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Computational modeling of elastic properties of carbon nanotube/polymer composites with interphase regions. Part I: Micro-structural characterization and geometric modeling

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ABSTRACT

A computational strategy to predict the elastic properties of carbon nanotube-reinforced polymer composites is proposed in this two-part paper. In Part I, the micro-structural characteristics of these nano-composites are discerned. These characteristics include networks/agglomerations of carbon nanotubes and thick polymer interphase regions between the nanotubes and the surrounding matrix. An algorithm is presented to construct three-dimensional geometric models with large amounts of randomly dispersed and aggregated nanotubes. The effects of the distribution of the nanotubes and the thickness of the interphase regions on the concentration of the interphase regions are demonstrated with numerical results.

1. Introduction

Since carbon nanotubes (CNTs) were discovered in 1991, they have attracted considerable attention in most areas of science and engineering due to their excellent mechanical, thermal and electrical properties. These properties make CNTs ideal for a wide range of applications, including as advanced filler materials in polymer–matrix composites.

CNT/polymer composites have demonstrated promising multi-functional features. Electrical properties can be dramatically improved by the addition of a small proportion of CNTs (weight fraction <1%) in the polymer matrix [1]. However, mechanical improvements have been underwhelming, with CNT/polymer composites exhibiting little or no improvement in their mechanical properties; added nanotubes even accelerated the overall damage process [2,3]. It has been determined that electrical and mechanical properties are both very dependent on the quality of the CNT dispersion as well as on the CNT concentration [4,5]. As a result, experimental and numerical studies have been devoted to understanding the relations between the structure of the CNT network and the effective properties of the CNT/polymer assembly [6,7].

Various types of simulation models have been used to study CNT/polymer composites, such as molecular dynamics, classical continuum mechanics and multiscale methods. However, these methods encounter some limitations when they are used to simulate CNT/polymer composites while trying to capture both the macroscopic length scale and the mesoscopic or microscopic structures. Molecular dynamics has been used to simulate interatomic interactions between a single CNT and polymer chains [8]. However, it is extremely difficult to implement molecular simulations of large-scale microstructures due to the limitations of current computing capabilities. Continuum mechanics models, usually resolved by the finite element method (FEM), have also been employed to predict the properties of CNT/polymer composites [9]. However, few simulations considered randomly interwoven CNT networks in nano-composites. The multiscale methods combine molecular dynamics and continuum mechanics, which are promising but not yet comprehensive approaches [10]. These computational models for CNT/polymer composites are covered in more detail in Section 3.

To tackle CNT/polymer modeling, it is worth mentioning the special characteristics of CNTs compared with other types of fillers. CNTs have very high aspect ratios which leads to complex CNT networks. The geometric microstructures of these networks directly affect the performance of the resulting composite [4,5,11]. Another feature of CNT reinforced polymers is that the surrounding polymer usually cannot be considered as uniform at the scale of the CNT. The most relevant physical evidence of this is the existence of the interphase region between the CNT and the bulk polymer. This interphase region can be associated with various physical reasons, mainly with the modification of the crystallization behavior

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of the polymer at the CNT interface or with the wrapping of the polymer chains around the CNTs [12,13]. However, the properties and structures of interphase regions have not been accurately quantified, which makes controlling and predicting the global properties of polymer–matrix nano-composites difficult [14]. It will be critical in predicting properties of CNT/polymer composites to generate a more realistic micro-structural model including CNT networks and polymer interphase regions.

The purpose of this communication is to characterize CNT/polymer composites by focusing on CNT distribution and interphase reinforcement. In Section 2, some micro-structural characteristics of CNT/polymer composites are highlighted. The current analytical and/or numerical methods for modeling the behaviors of CNT/polymer composites are briefly reviewed in Section 3. Section 4 outlines the assumptions that are the basis of our geometric modeling. In Section 5, we focus on the spatial distribution of CNTs in composites and propose a generation algorithm of three-dimensional (3D) random and/or aggregated CNT-networks. Numerical results are presented in Section 6.

2. Micro-structural characteristics of CNT/polymer composites

CNT-reinforced polymers reveal novel nano-scale structural characteristics that no classical micro-scale fiber-reinforced composites represent, such as CNT agglomeration and thick interphase region.

2.1. Network and agglomeration of CNTs in composites

Because CNTs have high aspect ratios, are easy to bend and develop strong attractions between each other [15], they tend to organize themselves in interwoven networks see Fig. 1(a). These networks [16,17] are critically beneficial for electrical percolation, effective conductivity and stress transfer [18].

The main challenge from an experimental point of view remains to obtain homogeneous dispersion of CNTs in the matrix during sample preparation [11]. Despite efforts to achieve randomly distributed networks, CNTs tend to agglomerate into "clusters". CNTs compactly interlace with one another to form agglomerations that are characteristic of CNT/polymer composites see Fig. 1(b). This agglomeration results from long-range interactions due to Van der Waals forces and Coulomb attractions [11,19]. Clusters can be of various sizes and shapes depending on the composite preparation technique [4,20] and they can reduce the mechanical and electrical properties of the composites [5,21]. The effect of CNT agglomerations on the effective properties of nano-composites has to be understood especially in numerical simulations [22], because it is very costly and almost impossible to get a perfect dispersion of CNT at high CNT concentrations.

2.2. The interphase region of CNT/polymer composites

Recently, researchers have begun to pay attention to the effects of the interphase regions between CNTs and the bulk resin [12,14]. Indeed, the fraction of interphase regions may be higher than that of the CNTs (see Fig. 2, where microfibers of threaded CNTs induce trans-crystallization of a polypropylene matrix).

The diameter of a CNT is at a scale similar to that of individual polymer chains. A typical single-walled carbon nanotube (SWCNT) has a diameter close to 1 nm [23] and the more commonly used multi-walled carbon nanotube (MWCNT) has a diameter ranging from 2 to 20 nm [24,25]. In comparison, the diameter of a benzene ring, which is often part of polymer (resin) chains, is around 0.6 nm [26]. Thus, interphase regions around CNTs easily form by wrapping [27],crystallizing [16,28] or aggregating [29] polymers. Furthermore, these interphase regions might consist of multiple polymer layers that gradually get "looser" away from the CNT [30]. These polymer interphase regions can be very thick, twice (or more than twice) the diameter of the CNTs [24,27,30] and have better mechanical properties than the bulk matrix [31,32].

An explanation for the improvement in properties in the polymer interphase region close to the CNT can be attributed to various reasons, one of them being a reordering of the polymer chains that gradually goes to a more crystalline phase. For instance, it is well known that while the modulus of amorphous polyethylene (PE) ranges from 0.1 to 1 GPa [33], ultra-high molecular weight PE fibers, which have an ordered structure of polymer chains, can have moduli as high as 117 GPa [33]. Additionally, Barber et al. revealed that polymer phases around a CNT show high resistance to stress [32], which suggests the existence of strong adhesion and effective stress transfer [34].

However, this interphase component with improved properties and high concentration has not received attention from a modeling point of view [14]. This lack of attention may be caused by two reasons: (1) a higher concentration of interphase regions is not common in traditional materials usually simulated and (2) there is no method available to characterize and measure the properties of the interphase region in nano-composites accurately. Our aim here is to propose a pragmatic model that would naturally account for the existence of this interphase region.

3. Approaches to simulate CNT-reinforced composites

So far, various modeling and simulation methods have been proposed to predict the mechanical properties of CNT-reinforced

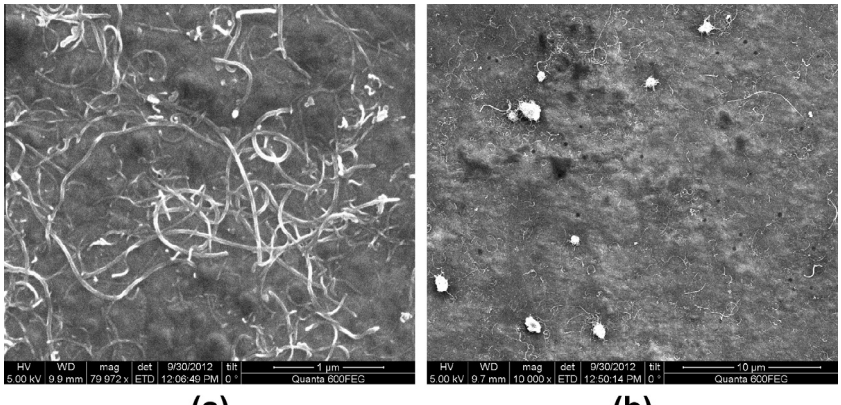

Fig. 1. Scanning electron microscopy images of multi-walled CNT/epoxy composites: (a) CNT network and (b) observation of CNT agglomerations.