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Effects of the distribution and geometry of carbon nanotubes on the macroscopic stiffness and microscopic stresses of nanocomposites

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Abstract

In this paper, effects of spatial distribution and geometry of carbon nanotubes (CNTs) on the macroscopic stiffness and microscopic stresses of CNT reinforced polymer composites are investigated based on the multi-scale homogenization theory. An effective fiber model with transversely isotropic constitutive relationship is utilized to describe the nanotube including the surrounding thin matrix layer. Regular and staggered arrays with straight or wavy nanotubes are simulated. The influence of the aspect ratio and volume fraction of CNT, the end gap between two coaxial nanotubes and the distance between two parallel nanotubes on the nanocomposites are also investigated. A new solution method is applied to the homogenization analysis. Numerical results of macroscopic stiffness and microscopic stresses are presented and the influence of various parameters of spatial distribution and geometry of CNTs is discussed in detail.

Keywords: A. Carbon nanotubes; A. Nanocomposites; C. Elastic properties; C. Multiscale modeling

1. Introduction

Carbon nanotube has become a fashion word of nanotechnology since 1991 because of its various unique and exciting physical and mechanical properties. Very small diameter, large aspect ratio, extremely high strength and stiffness naturally make the CNT to become a kind of most attractive reinforcement for polymer matrix composites. Many researches have been conducted to develop CNT reinforced composites in the past 15 years, as reviewed by Thostenson et al. [1], Andrews and Weisenberger [2], and Lau and Hui [3]. The mechanical properties of a single nanotube [4–8], the functionalization and purification of CNTs [9,10], and the constitutive modeling of a single nanotube including the local polymer surrounding the nanotube and the nanotube/polymer interface [11,12] have been extensively studied. However, it is recognized that there is still a long way to go to create CNT reinforced composites fully realized the potentials of high stiffness and strength of CNT. Many of the reported CNT polymer composites have not presented anticipated macroscopic properties such as high stiffness and strength although the individual CNTs have excellent mechanical properties. There are many reasons which may influence the macroscopic mechanical properties of nanocomposites, such as the dispersion, alignment, and waviness of CNTs. Therefore it is necessary to investigate the effects of these factors on the macroscopic properties of composites experimentally and analytically at multi-scale levels.

In the analytical researches of individual nanotubes and the interface of nanotube/matrix, molecular mechanics at the atomic scale is efficient. However, it is exceedingly difficult to apply the molecular mechanics to the whole nanocomposite. Continuum mechanics is still available for the investigation of the macroscopic mechanical properties of nanocomposites. According to the equivalent-continuum modeling proposed by Odegard et al. [11], a nanotube is modelled as an effective fiber and then the analytical and numerical methods developed in the study of traditional short-fiber reinforced composites can also be useful for

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nanocomposites. There are many theoretical and numerical methods for the prediction of macroscopic stiffness of short-fiber reinforced composites [13–18]. Halpin–Tsai equation [16] and Mori–Tanaka method (e.g. [17,18]) are two popular theoretical methods. Modified Halpin–Tsai equation was used to predict the macroscopic elastic constants of CNT polymer composites in [19] and Mori–Tanaka method was also applied to CNT polymer composites with long wavy nanotubes in [20,21]. However, these two methods have a common shortcoming that they cannot accurately reveal the interactions between neighboring nanotubes and cannot evaluate the micro-stresses involving with individual nanotubes because of the limitation of their analytical models.

Parallel to the above theoretical researches, numerical approaches have also been developed based on the analysis of a basic unit cell by finite element method (FEM) in the past years. In general, numerical approaches can be roughly classified into average-field method and homogenization method. These two methods are available for the evaluation of macro-stiffness and micro-stresses of nanocomposites at the same time. The average-field method (e.g. [22]) is developed based on the physical viewpoint that the macroscopic material properties obtained from experiments represent the properties of volume average. In contrast, the homogenization method (e.g. [23]) is developed based on the mathematically multi-scale perturbation theory. Chen and Liu [24] employed the average-field method to predict the macroscopic properties of CNT polymer composites with straight nanotubes. However, it is difficult to impose exact periodic conditions along the boundary of a unit cell with asymmetric and complicated microstructures in the average-field method [25]. On the other hand, in the homogenization method, a characteristic function is introduced into the analysis to relate the microscopic displacements to the macroscopic displacements, which makes it possible to express the exact periodic conditions formally along the boundary of the unit cell. However, since the integral equation related to the characteristic function is inhomogeneous, two computational steps of imposing initial strains and periodic displacement conditions need to be performed to solve the inhomogeneous integral equation in the conventional solution method. These calculation steps are obviously inefficient. To overcome this shortcoming, a new solution method has been developed recently in [26]. A homogeneous integral equation has been derived in stead of the conventional inhomogeneous integral by introducing a new characteristic function. Consequently, the computational step of imposing initial strains is omitted, which significantly simplifies the computational process.

Based on the above theoretical and numerical analysis methods, the influence of spatial distribution and geometrical shapes of traditional long and short fibers on composites have been studied in detail. However, it is difficult to directly apply these results to CNT polymer composites since CNTs have many different characteristics from traditional fibers. High volume fraction of CNT is difficult for us to obtain high stiffness and strength of composites and most nanotubes in composites are not as straight as traditional fibers. Thus, further study on the influence of spatial distribution and waviness of CNTs on the macroscopic and microscopic mechanical properties of nanocomposites seems to be necessary in order to explore an effective method for fabricating CNT polymer composites.

In this paper, an effort on the modeling of CNT polymer composite at the continuum level is made based on the multi-scale homogenization theory and the new solution method. The effective fiber model with transversely isotropic constitutive relationship [11] is utilized to describe the nanotube including the thin surrounding matrix layer. Regular and staggered arrays with straight or wavy nanotubes are simulated. The influence of the aspect ratio and volume fraction of CNTs, the end gap between two coaxial nanotubes, and the distance between two parallel nanotubes on the macroscopic and microscopic mechanical properties are also investigated.

2. Effective fiber model for nanotubes

In the constitutive modeling of CNT polymer composites, the simple assumption of perfectly bonded nanotube/polymer interface, used in the modeling of fiber/polymer interface for traditional fiber reinforced polymer composites, is not always available because of the extremely small diameter of nanotubes. Interactions between the nanotube and the surrounding polymer are rather complex and need to be investigated at molecular scale. Three steps usually need to be proceeded in order to model the constitutive relationship of CNT polymer composites. One is the constitutive modeling of individual nanotubes, the second is the modeling of the interface of nanotube/polymer, the third one is the modeling of nanotube/polymer composites. At the first two steps, molecular mechanics is an effective tool. Extensive experimental and theoretical studies have been conducted in the constitutive modeling of a single and the interface of nanotube/polymer, as described in [1–3]. This paper focuses on the third step. An effective fiber model [11] with transversely isotropic constitutive relationship, as shown in Fig. 1, is utilized to describe the nanotube including the interface and the surrounding polymer. In this model, the length of the effective fiber is equal to the nanotube length, the diameter of the effective fiber is 1.8 nm, and the volume fraction of nanotube in the effective fiber model is 34% if the nanotube is assumed as a hollow cylinder with a wall thickness of 0.34 nm. The five independent elastic constants of the effective fiber are

$$C^{f}_{11} = 457.6, \quad C^{f}_{12} = 8.4, \quad C^{f}_{22} = 14.3, \quad C^{f}_{23} = 5.5, \quad C^{f}_{44} = 27.0 \text{ (GPa)},$$

where subscript 1 denotes the fiber direction, subscripts 2 and 3 denote the two directions perpendicular to the fiber in the isotropic plane, respectively. The other stiffness constants can be calculated as follows: