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Multiscale micromechanical modeling of the constitutive response of carbon nanotube-reinforced structural adhesives

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ABSTRACT

Appropriate formulations are developed to allow for the atomistic-based continuum modeling of nano-reinforced structural adhesives on the basis of a nanoscale representative volume element that accounts for the nonlinear behavior of its constituents; namely, the reinforcing carbon nanotube, the surrounding adhesive and their interface. The newly developed representative volume element is then used with analytical and computational micromechanical modeling techniques to investigate the homogeneous dispersion of the reinforcing element into the adhesive upon both the linear and nonlinear properties. Unlike our earlier work where the focus was on developing linear micromechanical models for the effective elastic properties of nanocomposites, the present approach extends these models by describing the development of a nonlinear hybrid Monte Carlo Finite Element model that allows for the prediction of the full constitutive response of the bulk composite under large deformations. The results indicate a substantial improvement in both the Young's modulus and tensile strength of the nano-reinforced adhesives for the range of CNT concentrations considered.

1. Introduction

It has been recognized for some time that the mechanical properties of polymeric materials can be engineered by fabricating composites that are comprised of different volume fractions of one or more reinforcing phases. A number of techniques have been considered to improve the mechanical properties of structural adhesives. They included the addition of carbon, nylon or glass micro-fibers, rubber and liquid rubber precipitates, reactive ductile diluents and inorganic hybrid particles, among others. Whilst some improvements in bond properties have been observed (Kawashita et al., 2008; Takemura, 2007), these additives also led to reductions in high temperature service capabilities, low impact strength, and poor shrinkage characteristics (Petrie, 2006). As time has progressed, practical realization of composites has begun to shift from micro-scale composites to nanocomposites, taking advantage of the unique combination of mechanical and physical properties of *nanofillers* (fillers with a characteristic dimension below 100 nm). There are a number of advantages associated with dispersing nanofillers in polymeric materials. While some credit can be attributed to the intrinsic properties of the fillers, most of these advantages stem from the extreme reduction in filler size combined with the large enhancement in the specific surface area and interfacial area they present to the matrix phase. In addition, whereas traditional composites use over 40 wt% of the reinforcing phase, the dispersion of just a few weight percentages of nanofillers into polymeric matrices could lead to dramatic changes in their mechanical properties with added functionalities.

In this work, we propose to reinforce the adhesive layer through the homogeneous dispersion of only a small fraction of carbon nanotubes (CNTs). CNTs are regarded as one of the most promising reinforcement materials for the next generation of high-performance structural and multifunctional composites (Endo et al., 2004). These molecular scale tubes of graphitic carbon have outstanding mechanical, thermal and electrical properties. In fact, some CNTs are stronger than steel, lighter than aluminum, and more conductive than copper (Moniruzzaman and Winey, 2006). Theoretical and experimental studies have shown that CNTs exhibit extremely high tensile modulus (1 TPa) and strength (150 GPa). In addition, CNTs exhibit high flexibility, low density (1.3–1.4 g/cm^3), and large aspect ratios (1000 s). Due to this unique combination of physical and mechanical properties, CNTs have emerged as excellent candidates for use as tailoring agents in polymeric materials to yield the next generation nanocomposites.

The design and fabrication of nano-reinforced adhesive composites requires rigorous characterization and analysis. Excellent

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nanotube properties do not necessarily translate into the same properties for the bulk composite. Several issues pertaining to the alignment, dispersion, aspect ratio, orientation, and load transfer need to be optimized in order to achieve the best properties of the composite. Two approaches have generally been adopted in treating this class of materials, namely, experimental and theoretical. Although there exists plenty of notable experimental efforts, these are severely hindered by the technical difficulties encountered during the manipulation, fabrication, and processing of CNTs and their composites. As such, there exists significant variability amongst experimental results and no set standards exist to streamline the manufacturing process. This has motivated the use of theoretical and computational approaches to predict the effective mechanical properties of bulk nano-reinforced composite systems.

Recently, an interfacial cohesive law has been developed by Jiang et al. and applied to study the interaction between CNT walls (Lu et al., 2007) and CNT polymer composites (Jiang et al., 2006). The cohesive law was used in a micromechanical analysis to predict the stress–strain behavior of CNT polyethylene composites (Tan et al., 2007). The predicted stress–strain curves displayed an intermittent decrease in both stress and strain due to the interface softening behavior displayed in the cohesive law. The studies showed that CNTs indeed improve the mechanical behavior of composites at small strain. However, the improvement disappears at relatively large strain because the debonded nanotubes behave like voids in the matrix and may even weaken the composite.

Chen and Liu (2004) and Liu and Chen (2003) evaluated the effective mechanical properties of CNT polymer composites using a square representative volume element (RVE) based on continuum mechanics. They were able to extract the effective elastic mechanical properties of both discontinuous and continuous CNT polymer composites by analyzing the RVE under a variety of loading conditions. They found that with the addition of only about 3.6% volume fraction of the CNTs, the stiffness of the composite in the CNT axial direction can increase as much as 33% for the case of long CNT.

Lusti and Gusev (2004) used finite element methods to investigate the effect of CNT orientation, aspect ratio and volume fraction on the effective elastic properties of CNT polymer composites. They considered fully aligned, two-dimensional random in-plane and three-dimensional random orientation states at various CNT concentrations. In their study the CNTs were modeled as massive cylinders which were randomly distributed in a computational cell using a Monte Carlo (MC) algorithm. Their results show that fully aligned nanotubes lead to a significant enhancement in the longitudinal properties whereas two dimensional random in-plane and three-dimensional randomly oriented nanotubes increase the effective properties considerably less, but equally, in more than one direction.

Several micromechanical schemes including sequential homogenization and various extensions of the Mori–Tanaka method were compared in a recent study of the elastic properties of SWCNT-based polymers by Selmi et al. (2007). The comparative study showed that for all composite morphologies considered (fully aligned, two-dimensional in-plane random orientation, and three-dimensional random orientation) the two-level Mori–Tanaka/Mori–Tanaka approach delivered the best predictions when validated using both experimental and finite element (FE) results.

The above micromechanical investigations of the effective mechanical properties of CNT-reinforced composites typically employ linear analytical formulations such as the Mori–Tanaka scheme and its derivatives. These investigations certainly assist in understanding the effects of such parameters as CNT concentration, aspect ratio, and orientation upon the linear elastic properties of the bulk composite. However, it is also of interest to the scientific community to understand how these parameters govern the full constitutive response of the nanocomposite subject to large deformations. In this study, we present an initial prediction of the full constitutive response of the bulk nano-reinforced adhesive under large tensile deformations. Appropriate formulations are developed to allow for the atomistic-based continuum modeling of nano-reinforced structural adhesives on the basis of a nanoscale RVE. The newly developed RVE is then used with analytical and computational micromechanical modeling techniques to investigate the homogeneous dispersion of the reinforcing element into the adhesive upon both the linear and nonlinear properties. A schematic of this approach is provided in Fig. 1. This approach was also adopted in our earlier works (Meguid et al., 2010) in the analysis of the effective elastic moduli of nanocomposites containing aligned and randomly distributed CNTs. However, there are a number of fundamental differences in the present approach that are worth noting. First, the RVE is formulated for a specific two-component epoxy system with homogenous material properties. Unlike our previous publication which focused on a generic polymer with a discrete and aligned chemical structure. Secondly, in the current micromechanical study we divert from our previous work by assuming transversely isotropic material symmetry for the reinforcing RVE. Finally, in the present computational approach, we extend our previous efforts by adopting traditional continuum FE concepts coupled with MC techniques to develop large scale three-dimensional micromechanical models that can be used to predict the resulting stress and strain fields in the nanocomposite for large deformations.

2. Atomistic-based continuum modeling

A three-dimensional nonlinear representative volume element (RVE) is developed to study the nano-reinforced adhesive system. The RVE consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT-epoxy interface, as depicted in Fig. 1. Due to the inherent nano-scale involved in simulating CNT structures, an atomistic description is incorporated. First, the carbon–carbon (C–C) covalent bonds in the CNT structure are described using the Modified Morse interatomic potential. Secondly, the atomic van der Waals (vdW) interactions between the atoms in the CNT and the atoms in the adhesive matrix are described using the Lennard–Jones (LJ) interatomic potential. This description implies the assumption of a non-bonded interfacial region. The atomistic-based continuum (ABC) multiscale modeling technique is used to model the components of the RVE. The approach adopted here extends the earlier work of Wernik and Meguid (2011). However, for the sake of completeness, we provide a brief outline of the method detailed in our earlier work.

Fundamental to the proposed concept is the notion that a CNT is a geometrical space-frame-like structure and the primary bonds between two nearest-neighboring atoms act like load-bearing beam members as depicted in Fig. 2. As in traditional FE models, nodes are used to connect the beam elements to form the CNT structure. In this case, the nodes represent the carbon atoms and are defined by the same atomic coordinates. We adopt the Modified Morse interatomic pair potential with an added angle-bending term to describe the atomic interactions in the CNT. The parameters used for the potential in this study are the same as those adopted by Belytschko et al. (2002), and are presented in Table 1. The Modified Morse potential is given by:

$$E = E_s + E_b \tag{1}$$

$$E_s = D_e\left(\left[1 - \exp^{-\beta(r-r_0)}\right]^2 - 1\right) \tag{2}$$