A mathematical model for the description of the electrical conductivity of graphene / polymer nanocomposites

Yahya Öz
Group Leader, Turkish Aerospace, Department of Innovation, Advanced Materials, Processes and Energies Technology Center, Kahramankazan, Ankara 06980, TR
E-mail: yahya@unam.bilkent.edu.tr

Abstract. The dispersion of nanomaterials such as graphene has a major influence on the electrical conductivity in nanocomposites with a polymer matrix. For the description of this effect a continuum model is presented. Within this model, the percolation threshold is determined. Moreover, a distributional analysis is used for the purpose of taking electron hopping between graphene into account. Hence, interfacial conductivity enhanced by tunneling is also included in this study. Recent measurements of nanocomposites that are used for aerospace applications are compared with the results of the presented model and show good agreement between model and experiment.

1. Introduction
Gaining functional properties by use of nanomaterials as fillers in a polymer matrix is of great interest for aerospace and other industrial applications [1]. Especially carbon-based nanomaterials like graphene and carbon nanotube (CNT) with high electrical conductivity are currently studied for this purpose. These materials can form a conductive network and hence, a percolation threshold can be observed [2]. However, homogeneous dispersion of nanomaterials is typically quite hard to accomplish. Besides the process of nanofiller introduction, the oxidation of the nanomaterial as well as interaction energies between filler and matrix play a role during the possible formation of agglomerates which has an influence on the percolation threshold.

The theoretical study of the percolation threshold is of great interest [3, 4, 5, 6]. Hence, a continuum model is studied in this manuscript for this purpose. Moreover, the presented model takes agglomeration, imperfect interfaces and electron hopping between the nanomaterial into account.

2. The Model
2.1. Geometry of agglomeration
Nanofillers like graphene or CNT tend to form agglomerates which are assumed to be spheroids described by the aspect ratio $\frac{a}{c}$ within the framework of this presented model. Due to the agglomerates, two regions with low and high amount of nanofiller can be found inside of the nanocomposite. Thus, the complete volume of the nanocomposite is split into two sections, where the volume concentrations are given by $\Sigma_l$ and $\Sigma_h$. The volume concentrations of polymer and...
nanofiller inside of these two regions are given by $\Sigma^{(l/h)}_1$ and $\Sigma^{(l/h)}_1$, respectively. Note that the sum of each set of volume concentrations is equal to one. This construction leads to the volume fraction $\Sigma_1$ of the nanofiller given by

$$\Sigma_1 = \Sigma^{(l)}_1 + (\Sigma^{(h)}_1 - \Sigma^{(l)}_1)\Sigma_h,$$

(1)

which is typically the parameter in experiments. Due to Eq. (1) we find $\Sigma_h = \Sigma^{(l)}_1 = 0$ for $\Sigma_1 = 0$ and $\Sigma^{(l)}_1 = \Sigma^{(h)}_1 = 1$ for $\Sigma_1 = 1$. Hence, $\Sigma^{(h)}_1$ can be chosen as a free parameter $1 \geq b \geq 0$ for $\Sigma_1 = 0$. This construction allows the relationship between $\Sigma^{(h)}_1$ and $\Sigma_1$ to be selected by an assumption. The monotonically strictly increasing linear function $\Sigma^{(h)}_1 = b + (1 - b)\Sigma_1$ is chosen for our application because of $\Sigma^{(h)}_1 |_{\Sigma_1 = 0} = b$ and $\Sigma^{(h)}_1 |_{\Sigma_1 = 1} = 1$. Hence, $b$ can be interpreted as control parameter for agglomeration. $b = 0$ indicates a nanocomposite without any agglomeration. In contrast, $\Sigma^{(h)}_1/\Sigma_1$ specfies the amount of nanofiller inside the agglomerate that occurs for $b > 0$.

2.2. Electron hopping
Increasing the amount of integrated nanofiller inside of the polymer matrix decreases the interface resistivity which is initially given by $\rho_0$. This effect occurs due to the increasing electron hopping between the nanomaterials while they come closer to each other. This quantum effect is incorporated into the model presented in this study by the distribution in Eq. (2)

$$\rho_{\Sigma',\beta} (\Sigma) = \left(1 + e^{-\beta (\Sigma - \Sigma')}\right)^{-1}.$$

(2)

Due to $\rho''_{\Sigma',\beta} (\Sigma') = 0$ and $\rho''_{\Sigma',\beta} (\Sigma') = -\frac{\beta^2}{\Sigma}$ an inflection point exists at $\Sigma = \Sigma'$. Moreover, $\rho_{\Sigma',\beta} (\Sigma) = \frac{1}{2} + \frac{\beta}{4} (\Sigma - \Sigma') + \mathcal{O}\left((\Sigma - \Sigma')^3\right)$ shows that $\beta$ is a parameter that describes the rapid change of the distribution at $\Sigma \approx \Sigma'$. The codomain of the distribution is $\left[\left(1 + e^{\beta \Sigma'}\right)^{-1}, \left(1 + e^{-\beta (1-\Sigma')}\right)^{-1}\right]$ and $\rho_{\Sigma',\beta} (\Sigma') = \frac{1}{2}$ holds. Hence, the interface resistivity for any amount $\Sigma_1$ of nanofiller with percolation threshold at $\Sigma_1'$ integrated inside the polymer matrix is given by

$$\frac{\rho (\Sigma_1)}{\rho_0} = \frac{\rho_{\Sigma',\beta} (1) - \rho_{\Sigma',\beta} (\Sigma_1)}{\rho_{\Sigma',\beta} (1) - \rho_{\Sigma',\beta} (0)}$$

(3)

with the desired initial resistivity $\rho_0$ at $\Sigma_1 = 0$.

2.3. Continuum model
The measurable conductivity $\sigma_e$ of a composite with two phases, filler and matrix, can be determined by the implicit Eq. (4)

$$3\Sigma_0^0 \sigma_e - \sigma_0 + 2\sigma_e \Sigma_0^0 \sigma_e = \frac{\Sigma_1}{3} \left( \frac{2 (\tau (\sigma_1 - \sigma_e) - 2\sigma_1 \sigma_e S_{11} (1 + 2\alpha) \rho (\Sigma_1))}{\tau (\sigma_e + S_{11} (\sigma_1 - \sigma_e)) + 2\sigma_1 \sigma_e S_{11} (1 - S_{11}) (1 + 2\alpha) \rho (\Sigma_1)} \right)$$

$$+ \left( \frac{\tau (\sigma_3 - \sigma_e) - 2\sigma_3 \sigma_e S_{13} (1 + 2\alpha) \rho (\Sigma_1)}{\tau (\sigma_e + S_{13} (\sigma_3 - \sigma_e)) + 2\sigma_3 \sigma_e S_{13} (1 - S_{13}) (1 + 2\alpha) \rho (\Sigma_1)} \right)$$

(4)

where $\sigma_0$ is the isotropic conductivity of the polymer matrix, $\sigma_1 = \sigma_2$ the conductivity in the isotropic plane of graphene / or CNT and $\sigma_3$ the conductivity in the normal direction. $S_{11}$ and
$S_{33}$ are given by Eq. (5)

\[
S_{11} = \begin{cases} 
\frac{\alpha}{2(1-\alpha^2)^2} \left( \arccos \alpha - \alpha \sqrt{1-\alpha^2} \right), & \alpha < 1, \\
\frac{\alpha}{2(\alpha^2-1)^2} \left( \alpha \sqrt{\alpha^2-1} - \text{arcosh} \alpha \right), & \alpha > 1,
\end{cases}
\]

\[S_{33} = 1 - 2S_{11}\]

with the nanomaterial aspect ratio $\alpha$. Eq. (4) was derived by use of wave scattering [7], Eshelby $S$-tensors [8], effective medium theory [9, 10, 11, 12, 13] and geometry of the nanocomposites [14, 15]. Furthermore, the imperfect interface between nanomaterial and polymer matrix is taken into account in Eq. (4) by modeling the interface with an isotropic thin layer with thickness $t$ and low electrical conductivity as well as nanomaterial thickness $\tau$ [16].

This result can be used for the determination of the percolation threshold. For the sake of simplicity the polymer matrix is assumed to be perfectly insulating, i.e. $\sigma_0 = 0$. Eq. (4) turns into a quadratic equation in $\sigma_e$, where $\sigma_e \notin \mathbb{R}^+_0$ for $\Sigma_1 < \Sigma_1'$ with a critical value $\Sigma_1'$. However, the percolation threshold $\Sigma_1 = \Sigma_1'$ leads to $\sigma_e = 0$. Hence, we find the percolation threshold by fitting the solutions in $\sigma_e$ of Eq. (4) to the experimental data.

3. Results

The electrical conductivity of different polyether ether ketone (PEEK) / graphene samples prepared by wet mixing was obtained by an electrometer. The detailed study of these samples has to be presented in a separate publication though. However, we consider the results for the electrical conductivity in this study and compare them with the fitting process resulting from Eq. (4).

![Figure 1](image_url)

**Figure 1.** Experimental data for in total six different PEEK / graphene nanocomposites are depicted with black dots. As predicted, the electrical resistivity goes down rapidly with addition of GNP since neat PEEK is an insulator with an electrical conductivity of $(3 \pm 1) \cdot 10^{-10}$ $\Omega$m. Note that the percolation threshold seems to be in the range of 0.6 and 0.8 % volume concentration. Correspondingly, further measurements must be carried out in this area. However, the black curve which shows the result of the fitting process proofs that the methodology presented in this study is applicable for these kind of nanocomposites.
The percolation threshold is determined at a volume concentration of 0.72 %. During the computations the electrical conductivities \( \sigma_1 \) and \( \sigma_3 \) were taken as \( 2.5 \times 10^4 \, \text{S/m} \) and \( 25 \, \text{S/m} \), respectively. The agglomerates are assumed to have a thickness of \( \tau = 50 \, \text{nm} \), the initial interface resistivity is taken as \( \rho_0 = 5 \times 10^{-9} \, \Omega\text{m} \) while \( b \) is chosen as 0.05. The aspect ratio for the agglomerates was assumed to be 0.1. There is a certain range for the fitting parameter \( \beta \), since further measurements must be carried out in the vicinity of the percolation threshold. The result for \( \beta = 10 \) is given in Fig. 1. Overall, it can be observed that the presented model fits the measurements. Furthermore, even low amounts of graphene can lead to a conductive network, which is very useful for industrial purposes such as aerospace applications due to the cost of nanomaterials.

In the continuum model presented in this study the percolation threshold depends on the state of dispersion of the nanomaterial and the geometry of the agglomeration. Note that the threshold increases for spherical agglomerates. In addition, two competing mechanisms are embedded into the framework of the continuum model. The imperfect interface between filler and matrix lowers the upper bound of the effective conductivity. Contrarily, the electron hopping increases it to a certain extent. Hence, the bound observed in experiments can be determined from the model.

4. Conclusions
For the purpose of determining the percolation threshold of a nanocomposite a continuum model was presented in this study. The model takes both phases of the nanocomposite, nanofiller and polymer matrix, into account. Moreover, imperfect interface and electron hopping were embedded in the framework of the model.

Comparison of experimental data with the model shows that the behaviour of nanocomposites that are useful for aerospace applications can be modeled by the presented methodology. A successful determination of the percolation threshold was demonstrated.

Acknowledgments
The author acknowledges financial support by the Scientific and Technological Research Council of Turkey within the support program 1515 for research and laboratory developments within the project 5189901. Moreover, the author is grateful to the Bilkent University Institute of Materials Science and Nanotechnology for providing the needed infrastructure.

References
[1] Stankovich S, Dikin D A, Dommett G H B, Kohlhaas K M, Zimney E J, Stach E A, Piner R D, Nguyen S T and Ruoff R S 2006 Nature 442 282-286
[2] Chen H, Müller M B, Gilmore K J, Wallace G G and Li D 2008 Adv. Mater. 20 3557-3561
[3] Prasher R and Evans W 2006 Appl. Phys. Lett. 89 143119
[4] Li J, Ma P C, Chow W S, To C K, Tang B Z and Kim J-K 2007 Adv. Funct. Mater. 17 3207-3215
[5] Li C, Thostensen E C and Chou T-W 2007 Appl. Phys. Lett. 91 223114
[6] Xie S H, Liu Y Y and Li J Y 2008 Appl. Phys. Lett. 92 243121
[7] Maxwell J C 1873 A Treatise on Electricity and Magnetism (Cambridge: Cambridge University Press)
[8] Eshelby J D 1957 Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 241 376-396
[9] Hill R 1963 Journal of the Mechanics and Physics of Solids 11 357-372
[10] Hill R 1965 Journal of the Mechanics and Physics of Solids 13 313-222
[11] Walpole L J 1966 Journal of the Mechanics and Physics of Solids 14 151-162
[12] Walpole L J 1966 Journal of the Mechanics and Physics of Solids 14 289-301
[13] Walpole L J 1969 Journal of the Mechanics and Physics of Solids 17 235-251
[14] Hori M and Nemat-Nasser S 1993 Mechanics of Materials 14 189-206
[15] Nemat-Nasser S and Hori M 1998 Micromechanics: Overall Properties of Heterogeneous Materials (Amsterdam: Elsevier)
[16] Mori T and Tanaka K 1973 Acta Metallurgica 21 571-574