Modeling Carbon Nanotube Electrical Properties in CNT/Polymer Composites

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Abstract In this work it is demonstrated that the capacitance between two cylinders increases with the rotation angle and it has a fundamental influence on the composite dielectric constant. The dielectric constant is lower for nematic materials than for isotropic ones and this can be attributed to the effect of the filler alignment in the capacitance. The effect of aspect ratio in the conductivity is also studied in this work. Finally, based on previous work and by comparing to results from the literature it is found that the electrical conductivity in this type of composites is due to hopping between nearest fillers resulting in a weak disorder regime that is similar to the single junction expression.

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1 Introduction

One attempt to increase the application range of polymers is to incorporate nanoscale fillers, which usually have intrinsically high electrical conductivity, into the polymeric matrix. Among nanoscale modifiers, carbon nanotubes (CNT) present high electric conductivity (103–104 S/cm), and high tensile strength [1]. These facts, coupled to their relatively easy incorporation and dispersion in polymers, also raised the interest in CNT to provide solutions to some problems in composite applications [2–4]. However, in order to properly tailor the composite material properties for specific applications, the relevant conduction mechanisms must be better understood, in fact for these particular composites, the nanotube concentration, aspect ratio, and dispersion significantly affects the material response [2–4].

Models have been developed that can predict, to some extent, the effect on the permittivity of adding conductive fillers to a lossless dielectric matrix [5, 6]. The effective mean-field medium concept is the foundation for most of the empirical models. The main drawback of these models is that they fail to predict the composite dielectric behavior near the percolation threshold, defined as the critical point where the physical properties have singularities and show scaling behavior [7, 8].

The inclusion of carbon conductive fillers in a dielectric matrix enhances composite electrical properties. The most remarkable aspect of these composites is that after the percolation threshold—the critical point where physical properties strongly change—there is a high divergence in the electrical properties. This is explained with the formation of a network system of the fillers and by the decrease of the correlation length ($\xi \sim |p - p_c|^{-\nu}$) for increasing mass fraction of the fillers as stated by the percolation theory [9, 10]. The correlation length is the average distance of two sites belonging to the same cluster, and the percolation exponent v has the value ~ 0.88 for 3D percolation. Most physical quantities diverge at the percolation threshold and this divergence can be related with the correlation length. For instance, the conductivity (Σ) of random mixtures of superconducting (fraction p) and normal-conducting ($1-$p) elements, near the percolation threshold has a power law dependence ($\Sigma \sim |p - p_c|^{-s}$). The exponent s also appears in the critical behavior of the dielectric constant in random systems [9]; it is called the superconducting exponent and has the value of 0.75 ± 0.04 [11] for the 3D case.

In this way, the composite dielectric constant near the percolation threshold can be predicted by the power law in Eq. (1) [12–14].

$$\varepsilon_{\mathrm{eff}} \propto |\Phi_c - \Phi|^{-s}, \Phi \rightarrow \Phi_c \tag{1}$$

where s is a universal critical exponent that depends only on the system dimension, Φ is the volume fraction and Φc is the critical concentration at which an infinite cluster appears. For $\Phi > \Phi$c, a cluster spans the system, whereas for $\Phi < \Phi$c there is no spanning cluster and the system is comprised of many small clusters.

Several numerical models have been developed studying the effect of adding conductive fillers to a low loss dielectric matrix on the composite dielectric constant and dielectric strength. They can be divided in lattice-based models [15–18] and continuum models [19, 20], however, the latter models do not take the inclusion of high-aspect ratio fillers in consideration for the calculation of the composite effective dielectric constant. In a previous work [21] it was demonstrated that the critical concentration is related to the formation of capacitor networks and that these networks give rise to the high variations in the electrical properties of the composites. It is demonstrated that the dielectric constant and the dielectric strength of the composite are highly dependent on the distribution of the nanotubes, resulting in high deviations of the electrical properties.

The composite conductivity is generally described by the percolation theory [12–14], predicting a power law relation, as shown in Eq. (2).

$$\sigma \propto \sigma_0 (\Phi - \Phi_c)^t, \Phi \rightarrow \Phi_c \tag{2}$$

where t is a universal critical exponent that depends only on the system dimension. Interestingly, the predictions of the percolation theory and the excluded volume theory are not verified for CNT/polymer composites, as can be seen in recent reviews [2, 22]. In addition in studies on the percolation and excluded volume theory, several authors tried to cope with the effect of the volume fraction, clustering and anisotropy in the conductivity of CNT/polymer composites. In this section, the most relevant studies to our work will be reviewed. Dalmas et al. [23] modeled the conductivity in 3D fibrous networks using "soft-core" cylinders. They studied the effect of fiber tortuosity and fiber–fiber contact conductivity in the composite electric conductivity. It was found a good agreement between simulation and experimental results with one adjustable parameter, the fiber tortuosity. The latter authors also demonstrate that an increase of the fiber tortuosity decreases the fiber radius of gyration leading to a smaller effective aspect ratio. The existence of contact conductivity was also proposed by Hu et al. [24] using "soft-core" cylinders. The influence of aspect ratio, electrical conductivity, aggregation and shape of CNT in the composite electric conductivity was also studied. It was found, similarly to Dalmas et al. [23], that the percolation threshold increases with the fiber tortuosity. Nonetheless, the fiber tortuosity has a limited effect on the global composite conductivity. In addition, Hu et al. [24] found that the aggregation has a significant effect on the composite conductivity: the composite conductivity decreases with increasing aggregation. The contact resistivity was also investigated by Sun et al. [25] in a continuum model. The authors conclude that the contact and tunneling resistance must be controlled in order to achieve high conductive CNT/polymer composites. Finally White et al. [26] investigated the effect of CNT orientation using "soft-core" cylinders. It was found that there is a critical degree of orientation above which the electrical conductivity decreases. The work of Berhan et al. [27, 28] demonstrated that the use of hard-core fibers is more appropriate for modeling the electrical percolation onset in nanotube-reinforced composites. In the same work they also verified that the percolation threshold is independent of the fiber waviness for high aspect ratio fibers. Thus, the CNT can be modeled as a straight cylinder-hard-core ones—with an effective aspect ratio.

Carbon nanofiber/epoxy conductivity can be described by a single junction expression [29]. In recent work [30, 31] it was established that the conductivity for CNT/polymer composites is due to hopping between nearest fillers resulting in a weak disorder regime that is similar to the single junction expression. Also in [30], a new formula for the percolation threshold was proposed and speculated that a good cluster distribution will give better electrical properties. It was also demonstrated that the formation of a capacitor network is the key aspect for the dielectric response of the composite. Computer simulations and experimental results show that the conductivity of CNT/polymer composites can be described by hopping between nearest fillers resulting in a weak disorder regime. It was shown that when hopping between fillers is introduced in the composite conductivity simulation, using hard-core cylinders, no critical degree of orientation is found above which the electrical conductivity decreases, in contrast to the work of White et al. [26].

2 Results and Discussion

The effects of the relative orientation of the nanotubes and the distance between them on the capacitance are some of the key parameters defining the final macroscopic response of the nanocomposites. Figure 1 shows the capacitance variation for a pair of cylinders when the relative orientations are changed, for the calculation of the capacitance, it was used a capacitance extraction algorithm as described in [32].

The results for the capacitance with increased rotation angles are shown in Fig. 1. In this study, the cylinders are initially placed parallel to each other, with an axial orientation along the y-axis. Then, the capacitance is calculated under maintaining the first cylinder fixed and rotating the other cylinder about the x-axis, or about the z-axis.

There is a significant influence of the rotation of the cylinder about the z-axis, since the distance between cylinders decreases considerably, in fact up to half the original distance at 90° and 270° rotation angles (even though the surface area that is at the minimum distance at these angles is much smaller than at 0° and 180°). However, the capacitance is not significantly affected by rotation about the x-axis, even at a 90° rotation angle, implying that in practical terms, the distance has a much stronger effect than the rotation angle.

The value of the capacitance does not change considerably with the rotation around a plane parallel to the fixed cylinder. This occurs because even at large rotations of one cylinder about the x-axis, only the center region of the two cylinders are at the minimum distance between them but the distance between any other points on the surface of the two cylinders is not significantly different.

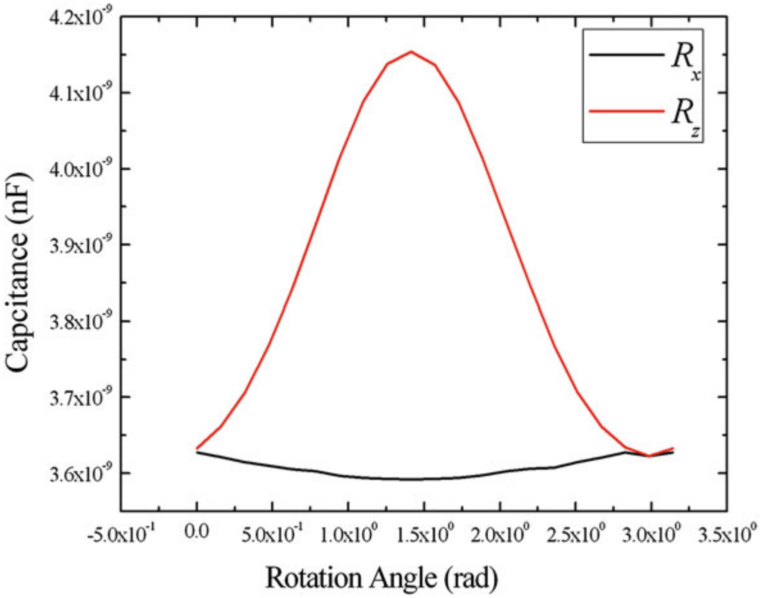

Fig. 1 Capacitance variation for a pair of cylinders when the relative orientations are changed

The influence of the filler–filler capacitance in the composite dielectric constant can be seen in [33]. In [33] it is presented the results for the dielectric constant for cylinders with an isotropic distribution and a nematic distribution. The latter results are then compared with two different aspect ratios. The fact that nematic materials show a lower dielectric constant than isotropic ones is related to the zenith angle. It was demonstrated in Fig. 1 that parallel cylinders exhibit a lower capacitance, so the lower value for the composite dielectric constant is related to the filler alignment.

One important aspect in this type of composites is the conductivity for different aspect ratio as presented in Fig. 2. The details of the simulation can be found in [31]. As can be seen the conductivity increases with increasing aspect ratio. Applying the power law defined by the percolation theory, Eq. (2) with the equation for the percolation threshold presented in [30], results in $t \sim 1.0$ with $R^2 \sim 0.97$ for all fits. The latter value for the critical exponent is equal to that predicted by the effective medium theory [10] (EMT). The fact that the value for the critical exponent deviates from the classical ones in a 3D dimension system ($t = 2$) can be related with the way that the network is formed and can be also a consequence of the used formula for the percolation threshold. This point is very interesting and is being studied analytically. It is to notice that experimental values found in the literature [22] range from 1 to 4. The observed increase of the conductivity with the aspect ratio is in agreement with [24] and can be explained by a decrease in the percolation threshold for increasing filler aspect ratio. Also in [31] it is presented the value of the composite conductivity for different degrees of

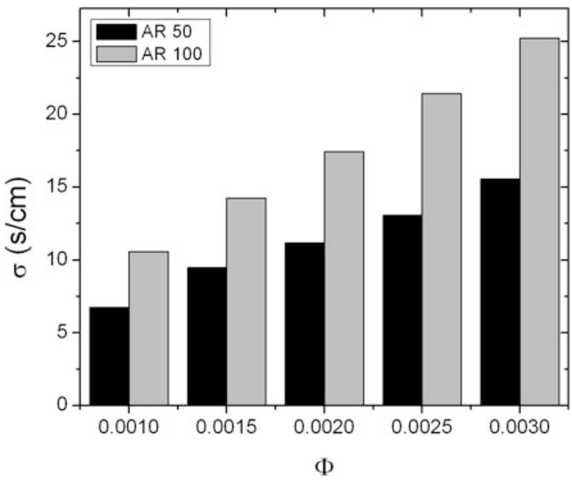

Fig. 2 The influence of the aspect ratio on composite conductivity

axial alignment, as per Eq. (3), and different volume fractions. A decrease in the conductivity for the more anisotropic composites can be observed, with this effect being more prominent at higher volume fractions.

$$S = \left(3\langle\cos^2\theta\rangle - 1\right)/2 \quad (3)$$

It should be noted that in our simulations the conductance of the cylinder (CNT) is independent of the filler length, contrary to [23–25]. Furthermore, as the present model does not assume a contact resistance, the composite conductivity results only from the CNT with $\delta_{\max}$ controlling the hopping length for the same aspect ratio. In this way, $\delta_{\max}$ is a parameter that can be associated to the dielectric matrix, i.e., different types of polymer will correspond to different values of $\delta_{\max}$. For instance, in epoxy composites, increasing the post-cure temperature will increase the cross-link density [34] increasing the composite conductivity [35]; this can be seen as an increase on the value of $\delta_{\max}$.

Comparing to the results in [26], a critical value for the axial alignment is not observed, but only a decrease in conductivity. This decrease in conductivity can be explained by an increase of the number of fillers that is necessary to transverse the domain between the applied electrodes. Increasing the number of fillers will increase the number of resistors and hence decrease the conductivity. Thus, increasing anisotropy changes the conductivity to lower values due to a higher number of fillers that are necessary to transverse the domain. Furthermore, as the number of fillers in the domain increases—by increasing the volume fraction—the difference between isotropic and anisotropic composite conductivity will be larger.

In [31] it is also demonstrated that there is a substantial difference in the conductivity between cylinders aligned perpendicular (S = 1) and parallel (S = −0.5)

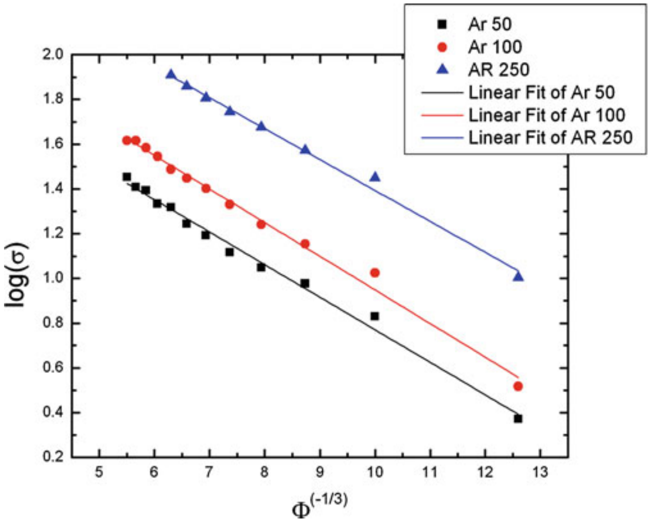

Fig. 3 Logarithm plot of the conductivity for three types of fillers versus volume fraction

to the measurement direction. This difference in conductivity is in agreement to recent experimental work [36], and is explained by the higher number of fillers necessary to transverse the domain (S = 1), which has a lower bound when S = −0.5.

In Fig. 3 it is presented the results of the linear fits of log(σ) $\sim\Phi-1/3$ for the latter simulations. As described in [31] it was used for the conductivity, in the performed simulations, hopping between nearest neighbors.

The linear fits in Fig. 3 have a $R^2\sim 0.99$ and we also like to stress that the same results were obtained for carbon nanofibers composites [29, 37, 38]. The latter linear fits indicates that the main conduction mechanism for composites where the filler is a CNT is due to hopping between nearest fillers resulting in a weak disorder regime that is similar to the single junction expression, as discussed in [30].

In [29] it was observed that the composites have some clusters that are evenly distributed in the domain and in [30] it is proposed that a highly dispersed cluster can raise the composite conductivity. This latter indication must be further tested but is an important aspect that must be considered in designing the CNT/Polymer composites for specific applications.

3 Conclusion

In this work it is demonstrated that the capacitance between two cylinders increases with the rotation angle between them and it has a fundamental influence on the composite dielectric constant. The dielectric constant is lower for nematic materials than for isotropic ones and this can be attributed to the effect of the filler alignment in the capacitance. Also in this work it was studied the effect of aspect ratio on the conductivity. Finally, based on early work, and by comparing to results from the literature, we found that the conductivity in this type of composites is due to hopping between nearest fillers resulting in a weak disorder regime that is similar to the single junction expression.

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