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A computational analysis of the percolation threshold and the electrical conductivity of carbon nanotubes filled polymeric materials

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Percolation of individual single walled carbon nanotubes (SWCNTs) and of SWCNT bundles dispersed in a non-interacting polymeric matrix has been analyzed computationally using an analytical model and a numerical simulation method. While the analytical model used is strictly valid only in the limit of an infinite length-to-diameter aspect ratio of the dispersed phase, good agreement is found between its predictions and the ones obtained using a computationally-intensive numerical method for the aspect ratios as small as 350. Since the aspect ratio of the individual SWCNTs is on the order of 1,000–10,000, this finding suggests that the analytical model can be used to study SWCNT percolation phenomena.

An electrical network model is also applied to the percolating and near-percolating SWCNT clusters in order to compute the *dc* electrical conductivity of a CP2 polyimide + SWCNT composite material. A reasonably good agreement is obtained between the computational and the experimental results with respect to both the magnitude of the electrical conductivity and to its behavior in the vicinity of the percolation threshold.

1. Introduction

Electrically conductive polymeric materials are sought in many applications in which antistatic, electrostatic dissipative and electromagnetic shielding/absorbing properties are required. For instance, electromagnetic interference shielding is essential in many portable electronic devices (e.g. laptop computers, cell phones, and pagers) to prevent interference with and from other electronic devices. Since there is presently no suitable polymeric material which can meet these requirements, electrically conductive additives (metals, carbon black, etc.) are generally used in the electronic equipment cases made of a polymer-based material. However, such materials are frequently associated with significant increases in the weight and manufacturing cost, as well as with reduced surface quality and manufacturability. High electrostatic dissipative properties are required, for example, in automobile body parts which are increasingly being made of plastics. During electrostatic painting of such parts, a charge layer is formed as a result of the deposition of charged paint droplets forming the initial coat. Such a charge-layer electrostatically repels the additional incoming paint droplets, giving rise to a significant paint waste and to the associated environmental problems. One solution to this problem could be the use of a conductive primer coat but this would introduce an additional processing step and hence increase the cost. On the other hand, if the part being painted possesses a sufficient level of electrical conductivity, and it is grounded during the painting process, no charge build up takes place.

The variation of electrical conductivity of polymers containing a conductive additive (filler) with the volume fraction of the filler (often referred to as the "*filler loading*") typically shows a classical S-curve behavior. That is, up to a critical loading (generally referred to as the "*percolation threshold*"), the bulk conductivity increases very slowly with the filler loading. At the percolation threshold, the conductivity undergoes an abrupt increase (of several orders of magnitude). At post percolation threshold levels of the filler loading, electrical conductivity again becomes a weak function of the volume fraction of the conductive additive. This behavior is well understood and it is attributed to the establishment of multiple, continuous paths through the conductive phase at the percolation threshold. Typically,

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an experimentally established percolation threshold is many times higher than the one which would be obtained if the particles of the conductive phase could be placed in the optimum positions to form a continuous network. Reduction of the experimental percolation threshold is very important since excessive filler loading may compromise the weight, mechanical properties and manufacturability. For example, in many polymers, carbon black loading levels as high as 50 vol% are required to reach the necessary level of electrical conductivity [1]. However, these high levels of the carbon black seriously degrade mechanical properties of the resulting polymer-matrix composite rendering it unmoldable [1].

In recent years, the potential of carbon nanotubes as electrically conductive fillers have been actively studied. Since their discovery in 1991 [2], carbon nanotubes have been the subject of intensive investigation primarily due to the unique combination of mechanical, electrical and chemical properties they possess. Depending on the fabrication method used, carbon nanotubes appear either predominantly as single-walled carbon nanotubes (SWCNTs) or as multi-walled carbon nanotubes (MWCNTs). SWCNTs, predominantly produced in carbon ablation and are discharge processes, can be described as single graphene sheets rolled up into a cylinder and capped with hemi-fullerenes at each end. Depending on their diameter and the spiral conformation (chirality), SWCNTs can be either semiconducting or metallic. Mechanical properties of SWCNTs are quite remarkable; their elastic modulus is typically above 1TPa, and they can undergo very large non-uniform (even highly localized) reversible deformations. Except for their ends and the locations of topological defects (e.g. 7-5-5-7 and Stone-Wales defects), SWCNTs are generally not very reactive.

MWCNTs are generally produced during thermal decomposition of the carbon precursors. Due to a weak inter-walls bonding, MWCNTs have generally inferior mechanical properties relative to those of the SWCNTs. Their electrical properties are similar to those of the SWCNTs although they cannot be easily correlated with their chirality. Chemical properties of the MWCNTs are dominated by the structure of their outer wall and are, hence, similar to the ones of the SWCNTs.

As mentioned earlier, carbon nanotubes have been actively investigated in recent years, as electrically conductive fillers in a polymeric matrix [3]. In particular, SWCNTs appear to be very attractive due to their high (ca. 10^6–10^7 Ω^{-1} m^{-1}) electrical conductivity and a high (ca. 10^3–10^4) length-to-diameter aspect ratio (the diameter of the SWCNTs is typically around 1nm while their length is on the order of 1 μm = 1,000 nm). For comparison, the aspect ratio in carbon black is typically 1–2. As shown schematically in Fig. 1a and b, the percolation threshold decreases with an increase in the aspect ratio, as slender additive particles are capable of forming a continuous network at a lower level of the filler loading. In a number of investigations [3], it has been established that the percolation threshold for SWCNTs in various non-interacting polymers is significantly lower than 1%. At such low levels of the filler loading, the flowability of the SWCNT-loaded thermoplastic melt or un-polymerized thermosetting resin is not significantly compromised ensuring a good processibility of these materials.

The percolation phenomenon of the additive phase has been studied extensively over the last two decades or more. Numerous analytical and numerical models [4–11] have been proposed which, with various degrees of success, account for the experimentally observed percolation thresholds. However, these models generally ignore the potential role that the interactions between filler particles can have on the percolation threshold. Such interactions, or more precisely, the van der Walls interactions, are often found to be significant in the case of SWCNTs dispersed in polymers and hence must be included into the percolation models. Hence, the objective of the present paper is to attempt to include the inter-SWCNT interactions into an analytical and a numerical model for the percolation threshold and to quantify the effect of such interactions.

The organization of the paper is as follows: The descriptions of an analytical and a numerical computational method used to determine the percolation threshold for SWCNTs dispersed in a non-interacting polymeric matrix are presented in Sections 2.1 and 2.2, respectively. The computer program used to compute the electrical conductivity of a polymer containing SWCNT fillers is described in Section 2.3. The main results obtained in the present work are presented and discussed in Section 3, while the key conclusions resulted from the present study are summarized in Section 4.

2. Computational procedure

2.1. Analytical percolation model

There are several analytical models capable of predicting the percolation threshold for high length-to-diameter aspect-ratio cylinder-like particles of a discrete (minor) phase (such as a dispersion single SWCNTs or SWCNT bundles) embedded into a non-interacting matrix (the major) phase [4–11]. The basic ideas defined in these models are used in the present work to predict the percolation threshold single and bundled SWCNTs dispersed in a non-interaction polymeric matrix.

According to the analytical models [4–11], the number of SWCNTs at the percolation threshold, ρ_c, in the limit of an infinite nanotube length-to-diameter aspect ratio, is defined as:

$$\rho_c = \frac{V}{V_{ex}} \tag{1}$$

where V is the specimen volume and V_{ex} is the nanotube excluded volume. The excluded volume of an object is generally defined as the volume associated with that object which is not accessible by the center of mass of another (similar or identical) object. Following a simple geometrical argument, this volume for a SWCNT,

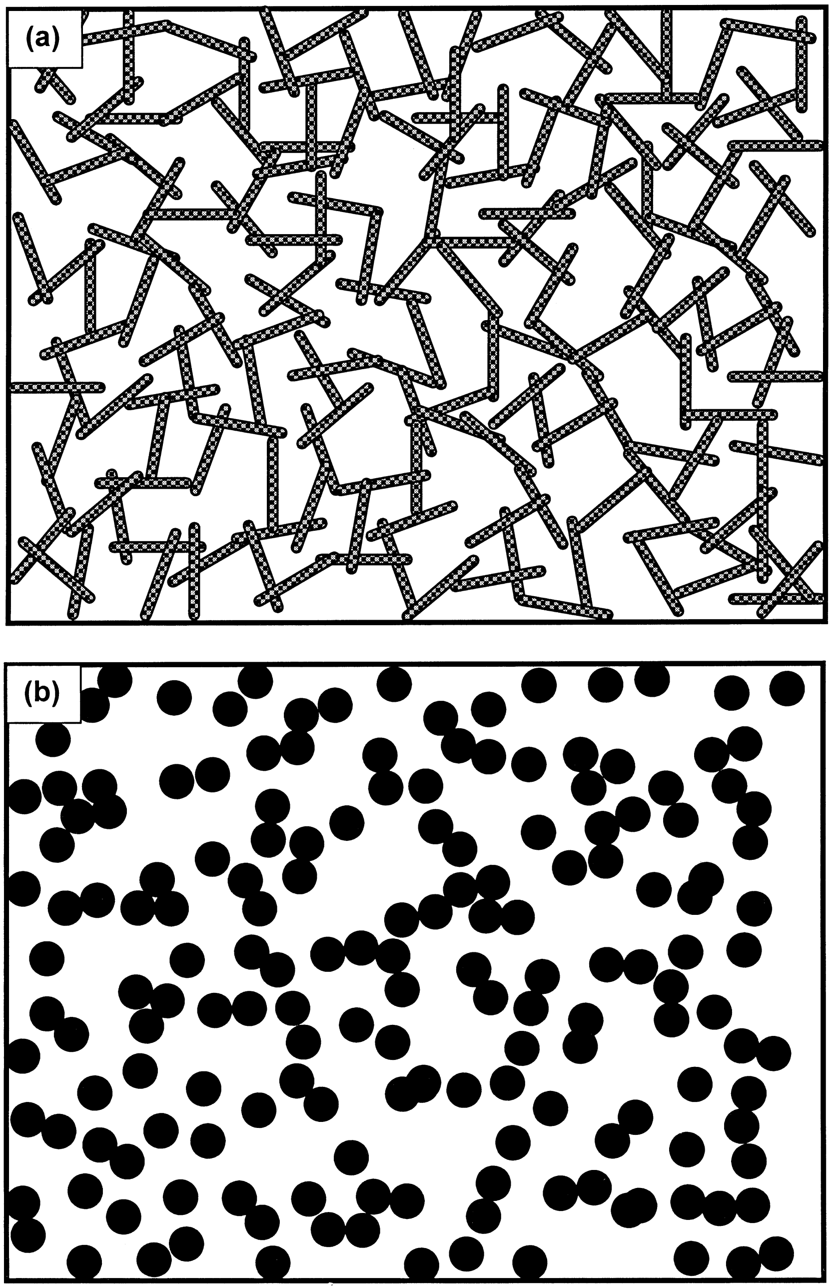

Figure 1 (a) A two-dimensional schematic of the percolation of randomly-dispersed high aspect-ratio particles; (b) the corresponding non-percolating microstructure for circular particles at the same area fraction as in (a).

modeled as a cylinder of length l, and radius r, capped at each end with a hemisphere, is defined as [4–11]:

$$V_{\mathrm{ex}} = \frac{32}{3}\pi r^3 + 8\pi l r^2 + 4l^2 r \langle \sin(\theta) \rangle. \tag{2}$$

The term $\langle \sin(\theta) \rangle$, the average value of $\sin(\theta)$, describes the degree of SWCNT alignment with θ being the angle between two SWCNTs. When the SWCNTs are perfectly aligned ($\theta = 0$), $\langle \sin(\theta) \rangle = 0$. On the other hand, for a random distribution of the SWCNT orientations, starting from the expression for a solid angle, Ω:

$$\Omega = 4\pi \sin^2(\theta/2) \tag{3}$$

the probability density distribution function for θ, $f(\theta) = (1/4\pi) d\Omega/d\theta$, (the 4π normalization factor is used to satisfy the condition $\int_0^\pi f(\theta) d\theta = 1$) has been derived as:

$$f(\theta) = 0.5 \sin\theta \tag{4}$$

and hence the $\langle \sin(\theta) \rangle$ term is evaluated as:

$$\langle \sin(\theta) \rangle = \int_0^\pi f(\theta) \sin(\theta) d\theta = \int_0^\pi 0.5 \sin^2\theta \, d\theta = 0.25\pi \tag{5}$$

A truly random distribution of the SWCNTs cannot be generally expected since the SWCNTs tend to interact with each other and to promote their mutual alignment. This is simply the result of the fact that van der Waals interactions between the aligned SWCNTs are stronger giving rise to a lower energy of the system.

Consequently, the orientation of the SWCNT is not expected to be uniform but rather skewed in the direction of aligned nanotubes. Before the equilibrium orientation distribution of the SWCNTs can be determined, one must first quantify the variation of the potential energy of two nanotubes with the mis-orientation angle θ and with the inter-nanotube distance. Toward that end, the van der Waals interaction energy between two carbon atoms, E_{CC}, separated by a distance d, is expressed using the following 12-6 Lennard-Jones potential [12]:

$$E_{\mathrm{CC}}(d) = \frac{C_{12}}{d^{12}} - \frac{C_6}{d^6} \tag{6}$$

where the interaction parameters C_{12} and C_6 have the values of 2.48×10^{-8} eVnm^{12} and 2.0×10^{-5} eVnm^6, respectively [12]. In addition, a Lennard-Jones potential cut-off distance (the inter-atomic distance beyond which the atoms are assumed not to interact) is set to 1.64 nm [12]. To find the total interaction energy between two SWCNTs, all pair interactions between the atoms of the two nanotubes must be included. The orientation of the two SWCNTs can be defined by the relative position vector of their centers, r_{12}, and by the orientation vectors of their axes, w_1 and w_2, respectively. The total van der Waals interaction energy between the two SWCNTs, E_{int}, can then be defined by the following double surface integral:

$$E_{\mathrm{int}}(r, w_1, w_2) = \int_{S_1} dS_1 \int_{S_2} dS_2 E_{\mathrm{cc}}(|s_1 - s_2|)\sigma^2 \tag{7}$$

where S_1 and S_2 denote the surfaces of the two SWCNTs while s_1 and s_2 are the position vectors of the surfaces elements dS_1 and dS_2, respectively and the atomic surface density σ is assigned the following value: $\sigma = 38.3$ nm^{-2} [12].

While there is no closed-form solution for the double surface integral given on the right hand side of Equation 7, the numerical evolution of this integral using a numerical procedure (e.g. a multi-dimensional trapezoidal rule) is trivial. The results of the numerical computation of the variation of interaction energy for two SWCNTs with an misorientation angle, θ, normalized by the interaction energy between the same two SWCNTs in a mutually orthogonal orientation, $E_{\mathrm{int},\theta}/E_{\mathrm{int},\theta} = \pi/2$ at two different values of the nanotubes centers distances, $|r_{12}|$, are shown in Fig. 3. Nanotubes with a typical length-to-diameter aspect ratio $l/2r = 10^3$ and with a typical radius $r = 0.7$ nm, are considered in Fig. 3. The two values of the nanotubes centers distances correspond respectively to: (a) the equilibrium van der Waals separation of two parallel SWCNTs (2×0.7 nm $+ 0.17$ nm $= 1.57$ nm) where a value of 0.17 nm is used for the van der Waals separation of two carbon atoms and (b) a separation of two parallel SWCNTs at which the shortest distance between the carbon atoms of the two nanotubes is equal to the van der Waals cut-of distance (2×0.7 nm$+ 1.64$ nm $= 3.04$ nm). The results shown in Fig. 3 suggest that the $E_{\mathrm{int},\theta}/E_{\mathrm{int},\theta=\pi/2}$ vs. θ, is only weakly dependent on the inter-nanotube distance and that it could be fitted by a polynomial of the six order as:

$$\begin{aligned} E_{\mathrm{int}(\theta)} &= E_{\mathrm{int}(\theta=\pi/2)}(3.90\theta^6 + 19.63\theta^5 + 35.92\theta^4 \\ &\quad + 27.38\theta^3 + 6.61\theta^2 - 1.13\theta \\ &\quad + 2.96) 0 \le \theta \le \pi/2 \\ E_{\mathrm{int},\pi/2+\theta} &= E_{\mathrm{int},\pi/2-\theta} 0 \le \theta \le \pi/2 \end{aligned} \tag{8}$$

The curve corresponding to the fitting polynomial of the sixth order given in Equation 8 is displayed in Fig. 2 using a dotted line and labeled "*Fitting Polynomial*".

The probabilistic density distribution function for the orientation of SWCNTs is next defined as:

$$f(\theta) = \frac{1}{Z} \sin(\theta) \exp\left(- \frac{E_{\mathrm{int},\theta} - E_{\mathrm{int},\theta=0}}{RT} \right) \tag{9}$$

where Z is a normalization factor which ensures that $\int_0^\pi f(\theta) = 1$, R is the universal gas constant and T ($= 295$ K) is the temperature. Once the probability density distribution function $f(\theta)$ is defined, the $\langle \sin(\theta) \rangle$ term can be evaluated using the left-most relation in Equation 5. This procedure yielded $\langle \sin(\theta) \rangle = (0.053 - 0.11)\pi$ for the range of values for the nanotubes centers distances shown in Fig. 2. This finding suggests a significant deviation of the "equilibrium" orientation of SWCNTs from a random distribution ($\langle \sin(\theta) \rangle = 0.25\pi$) toward an aligned arrangement of the nanotubes ($\langle \sin(\theta) \rangle = 0$).

Once the $\langle \sin(\theta) \rangle$ term is defined, the excluded volume can be calculated and the volume fraction of the nanotubes at the percolation threshold, ϕ_c, computed as:

$$\phi_c = \frac{\rho_c V_{\mathrm{SWCNT}}}{V} \tag{10}$$

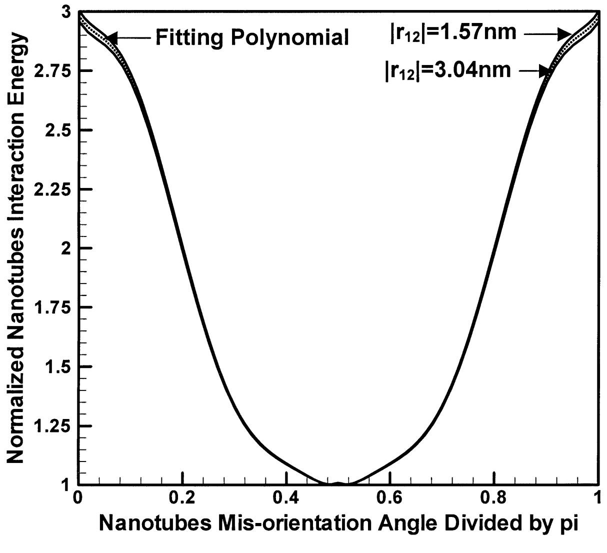

Figure 2 Variation of the normalized van der Waals interaction energy between two SWCNTs as a function of their mis-orientation angle and the nanotubes centers distance, $|r_{12}|$.

where the volume of a SWCNT, V_{SWCNT}, is defined as:

$$V_{\text{SWCNT}} = \frac{4}{3}\pi r^3 + \pi l r^2 \tag{11}$$

It should be noted that the procedure presented above is strictly valid only in the limit of an infinite nanotube length-to-diameter aspect ratio ($l/2r \to \infty$). Therefore, a numerical simulation method is used in the next section to recalculate the percolation thresholds for the single SWCNTs and for the bundles consisting of three, seven, and nineteen closely-packed SWCNTs. While numerical methods may suffer from a number of limitations (primarily associated with the fact that they typically require a large number of simulation runs in order to obtain a statistically accurate solution), they are generally considered more reliable at smaller values of the aspect ratio.

2.2. Numerical simulations of percolation

Since the analytical model presented in the previous section is strictly valid only in the limit of an infinite ($l/2r$) aspect ratio, numerical simulations are also used for determination of the number density (or the volume fraction) of the SWCNTs at the percolation threshold. The simulations are carried out using the following procedure:

(a) First, a cubic unit cell is constructed, and the periodic boundary conditions applied over the surfaces of the unit cell. The size of the unit cell is varied in order to determine a potential dependence of the computed percolation threshold on the unit-cell size.

(b) SWCNTs are next added (one at a time) into the unit cell by selecting five random numbers. Three of these random numbers are chosen from a uniform distribution and are used to define the coordinates for the center of mass of a nanotube. The other two random numbers are used to specify the components of the unit vector along the nanotube axis. These two random numbers are chosen in accordance with the density distribution functions given by either Equation 9 or Equation 4, depending on whether the effect of van der Waals interactions on the orientation distribution of the carbon nanotubes is considered or not. This is done by first generating a random number *ran* distributed uniformly in the range (0, 1) and then using the method of inversion of the cumulative distribution function [13] to compute the nanotubes mis-orientation angle, θ, as:

$$\theta = F_{\theta}^{-1}(ran) \tag{12}$$

where $F_{\theta}()$ is the cumulative distribution function corresponding to the probability density function given by Equations 4 and 9. Once the coordinates for the center of mass and the orientation of a SWCNT are specified, and using the SWCNT length ($l = 3\ \mu$m), the coordinates of the end points of the SWCNT in question are defined.

(c) Each time after a new SWCNT is added into the unit cell, it is checked if it is in contact with one or more of the SWCNTs already present in the unit cell. This is done by determining the minimum distance between the axes of the SWCNT in question and the axes of the remaining SWCNTs. If such distance for two SWCNTs is smaller than the nanotube diameter ($2r$), the SWCNTs are considered to be in contact. The minimum distance between the axes of two SWCNTs is determined using the procedure proposed by Allen *et al.* [14]. This procedure involves two steps: (i) First, the shortest distance, d_{normal}, between the two "carrier" lines, (the lines containing the axes of the two SWCNTs) is determined. It should be noted that the vector along this shortest distance is normal to both carrier lines; and (ii) the two carrier lines are next projected onto a plane whose normal is co-linear with the vector along d_{normal}, and the shortest in-plane distance between the two SWCNTs, $d_{\text{in-plane}}$, computed using a simple geometric procedure. The shortest spatial distance between the two SWCNTs, d_{SWCNT}, is then calculated as: $d_{\text{SWCNT}} = \sqrt{d_{\text{normal}}^2 + d_{\text{in-plane}}^2}$.

(d) When two SWCNTs are found to be in contact, their minimum distance is generally smaller than $2r$ which means that the two SWCNTs penetrate each other. Since such penetration is an un-physical phenomenon, the added SWCNT is translated in a randomly selected direction until the minimum distance between the two SWCNTs becomes equal $2r$. Formation of the clusters consisting of touching nanotubes is handled using the tree-based union/find algorithm proposed by Newman and Ziff [15].

(e) As SWCNTs are added and clusters are formed by the contacting SWCNTs, an algorithm is activated to check if any of the clusters extends over the entire unit cell. Once a cluster which extends over the entire unit cell is detected, the simulation is terminated, and the number of SWCNTs, the volume of a nanotube and the volume of the unit cell used to determine the SWCNT volume fraction at the percolation threshold. While calculating the volume fraction of SWCNTs at the percolation threshold, for the SWCNTs extending over the cell boundary only the volume of their segments lying within the unit cell are considered.

2.3. Computation of the electrical conductivity

Electrical conductivity of the polymer containing a dispersion of the SWCNTs is calculated using the SPICE 3 computer program which was originally created and currently maintained at the Electrical Engineering and Computer Science Department at the University of California at Berkeley [16]. SPICE 3 is a general-purpose circuit simulation program for nonlinear *dc*, nonlinear transient, and linear *ac* analyses. Circuits analyzed may contain resistors, capacitors, inductors, mutual inductors, independent voltage and current sources, four types of dependent sources, lossless and lossy transmission lines, switches, uniform distributed *RC* lines, and the five most common semiconductor devices: *diodes*, *BJTs*, *JFETs*, *MESFETs*, and *MOSFETs*. The *dc* analysis portion of SPICE 3 used in the present work determines the *dc* operating point of a circuit in which inductors are shorted and capacitors opened. A *dc* analysis is automatically performed prior to a transient analysis to determine the transient initial conditions, and prior to an *ac* small-signal analysis to determine the linearized, small-signal models for nonlinear devices. If requested, the *dc* small-signal value of a transfer function (ratio of output variable to input source), input resistance, and output resistance is also computed as a part of the *dc* solution. The *dc* analysis can also be used to generate *dc* transfer curves: a specified independent voltage or current source is stepped over a user-specified range and the *dc* output variables are stored for each sequential source value.

Since the electrical conductivity of a typical polymer-matrix material such as CP2, an aromatic colorless polyimide used in the work of Ounaies *et al.* [3], is typically around 10^{-17}–10^{-18} S/cm and thus at least 22 orders of magnitude smaller than that of SWCNTs (typically 10^4–10^5 S/cm), the electrical conductivity in a polymeric material containing percolating SWCNTs clusters is assumed to be controlled by the SWCNTs. When the concentration of SWCNTs in the polymeric matrix is lower than the percolation threshold, non-percolating SWCNTs clusters are assumed to be bridged by fibers of the polymeric-matrix material whose diameter (and hence electric conductance) is taken to scale with the volume fraction of the polymer. Additional details regarding the calculation of the electrical conductivity of the polymeric material containing a hypo-percolation-threshold volume fraction of the SWCNTs is given in Section 3.3. It should be also noted that in order to eliminate unnecessary computation, all SWCNT end segments and the segments intersecting the faces of the unit cell orthogonal to the direction of current flow are excluded during calculation of the electrical conductivity.

3. Results and discussion

3.1. Analytical percolation model

The analytical model developed in Section 2.1 is used in this section to compute the percolation threshold for single SWCNTs and SWCNT bundles dispersed in a non-interacting (polymeric) matrix.

To determine the percolation threshold for the single SWCNTs, Equations 2 and 11 are substituted into Equation 10 and the average values for the nanotubes radius, $r = 0.7$ nm, and for the nanotubes length, $l = 3\,\mu$m, as reported by Ounaies *et al.* [3] are used. Under the assumption of a random orientation distribution of the SWCNTs ($\langle\sin(\theta)\rangle = 0.25\pi$), this procedure yielded the SWCNT volume fraction at the percolation threshold $\phi_c = 0.000233$, which is less than one half of the experimental value (=0.0005 ± 0.00015) reported by Ounaies *et al.* [3]. When van der Waals interactions between the SWCNTs are taken into account ($\langle\sin(\theta)\rangle = (0.053{-}0.11)\pi$), the SWCNT volume fraction at the percolation threshold is in a range between 0.000425 and 0.000876. These values are in a much better agreement with their experimental counterpart, $\phi_c = 0.0005 \pm 0.00015$.

The computed percolation threshold values discussed above are obtained under the assumption that SWCNTs are dispersed as single nanotubes within the polymer matrix. Since a complete separation of the SWCNT ropes (the clusters of closely packed parallel nanotubes obtained during fabrication of the SWCNTs) into individual nanotubes is generally not attainable due to the van der Waals type of attraction between the closely spaced nanotubes, it is important to assess how a potential lack of complete separation of the SWCNT ropes into individual nanotubes (or a potential reagglomeration of the nanotubes into bundles) affects the SWCNT volume fraction at the percolation threshold. Toward that end, the bundles consisting of three, seven and nineteen touching parallel SWCNTs arranged on a triangular (close-packed) lattice are considered (Fig. 3). The calculation is simplified by treating such bundles as having a cylindrical shape and being terminated with hemi-spherical end caps. Hence, the length of the cylindrical portion of such bundles is the same as that of the individual SWCNTs while their radius is increased. This, in turn, causes the aspect ratio ($l/2r$) to decrease with the number of SWCNTs in the bundle (Table I). It should be noted that a 0.34 nm van der Waals wall-to-wall separation of the adjacent nanotubes is used in Table I when calculating the radii of the three-, seven-, and nineteen-SWCNT bundles [12]. The effect of the number of nanotubes in the bundle, under both the condition of a random orientation distribution of the nanotube bundles and the condition of a partial alignment of the bundles due to the bundle-bundle van der Waals interactions, on the volume fraction of SWCNTs at the

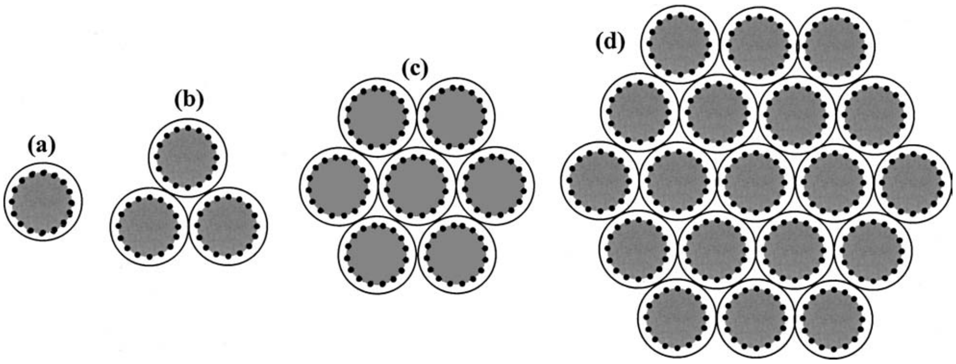

Figure 3 Schematics of: (a) a single SWCNT and (b)–(d) three-, seven- and nineteen-SWCNT bundles, respectively. Dots are used to represent nanotubes walls while the lines are used to represent van der Waals radii.

TABLE I The effect of SWCNT bundling on the percolation threshold volume fraction as predicted by the analytical model

Number of SWCNTs in the bundle	Bundle radius (nm)	Bundle length (μm)	Bundle aspect ratio	Percolation threshold volume fraction (Random orientation)	Percolation threshold volume fraction (SWCNT interactions)
1	0.70	3.0	2143	0.000233	0.000528–0.001091
3	1.86	3.0	807	0.000262	0.000592–0.001215
7	2.61	3.0	575	0.000435	0.000980–0.002001
19	4.35	3.0	345	0.000705	0.001580–0.003191

percolation threshold as predicted by Equation 10 in conjuction with Equations 2 and 11 is shown in Table I. The results displayed in Table I show that as the number of SWCNTs in the bundle increases, the SWCNT volume fraction at the percolation threshold also increases. Furthermore, under the assumption of a random orientation distribution of the SWCNTs or their bundles, if on average the SWCNTs are dispersed as seven- and nineteen-nanotube bundles, the agreement between the model prediction (0.000435–0.000705) and the experiment (=0.0005 ± 0.00015) is excellent. However, it should be noted that as the aspect ratio decreases, the analytical approach used, which is strictly valid only in the $l/2r \to \infty$ limit, becomes less reliable. Therefore, the numerical simulation method developed in Section 2.2 is used in the next section to recalculate the percolation thresholds for the single SWCNTs and for the three-, seven-, and nineteen-nanotube bundles.

It should be noted that if the equations presented in Ref. [9] are used to compute the percolation threshold under the random-distribution conditions, the values obtained are in a somewhat better agreement with the experimental ones. Nevertheless, when the effect of SWCNT interactions is included in the equations presented in Ref. [9], the values of the percolation threshold are found to increase in the same way as the values listed in Table I. This finding suggests that, while the values of the percolation threshold are generally effected by the analytical model used, the effect of nanotubes interactions is significant but weakly affected by the choice of the analytical model.

3.2. Numerical simulations

The numerical model developed in Section 2.2 is used in this section to compute the percolation threshold for the individual SWCNTs and for the three-, seven-, and nineteen-SWCNT bundles dispersed in a non-interacting (polymeric) matrix. Examples of the percolating clusters consisting of randomly-distributed (non-interacting) SWCNTs and of SWCNTs interacting through the van der Waals forces are displayed in Fig. 4a and b, respectively. It should be noted that in order to increase clarity of the nanotube structures displayed in Fig. 4a and b, only the SWCNTs associated with the percolating clusters are shown and these nanotubes are displayed using a radius which is 100 times larger than the actual nanotube radius. A comparison of the nanotube structures displayed in Fig. 4a and b shows that, as established in the previous section using the analytical percolation model, interactions between the nanotubes which give rise to their mutual local (short-range) alignment increases the percolation threshold.

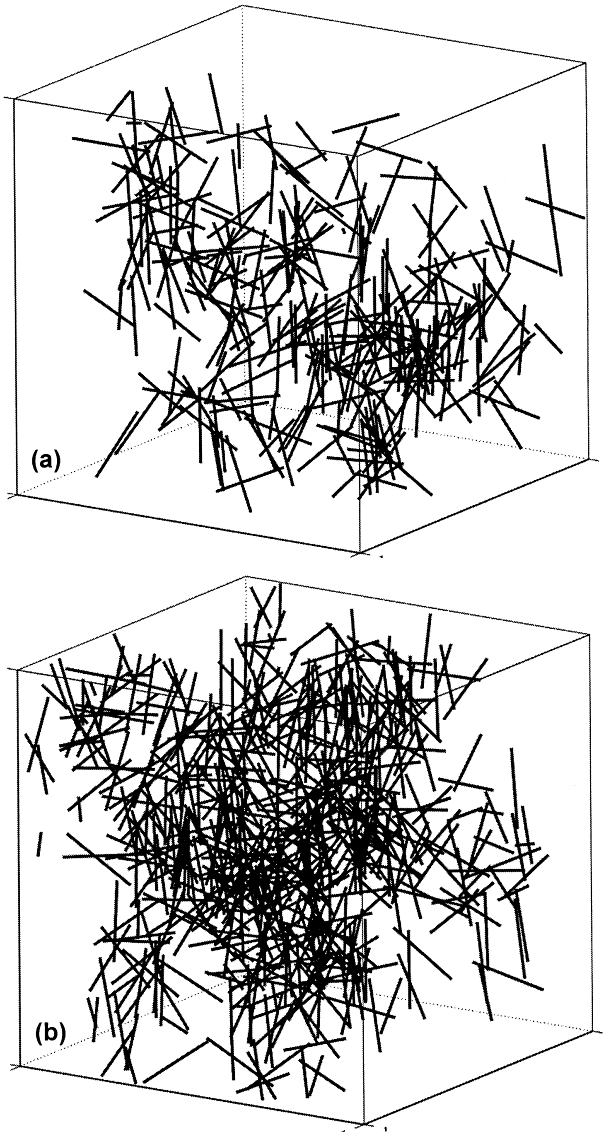

Figure 4 Typical structure of a percolating cluster in the cases of: (a) a random distribution of the SWCNTs and (b) the SWCNTs interacting via the van der Waals forces.

The numerical simulation results of the computation of the percolation threshold in the case of isolated SWCNTs and of three-, seven-, and nineteen-SWCNT bundles are shown in Table II. The results shown in Table II contain the mean values and the standar deviations for 50 numerical simulations in each case. The results displayed in Table II show that, as expected, the percolation threshold increases with an increase in the number of SWCNTs in the bundle and as a result of the van der Waals interactions between the nanotubes.

TABLE II The effect of SWCNT bundling on the percolation threshold volume fraction as predicted by the numerical model (The results shown for each case correspond to the mean values and the standard deviation of ten simulations)

Number of SWCNTs in the bundle	Bundle radius (nm)	Bundle length (μm)	Bundle aspect ratio	Percolation threshold volume fraction (Random orientation)	Percolation threshold volume fraction (SWCNT interactions)
1	0.70	3.0	2143	0.000201 ± 0.000044	0.000512 ± 0.000069
3	1.86	3.0	807	0.000332 ± 0.000031	0.000873 ± 0.000124
7	2.61	3.0	575	0.000492 ± 0.000063	0.001546 ± 0.000346
19	4.35	3.0	345	0.000853 ± 0.000061	0.002495 ± 0.000497

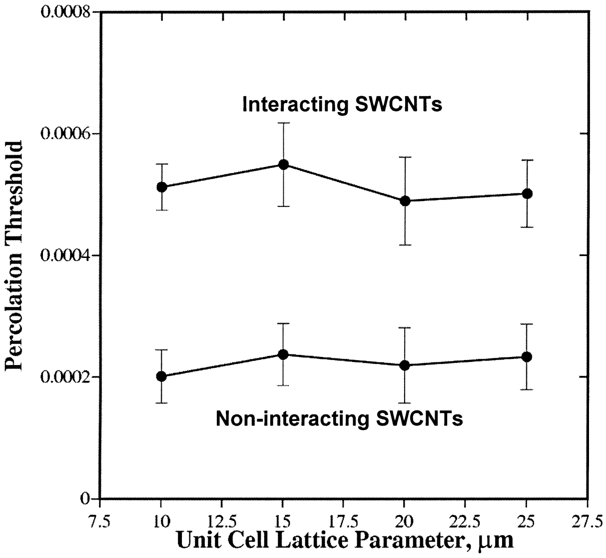

Figure 5 Effect of the unit cell size on the percolating threshold in the cases of a random distribution of the SWCNTs and the SWCNTs interacting via the van der Waals forces.

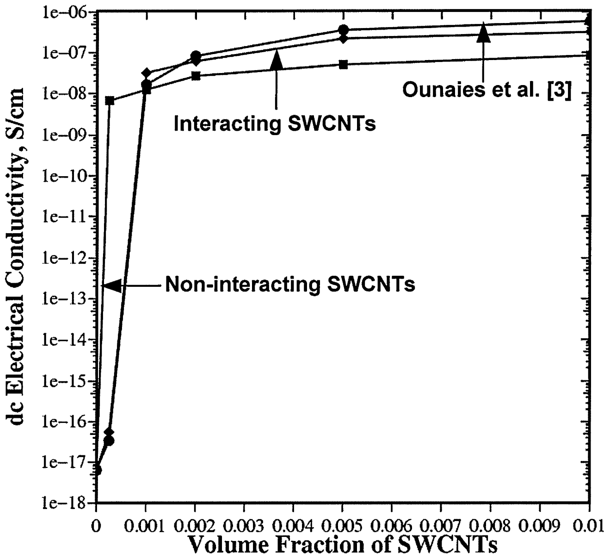

Figure 6 Effect of the volume fraction of the SWCNTs on the *dc* electrical conductivity of CP2 polyimide + SWCNT composites.

Furthermore, a comparison of the corresponding results shown in Tables I and II shows that the agreement between the predictions of the analytical and the numerical models are quite good. This is particularly the case for the individual SWCNTs. This finding suggests that the simpler and computationally less demanding analytical model can be used to predict the percolation threshold for cylinder-like particulates with an aspect ratio as low as ca. 350.

Since the numerical calculations of the percolation threshold are carried out under the periodic boundary conditions, the size of the unit cell used in the computation can in general have an effect on the computational results. To assess the potential effect of the size of the unit cell on the computed percolation threshold, numerical simulations of the percolation of isolated SWCNTs in the absence and in the presence of inter-SWCNT interactions are carried out at four different values of the unit cell size. The results of these simulations are displayed in Fig. 5. The results shown in this figure indicate that the unit cell size (within the range examined) has a very weak effect on the computed percolation threshold.

3.3. Computation of the electrical conductivity

The electrical network computational method described in Section 2.3 is utilized in this section to compute the variation of the *dc* electrical conductivity of a CP2 polyimide + SWCNTs composite. As stated earlier these type of polymer matrix composites were used by Ounaies *et al.* [3], and the experimental results of Ounaies *et al.* [3] pertaining to the effect of the volume fraction of SWCNTs on the (bulk) *dc* electrical conductivity in this material are displayed in Fig. 6. As seen, the *dc* electrical conductivity changes by about nine orders of magnitudes in the SWCNT volume fraction range between 0.0002 and 0.0010. In sharp contrast, at the SWCNT volume fraction levels outside this range, the *dc* electrical conductivity changes much more slowly. Specifically, at SWCNT volume fraction levels lower than 0.0002, the *dc* electrical conductivity increases with an increase in the SWCNT volume fraction between 6.3×10^{-18} S/cm (the *dc* electrical conductivity of the CP2 polyimide) and $\sim 3 \times 10^{-17}$ S/cm. At SWCNT volume fraction levels in excess of 0.0010, on the other hand, the *dc* electrical conductivity increases with an increase in the SWCNT volume fraction between 1.6×10^{-8} S/cm and 3×10^{-7} S/cm. The S-shaped character of the *dc* electrical conductivity vs. the SWCNT volume fraction relationship shown in Fig. 6 is an indication of the percolation transition with the percolation threshold being around 0.0005.

As discussed in Section 2.3, the *dc* conductivity of the composite material at the SWCNT volume fractions exceeding the percolation threshold is assumed to be dominated by current conduction through the percolating

SWCNT clusters. At volume fractions lower than the percolation threshold, non-percolating SWCNT clusters are assumed to be bridged by fibers of the CP2 polymeric material. The cross section area of such CP2 fibers is set equal to the surface area of unit cell face. The non-percolating SWCNT clusters in the composite material containing a hypopercolation threshold volume fraction of the SWCNTs are generated in the following way: First, a configuration containing a SWCNT percolating cluster is generated using the procedure described in Section 2.2. Then, the required number of SWCNTs is at random replaced with the CP2 fibers in order to obtain the target hypo-percolation threshold volume fraction of the SWCNTs.

The computational results pertaining to the effect of the volume fraction of SWCNTs on the *dc* electrical conductivity in the corresponding CP2 polyimide matrix composites are also shown in Fig. 6 both for the non-interacting and for the interacting SWCNTs. The results displayed in Fig. 6 show that, as expected, van der Waals interactions between the SWCNTs give rise to an increase in the computed percolation threshold. Also, the computed percolation threshold for the interacting SWCNTs is in significantly better agreement with the experimental one. Furthermore, absolute values of the *dc* electrical conductivity both at the hypo- and at the hyper-percolation threshold volume fraction levels of the SWCNTs are in reasonably good agreement with their experimental counterparts.

The post percolation threshold behavior of the *dc* electrical conductivity in composite materials is often modeled using the following power law:

$$\sigma = A(\phi - \phi_c)^t \tag{13}$$

where σ is the *dc* electrical conductivity, ϕ, the SWCNT volume fraction and A and t percolation parameters. Linear least-squares fitting of the $log\,\sigma$ vs. $(\phi - \phi_c)$ computed results yielded $A = 1.6 \times 10^{-6}$ S/cm and $t = 0.87$ for the non-interacting SWCNTs and $A = 2.0 \times 10^{-5}$ S/cm and $t = 1.17$ for the interacting SWCNTs. The latter set of data is in somewhat better agreement with their experimental counterparts ($A = 6.7 \times 10^{-4}$ S/cm and $t = 1.38$) obtained using the results of Ounaies *et al.* [3]. It should be noted that the ϕ_c values listed in Table II which were obtained using the numerical model and, thus, deemed most reliable, are used in this procedure. The value $t = 1.17$ is not in a very good agreement with the theoretical value of $\sim$2 predicted by Sahimi [17] for three-dimensional percolating systems. However, the value of ϕ_c used generally can have a significant effect of the value of t. This is found to be the case in the present work where the use of the analytical values for ϕ_c form Table I yields $t = 1.79$ which is in a significantly better agreement with its theoretical counterpart.

4. Conclusions

Based on the results obtained in the present work, the following main conclusions can be drawn:

1. A relatively simple analytical percolation model based on the concept of an excluded volume gives rise to the values of the percolation threshold for a dispersion of single-walled carbon nanotubes (SWCNTs) and SWCNT bundles within a non-reactive polymeric matrix which are within few percents of the percolation threshold values obtained using a more accurate, but computationally quite intensive numerical approach.
2. Van der Walls interactions between the SWCNTs and the associated mutual local alignment of the nanotubes gives rise to an increase in the computed percolation threshold making it very comparable with its experimental counterpart.
3. The *dc* electrical conductivity of polymer matrix materials containing SWCNT fillers can be successfully predicted using an electrical network analysis.

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