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Multifidelity multiscale modeling of nanocomposites for microstructure and macroscale analysis

Ashwin Rai[a], Aditi Chattopadhyay[b,*]

[a] Graduate Research Associate, School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287, United States
[b] Regents' Professor & Ira. A Fulton Professor of Engineering, School for Engineering of Matter, Transport, and Energy, Arizona State University, Tempe, AZ 85287, United States

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ABSTRACT

A high-fidelity multiscale modeling framework that integrates information from atomistic simulations pertaining to polymer chain sliding and bond dissociation is utilized to study damage evolution and failure in carbon nanotube (CNT)-reinforced nanocomposites. The nanocomposite constituents (microfiber, polymer, and CNTs) are explicitly modeled at the microscale using representative unit cells (RUCs). The modeled constituents are subsequently employed in a multiscale framework to describe damage initiation and propagation in these systems under transverse loading. Two CNT architectures, randomly dispersed and radially grown, are investigated. Damage initiation sites and damage evolution trends are studied, with results indicating that the presence of CNTs causes a unique stress state at the sub-microscale. This can lead to accelerated damage progression, which can be mitigated by architectural reconfiguration of the CNTs. Additionally, the Schapery potential theory is extended to develop an orthotropic nonlinear damage model that captures global behavior of the nanocomposite RUCs in a computationally efficient manner, and can be utilized as a numerical surrogate for structural scale nanocomposite analysis.

1. Introduction

Structural nanocomposites in the recent literature have shown to offer many potential and promising applications for aerospace and civil technologies [1,2]. For instance, nanocomposites that use carbon nanotubes (CNTs) for nanoscale reinforcement in a polymer matrix, have exhibited significant improvements in mechanical properties over conventional polymer based material systems [3,4]. In particular, carbon fiber composites reinforced with a polymer matrix containing randomly dispersed CNTs have shown to provide marked improvements in mechanical strength, interlaminar fracture resistance, energy absorption, and thermomechanical properties [5–7] compared to traditional carbon fiber reinforced polymer (CFRP) composites. However, it has also been observed that the nanocomposite characteristics do not scale linearly with size, and there exist large disparities in microscale and structural scale properties, such as stiffness and failure strengths [8]. Similarly, macroscale systems with CNTs embedded in their matrix, display only a marginal increase in fracture properties [9,10] with some studies indicating also reduced strength and fatigue life when compared to predicted values [11]. Such discrepancies are largely attributed to microscale architectural irregularities in the randomly dispersed nanofillers, such as misalignment, agglomerations, and poor dispersion of the CNTs [12,13]. To mitigate these drawbacks, recent advances in nanotechnology techniques have been exploited to engineer novel CNT architectures, including nanoforests [14–16], which utilize appropriate substrates for the growth of highly aligned dense mats of CNTs, fuzzy fibers [17], which contain CNTs radially grown on the microfibers, and CNT ropes [18], which harness the ultra-long strands of CNTs as a replacement for microfibers. Fuzzy fiber architecture, in particular, has shown to provide increased in-plane strength, interlaminar shear strength, and fracture properties [19]]. However, the observed improvements in properties due to the addition of CNTs is generally lower than the predicted theoretical values [20].

Possible causes for discrepancies between experimental results and theoretical predictions of the CNT nanocomposite properties may be the modeling approaches used for predicting material properties and behavior. These approaches are often not appropriate for a complex heterogeneous material system, such as the CNT/CFRP. Conventional methodologies predict structural scale properties using one of two approaches: a top-down approach based on a bulk material analysis such as smeared material techniques [21,22], or a bottom-up approach that uses mean field techniques, such as the Mori-Tanaka or the composite

* Corresponding author.
E-mail address: aditi@asu.edu (A. Chattopadhyay).

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cylinder assemblage techniques [23,24]. In the top-down approach, the macroscale bulk material analysis that is used cannot successfully capture the unique stress states at the sub-microscale, particularly where the CNT has a dominant load transfer effect, and can thus lead to unreliable failure predictions. Additionally, such approaches require large-scale experimental data to produce meaningful results. Mean field micromechanical techniques, on the other hand, tend to overestimate mechanical properties due to the assumption of overly simplistic repeating unit cells (RUCs), which in turn fail to account for the stochasticity in the microscale constituent properties and arrangement. In either case, the interaction of the CNTs and the polymer molecules at the nanoscale is entirely ignored.

In the case of CNT nanocomposites, recent studies suggest that the unique stress state at the nanoscale may lead to a divergence in observed and predicted response at the higher length scales [25]. Subramanian et al. developed a linear and post-linear multiscale approach for CNT-enhanced epoxy polymers by combining molecular dynamics (MD) simulations and the continuum mechanics approach [26]. In their study, the stress-strain response at the nano- and the sub-microscale was seen to be significantly different from the average bulk stress-strain response of the nanocomposite, indicating local stress concentrations, which can then lead to accelerated local damage initiation as demonstrated in [27]. Recent atomistic scale studies also show that bond formation and bond breakage phenomena of the polymer molecules may have significant impact on the macroscale elastic and damage behavior of CFRPs [25,26,28,29], a phenomenon not typically accounted for in conventional continuum modeling techniques.

Based on the above discussion, it is clear that a necessary first step to achieve a systematic understanding of the behavior of nanocomposite materials at the higher length scales requires comprehensive understanding of the mechanics of load transfer between the nanofiller, the matrix, and the microfiber. One approach for such an investigation could be through extensive experimental characterization as seen in [30]; however, the large number of physical variables and their complex interactions involved in the process makes for a daunting task. An alternative would be to develop new computational tools, which include nanoscale mechanics to resolve atomistic interactions used in the investigation of the physical phenomena associated with the load transfer and damage mechanisms in CNT/CFRPs.

Numerous CFRP analyses with atomistic integration have been performed in the past. They include using a combination of molecular mechanics (MM) or molecular dynamics (MD) simulations and averaging techniques, such as elastic homogenization based micromechanics [20,31], statistical techniques such as Monte Carlo methods [32], or adopting a fully continuum mechanics finite element (FE) approach [33]. While homogenization provides reasonably accurate results for elastic analysis, it can also result in imprecise outcomes for inelastic and damage analyses due to the loss of spatial variability in stress and strain fields [34]. Similarly, statistical techniques may require an inordinately large number of simulations to achieve an accurate characterization of the complete nonlinear behavior spectrum. For example Monte Carlo simulations of amorphous polymer deformation have to be severely limited in the spatial and temporal domain to obtain practical results [32]. It has also been shown that investigating stochastic properties of composite materials with m uncertain variables may lead to a N^m increase in computation time which can only be decreased slightly using improved sampling schemes such as the Latin Hypercube Sampling [35]. Finally, FE methods often fail to capture the fidelity at atomic scales due to the breakdown of the assumptions in continuum mechanics. Zeng et al., provide a thorough comparison of the various methodologies along with the advantages and disadvantages of each method [36].

In the literature there is considerable emphasis on deriving rigorous mathematical theories for describing the stress state of heterogeneous media, wherein the nanoscale mechanics is integrated using various forms of homogenization, such as the variational asymptotic homogenized micromechanics models [37,38]], eigen-deformation based reduced order models [39,40], mathematical homogenized micromechanics coupled with diffused damage models [41], and *ad hoc* mathematical functions such as the boundary condition free micromechanics theory [42]. Recent studies have also used concurrent and semi-concurrent coupled FE and MD simulations to capture nanoscale mechanics explicitly [43]. However, the nanoscale mechanics used in these works utilize empirical force fields that are inadequate for capturing fundamental nonlinearities at the nanoscale, e.g., bond breakage of polymer chains [26]. Moreover, when reactive bond order force fields are used in these methods, the implementation becomes computationally infeasible. It has also been shown that there are certain localized phenomena, e.g., stress recovery proceeding initial softening and damage saturation, which can only be observed explicitly, by modeling the nanoscale substructures using reactive bond order force fields [27].

In this paper, a novel multiscale methodology is presented, which includes nanoscale mechanics to resolve atomistic interactions, to investigate the physical phenomena associated with the load transfer and damage mechanisms in CNT/CFRPs. Each constituent of the CNT/CFRP material system is explicitly modeled and assembled into a realistic microscale representative unit cells (RUCs) using the finite element (FE) method. The matrix constituent is modeled using a physical damage evolution law that uses the fundamental covalent bond dissociation information obtained from MD simulations of the polymer molecules and chains, implemented using the reactive force field (ReaxFF) [44]. Since the CNTs are modeled explicitly, a thorough post-linear investigation of the interaction between the CNTs and the matrix constituent is also performed. This study provides insights into the load transfer mechanism, and the damage initiation and propagation phenomenon, in randomly dispersed CNT nanocomposites and radially grown fuzzy fiber nanocomposites, at the sub-micro and micro length scales. Additionally, a surrogate orthotropic material model based on the Schapery potential theory [45], which reproduces the nanopolymer behavior, is also developed. The material model is calibrated with the response obtained from the high-fidelity nanocomposite model, and applied to a microscale 3D subcell-based sectional micromechanics framework [46], to replicate the global behavior of the high-fidelity RUC. The calibrated Schapery/Subcell equations can be easily applied as a user defined material model within laminated plate theories in most finite element software packages for rapid damage and failure analysis of CNT enhanced composite components such as skis, golf shafts, baseball bats, tennis rackets etc. The models presented in this paper may also allow these material systems to be used in critical structural and multifunctional roles which is currently avoided due to the uncertainty in material behavior predictions. This paper also sets the procedure and workflow for similar investigations with different epoxy matrix, carbon fiber, or CNTs and thus help composite designers in making optimum use of these material systems.

2. Constituent and model generation

This section details the methodology used to generate the explicit RUC of the CNT/CFRP material system. The three constituents of the nanocomposite, (i) microfiber (ii) polymer (iii) CNTs, are generated individually and then combined in a single model within the FE framework using the commercial FE software, ABAQUS, thereby permitting the inclusion of deterministic or stochastic geometric and material properties. The algorithms and the methods for introducing stochasticity for all three constituents are also briefly described.

MD simulations of DGEBF (Di-Glycidyl Ether of Bisphenol F) epoxy and DETA (Di-Ethylene Tri-Amine) hardener simulating the curing process are performed to yield a distribution of the most likely cross-linking degree for this system. Additionally, MD simulations are used to determine the relationship between the cross-linking degree and material properties by recording the response of the MD unit cells under