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The influence of matrix mediated hopping conductivity, filler concentration, aspect ratio and orientation on the electrical response of carbon nanotube/polymer nanocomposites

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Abstract

A model to simulate the conductivity of carbon nanotube/polymer nanocomposites is presented. The proposed model is based on hopping between the fillers. A parameter related to the influence of the matrix in the overall composite conductivity is defined. It is demonstrated that increasing the aspect ratio of the fillers will increase the conductivity. Finally, it is demonstrated that the alignment of the filler rods parallel to the measurement direction results in higher conductivity values, in agreement with results from recent experimental work.

Keywords: A. Nano composites; A. Polymer-matrix composites; B. Electrical properties; C. Modelling

Introduction

One attempt to increase the application range of polymers is through the incorporation of nanoscale fillers with intrinsically high electrical conductivity into the polymeric matrix. Among nanoscale modifiers, carbon nanotubes (CNT) present high electric conductivity (10^3 - 10^4 S/cm) and tensile strength [1]. These facts, together to the relatively easy incorporation and dispersion into polymers, raised the interest in CNT to provide solutions to some problems in composite applications [2]. In order to be used in tailored composite applications, the conduction mechanism must be understood. The composite conductivity is generally described by the percolation theory [3], predicting a power law relation:

$$\sigma \propto \sigma_0 (\Phi - \Phi_c)^t, \text{ for } \Phi > \Phi_c \quad (1)$$

where t is a universal critical exponent that depends only on the system dimension, Φ is the volume fraction and Φ_c is the critical concentration at which an infinite cluster appears. For $\Phi > \Phi_c$, a cluster spans the system, whereas for $\Phi < \Phi_c$ the spanning cluster does not exist and the system is comprised of many small clusters. 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 [4, 1]. In addition to 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. Dalmás *et. al.*[5] modelled the conductivity in 3D fibrous networks using “soft-core” cylinders. They studied the effect of fibre tortuosity and fibre-fibre contact conductivity in the composite electric conductivity. It was found a good agreement between simulation and experimental results with one adjustable parameter, the fibre

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.* [6] 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.*[5], that the percolation threshold increases with the fibre tortuosity. Nonetheless, the fibre tortuosity has a limited effect on the global composite conductivity. In addition, Hu *et. al.*[6] found that the aggregation has a significant effect on the composite conductivity: the composite conductivity decreasing with increasing aggregation. The contact resistivity was also investigated by Sun *et. al.*[7] in a continuum model. The authors conclude that the contact and tunnelling resistance must be controlled in order to achieve high conductive CNT/polymer composites. Finally White *et. al.* [8] 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.* [9] demonstrated that the use of a 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. Therefore, it can be concluded that CNTs can be modeled as straight hard core cylinders with a given effective aspect ratio.

In a previous paper [10], we demonstrated that CNT/Epoxy conductivity can be described by a single tunnel junction expression: $\sigma_{DC} = \sigma_0 \exp(-2\chi_t d)$ [11], where

$\chi_i = \sqrt{2mV(T)/\hbar^2}$, m represents the mass of the charge carriers, d the barrier width and $V(T)$ the temperature modified barrier height [12]. In the present work, it is shown that the polymer matrix can also play an important role in the overall conductivity of the composites and that hopping mediated by the polymer matrix can explain the conductivity of CNT/polymer composites. In this way, a new model, based on “hard-core” cylinders with no contact resistance, is proposed.

Results and discussion

The influence of the matrix mediated hopping conductivity on the composite conductivity for different values of the aspect ratio and filler orientation was studied. For isotropic composites, fibers are initially positioned in 3D space with a derivation of a sequential packing algorithm [13-15]. In this process, a cylinder position is accepted if the minimum distance to any other cylinder is larger than the cylinder diameter; otherwise, the position is rejected and a new one is tested until it can be placed. This process is repeated until the desired volume fraction is achieved. Once the generation of the composite is completed, a resistor network is extracted by assigning a resistor between two rods that are at a minimum distance lower than some threshold, δ_{\max} , the maximum value for the minimum separation distance. To complete the process we extract the list of connected bonds using the depth-first search algorithm [16]. After the generation of the microstructure, the conductivity can be found using the matrix representation for a resistor network and the Kirchhoff's current laws [17]. More precisely, the linear system is solved using the incomplete Cholesky conjugated gradient method. A range of volume fractions were generated in a cube of side 25000 nm for isotropic cases corresponding to a range of

~800 to 14000 cylinders with length 5000 nm and a diameter value that depends on the aspect ratio, no periodic boundary conditions were used. Five different materials were evaluated and an error of 5% in the calculated conductivity was determined. For the anisotropic study, the axial orientation parameter is initially defined as:

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

where S varies from -0.5 to 1; 0 for a isotropic composite (Figure 1, left), 1.0 for cylinders with a parallel orientation (Figure 1, right) and -0.5 for cylinders with perpendicular orientation. In our case, $S=1$ corresponds to a composite with cylinders oriented perpendicular to the measurement direction and $S=-0.5$ to cylinders oriented parallel to the measurement direction. For the anisotropic materials the zenith angle is determined by a Gaussian distribution in $\cos \theta$ and randomly placement of the cylinders in domains following the previous stated procedure for the isotropic composites. The alignment was evaluated using Equation (2) and a range of volume fractions were generated in a cube of side 25000 nm which corresponds to ~800 to 10000 cylinders with length of 5000 nm and a diameter of 50 nm.

It has been previously demonstrated that the conductance of CNT/polymer composites can be explained by a transition from a strong disorder regime into a weak disorder one [18]. With the latter in mind, the bonds between two fillers have an assigned conductance defined as:

$$G = G_0 e^{-a[0,1]} \quad (3)$$

where G_0 is the filler conductance for metallic armchair CNT having the value of $4e^2/h$ [18], with e being the electron charge, h the Planck constant, a a constant that controls the disorder strength and $[0,1]$ the interval of a uniform distribution between 0 and 1. Equation (3) is similar to the expression of Miller *et. al.* [20] for hopping at room temperature: $\sigma_{ij} = \sigma_0 \exp\left(-\frac{x_{ij}}{x_0}\right)$, where x_{ij} is the distance between two fillers – in our case the minimum distance between two rods; x_0 is the scale over which the wave function decays in the matrix and σ_0 the dimension coefficient. It is assumed that the CNTs are rigid and randomly placed. For the simulated volume fractions, CNT-CNT contact will occur with a very low probability. In this way, contact resistance is not included in the simulations.

Also in [18], the following relation is obtained for isotropic composites:

$$\Phi_c = \frac{D^2}{2\delta_{\max} L} \quad (4)$$

where D is the fiber diameter, L the fiber length and δ_{\max} the maximum value for the rod minimum separation distance related to the conduction mechanism: hopping. Equation (4) is similar to the one obtained in [21]. The disorder constant “ a ” is related to δ_{\max} [18] and in this work we restrain ourselves to the weak disorder regime. This regime has already been observed experimentally [10,18,22] and can be described by the following linear relation: $\log(\sigma) \sim \Phi^{-1/3}$ [18]. For that, we set $\delta_{\max} = \xi$, with ξ being the correlation length that depends on the length of the optimal path between two fillers [18]. Resulting in “ a ” value close to the unit, meaning, in the weak disorder regime where all bonds contribute to the conductivity.

The conductivity for different aspect ratio is presented in Figure 2: The conductivity increases with increasing aspect ratio. Applying the power law (Figure 2 inset) defined by the percolation theory, Equation (1) with Equation (3), 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 [17] (EMT). The fact that the value for the critical exponent deviates from the classical ones in a three dimensional system ($t=2$) is related to the way in which the network is defined and it is also a consequence of the used formula for the percolation threshold. It is to notice that the experimental values for t found in the literature [4] range from 1 to 4. The observed increase of the conductivity with the aspect ratio is in agreement with [6] and can be explained by a decrease in the percolation threshold for increasing filler aspect ratio.

It should be noted that in our simulations the conductance of the cylinder (CNT) is independent of the filler length, contrary to [5-7]. Furthermore, as the present model does not assume a contact resistance, the composite conductivity results only from the CNT with δ_{\max} controlling the hopping length for the same aspect ratio. In this way, δ_{\max} is a parameter that can be associated to the dielectric matrix, i. e., different types of polymer will correspond to different values of δ_{\max} . For instance, in epoxy composites, increasing the postcure temperature will increase the cross-link density [23] increasing the composite conductivity [24]; this can be seen as an increase on the value of δ_{\max} .

Figure 3 shows that the conductivity increases with δ_{\max} for fibers with the same aspect ratio (100). Increasing δ_{\max} will increase the number of fillers that are available to conduction, decreasing the number of bonds to transverse the domain, i.e., decreasing the length of the optimal path [18]. Also, as stated by Equation (4), an increase of δ_{\max} will

decrease the percolation threshold. As stated before, the parameter δ_{\max} can be easily related, e.g., to the cross-link density and hence depends on the nature of the polymeric matrix. Aside from the relation between δ_{\max} and the polymer, the latter parameter is linked with the disorder strength (“ a ”) as previously discussed. This disorder constant, “ a ”, can be linked to the variables in the Miller hopping formula [20]. Therefore, δ_{\max} is also related to the conduction mechanism, i. e., hopping mediated by the matrix. As final remark to Figure 3, the high values for δ_{\max} is a consequence of setting δ_{\max} equal to the correlation length that depends on the length of the optimal path between two fillers [18].

In Figure 4 are presented the values of the composite conductivity for different degrees of axial alignment (Equation (2)) 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. Comparing to the results in [8], 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.

Figure 4 also shows that there is a substantial difference in the conductivity between cylinders aligned perpendicular ($S=1$) and parallel ($S=-0.5$) to the measurement direction. This difference in the conductivity is in agreement to recent experimental work [25] and

is explained by the higher number of fillers necessary to transverse the domain ($S=1$) which has a lower bound when $S=-0.5$.

Conclusions

In this paper it is proposed a new model for CNT/polymer composites based on “hard-core” cylinders with no contact resistance. It is shown that hopping mediated by the polymer matrix can explain the conductivity of the composites. The simulations demonstrate that increasing aspect ratio will increase conductivity. On the other hand, increasing the anisotropy will decrease conductivity; this effect is more evident at higher volume fractions. Finally, it is demonstrated that the alignment of rods parallel to the measurement direction results in higher conductivity values, in agreement to recent experimental work.

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References

- [1] M. H. Al-Saleha and U.Sundarara, Carbon 47, 2 (2009).
- [2] E. T. Thostenson, C.Li, and T.-W. Chou, Compos. Sci. Technol. 65, 491 (2005).
- [3] D. Stauffer and A.Aharony, Introduction To Percolation Theory, Taylor and Francis, London (1992).
- [4] W. Bauhofer and J. Z. Kovacs, Compos. Sci. Technol. 69, 1486 (2009).
- [5] F. Dalmas, R. Dendievel, L. Chazeau, J. Cavaille, and C. Gauthier, Acta Mater. 54, 2923 (2006).
- [6] N. Hu, Z. Masuda, Y. Cheng, and G. Yamamoto, Nanotechnology 19, 215701 (2008).
- [7] X. Sun, M. Song, Macromol.Theory Simul. 18, 155 (2009).
- [8] S. I. White, B. A. DiDonna, M. Mu, T. C. Lubensky, and K. I. Winey, Phys. Rev. B 79, 24301 (2009).
- [9] L Berhan and A M Sastry, Phy. Rev. E 75, 41121 (2007).
- [10] P. Cardoso, J. Silva, A. J. Paleo, F. W J van Hattum, R. Simões, and S. Lanceros-Mendez, Phys Status Solidi A 207, 407 (2009).
- [11] T. A.Ezquerria, M.Kulescza, and F. J.Baltá-Calleja, Synth. Met. 41, 915 (1991).
- [12] H Kawamoto and E J Sichel, Carbon Black-polymer Composites, Marcel Dekker, New York (1982).
- [13] M. J Vold, J. Phys. Chem. 63, 1608 (1959).

- [14] R. Simoes, J. Silva, S. Lanceros-Mendez, and R. Vaia, *J. Mater.Sci.* 45, 268 (2009).
- [15] R. Simoes, J. Silva, R. Vaia, V. Sencadas, P. Costa, J. Gomes, and S. Lanceros-Mendez, *Nanotechnology* 20, 35703 (2009).
- [16] T. H.Cormen, C. E.Leiserson, R. L.Rivest, and C. Stein, *Introduction To Algorithms*, MIT Press, Cambridge (2001).
- [17] S. Kirkpatrick, *Rev. Mod. Phys.* 45, 574 (1973).
- [18] J. Silva, R. Simões, S. Lanceros-Mendez, and R. Vaia, *Phys. Rev. B* **submitted**, (2010).
- [19] J.-C. Charlier, X. Blase, and S. Roche, *Rev. Mod. Phys.* 79, 677 (2007).
- [20] A. Miller and E. Abrahams, *Phys. Rev.* 120, 745 (1960).
- [21] A. V. Kyrlyuk and P. van der Schoot, *PNAS* 105, 8221 (2008).
- [22] A.Allaoui, S. V.Hoa, and M. D. Pugh, *Compos. Sci. Technol.* 68, 410 (2008).
- [23] I. Irurzun, J. Vicente, M. Cordero, and E. Mola, *Phys. Rev. E* 63, 1 (2000).
- [24] G. Faiella, F. Pscitelli, M. Lavorgna, V. Antonucci, and M. Giordano, *Appl. Phys. Lett.* 95, 153106 (2009).
- [25] A. Dombovari, N. Halonen, A. Sapi, M. Szabo, G. Toth, J. Mäklin, K. Kordas, J. Juuti, H. Jantunen, and A.Kukovecz, *Carbon* 48, 1918 (2010).

Figure Captions

Figure 1: representation of an isotropic virtual material (left) and an anisotropic material (right). For all simulations the domain is larger than the one presented here.

Figure 2: conductivity versus volume fraction for three different aspect ratios. Inset log-log plot and linear fit with Equation 1 and the critical volume fraction given by Equation 3.

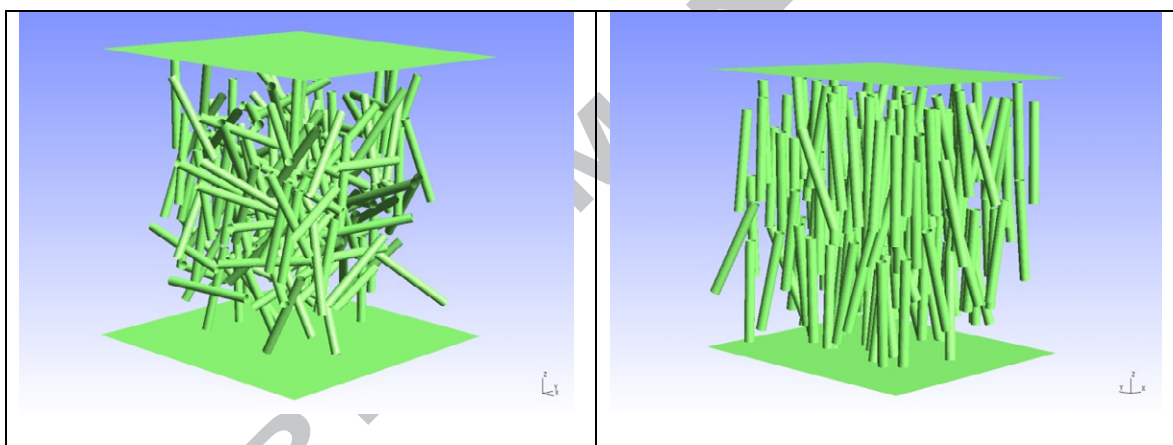
Figure 3: conductivity as a function of the volume fraction for several values of δ_{\max}

Figure 4: conductivity as a function of axial alignment (S).

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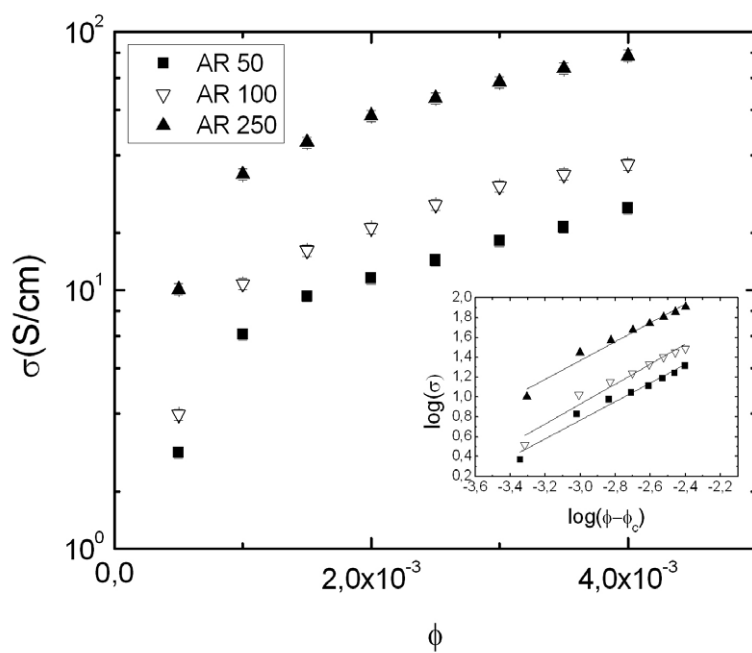
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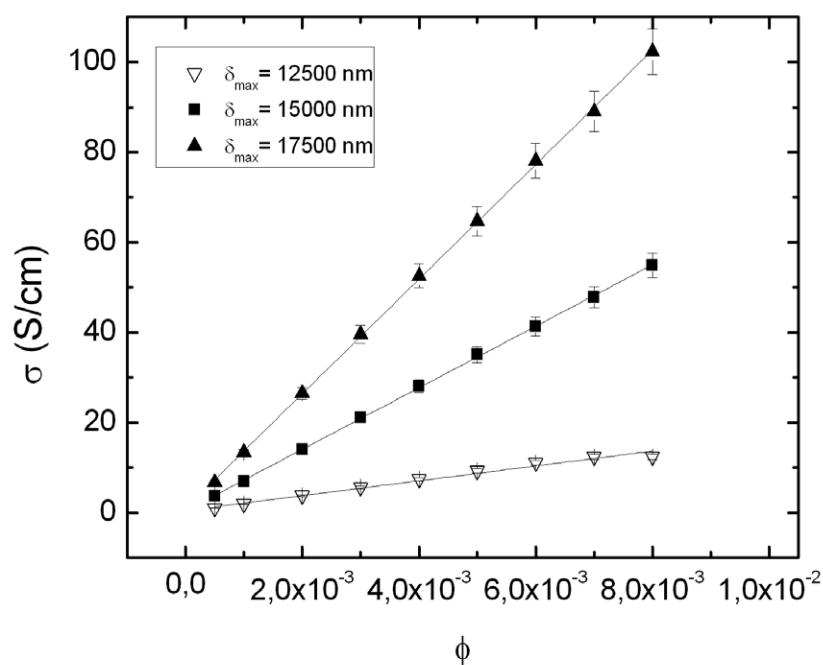
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Figure 3: conductivity as a function of the volume fraction for several values of δ_{\max}



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Figure 4: conductivity as a function of axial alignment (S).

