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Carbon nanotube agglomeration effect on piezoresistivity of polymer nanocomposites

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ABSTRACT

Carbon nanotube (CNT) agglomeration exists inevitably in all CNT-polymer composites. This paper quantified the effect of CNT agglomeration on the piezoresistivity of CNT-polymer composites. A new multiscale model of 3-dimensional deformable CNT percolating networks has been developed, where the CNT agglomerates were modeled as second phases embedded randomly in the polymer matrix. The newly developed model agrees quantitatively with experimental data. The study found that the CNT agglomeration is responsible for the reduced electrical conductivity and nonlinearity of piezoresistivity with respect to the zero strain. Its effect can be quantified by the newly developed model. Parametric analyses were conducted to show the effects of morphology and electrical properties of CNTs, the Poisson's ratio of CNT-polymer composites and the extent, internal density and size of CNT agglomeration on the electrical conductivity and piezoresistivity. The current work provides a useful analysis tool for designing smart sensing and multifunctional polymer composites.

1. Introduction

Carbon nanotubes (CNTs) have great potential in fabricating high-performance and multifunctional polymer composites due to their good electrical conductivity, ultra-small diameter, high aspect ratio, and lightweight [1–5]. The performance of these composites is highly affected by the distribution of CNTs in polymers, where the CNTs tend to attract each other and form large particle clusters or agglomerates [6]. Investigations find that the presence of CNT agglomerates will significantly reduce the electrical properties of CNT-polymer composites compared with theoretical predictions that are based on the assumption of uniform distribution of CNTs in polymers [7–9]. Many efforts have been devoted to disperse CNTs into polymer matrices uniformly [10–14] in order to reach the theoretical properties of CNT-polymer composites. Although effective, studies founded that even the well-dispersed CNTs in polymers could re-agglomerate in the subsequently curing process [15]. The situation becomes worse at high CNT loadings. Therefore, it is imperative to quantify the effect of CNT agglomeration on the electrical properties precisely since the CNT agglomeration is inevitable.

Currently, many progresses have been made in this area. Compared with the extensive experimental works [16–18], relatively limited analytical and numerical efforts have been devoted to this field [19]. Analytical studies usually adopt the Mori-Tanaka averaging method to model the piezoresistivity by the average electric field. For instance, Seidel and Lagoudas [20] estimated the electrical conductivity of CNT-polymer composites by the Mori-Tanaka method in the micromechanics domain. Using the similar approach, Pham [21] evaluated the effective piezoresistivity of CNT-polymer composites based on the nanoscale Simmons' tunneling resistance [39] at CNT junctions. Wichmann et al. [22] investigated the influence of strain range on the piezoresistivity by a combination of Simmons' tunneling resistance and simplified CNT resistor networks. Ren and Seidel [9] studied the macroscale piezoresistivity of CNT-polymer composites based on the nanoscale Simmons' tunneling resistance and CNT intrinsic piezoresistivity by a computational micromechanics finite element approach. Although successful, these models predict the piezoresistivity of CNT-polymer composites qualitatively and no CNT agglomeration is considered. To provide accurate and quantitative predictions of the piezoresistivity, numerical approaches have been developed, which are generally based on the statistical percolating network theory of randomly distributed CNTs in polymers and the Monte Carlo simulations. For instance, Theodosiou et al. [24] analyzed the nanoscale piezoresistive response of CNTs and then derived averaged or

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effective piezoresistivity of CNT-polymer composites at macroscale by a numerical CNT percolating network model. Yasuoka et al. [25] showed that the macroscale piezoresistivity is nonlinear due to the tunneling effect at CNT junctions and is inversely proportional to CNT loadings by an electrical circuit analog to percolating networks. In the report by Alamusi et al. [26], the piezoresistivity of CNT-polymer composites was modeled by assuming CNTs translating and rotating rigidly in polymer matrices when subject to an external strain [27]. Li and Chou [28] analyzed the effective electrical resistance of the percolating network by considering the nanoscale tunneling and intrinsic resistances of CNTs and then averaging through the finite element method of an electrical circuit analog to percolating networks. Wang et al. [29] studied numerically the dependence of piezoresistivity on the Poisson's ratio of polymer matrix by power-law-type resistor networks analog to the CNT percolating networks. Up to date, none of these analytical or numerical approaches can accurately quantify the significant reduction in electrical conductivity, piezoresistivity, and piezoresistive sensitivity to CNT loadings of CNT-polymer composites due to CNT agglomeration.

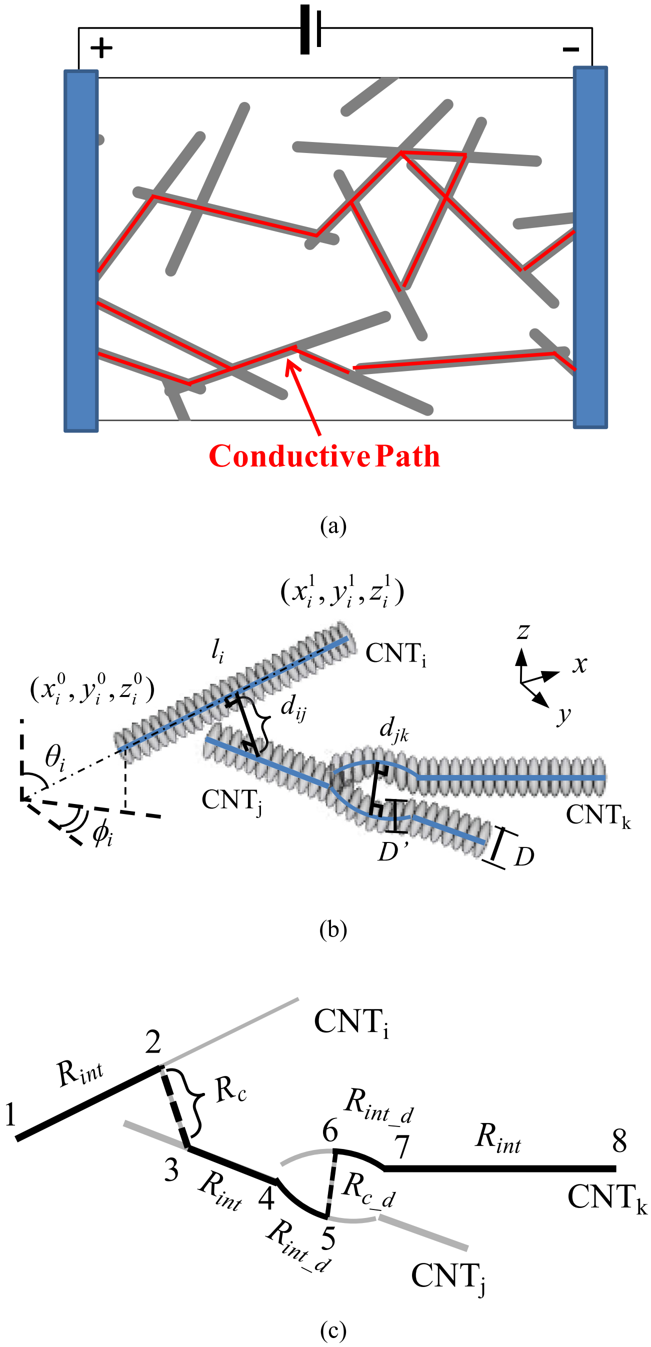
To address the discrepancy between the experiments and the theory, a 3D multiscale percolating network model has been developed here to model the electrical conductivity and piezoresistivity of CNT-polymer composites quantitatively, where the effects of CNT agglomeration and deformation (wall deformation and tube-bending) are considered. The effect of CNT agglomeration on the electrical properties has been modeled at three different scales, ranging from the nanoscale, to the mesoscale and to the macroscale. The model agrees quantitatively with the experimental data [31] of CNT-polymer composites with and without significant CNT agglomeration. The analysis results reveal that the CNT agglomeration is responsible for the reduced electrical conductivity, piezoresistivity, sensitivity of piezoresistivity to CNT loadings and nonlinearity of piezoresistivity with respect to zero strain. The study also finds that the CNT deformation is one of the major mechanisms that affect the electrical conductivity and piezoresistivity. Finally, parametric studies show the different dependences of piezoresistivity of CNT-polymer composites on the Poisson's ratio of composites, the size of CNT agglomerates, and the morphology and intrinsic resistance of CNTs.

Compared to the existing models, the novelty of the new model is that the CNT agglomerates are considered and modeled as second phases embedded in the 3D CNT percolating network and the CNT bending and wall deformation are modeled at CNT junctions. The new model improves the representation of 3D CNT percolating network for agglomerated CNT-polymer composites and is capable of quantifying the effect of CNT agglomeration on composites' electrical conductivity and piezoresistivity. The outcome of the current work would provide useful information and an optimization tool for the design of smart sensing and multifunctional polymer composites.

2. Multiscale modeling methodology

2.1. CNT percolating network in a polymer matrix

It is well known that the electrical resistance of CNT-polymer composites can be represented by the resistance of CNT percolating networks inside the composites [3,32]. As shown in Fig. 1(a), each CNT in the network is assumed as a straight and caped cylinder with length of L and diameter of D initially. The CNTs are assumed deformable (tube-bending or wall flattening) to avoid CNT overlap at crossed CNT junctions in the network [33]. Assume CNTs are randomly distributed in a representative volume cuboid with dimensions of $L_x \times L_y \times L_z$. Thus, the coordinates of starting point and the azimuthal and polar angles (ϕ_i, θ_i) of each CNT are generated randomly [32],



(a)

(b)

(c)

Fig. 1. Schematic of (a) an electrical conductive CNT network in a polymer matrix, (b) detailed CNTs and CNT junctions in network, and (c) electrical resistance of a typical conductive path (Thick solid, dotted and thin solid lines represent conductive paths formed by CNTs, CNT junctions and CNT parts that are not involved in a conductive path, respectively).

$$\begin{aligned}&(x_i^0, y_i^0, z_i^0) = \left(L_x \times Rand, L_y \times Rand, L_z \times Rand\right),\\&(\phi_i, \theta_i) = \left(2\pi \times Rand, \cos^{-1}\left(2Rand - 1\right)\right)\end{aligned} \tag{1}$$

where i is the index of i-th CNT and '$Rand$' denotes uniformly distributed random numbers in the interval [0, 1].