Monte Carlo model for the study of percolation thresholds in composites filled with circular conductive nano-disks

Amirhossein Biabangard Oskouyi, Pierre Mertiny*

University of Alberta, 4-9 Mechanical Engineering Building, Edmonton Alberta T6G 2G8, Canada

Abstract

The subject of the study described in this paper is the percolation threshold of composites with conductive nano-scale fillers. Specifically, a three-dimensional continuous Monte Carlo algorithm was developed to determine the percolation threshold of polymers filled with two-dimensional conductive circular nano-disks. The Monte Carlo simulation provides the threshold value of the filler loading when at least one percolation network is formed. A scaling study was carried out to determine the minimum dimension of the representative unit volume that ensures a percolation threshold that is independent of the unit cell size. The effect of the aspect ratio of the nano-particles and the tunneling distance on the percolation threshold was investigated employing the developed model.

Keywords: Percolation threshold; Monte Carlo modeling; Nano-disk filler; Conductive composites

1. Introduction

Electrically conductive polymers have garnered the attention of researchers in recent decades. One reason for the growing interest is the piezoresistivity of conductive polymers which make them a good candidate for deformation/strain sensors [1-4]. By increasing the amount of conductive particles dispersed within a non-conductive polymer, a critical volume fraction of particles is reached at which the polymer exhibits a transition from a nonconductive to a conductive phase. This critical volume fraction is called the percolation threshold [5]. For volume fractions higher than the percolation threshold, the conductivity of the polymer was found to obey a power-law conductivity behaviour, i.e.

$$\sigma = (\varphi - \varphi_c)^s$$  \hspace{1cm} (1)

where $\varphi_c$ is the percolation threshold and $\varphi$ and $s$ are the filler volume fraction and a constant, respectively.

A great number of experimental works have been devoted to determining the percolation threshold for different conductive inclusions [1-15]. Numerical modelling based on the Monte Carlo method is commonly employed to study the percolation threshold for fillers with different geometry. Consiglio et al. [8] determined the percolation...
threshold for spherical fillers, like carbon black, through Monte Carlo modelling. Likewise, Wang and Ogala [9] developed a continuum Monte Carlo model to predict the percolation threshold of conductive polymers filled with spherical conductive inclusions. In their study, fillers were considered as spheres with a hard core and a soft shell, and the effect of the soft shell thickness on the percolation threshold was examined. Taya et al. [10] studied the piezoresistivity and percolation threshold of conductive composites with straight fibres. Their study on piezoresistivity was based on affine transformation and an incompressibility of composite assumption. Hu et al. [11] studied the tunneling effect on the conductivity of carbon nano-tube based composites. They employed a Monte Carlo technique to evaluate the percolation threshold dependence on tunneling resistance. They also investigated the piezoresistivity effect through affine transformation and a Cholesky conjugate gradient method. Ma and Gao [12] developed a three-dimensional Monte Carlo model to study the percolation threshold and conductivity of composites filled with curved fibres. In this study, arm-shaped fibres were considered. Balberg and Anderson [13] derived an expression for the excluded volume fraction for stick-shaped inclusions. They further discussed the relationship between the percolation threshold and the excluded volume fraction associated with the inclusions. In [14] Li and Chou investigated the effect of fibre waviness on electrical conductivity and percolation threshold of conductive composites. Also considered in this work was the effect of waviness on the critical exponent of the power-law conductivity equation. In another study by the same authors [15], a two-dimensional continuum percolation model for nano-composites with arbitrary shapes through Monte Carlo modelling was developed. The shape of the filler was approximated using polygons.

Reviewing the technical literature revealed a lack of work pertaining to disk-shaped inclusions, such as graphene nano-platelets. The present authors thus developed a three-dimensional continuum Monte-Carlo model to study the percolation threshold for a matrix filled with circular nano-disks. The conductive filler was modelled as circular nano-platelets that are randomly dispersed in a cubic representative volume element (RVE). The developed model was employed to determine the critical volume fraction which leads to a percolation network. The effects of RVE scaling as well as of the controlling parameters were studied, including the nano-disk size and aspect ratio, and the electron tunneling distance. A dimensional analysis of the simulation results provided a dimensionless variable which plays a dominant role for the percolation threshold of matrices modified with circular nano-platelet particles.

2. Formulation

2.1. Model creation

In order to predict the critical volume fraction for the onset of electrical conductivity, a three-dimensional continuum Monte Carlo model was developed. The model is based on a cubic RVE with edge length $L$ that is filled with randomly distributed and oriented conductive circular nano-disks. A group of nano-particles that are electrically connected shall be called a cluster. A cluster that connects the two parallel faces of the RVE constitutes a percolation network, and the fibre volume fraction at the inception of the percolation network is called the percolation threshold. Each circular nano-disk is identified by the coordinate of the circular disk centre, $P(x,y,z)$, and a normal vector, $\mathbf{n} = (n_1, n_2, n_3)$, that indicates the normal to the plane on which circular nano-disk lies. Point $P$ and vector $\mathbf{n}$ are generated using pseudo random number generator (RNG) algorithms that provide for uniformly dispersed particles inside the RVE.

Choosing a reliable RNG plays an important role in the accuracy of Monte Carlo simulations. Diaz et al. [16] assessed the suitability of different pseudo RNG algorithms. They utilized different well-known RNG algorithms to develop a Monte Carlo based model for a gamma-ray spectrometry problem. Their results indicate the suitability of the Mersenne Twister (MT) RNG algorithm for Monte Carlo applications. The MT algorithm was developed by Matsumoto and Nishimura [17]. It has a long period ($2^{19937} - 1$). Several studies confirmed good randomness of the MT algorithm, which makes it a good candidate for Monte Carlo simulations. In this study the MT algorithm was employed to first provide the coordinates of a circular disk centre, followed by the generation of a random normalized vector that represents the normal vector to the circular disk plane. In some of the published works [9, 11-12], the orientation vectors (which origins and end points are located in the centre and span to the surface of a unit sphere respectively) were obtained by generating elevation angles $\theta$ and inclination angles $\psi$, which correspondingly are bound in a spherical coordinate systems by $[-\pi/2, \pi/2]$ and $[0, 2\pi]$. But, it should be noted that an elevation angle...
that is uniformly distributed in \([-\pi/2, \pi/2]\) does not provide a uniform distribution of points on the surface of a unit sphere. In fact, a uniform distribution on the unit sphere surface is achieved if \(\theta\) is chosen as a weighted distribution between \(-\pi/2\) and \(\pi/2\) where the weight of the distribution is \(\sin(\theta)\) \[18\]. In the present study a different algorithm was employed to generate points that are uniformly distributed on a unit sphere. As in other works these points then describe the normal vectors to the planes on which the circular disks lie. Marsaglia \[19\] offered an effective method to generate a sequence of points that are uniformly distributed on a unit sphere. The employed algorithm generates two random parameters \(\beta_1\) and \(\beta_2\) independent uniform on \((-1, 1)\) until \(S = (\beta_1)^2 + (\beta_2)^2 < 1\), then forms:

\[
\mathbf{n} = \left(2\beta_1(1-S)^{1/2}, 2\beta_2(1-S)^{1/2}, 1-2S\right)
\]  

Employing the discussed algorithm provides the position and normal vectors of the circular nano-disks that can be added to the RVE. When dealing with Monte Carlo simulations for stick-shaped particles like carbon nano-tubes, particles generated by the algorithm can directly be added to the RVE. This is due to their high aspect ratio, i.e. their thickness is negligible in comparison with their length, and particles can thus be considered two-dimensional. But in a Monte Carlo simulation of circular nano-disks, a geometric feasibility study should be carried out for a newly generated nano-disk that is to be added to the RVE. The new nano-disk must not intersect existing disks inside the RVE. Considering Fig. 1, if disk \(D_2\) intersects disk \(D_1\), their intersection is the segment of a line. This line is given by the cross product of the normal vectors of the planes on which the two disks lie \((\mathbf{L} : \mathbf{n}_1 \times \mathbf{n}_2)\). According to Fig. 1, \(\overline{o_1p_1}\) and \(\overline{o_2p_2}\) are the shortest distances of the centres of the disks from the intersection line. \(M_i\) and \(N_i\) are the intersections of \(i^{th}\) circle and line \(\mathbf{L}\). The disks intersect when

\[
\overline{o_1p_1} < R \text{ and } (M_iN_i + M_2N_2) < 2\overline{p_1p_2}
\]  

where \(R\) is the radius of the disks. Only in the case of non-intersecting disks would newly generated nano-disks be added to the RVE, which occurs until a percolation network is formed between two parallel faces of the RVE.

2.2. Connection criterion

The electrical connectivity between adjacent nano-disks stems from the tunneling effect within the polymer matrix. As shown in Fig (2) the matrix acts as a resistor through which electrical current can pass through and connect to the adjacent particle. The tunneling resistivity of the polymer can be approximated by Eq. 4 \[2\].

\[
R_{\text{tunl}} = \frac{h^2d}{Ae^2\sqrt{2m\lambda}} \exp\left(\frac{4\pi d}{h}\sqrt{2m}\right)
\]  

where \(R_{\text{tunl}}\) is the electron tunneling resistance, \(m\) the mass of an electron, \(h\) the Planck’s constant, \(\lambda\) the barrier height of the polymer, \(e\) the quantum of electricity, \(d\) the tunneling distance and \(A\) the cross-sectional area of tunnel.
Figure (3) illustrate the variation of the tunneling conductivity with respect to the tunneling distance. The conductivity was simulated for three different barrier heights, i.e. $\lambda = 0.5, 1.0, 1.5$ ev. As shown in Fig. 3, the conductivity drops drastically for distances greater than a certain value. Hence, an approximate cutoff distance, $d_t$, can be determined so that for distances greater than $d_t$, the tunneling conductivity and electron hoping is neglected.

When a new particle is added to the RVE, the developed algorithm determines the shortest distances between the newly added particle and adjacent particles. As illustrated in Fig (2), two disks would be considered electrically connected by a tunneling resistor if the shortest distance is less than $d_t$. In this case the particles would be grouped as a cluster. Nano-disks are added to the RVE until a cluster emerges that connects two parallel sides of the RVE. Such a cluster is named a percolation network, and the volume of particles added to the RVE constitutes the critical volume fraction, i.e. the percolation threshold which is given as $q_c = N_c t \pi R^2 / L^3$, where $N_c$ is the number of the disk existing in the RVE at the onset of the percolation and $t$ is the thickness of the nano-disks. Figure 4 illustrates a percolation network and a cluster. To determine the shortest distance between two circular disks in three-dimensional space the algorithm developed by Almohamad and Selim [20] was used. Figure 5 illustrates the concept of the algorithm. In order to calculate the shortest distance between two disks, a point on disk 2 corresponding to the shortest distance of the centre of disk 1 from disk 2 is determined. The procedure is repeated for disk 2, so that points $p_1$ and $p_2$ are found. In the next step the points corresponding to shortest distance of $p_1$ from disk 1 and $p_2$ from disk 2 are determined ($q_1$ and $q_2$). The shortest distance is the minimum of the $p_1q_1$ and $p_2q_2$.

3. Result and Discussion

A computer code was developed in the FORTRAN programming language to study percolation problems for circular nano-disks. Considering the high computational cost of Monte Carlo simulations the code was written employing the message passing interface technique which enables the usage of multiple processors. The code was run on a general purpose Linux Cluster. The effect of different control parameters including the size of the nano-disks, the tunneling distance, and the size of the RVE, and scaling effects were examined.
3.1. RVE size effect

The RVE must have a large enough size so that the effect of the RVE boundary are negligible and simulation results can be generalized to larger samples. Figure 6 shows critical volume fractions for two different tunneling distances. The disk radius was set to 350 nm. For all simulations in this study the disk thickness was fixed to 0.345 nm, which corresponds to the thickness of graphene nano-platelets. Figure 6 demonstrates that the RVE size has no effect on the percolation threshold when the ratio of $L/d_t$ is greater than 35.

3.2. Conductivity criterion

The conductivity criterion described thus far is the existence of a percolation network connecting two parallel sides of the RVE. In this case, current can pass through the sample in this one direction, whereas between its other parallel sides the RVE still acts as an insulator. In other words, the RVE properties are not homogeneous. An alternative conductivity criterion may be defined, i.e. filler is added to the RVE until all parallel faces are mutually connected by percolation clusters. The resulting RVE would be conductive in all directions. Figure 7 shows a comparison of percolation thresholds based on both possible criteria. It can be observed that differences in percolation threshold between the two different criteria are diminutive.
3.3. Critical volume fraction

Figure 8 shows the percolation threshold with respect to the nano-disk size. This simulation was carried out for different tunneling distances. The data indicates that the percolation threshold increases monotonically with increasing particles size. Consequently, nano-disks with smaller radii produce lower percolation thresholds. Furthermore, polymers with greater tunneling distance need less filler volume to become conductive.

3.4. Dimensional analysis

A dimensional analysis was carried out to identify a dimensionless parameter that plays a dominant role in attaining a critical volume fraction. Considering the percolation threshold $\varphi_c$ to be a function of the geometric variables, i.e. $\varphi_c = f(R, d, t)$, $\varphi_c$ was found to be a linear function of the dimensionless parameter $t R d_i^{-2}$, see Fig. 9.

4. Conclusions

In this study a novel method based on three-dimensional continuum Monte Carlo modelling was developed to predict the critical volume fraction for composites filled with conductive circular nano-disks. Different aspects of the problem including RVE size effects were studied. Results obtained from this study indicate the reliability of the developed numerical method. The dimensional analyses provide a comprehensive understanding about the control parameters and their contribution to the percolation threshold for conductive circular nano-disks.

References