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On the mechanism of piezoresistivity of carbon nanotube polymer composites

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ABSTRACT

Carbon nanotube (CNT) polymer composites exhibit strong nonlinear and asymmetric piezoresistivity about zero strain in tensile and compressive strain states. The existing models explain the characteristic qualitatively but not quantitatively. This paper attempts to understand the mechanisms of this piezoresistivity by developing a new 3-dimensional percolation CNT network model, where the effect of CNT deformation (wall indentation and tube bending) is considered for the first time. The predicted electrical conductivity and piezoresistivity agree with experiments quantitatively, which reveals that the CNT deformation is a dominant mechanism for the nonlinearity and asymmetry of piezoresistivity of CNT-polymer composites. Parametric studies have been conducted to show the effects of morphology and electrical properties of CNTs, work functions and Poisson's ratio of polymer on the piezoresistivity of CNT-polymer composites for future application in nanosensing composites.

1. Introduction

Carbon nanotube (CNT) polymer composites with extraordinary electrical properties have received considerable attention recently [1–5]. It has been well established that (i) the effective electrical conductivity of CNT enhanced polymer composites obeys a percolation-like power law [1], (ii) the electrical conductivity varies when a mechanical strain is applied [2], and (iii) the current–voltage characteristic of the CNT-polymer composites exhibits a non-ohmic behavior, an indication of quantum tunneling conduction mechanism [3]. These electrical properties are generally attributed to the formation of conductive CNT percolation networks within the CNT-polymer composites [1], which are heavily dependent on parameters, such as, the electronic band structure and morphology of CNTs [6], the tunneling resistance at crossed CNT junctions [7], and the morphology of the CNT percolation networks [8]. Existing works have shown that these parameters are sensitive to mechanical deformation [9]. Hence, the electrical conductivity of CNT-polymer composites is strain or stress dependent, similar to the piezoresistive behavior of conventional strain sensors but with much higher sensitivity [10]. The enhanced piezoresistivity of CNT-polymer composites has enormous potential applications in highly sensitive resistance-type strain/force sensors [11], in-situ structural monitoring [12], and wearable sensing electronics [13], just to name a few. Numerous experiments have been conducted on the electrical conductivity and piezoresistivity of CNT-polymer composites and their sensing applications [5,14,15]. However, systematic analytical and numerical studies in this area are very limited to date.

The comprehensive understanding of the electrical conductivity of CNT-polymer composites is imperative in investigating the piezoresistivity. Both analytical and numerical studies have been conducted in this area. Some analytical approaches for the electrical conductivity were based on either the continuum percolation theory of 3D cylinders [3] or the micromechanics with a representative volume element [16]. In these approaches, CNTs were modeled as capped cylinders with finite length L and diameter D. Other analytical approaches modeled CNTs as ellipsoidal inclusions uniformly distributed in 3D space [17] to estimate the percolation threshold and electrical conductivity using the theory of Ponte Castaneda–Willis microstructure and Hashin–Shtrikman upper bound. While the analytical approaches are able to provide qualitative explanations of the effective electrical conductivity of CNT-polymer composites, significant efforts are needed to yield better quantitative predictions of the electrical properties of CNT-polymer composites comparable to the experimental measurements [16]. Unlike their analytical counterparts, the numerical approaches [3,8,18–25] are based on the assumption of random distribution of CNTs in polymers, the traditional statistical percolation theory, and the

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Monte Carlo simulations. Generally, they are able to provide acceptable quantitative predictions of the electrical conductivity at and after the percolation threshold. Early numerical studies were mainly used to augment the analytical calculations for the critical CNT loadings at the percolation threshold. In these approaches, it was commonly assumed that (i) the CNTs were rigid, straight and capped cylinders with finite length L and diameter D and (ii) the contact resistance at CNT junctions was zero if the distance between central axes of the CNTs is less than or equal to the diameter of CNTs [3,7]. However, the rigid assumption resulted in CNT overlap due to the neglect of the Van der Waals repulsive forces in the real materials. Consequently, the predicted percolation thresholds of electrical conductivity of MWCNT (multi-walled carbon nanotubes)-polymer composites were significantly greater than the experimental measurements [26]. On the contrary, the experimental percolation thresholds of SWCNT (single-walled carbon nanotubes)-polymer composites are greater than the numerical predictions [27]. To address the discrepancy, curved CNT models were proposed [28] and the tunneling effect at CNT junctions was included by the Simmons model [29] with limited success. However, the assumption of large and flat contact surfaces in the Simmons model results in zero contact resistance as the distance diminishes between the adjacent CNT walls, which contradicts the experimental observations [30] and overestimates the electrical conductivity significantly. To rectify this problem, a solution [7] was introduced by assuming the contact resistance as the sum of a tunneling resistance and a direct contact resistance, where the direct contact resistance is determined experimentally. However, the Simmons model cannot explain the difference in contact resistance between SWCNTs and MWCNTs observed in experiments [7]. The real CNT–CNT contact occurs at nanoscale and the contact region limits to only several atoms. It is reasonable to assume that the electron conduction at CNT junctions is approximated as one-dimensional ballistic transport [31]. Using the 1D Landauer-Büttiker (L-B) formula of electron transport theory, a new contact resistance model was developed by considering only the tunneling effect with two parameters: transmission probability and channel number [8,22–24]. The latter is the total number of conduction bands for all CNT walls and represents the different types of CNTs (SWCNTS or MWCNTs) at CNT junctions [32]. The model clarifies the mechanism of CNT contact resistance at CNT junctions by eliminating the direct contact resistance. Numerical analysis shows that the model improves the accuracy of electrical conductivity of SWCNT- and MWCNT-polymer composites, respectively. The model was further extended to include the effects of CNT alignment, bending, and agglomeration on the electrical conductivity [8,24]. In spite of these improvements, the numerical approaches still overestimate the overall electrical conductivity and the percolation thresholds, especially for the SWCNT-polymer composites, due to the unrealistic CNT overlap at CNT junctions. Experimental observations revealed that the CNT wall deformed transversely at CNT junctions when the distance between walls of adjacent CNTs was less than the Van der Waals distance [33,34]. The CNT deformation dramatically increases the intrinsic resistance of CNTs and decreases the CNT contact or tunneling resistance [30,35]. To attenuate the problem of CNT overlap, the effect of CNT wall deformation was considered in the models of the intrinsic and contact resistance recently [25]. The simulation results reveal that the CNT wall deformation is a major mechanism leading to the overall increase of electrical resistance of CNT percolation networks. The predicted electrical conductivity and percolation thresholds by the improved model agree well with experimental data quantitatively.

In the domain of piezoresistivity of CNT-polymer composites, many experimental investigations have been carried out and demonstrated that the strain induced electrical resistance change in CNT-polymer composites is highly nonlinear [36,37]. Furthermore, this piezoresistive behavior is asymmetric about the zero strain when subjected to tensile and compressive strains, where the piezoresistivity of compressive stress is much lower than that of tensile strain [9]. The experiments also revealed that the piezoresistivity sensitivity of CNT-polymer composites is much greater than that of metal and conventionally doped silicon strain gauges [38] and decreases as the CNT loading increases [9]. The mechanism of the piezoresistivity of CNT-polymer composites has been attributed qualitatively to three different aspects [14]. The first is the variation of CNT percolating network itself under strain. This includes two types of variations: (i) the breakdown of existing conductive paths or form of new ones due to the change of distance between CNTs at CNT junctions and (ii) the variation of conducting length of CNTs between two contacting points due to the movement of CNT junctions along CNTs. The second is the variation of tunneling resistance at CNT junctions due to the distance change between CNTs. The third is the piezoresistivity of CNTs resulting from CNT length changes, CNT beam type bending and wall indentation. Up to date, only a few studies [18,39–48] have explored the piezoresistive behavior and the associated mechanisms of CNT-polymer composites quantitatively. Analytical studies [40,41,45], usually employing the Simmons model [29], have tried to explain the mechanism of piezoresistivity in CNT-polymer composites. For instance, Wang et al. [45] studied the dependence of piezoresistivity on the Poisson's ratio of polymer matrix using a power law of resistor networks analog to CNT percolating networks and Wichmann et al. [40] investigated the influence of strain range on the piezoresistivity by a simplified resistor network model. Although successful, these models are limited to qualitative explanation of the mechanism of piezoresistivity. To overcome the limitation of these analytical approaches, numerical approaches have been developed. By using a multi-scale approach, Theodosiou et al. [18] analyzed the piezoresistive response of CNTs at nanoscale and the effective piezoresistive behavior of CNT-polymer composites at macroscale by a numerical CNT percolation model. The work concluded that the CNT piezoresistivity, instead of tunneling resistance at CNT junctions, was the dominant mechanism of piezoresistivity of CNT-polymer composites. Using an electrical circuit analogue to percolation network, Yasuoka et al. [41] showed that the piezoresistivity is nonlinear due to the tunneling effect at CNT junctions and is inversely proportional to the CNT loadings. Pham [44] developed a piezoresistivity model that is formulated utilizing a combination of percolation theory and micro-mechanics mean field analysis method. In the report by Alamusi et al. [42], the piezoresistivity of CNT-polymer composites was studied by using the Simmons' tunneling model [29] and the fiber reorientation model [49] together with the 3D rigid CNT percolation network model developed by Hu et al. [9]. However, these approaches considered only the strain-induced re-orientation of rigid CNTs and the resulting network changes in CNT-polymer composites. The contribution of CNT piezoresistivity was discarded. As the result, this approach only reflects the trend of piezoresistivity qualitatively with gross underestimation. Nevertheless, the study found that (i) the piezoresistivity is proportional to the ratio of the tunneling resistance to the total resistance, (ii) the alignment of CNTs with the strain direction results in the lower piezoresistivity, and (iii) the composites with a CNT loading near the percolation threshold exhibit higher piezoresistivity. Recently, the numerical work by Wang et al. [45], based on the tunneling model of Hu et al. [9], showed that the morphology (orientation and diameter) of