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Jang, Sung-Hwan

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PAPER

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PAPER

Effective electrical conductivity of carbon nanotube-polymer composites: a simplified model and its validation

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Sung-Hwan Jang and Huiming Yin

Department of Civil Engineering and Engineering Mechanics, Columbia University, 610 Seeley W. Mudd 500 West 120th Street, New York, NY 10027, USA

E-mail: yin@civil.columbia.edu

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Abstract

A simplified model is presented to predict the effective electrical conductivity of carbon nanotube (CNT)-polymer composite with different material proportions, which is validated by the experiments of multi-walled CNT/polydimethylsiloxane (PDMS) composites. CNTs are well dispersed in a PDMS matrix, and the mixture is then cured and cast into thin films for electrical characterization. The CNTs are assumed to be statistically uniformly distributed in the PDMS matrix with the three-dimensional (3D) waviness. As the proportion of CNTs increases to a certain level, namely the percolation threshold, the discrete CNTs start to connect with each other, forming a 3D network which exhibits a significant increase of effective electrical conductivity. The eight-chain model has been used to predict the effective electrical conductivity of the composite, in which the contact resistance between CNTs has been considered through the Simmons' equation. The eight-chain network features can be significantly changed with the modification to mixing process, CNT length and diameter, and CNT clustering and curling. A Gaussian statistics-based formulation is used to calculate the effective length of a single CNT well dispersed in the matrix. The modeling results of effective electrical conductivity agree with the experiments very well, which are highly dependent on a contact resistance between CNTs and the waviness of the CNTs. The effect of inner-nanotube distance and diameter of CNTs on the effective electrical conductivity of the CNT/PDMS composite is also discussed.

1. Introduction

CNTs have been proposed as a sensor material due to their excellent electric properties [1, 2]. The CNT's electrical conductance is highly sensitive to the mechanical strain. The gauge factor (GF) for a single CNT has been reported as high as 600–1000 [3]. However, it is not straightforward to use single CNTs in engineering tests due to their small size and high stiffness. Using CNTs to modify polymers provides a practical way to perform strain and fracture sensing. For example, they have been used as strain sensors or damage indicators due to their high strain sensitivity compared to conventional metallic-based strain sensors [4–6]. Hu *et al* [7] studied the strain sensitivity of epoxy-based composite with various types of CNT where the strain gauge factor reaches 20 under a static tensile loading using 1 wt.% of multi-walled carbon nanotube (MWCNT)/epoxy composites. In addition, MWCNT polymer-based composites have been used in various applications because of the superior material properties of CNTs in electrical [1, 2], thermal [8, 9], and mechanical aspects [10, 11].

Yin [12] invented a novel strain sensor made of ferromagnetic particles (FMPs) and CNTs in PDMS for a large strain capacity and a high sensitivity. FMPs and CNTs are mixed in a prepolymer under a high magnetic field. FMPs are aligned into chains [13–15]. The mixture is cured and solidified into a thin film, which is then tailored into a tape with the chain direction normal to the width direction. Although the electric conductivity of PDMS is extremely small, a properly chosen volume fraction of CNTs can significantly improve the effective conductivity of the mixture for good measurability. Moreover, FMP chains further improve the conductivity. Therefore, along the chain direction, the electric conductivity of the tape is much higher than in other directions.

Electrodes are attached onto the tape along the width direction with a certain spacing, and gauge leads are used to setup the measurement circuit. In an actual test, the tape will be glued to the surface of a test specimen. Because PDMS is so compliant, the tape will deform together with the specimen surface, which will lead to significant change of the electric conductivity of the tape, which can therefore sense the strain and fracture of the specimen. Because the FMPs are much larger than CNTs, the CNT modified PDMS can be considered as a matrix material for FMPs. The effective electrical conductivity of CNT modified PDMS is an important factor for sensor design and development because it not only determines the strain sensitivity or GF of the sensor, but also because it significantly affects the sensor fabrication and operation. The electrical behavior of CNT composites has been studied [16–18]. Yan *et al* [19] developed a model of the effective electrical conductivity for CNT composites incorporating the interface effect with an average field theory. Some empirical models based on percolation theory agree well with experimental data [18, 20]. However, they cannot predict the effective material properties for composites with a large range of CNT proportions and varying physical parameters, such as the length and diameter of CNTs.

The micromechanical approach provides a reliable method for predicting the effective material properties of the composites consisting of different kinds of components using the analysis of a representative volume element (RVE) or a unit cell [21]. Casas and Sevostianov [22] developed the micromechanical model to find the effective electrical conductivity of a complex cortical bone. They established the model based on the concept of a resistivity contribution tensor. Cantournet *et al* [23] proposed an eight-chain model which captures the physical deformation of an isotropic random network of an elastomer under different states of strain. They also applied the concept to MWCNT-elastomer composites for a large strain deformation behavior of the composites where the effect of MWCNTs is modeled via a constitutive element that tracks the motion of MWCNTs in the matrix.

The purpose of this paper is to develop a micromechanical model to predict the complex electric conduction behavior of CNT modified polymers with an increasing volume proportion of CNTs in PDMS. It is assumed that the CNTs are well dispersed in the PDMS, and clustering of CNTs or segregation of CNTs from the PDMS is not considered. When the proportion is below the percolation threshold, the CNTs are sparsely dispersed in the insulative PDMS matrix, and electron transport through the composite is very weak. As more CNTs are added, the discrete CNTs start to connect with each other forming a three-dimensional(3D) network, which exhibits a significant increase of effective electrical conductivity [24]. Although a single CNT can be treated as a one-dimensional(1D) cylinder, due to the large aspect ratio of its length to its diameter, it exhibits a 3D waviness with the distance between two ends much less than the CNT's actual length [25, 26], which can be described by the Gaussian statistics based formulation. The network of CNTs in the 3D volume is approximated by an eight-chain model in a unit cell. The contact resistance between CNTs has been considered through the Simmons' equation.

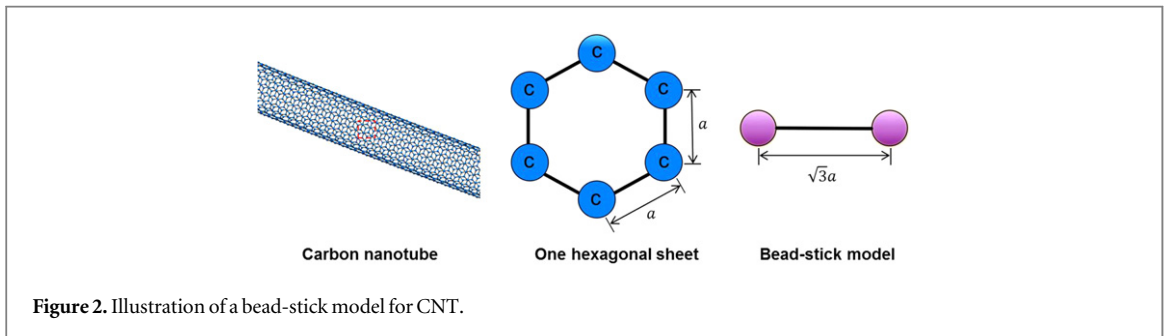
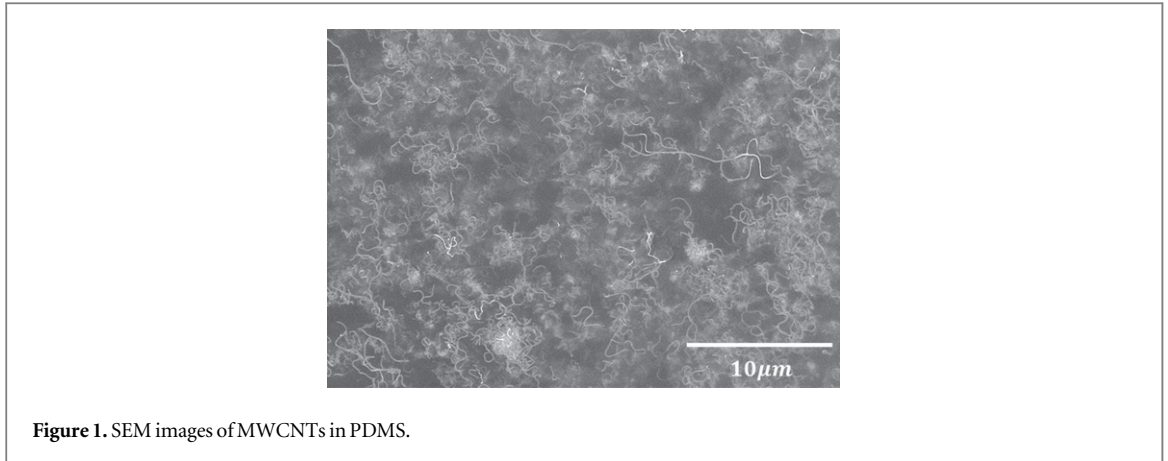
In what follows, a simplified model based on a unit cell is developed to predict the electrical conductivity of CNT/PDMS composites in section 2. The model takes into account the intrinsic and contact resistances of CNTs. Section 3 presents the experimental method to fabricate MWCNT/PDMS sensing composites using the solution casting method. Section 4 shows and discusses the modeling and the experimental results in terms of the critical volume fraction and the effective electrical conductivity at different volume fractions. The comparison between modeling and experimental results shows that the proposed model provides very good agreement for electrical conductivity of the MWCNT/PDMS composites. Section 5 provides some conclusive remarks.

2. Eight-chain model for effective electrical conductivity

When CNTs are mixed in a polymer, the microstructure significantly depends on the mixing effect and material proportion. The microstructure of PDMS containing 1 wt.% of well dispersed CNTs is shown in figure 1. Although a single CNT can be treated as a 1D cylinder, in a randomly dispersed CNT-polymer composite, a CNT exhibits a 3D curvature with random orientation. Because the polymer is electrically insulative, the electron transport through the CNT network significantly relies on the individual CNT's geometry, CNT-CNT connection, dispersion features and contact resistance. It has been a formidable task to simulate an actual CNT-polymer composite for its effective electric conductivity. This section will present a simplified model to idealize the network feature of CNTs and to predict the percolation threshold and the effective electrical conductivity.

2.1. Effective length of a single CNT

Consider the example of carbon nanotube in figure 2. The geometry can be represented by a repeating hexagonal sheet consisting of carbons. The carbon-carbon bond length is around 1.43Å even though it varies with different combinations [27, 28].



Although a single CNT on a nanoscale can be considered as a 1D hollow cylinder, due to its large aspect ratio, it exhibits a 3D waviness. The distance between two ends is much less than the CNT's length because of the fabrication process of CNT as well as the dispersion of CNTs in solvent. In order to represent the effective length of CNT for a curling effect, we consider a single CNT as numerous repeating segments where one hexagonal sheet of CNT is modeled as a bead-stick model, which has a length of $\sqrt{3}a$. The waviness of the CNT results from angles between two neighboring bead-stick units, which are caused by the mixing effort. Assume that a repeated unit is freely jointed to the neighboring unit randomly in a 3D space with an average angle denoted by γ . For simplicity, the total real length and the averaged effective end-to-end distance of a CNT in the 3D space can be, respectively, represented by the Gaussian chain statistics [29] as follows:

$$l_{\text{real}} = \sqrt{3} aN \quad (1)$$

$$l_{\text{eff}} = \sqrt{3} aN^{\frac{1}{2}} \sqrt{\left(\frac{1 + \cos \gamma}{1 - \cos \gamma}\right)} \quad (2)$$

where the carbon bond length $a \cong 1.43\text{\AA}$ and the segment number N should be very large, and a smaller γ represents a stiffer CNT which only allows small orientation. Combining the above two equations provides

$$l_{\text{eff}} = \sqrt{\sqrt{3} a \left(\frac{1 + \cos \gamma}{1 - \cos \gamma}\right)} \sqrt{l_{\text{real}}} \quad (3)$$

Although the angle γ may change with the mixing effort, in an average sense, it can be considered as a constant for a well-mixed CNT-polymer composite. Therefore, the above equation can be rewritten as

$$l_{\text{eff}} = k \sqrt{l_{\text{real}}} \quad (4)$$

where the constant $k = \sqrt{\sqrt{3} a \left(\frac{1 + \cos \gamma}{1 - \cos \gamma}\right)}$ with a dimension of $\sqrt{\text{length}}$ evaluates the waviness of CNTs in the composite. Therefore, given two end points of a CNT, the real length of the CNT can be calculated as

$$l_{\text{real}} = \left(l_{\text{eff}}/k\right)^2 \quad (5)$$

Notice that because γ cannot be measured by experiments, the constant k , which combines a and γ , will be obtained by a curve fitting of the effective material behavior of the composite. Therefore, it is a parameter to be

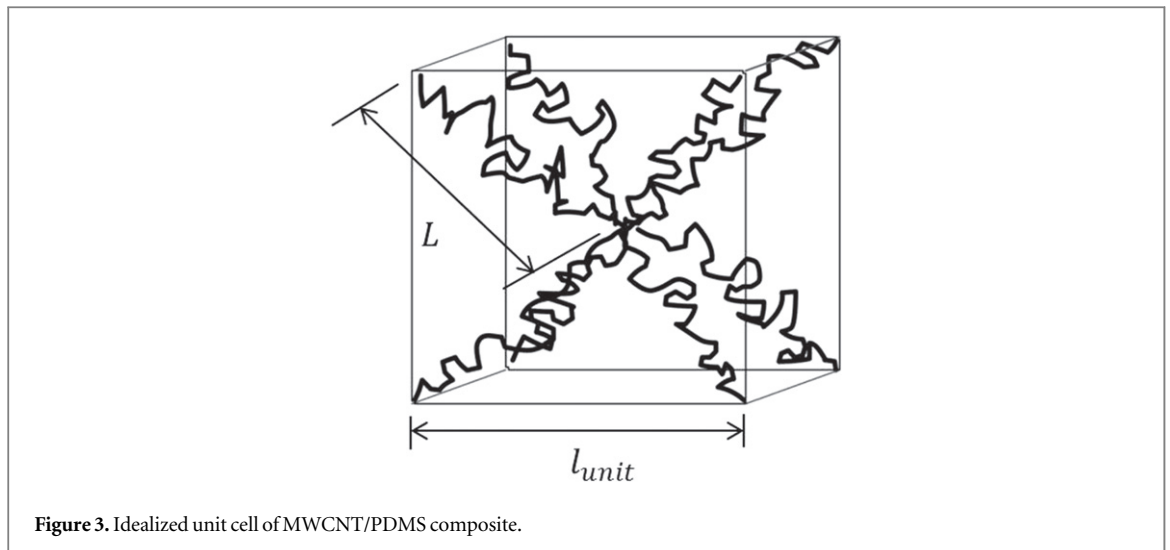


Figure 3. Idealized unit cell of MWCNT/PDMS composite.

determined in the data analysis. However, for one type of CNTs dispersed on a polymer through the same mixing process, one can approximately assume k is the same even if the volume fractions of CNTs are different.

2.2. Eight-chain model for CNT-polymer composites

When CNTs are well dispersed into a polymer matrix at a certain proportion, they connect to each other, forming a network, and significantly change the effective material properties of the polymer. Without considering any agglomeration of CNTs, a simplified unit cell has been proposed in figure 3 to describe the network effect on the effective electrical conductivity of the composite under the following assumptions:

1. The random isotropic CNT network in a polymer matrix is represented by the repeated cubic unit cells with eight CNTs along the diagonal directions [30, 31]. During the dispersion and fabrication process, because CNTs are well coated with polymer, CNTs approach each other at the joints but do not physically or chemically bond with a direct contact. Therefore, in this study, we only consider a contact resistance by the tunneling effect, which depends on CNT geometry, CNT-to-CNT gap, and polymer type among other factors [32].
2. Once a network forms, the ends of a CNT will come into contact with the ends of other CNTs disregarding the effect of cross joints for two CNTs coming into contact in the middle range of the CNTs. Due to the high contact resistance of the polymer, the electron transfer through the network will go through one end to another end of a CNT and then to another CNT by the tunneling effect. Therefore, the cross joints do not affect the electron transfer. Only end-to-end contact resistance between CNTs is considered due to a configuration of the unit cell model.
3. For each of the eight chains in the unit cell, the CNT is actually not straight and the real length of CNT can be calculated using equation (5).

Notice that in the present unit cell, when two CNTs cross each other, because the contact resistance is obviously higher than CNT's resistance, the electron transport will go through the CNT instead crossing-joint if the situation of other joints stays the same. Therefore, the cross-joint electron transport is not considered in this model. Indeed, this is a very rough approximation as well as a significant simplification, because this idea unit cell cannot really describe the complex microstructure of the network and the CNT's orientation may be inconsistent with the electrical current direction, where the cross-joint electron transport is very common. However, the proposed model provides a practical approach to evaluate the effect of CNT's length and volume fraction and the effect of CNT-CNT contact resistance. Despite this limitation, when the model is calibrated with the effective material behavior at a certain set of parameters, it can still provide very good predictions of this complex material system, as the end-to-end contact and the cross-joint contact produce the similar trend based on the Simmon's model.

Because PDMS exhibits an electrical conductivity of $10^{-13} \sim 10^{-14} \text{ S} \cdot \text{m}^{-1}$ [33], the polymer can be idealized to be non-conductive in this model. Therefore, electrical conduction only goes through one CNT to another in the non-conductive polymer matrix. Based on Assumption 2, the effective resistance of a single CNT consists of its intrinsic resistance and the contact resistance by the tunneling effect between the next CNTs.

$$R_{\text{CNT}} = R_i + R_c \quad (6)$$

where R_i is an intrinsic resistance of a CNT and R_c is a contact resistance between CNTs.

The estimation of conductance of a CNT is difficult since the conductance of a CNT depends on many parameters, such as the number of current carrying shells, number of conducting channels for each shell, intershell interactions, and the number of metallic shells [34]. In this study, a CNT is considered as a uniform cylinder, and thus its intrinsic resistance can simply be calculated as:

$$R_i = \frac{4L}{\pi D^2 \sigma_i} \quad (7)$$

where σ_i is the electrical conductivity of a CNT, L the length, and D the diameter of the CNT, respectively.

The contact resistance of CNTs dispersed in a polymer matrix also varies in a wide range [35, 36]. The contact resistance between CNTs in the polymer matrix should be higher than that without the matrix since a thin non-conductive polymer film exists between CNTs, which results in a dramatic increase in the contact resistance of the composites. The contact resistance of MWCNTs is described using Simmons's equation with the electrical tunneling effect between two CNTs separated by a thin polymer film [37].

$$R_c = \frac{h^2 t}{ae^2 (2m\varphi)^{1/2}} \exp\left(\frac{4\pi t}{h} (2m\varphi)^{1/2}\right) \quad (8)$$

where a is the contact area which is approximated by D^2 , e (1.6×10^{-19} J) is the unit electron charge, h (4.1357×10^{-15} eV s) is the Planck's constant, t is the inter-nanotube distance, m (0.511 MeV c^{-2}) is the mass of an electron, and φ is the potential barrier height. The inter-nanotube distance, t , is decreased when the volume fraction of CNTs is increased, which can be expressed as

$$t = \alpha (f_{\text{CNT}})^\beta \quad (9)$$

where f_{CNT} is the volume fraction of the CNTs and both α and β are material constants [38].

Here the volume fraction f_{CNT} is related to the unit cell size l_{unit} by

$$f_{\text{CNT}} = \frac{8 \left(\frac{\sqrt{3} l_{\text{unit}}}{2}\right)^2 \frac{\pi D^2}{4}}{l_{\text{unit}}^3} = \frac{\sqrt{3} \pi D^2}{l_{\text{unit}}^2} \quad (10)$$

Therefore, for a CNT/polymer composite, once R_i and R_c for a single CNT are obtained, the effective electrical conductivity of the CNT can be calculated by

$$\bar{\sigma}_{\text{CNT}} = \frac{1}{1 + R_c/R_i} \sigma_i \quad (11)$$

through which the CNT network can be idealized as perfectly connected CNTs with the effective electrical conductivity $\bar{\sigma}_{\text{CNT}}$.

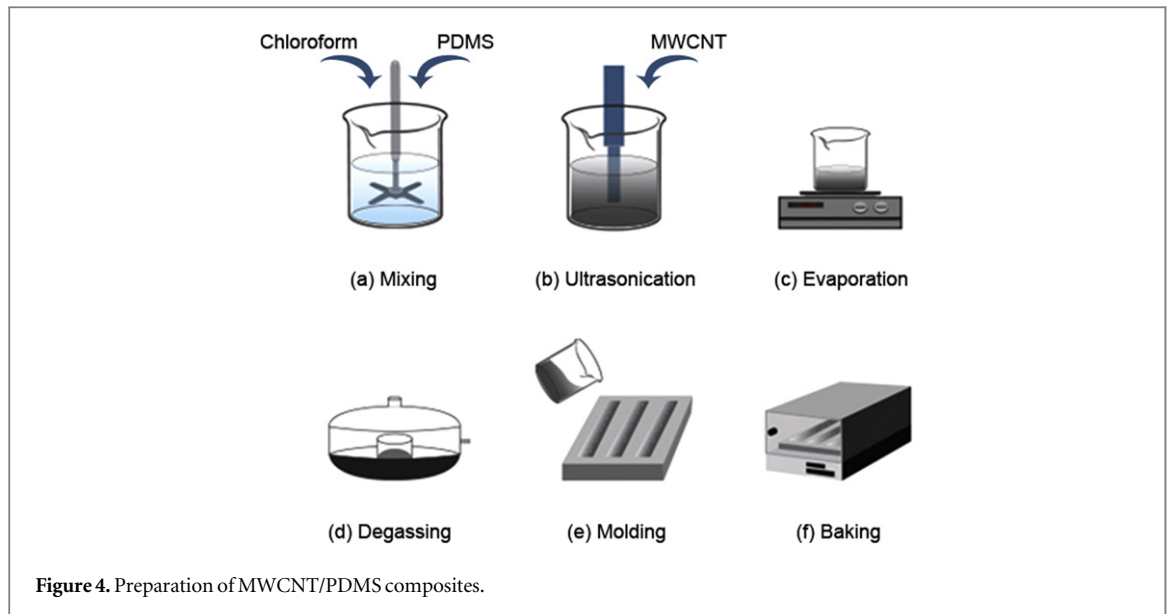
The effective resistance of a unit cell can be obtained by the equivalent circuit model based on a series-parallel resistance network. Total resistance of a unit cell can be written as

$$R_{\text{eff}} = \frac{1}{2} R_{\text{CNT}} \quad (12)$$

In the composite, electric current is considered to pass from the top surface to the bottom surface of the unit cell. Therefore, the effective electrical conductivity of the composite in the unit cell is determined by

$$\sigma_{\text{eff}} = \frac{l_{\text{unit}}}{R_{\text{eff}} A_{\text{unit}}} = \frac{1}{l_{\text{unit}} R_{\text{eff}}} \quad (13)$$

where l_{unit} is the edge length of the unit cell. Given the physical properties of a type of CNT, once the proportion of CNTs f_{CNT} is provided, the effective electrical conductivity of the CNT $\bar{\sigma}_{\text{CNT}}$ can be calculated by equation (11). On the other hand, the unit cell length l_{unit} and the corresponding real length of the CNT chain can also be calculated by equations (10) and (5). Therefore, the effective electrical conductivity of the composite σ_{eff} can be derived using equation (13). When the proportion of the CNTs is lower than the percolation threshold, the unit cell length is so large that the CNTs cannot connect to each other, so the conductivity will be extremely low, approaching zero. When the proportion of the CNTs is higher, one CNT may cross multiple unit cells forming a complex network.



3. Experiments

3.1. Material fabrication

In our experiments, chemical vapor deposition synthesized MWCNTs with a purity of above 95.0% (Research grade) and 85.0% (industrial grade) were both acquired from NanoLab (Newton, MA). Research graded MWCNTs were used for a percolation threshold of the composites. Two different lengths of MWCNTs (1–5 μm and 5–20 μm) were used, both of which exhibit a diameter of 15 nm. Industrial graded MWCNT was used to compare the modeling result over a large range of MWCNTs in the composite. Industrial graded MWCNT has 5–20 μm in the length and 10–30 nm in the diameter. PDMS elastomer (Sylgard 184) was obtained from Dow Corning, USA. Chloroform was used from Fisher Scientific as a dispersion agent in order to obtain well-dispersed MWCNTs in the matrix.

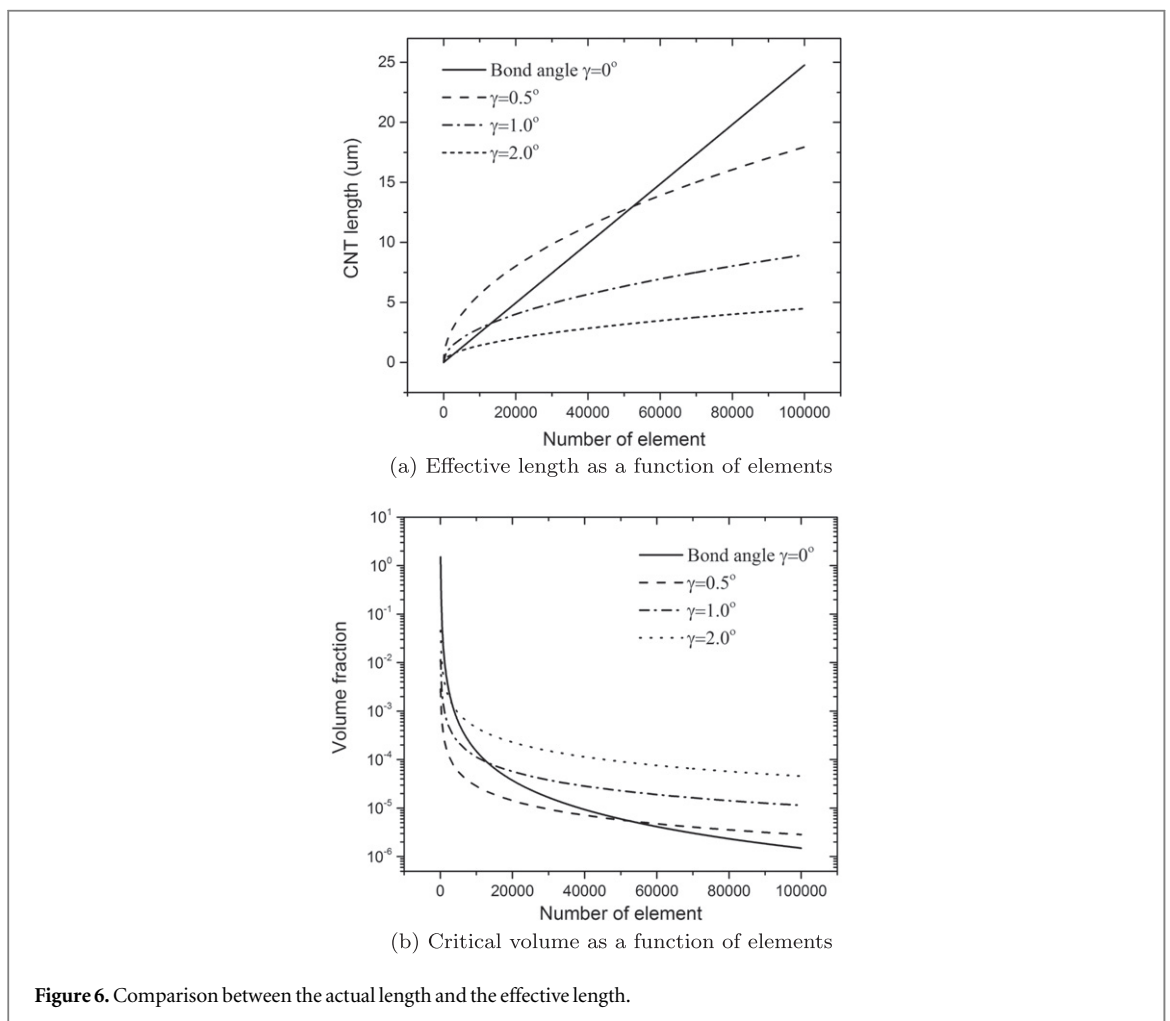
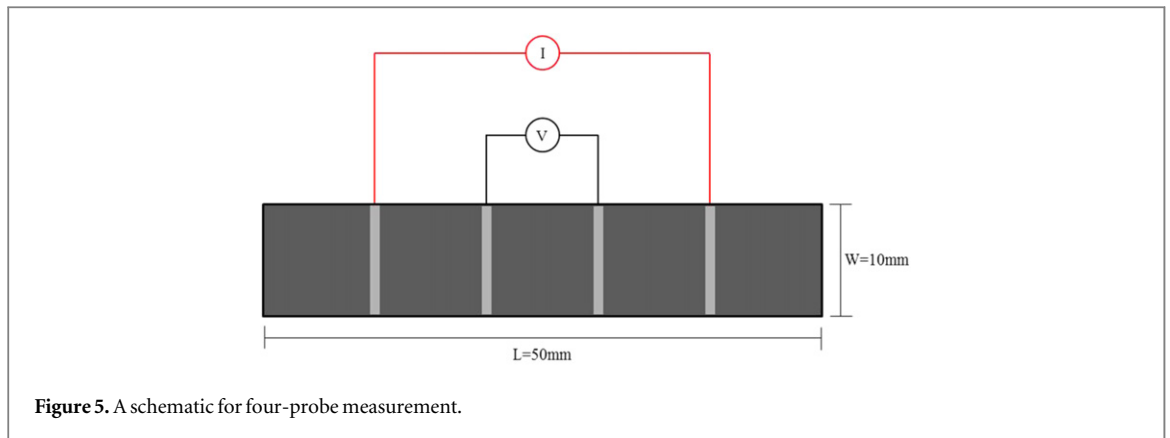
Different volume fractions of MWCNT/PDMS composites were fabricated by the solution casting method, as shown in figure 4. About 50.0 ml of chloroform was used as a solvent for the dispersion of MWCNTs which exist in large agglomerates due to van der Waals intermolecular force between MWCNTs. Chloroform was successfully used to disperse MWCNTs in PDMS compared to any other solvents, which dissolved PDMS base polymer easily and allowed high quality dispersion of MWCNTs [39]. MWCNT and PDMS were mixed with the solvent using a shear mixer for 3 min. A horn-type ultrasonicator was applied to break MWCNT agglomerates and thus made a proper dispersion of MWCNTs in the matrix. In this study, the ultrasonicator was operated in a pulse model (15 seconds on and 15 seconds off cycle) with 50% amplitude, which can reduce damage to MWCNTs from the heat, for 30 min. Then, the solvent was evaporated at a high temperature (90°C) for 24 h. A fully evaporated mixture was then mixed with a cross-link agent by a shear mixer for 3 min. Then, a vacuum chamber was used to remove air bubbles inside the polymer for about 30 min. Finally, the mixture was cured at 120°C for 1 hour. The composites with different volume fractions of MWCNTs were prepared for the measurements of electrical conductivity.

3.2. Characterization

The electrical conductivity of the composites was measured using a Keithley 6517 B for a high resistance of the composites, above $10^9 \Omega$, and Fluke 8846 A for a normal resistance of the composites. The four-probe measurement technique was employed to eliminate contact resistance between a probe and samples, as shown in figure 5. Each test specimen was cut into a rectangular shape (10 mm \times 50 mm \times \sim 1 mm) from the sheets. The thickness of the samples was examined using a scanning electron microscope (SEM). Silver paint was applied to all electrodes of the samples to minimize further induced resistance. Five replicas were tested for each case of the effective electrical conductivity. Volume resistance of the composites was measured at room temperature and thus the conductivity is calculated as

$$\sigma = \frac{L}{RA} \quad (14)$$

where L is a length between two inner electrodes, A is an area of the composites, and R is a resistance of the composites.



4. Results and discussion

In this study, we investigate the effect of the length of CNTs on the percolation threshold of electrical conductivity of CNT/polymer composites, and conduct a parametric study comparing our simulation and experimental data.

4.1. Effective length of CNT

Figure 6 shows a characteristic of the effective length of CNT by comparing to the actual length of CNT, number of element, and bond angles. Consider that the distance between two elements is 1.43 \AA and the diameter of CNT is 15 nm for the simulation. Figure 6(a) presents an effect of effective length in terms of the number of elements and the three different bond angles. A larger bond angle between two elements leads to shorter effective

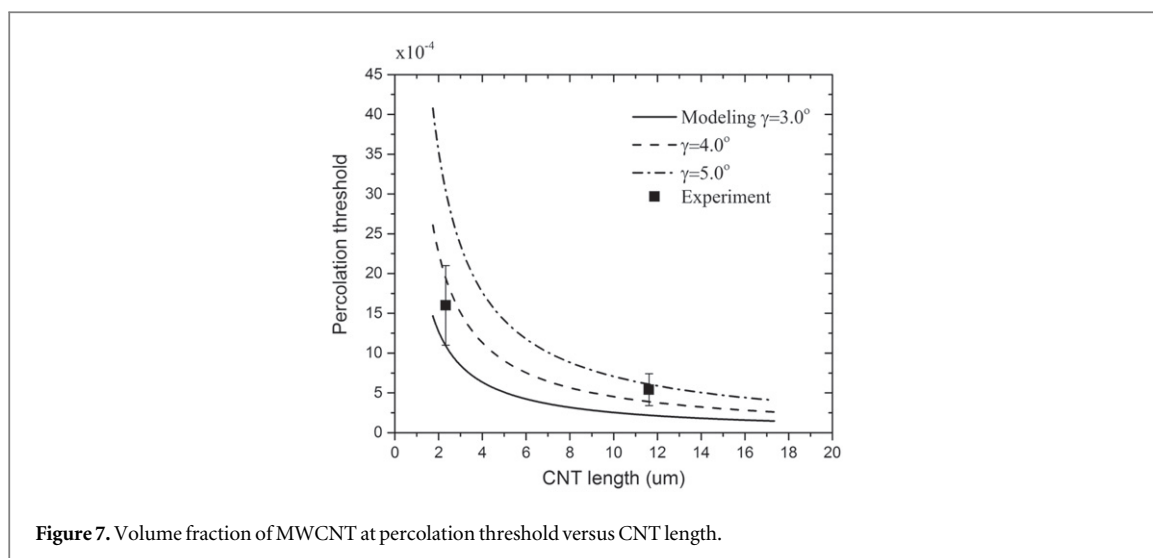


Figure 7. Volume fraction of MWCNT at percolation threshold versus CNT length.

length of CNT compared to the actual length. An interesting point is that the required number of element for the simulation is dependent on the bond angle based on the fact that actual CNT length is always larger than any effective length. For instance, our approach for considering the bond angle as 0.5° is effective only if the element number is higher than 50,000 in order to obtain a reasonable effective length of CNTs. Figure 6(b) shows the comparison of a critical volume of CNT between actual length and effective length. The eight-chain model is used so that the CNT length is related to the critical volume. Because the effective length of a CNT is lower than the actual length, it generally provides a higher critical volume compared to one using the actual CNT length. However, when the number of elements is small, our formulation is not applicable and may provide unreasonable results. As it controls the bond angle of the element, a higher critical volume fraction of CNTs is required to form a network for a higher bond angle.

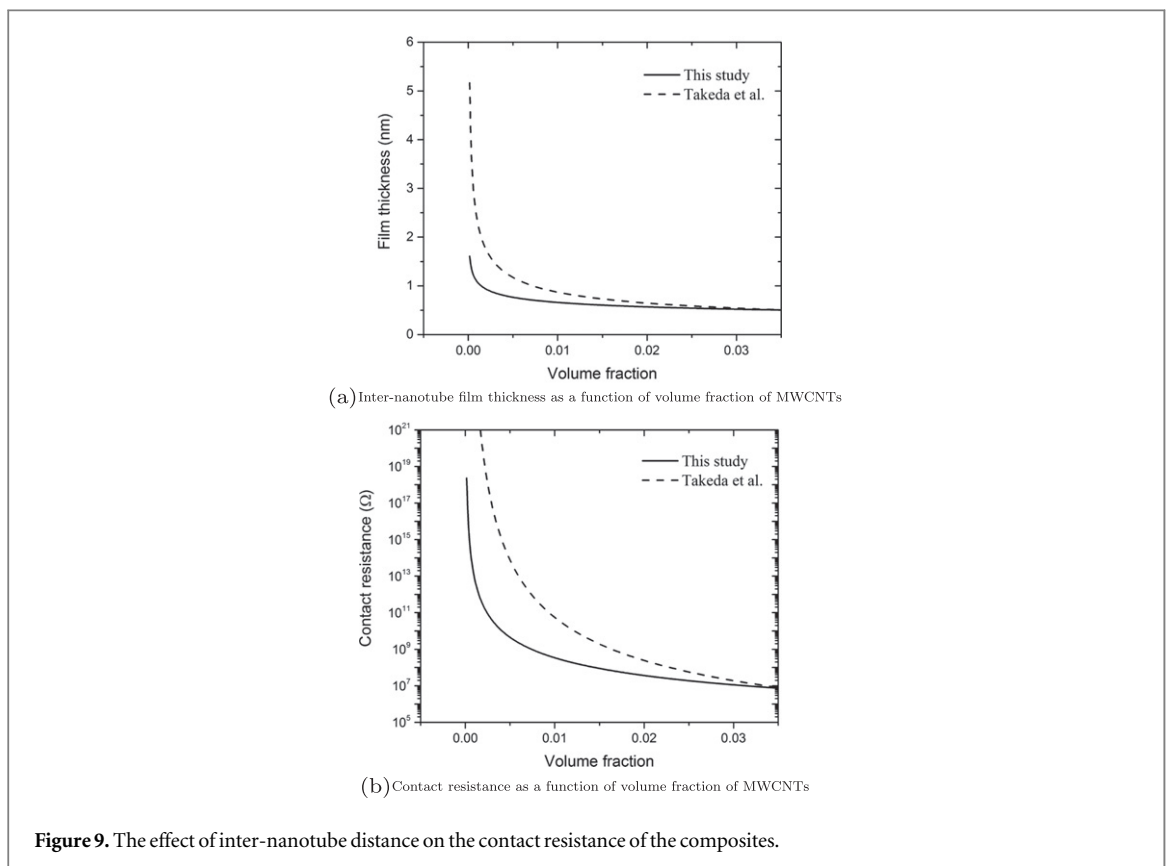
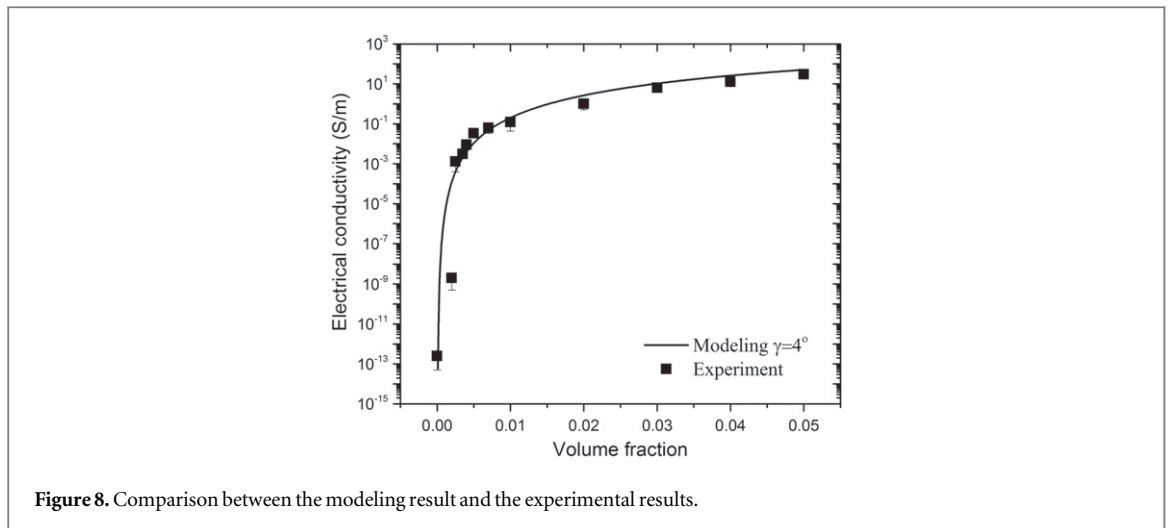
4.2. Percolation threshold

The percolation threshold is the critical volume fraction of a CNT/polymer composite to form a CNT network. In our modeling, the critical volume fraction is described by a unit cell incorporating eight MWCNT segments. Figure 7 represents a critical volume fraction as a function of CNT length and bond angle of CNT elements. It is found that physical changes of MWCNT affect the critical volume fraction. Increasing the length of MWCNTs leads to a low percolation threshold. Kim *et al* [40] examined the effects of an aspect ratio of the MWCNTs on the electrical percolation threshold. They found that the higher aspect ratio of MWCNTs had lower electrical percolation thresholds due to their ease of contact with other MWCNTs. Our experimental result also shows that a long length of MWCNT in PDMS has a lower critical volume fraction (0.00054) compared to a short length of MWCNT (0.00160). The discrepancy between results from Kim *et al* [40] and this study is very possibly due to the difference of the dispersion method of MWCNTs in these studies. In this simulation, the diameter of CNTs is selected as 15 nm. Our modeling provides good agreement with our experiment for a range of $3 \sim 5^\circ$ for the bond angle.

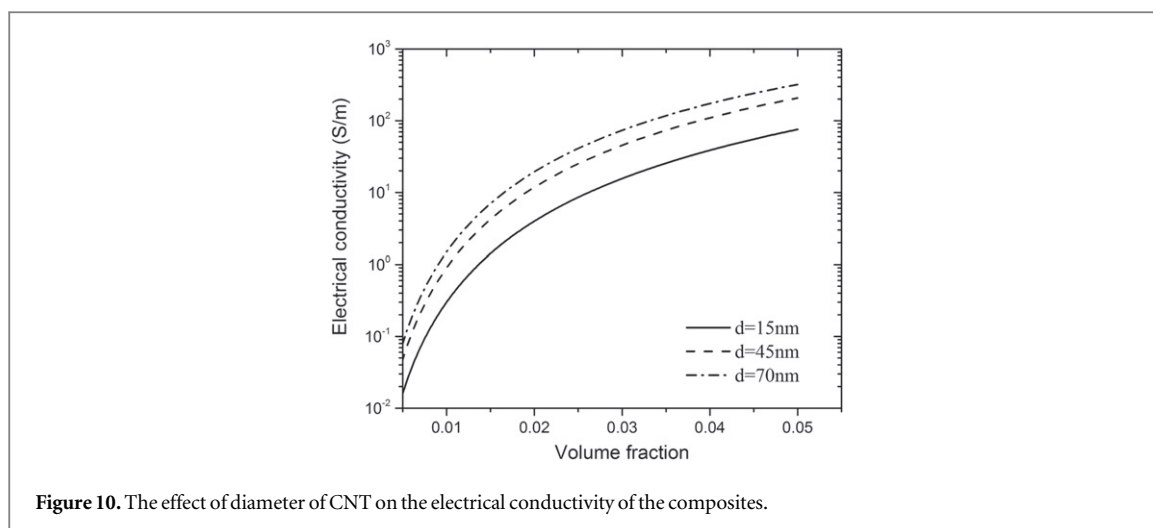
4.3. Effective electrical conductivity of MWCNT/PDMS composite

In order to compare our experimental results with the proposed model, we investigated material properties of MWCNT. The PDMS is generally known as a non-conductive material with a value of $2.5 \times 10^{-14} \text{ S} \cdot \text{m}^{-1}$ for the electrical conductivity. For simulation, the electrical conductivity of MWCNT is assumed to be $10^{-14} \text{ S} \cdot \text{m}^{-1}$, and length and diameter of MWCNT are $12.50 \mu\text{m}$ and 10.00 nm , respectively, considering the damage caused on physical properties of MWCNT during the sample preparation. The potential barrier height is also assumed to be 5.00 eV according to previous studies [41, 42]. Figure 8 shows a comparison of the modeling results and experimental data. From the experimental result, the percolation threshold level is around 0.11 vol.%, indicating that the dispersion of MWCNT is a kind of ideal state compared to other experiments [43, 44]. Two constants for the inter-nanotube distance can be determined using a fitting curve from the experimental data showing that $\alpha = 0.245$ and $\beta = -0.215$, respectively. The modeling result shows good agreement with the experimental data conducted at the percolation threshold as well as at a large volume fraction of MWCNTs in the composites.

The inter-nanotube distance is an important factor in MWCNT/PDMS composites because it affects the contact resistance of MWCNTs very much. Although it is generally known that the film thickness between two



MWCNTs varies with the volume fraction of MWCNTs in the composite and the contact resistance by tunneling effect decrease for more MWCNT in the composite, the two constants in the relationship for the inter-nanotube distance are quite different. For example, Mohiuddin and Hoa [45] reported that two parameters were estimated by a curve fitting from experimental data of MWCNT/PEEK (Poly Ether Ether Ketone) composite. Takeda *et al* [38] determined the inter-nanotube thickness based on other data [46, 47], where they estimated the upper limit of the film thickness for electrical tunneling as about 1.8 nm and the film thickness as around 1.2 nm in a transition region. Figure 9 shows a comparison of the inter-nanotube thickness of MWCNTs and the contact resistance of MWCNT with previous results. The inter-nanotube thickness decreases with an increasing in MWCNT volume fraction in the composite in all cases. The comparisons show that our parameters chosen in this study are reasonable for the simulation.



4.4. Effect of the diameter of MWCNTs

Figure 10 shows the influence of the diameter of MWCNT on the electrical conductivity of different volume fractions of MWCNT/PDMS composites. The electrical conductivity dependence on the diameter of MWCNT is observed from the modeling results, which indicate that smaller diameter of MWCNT contributed to decreasing overall electrical conductivity of MWCNT/PDMS composites. A similar result is observed in the experimental and modeling studies [48, 49]. This can be explained by the fact that for more MWCNTs at the same volume fraction, a more conductive network formation is created, resulting in higher electrical conductivity.

5. Conclusion

A micromechanical model based on the unit cell for predicting the effective electrical conductivity of MWCNT/PDMS composites has been proposed. The model was validated with the experimental results. It is found that the proposed model predicts the percolation threshold and effective electrical conductivity very well, which is governed by the tunneling effect between MWCNTs and the waviness of CNTs. The finding is valuable to sensor design and fracture indication. The present modeling can provide an informative way to estimate the electrical conductivity of CNT/polymer composites for strain sensor applications.

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