for storing energy and it is proportional to the charges stored in a capacitor. The spectrum shows that the relative permittivity decreases with increasing the frequency, reaching a value of 66 ± 2 for a frequency of 100 kHz.

It is considered that the frequency dependence of the dielectric constant of the MWNTs composites comes from three effects: (a) dispersion of MWNTs in polymer matrix; (b) polarization effects between MWNT clusters inside the mixture, and (c) anomalous diffusion within each cluster [33]. When in the presence of an AC electrical field, the charges move inside the MWNTs clusters according to the direction of the electrical field in each half cycle, and accumulate at the epoxy/MWNTs interfaces in the aggregates, imparting a dipole moment to a whole cluster in an isolated aggregate. The interfacial polarization in MWNT composites usually causes a high frequency dependence of the dielectric properties, being strongly affected by both the concentration and the characteristic of the nanotubes [34].

This behavior is an indicative that the highest levels of charge storage are found at lower frequencies (<10 kHz) and can be described by the Debye first-order dielectric dispersion model:

$$\varepsilon' = \varepsilon_{\infty} + \frac{\varepsilon_S - \varepsilon_{\infty}}{1 + (\omega\tau)^2} \qquad (3)$$

where ε′ is the real component of permittivity, $\varepsilon_s$ is the permittivity

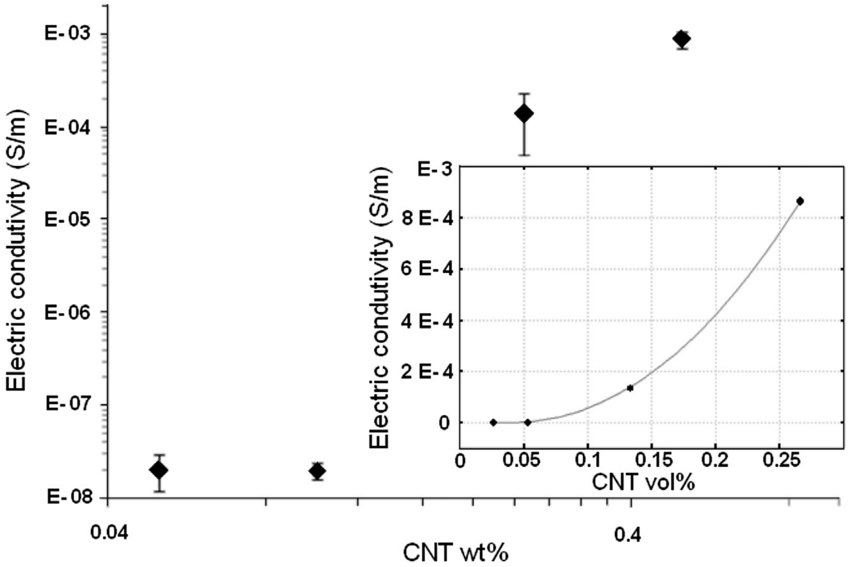

**Fig. 7.** Electrical behavior of epoxy matrix nanocomposites with different contents of randomly dispersed MWNTs. The inner graph shows the data fitting using Equation (1).

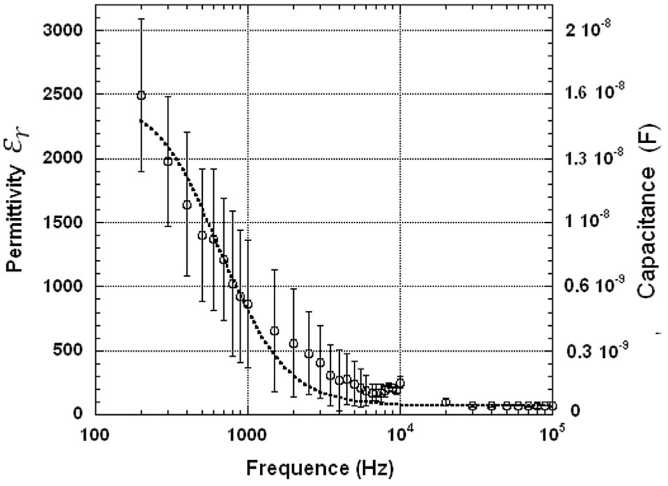

**Fig. 8.** Permittivity and capacitance spectrum of nanocomposites containing 0.5 wt% MWNT.

at low frequencies, $\varepsilon_\infty$ is the permittivity at high frequencies, ω and τ are the angular frequency of the electric field and the relaxation time of dipoles, respectively. This model is usually used to describe phenomena of absorption and dispersion in dielectric materials, but do not consider interactions between the particles. Other models, considering micromechanics based on the Mori-Tanaka [35] and composite cylinders [36] methods, can be used to introduce the effects of the interaction between nanotubes. Nonetheless, the Debye model, while simple, captures the essential physics of the problem and fits very well with the data obtained in this work.

By using Equation (3) it was possible to determine the relaxation time of the electric dipole ($6.0 \times 10^{-4} \pm 0.2 \times 10^{-4}$) s and the cut-off frequency, $\omega_0 = \tau^{-1}$, equal to 1.7 kHz, at room temperature. Above this level the dipoles do not respond efficiently to stimuli of the field. It is noted that the major capacitance level is obtained at frequencies smaller than the cut-off frequency (around $1.6 \times 10^{-8} \pm 0.4 \times 10^{-8}$ F at 200 Hz), due to dipoles stored at the nanotube/matrix interface. This behavior is related to the required time for the occurrence of charge motion at the interface between the nanotubes and the polymer matrix, since there is an inertial polarization due to the interaction between the constituents. There is the possibility that these charges jumped from one CNT neighbor to another, creating hopping polarization. This phenomenon also occurs in semiconductors, depending on the width and the height of the potential well, electrons can jump or tunnel from one site to another [37].

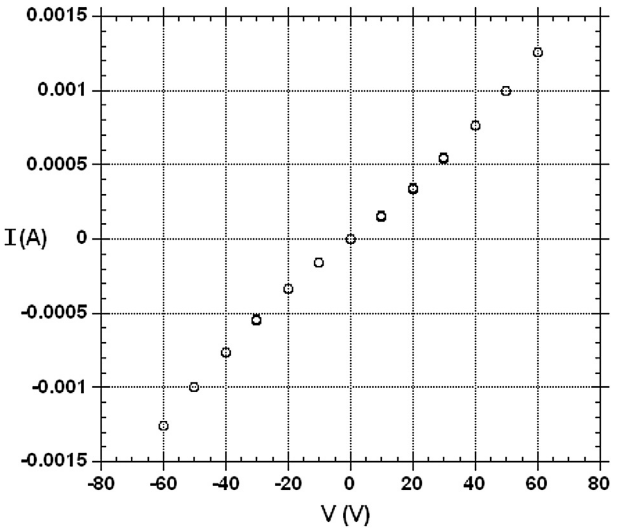

**Fig. 9.** Electrical current vs DC voltage plot for a 0.5 wt% MWNT nanocomposite.

Fig. 9 show the relationship between DC voltage and electric current of a sample with 0.5 wt% MWNT. The result indicates an ohmic behavior and that the nanocomposites do not present hysteresis. Considering the experimental parameters used here, i.e., room temperature and CNT concentration above the percolation threshold, the observed ohmic behavior was therefore expected, based on the results reported in the literature [38–41]. This ohmic nature indicates resistive contacts between CNTs in the composite, evidencing the formation of a percolating network. Thus, at sufficiently high concentrations of CNTs, such as 0.5 wt%, the composite behaves as a conductor. However, the relatively low maximum conductivity (around $10^{-3}$ S/m) corroborates the hypothesis of an insulating polymer layer between some CNTs or bundles, as proposed by other researchers [32,42].

## 4. Conclusion

The results indicate the possibility of manipulating carbon nanotubes in epoxy systems by applying an external electric field during the cure process, since CNTs may rotate and translate in viscous media. Therefore, it is possible to produce nanocomposites with controlled bulk electric conductivity and monitor the cure process, since a close relationship between conductivity and gel-time was found. The conductivity exponent and critical concentration found by the percolation theory were 2.0 and 0.038 vol%, respectively.

The dielectric parameters of aligned multi-walled carbon nanotubes (MWNT) networks in epoxy nanocomposites, over a wide frequency range, have been determined by impedance spectroscopy. The nanocomposites with CNT concentrations above the percolation threshold followed the Debye first order dispersion model, presenting interfacial and hopping polarizations with relaxation time and cutoff frequency of ca. $6.0 \times 10^{-4}$ s and 1.7 kHz, respectively. Nevertheless, the results confirm theoretical predictions showing that it is possible to use an AC electric field during the cure of epoxy resins to help the debundling of CNTs.

## Acknowledgments

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