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Computational and experimental study of electrical conductivity of graphene/poly(methyl methacrylate) nanocomposite using Monte Carlo method and percolation theory

Weiling Wang, Ahalapitiya H. Jayatissa *

Nanotechnology and MEMS Laboratory, Mechanical, Industrial, and Manufacturing Engineering Department, The University of Toledo, OH 43607, USA

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ABSTRACT

Graphene/insulator nanocomposite has potential applications in electric/magnetic shielding and printing circuit. It is necessary to develop fundamental knowledge of the transport mechanism of graphene/insulator nanocomposite and find the significant factors that control the electrical conductivity. A numerical model based on Monte Carlo method and percolation theory was developed for graphene/poly(methyl methacrylate) (PMMA) nanocomposite in this study. The contact resistance between graphene sheets was discussed, and the tunneling resistance played the determinant role in the overall resistivity. The effect of graphene size was studied using this model, results suggested that smaller the size of graphene sheet is, more conductive the composite is. Preliminary experimental results were compared with the simulation results, and they are in agreement, proving the accuracy of this numerical model.

1. Introduction

Graphene is composed of a single layer of carbon atoms arranged in a honeycomb pattern. Graphene can also be described as a one-atom-thick layer of graphite. Graphene was once thought impossible to exist; it was unexpectedly discovered by Novoselov et al. using scotch tape in 2004. Since its discovery, numerous studies have been directed toward graphene, and the superior properties of graphene have been recognized. The electronic properties of graphene were found to be exceptional. Novoselov et al. found that graphene exhibits a strong ambipolar electric field effect and its carrier mobility could reach $\sim$10,000 $cm^2 V^{-1} s^{-1}$ at room temperature [1]. Later on Geim et al. corrected the value to an excess of 15,000 $cm^2 V^{-1} s^{-1}$[2]. Chen et al. reported that the carrier room-temperature mobility of graphene on SiO_2 substrate is limited to 40,000 $cm^2 V^{-1} s^{-1}$ at a relevant carrier density of 1×10^{12} cm^{-2} [3]. Du et al. reported that when graphene is suspended, the low-temperature carrier mobility approaches 200,000 $cm^2 V^{-1} s^{-1}$ for carrier densities below 5×10^9 cm^{-2}, which corresponds to a conductivity of 6000 S/cm [4]. Because of its superior electrical conductivity and high surface to volume ratio, like carbon nanotube, graphene sheets have been added into polymer to make electrical conductive nanocomposite, which has potential applications in electric/magnetic shielding and printing circuit. Most research about graphene/polymer nanocomposite are focused on the synthesis method of graphene and polymer mixing and processing technique. Few researchers have done theoretical study on the electrical conductivity of graphene/polymer nanocomposite. It is necessary to develop fundamental knowledge of the factors that control composite conductivity to fully understand these materials.

Most existing models of the electrical conductivity of polymer composites are generally based on percolation theory. The term "percolation theory" was first introduced by Broadbent and Hammersley in 1957 [5], when they used a geometrical and statistical approach to solve the problem of fluid flow through a static random medium. Kirkpatrick extended the percolation theory to electron transport problems [6,7]. He studied numeric simulation for two dimensional and three dimensional lattices. The models he used could be characterized as lattice site and bond models. Pike and Seager have done computational studies using site and bond percolation models [8,9]. They studied the random lattice cases with a large computer. They used the Monte Carlo

* Corresponding author at: N. Westwood, Toledo, OH 43607, USA. Tel.: +1 419 530 8245.
E-mail address: ajayati@utnet.utoledo.edu (A.H. Jayatissa).

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method to generate random position parameters and other shape parameters. They developed hard core models for different shapes, including circles, squares, sticks, etc., and solved many random lattice percolation models in two and three dimensions. Li and Morris studied a special case for conductive adhesive using percolation theory [10]. They used a two dimensional square model to study the percolation threshold for an Ag flakes-epoxy system and the particle size effect. Their model predicts that the conductivity increases with contact force between Ag flakes and with broad particle size distributions. Li et al. studied the electrical conductivity of carbon nanotube-based composites [11]. They addressed the effect of nanotube contact resistance on the resistance of the composite. They concluded that the tunneling resistance between nanotubes plays a dominant role, and the maximum tunneling distance was found to be 1.8 nm using Monte Carlo simulations. Yu et al. did research in a similar manner, and they both used the tunneling current density formula derived by Simmons to calculate tunneling resistance [12]. Bao et al. have studied the electrical conductivity of carbon nanotube nanocomposites and the tunneling resistance [13]. To calculate the contact resistance, they used the Landauer–Bűttiker (L–B) formula to account for both tunneling and direct contact resistances. Few researchers have done computational modeling of graphene/polymer nanocomposite. Hicks el al. studied the case of graphene–polymer nanocomposite [14]. They studied the effect of aspect ratio of graphene sheets and size of device using their model. However, they did not study the tunneling distance effect in detail, and they didn't try to use various size of graphene sheets. Oskouyi el al. studied the conductivity and piezoresistivity of graphene platelets composites using a three-dimensional model [15]. The particle physical model used in their simulation is circular disk, which is not as close to reality.

In this study a simulation model was established based on Monte Carlo method and percolation theory. Effect of graphene sheet size on electrical conductivity, including thickness and area of graphene sheet, was investigated. Electrical conductivity of graphene/Poly(methyl methacrylate) (PMMA) nanocomposite produced by an innovative method was compared with simulation results, which is in good agreement with simulation results.

2. Electrical conductivity simulation method

Three dimensional simulation was developed following the flow chart as shown in Fig. 1. First, a physical model representing the filler, graphene, was constructed using a hard-core soft-shell rectangular prism model, as shown in Fig. 2. The hard core could not penetrate each other. 2a is the side of the hard core. The soft shell could penetrate each other physically, t_{shell} is the thickness of the soft shell. t is the thickness of graphene sheets. The soft shell represents the tunneling area which could allow electrons to hop from one graphene sheet to another. Since in experiments the graphene platelets tend to aggregate and stack with each other, the thickness of which is larger than the single layer graphene. In this simulation, thickness of graphene platelets was assumed to be 2 nm. The tunneling distance between graphene sheets was assumed to be 2 nm and thickness of soft shell was assumed to be 1 nm.

Second, a physical network was generated using Monte Carlo method. Monte Carlo method was used to generate the random position parameters of each graphene sheet, x_c,y_c, z_c and angle θ.

The same as the simulation model proposed by Hicks el al, we assumed that graphene sheets in composites mostly align themselves to the substrate [14,16,17]. The angle θ of prism is defined as the angle of the square side with the x axis of the coordinate, as shown in Fig. 3.

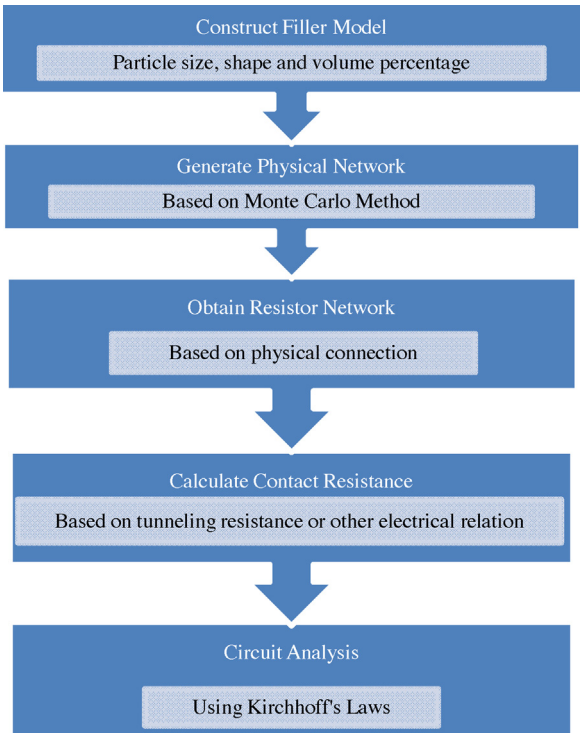

Fig. 1. Flow chart of electrical conductivity simulation.

Since the random number generated was nondimensional, i.e. in the range from 0 to 1,the position of center would be calculated as the generated random number multiplied by side length of the whole sample, and the angle of orientation on x–y plane would be generated random number multiplied by $\frac{\pi}{4}$, as:

$$x_c = \mathrm{L} \times \mathrm{random}(1),$$

$$y_c = \mathrm{L} \times \mathrm{random}(2),$$

$$z_c = \mathrm{L} \times \mathrm{random}(3),$$

$$\theta = \frac{\pi}{4} \times \mathrm{random}(4),$$

where L is the size of sample, random(n) is the random number generated by Monte Carlo method. The coordinates of x, y, z need to be rotated to represent the random oriented rectangular prism. In this study, we assum all the graphene sheets align to the substrate (x–y plane), the rotation matrix is given by:

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} \cos\theta & -\sin\theta & 0 \\ \sin\theta & \sin\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}.$$

The rectangular prism well aligned in space can be represented by:

$$|x' - x_c'| \le \mathrm{a},$$

$$|y' - y_c'| \le \mathrm{a},$$

$$|z' - z_c'| \le t.$$