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Investigation of damage mechanisms in CNT nanocomposites using multiscale analysis

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ABSTRACT

This paper examines microscale and sub-microscale damage mechanisms in carbon nanotube (CNT) reinforced nanocomposites. A multiscale modeling framework with a damage model developed from molecular dynamics simulation, is employed to study the physical mechanisms of damage initiation and propagation in CNT nanocomposites at the sub-microscale. Two CNT arrangements, randomly dispersed and entangled agglomerates, are examined. This investigation offers insights into damage properties of particular configurations of CNTs in a polymer matrix, in addition to specific understanding related to damage concentration effects around the filler material at the sub-microscale. High spatial CNT concentration differential is observed to affect damage initiation and rate of damage. It is further shown to result in sub-microscale crack initiation at low global strains, a phenomenon that is also observed at agglomeration boundaries, which results in CNT agglomerations to behave as crack initiation sites.

1. Introduction

The use of carbon nanotubes (CNTs) for structural and multifunctional nanotechnology applications is an area of growing scientific interest (Thostenson et al., 2001; Yu and Kwon, 2009). In particular, nanocomposites that use CNTs as reinforcing nanofillers in the polymer matrix have been shown to exhibit superior multifunctional properties under controlled environments (Balazs et al., 2006), such as improved stiffness (Dean et al., 2006), *in-situ* damage sensing (Datta et al., 2015), precise thermal management (Biercuk et al., 2002) and increased toughness (Coleman et al., 2006), thus presenting potential for unique applications. However, a critical obstacle preventing the integration of nanostructures into practical applications is the inability to scale the performance gains and multifunctional capabilities of nanocomposites for commercialization purposes (Sochi, 2012). In other words, a deep divide remains between the theoretical predictions and the experimental observations of the mechanical, strength, and damage properties of CNT-nanocomposites at the macroscale. These differences translate into limitations, e.g., minimal increase in fracture characteristics (Gojny et al., 2004; Qiu et al., 2007) and low strength and fatigue life compared to predicted values (Ren et al., 2004). Such discrepancies have been attributed to geometrical inconsistencies in the CNT composition at the sub-microscale, such as lack of alignment, agglomerations and poor dispersion of the CNTs (Wicks et al., 2010) that are not accounted for in most macroscale theoretical formulations. Limited efforts have been devoted to a comprehensive analysis of the cause of these discrepancies. Recent studies have shown that the local nanoscale and sub-microscale stress-strain response of nanocomposites can significantly differ from the average bulk response, with the local stress-strain response around the filler material indicating stress concentration sites (Subramanian et al., 2015). Such sub-microscale responses may lead to accelerated damage initiation and may account for the difference in theoretical and predicted macroscale response in these materials.

A number of computational methods have been used to understand the load transfer, elastic behavior, and damage mechanisms of nanocomposites at the nano and sub-microscales (Rai et al., 2016a; Subramanian et al., 2015; Seidel and Lagoudas, 2006; Valavala and Odegard, 2005; Fish and Wagiman, 1993). Molecular dynamics (MD) simulations demonstrate excellent compatibility for resolving the physics associated with load transfer between polymer chains and CNTs, which is possible due to the similarity in length scales between these components (Rahmat and Hubert, 2011). However, MD simulations require high computational times and hence are limited to unit cells of a few nanometers in size. Multiscale modeling methods, on the other hand, may be used for scaling the nanocomposite behavior along multiple length scales,

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since the prevailing mechanisms at the lowest length scale are resolved while maintaining stable solutions at the higher length scales through physical length scale bridging (Subramanian et al., 2015). Multiscale analysis using atomistic simulations is yet another method that is able to not only achieve the desired resolutions for obtaining realistic insights into load transfer and damage mechanisms at the sub-microscale in CNT nanocomposites, but also deliver simultaneously, an accurate far field response. Such a hybrid multiscale approach has been used for investigating the linear and elastoplastic response of CNT nanocomposites (Zhang et al., 2015; Yang et al., 2013; Yang and Cho, 2008), and can also calculate the most likely crosslinking degree of the epoxy after cure (Subramanian et al., 2015) as well as variations in mechanical response due to physical factors, such as CNT orientation, agglomeration, and CNT and polymer interface properties (Alian et al., 2015; Namilae and Chandra, 2005). The multiscale approach has shown to be applicable to a nanocomposite system while simultaneously being reasonably accurate at multiple length scales.

In their recent work, the authors have developed an atomistically informed continuum damage mechanics (CDM) based formulation that captures polymer damage under isothermal conditions and within operating temperatures lower than the glass transition temperature (Rai et al., 2016b). The methodology utilizes bond disassociation energy densities that are calculated from MD simulations of bond breakage in the epoxy polymer chains under load. The bond disassociation energy density is used to formulate the damage evolution curve for a CDM theory which also makes use of polymer mechanics to simulate polymer hardening/softening (Bouvard et al., 2010). This paper extends our previous work by applying the atomistically informed damage model to a CNT/polymer system to achieve a more sophisticated understanding of the load transfer, damage initiation, and propagation in CNT nanocomposites at the length scale of the filler material and its effects at the microscale. This work provides new insights into damage trends, crack initiation, and propagation at the sub-microscale of CNT nanocomposites, and can potentially assist in future nanoengineering of CNT material systems for optimal mechanical response for specific applications.

2. Formulations

This section briefly reviews the multiscale damage formulations developed by the authors (Rai et al., 2016a; 2016b).The developed model has been bench-marked against classical plasticity, and CDM models and verified for experiments involving pure polymer specimens in the following reference: (Rai et al., 2016b). The CDM framework is used to introduce damage at the continuum scale Lemaitre (2012); Chaboche et al. (2006), chosen due to the improved computational efficiency compared to fracture mechanics methods, and for its ability to develop thermodynamically consistent formulations (Coleman and Gurtin, 1967; Simo and Hughes, 2006). The elastic strain, $\underset{\sim}{\epsilon}^e$, the isotropic damage variable, D, the internal variable associated with polymer chain movement and entanglement, ξ, and the original density of the material, ρ_0, are used to define the Helmholtz specific free energy as:

$$\psi = \frac{1}{\rho_0}\bar{\psi}(\underset{\sim}{\epsilon}^e, D, \xi) \tag{1}$$

The Helmholtz free energy is further used to define the thermodynamic affinities associated with damage, D, and the internal strain due to chain entanglement in the polymer, ξ:

$$Y = -\frac{\partial\bar{\psi}}{\partial D} \qquad \textit{and} \qquad k = \frac{\partial\bar{\psi}}{\partial\xi} \tag{2}$$

The Helmholtz free energy is assumed to be a linear summation of the elastic and inelastic terms. Defining the stiffness matrix as $\underset{\approx}{L}$, the elastic term of the free energy is obtained using the constitutive relation and the equivalent strain concept (Lemaitre, 2012):

$$\bar{\psi}^e = \frac{1}{2}(1-D)\underset{\sim}{\epsilon}^e : \underset{\approx}{L} : \underset{\sim}{\epsilon}^e \tag{3}$$

Eq. (3) is used to derive Hooke's law as shown in Eq. (4):

$$\underset{\sim}{\sigma} = \rho\frac{\partial\psi}{\partial\underset{\sim}{\epsilon}^e} = (1-D_v)(1-D)\,\underset{\approx}{L} : \underset{\sim}{\epsilon}^e \tag{4}$$

The difference in density between the damaged and pristine material can be associated with damage due to volume changes using a dependent variable, D_v, such that $\frac{\rho}{\rho_0} = 1 - D_v$ (Chaboche et al., 2006). D_v is hence used to quantify the effects of void growth and increase in crack density per unit volume in the material.

The plastic potential is formulated such that the effects of damage and volumetric change is represented (Lemaitre, 1985):

$$\phi_p = \frac{\rho_0}{\rho}\frac{\sigma^*_{eq}}{1-D} - k - \sigma_y \leqslant 0 \tag{5}$$

where σ_y is the yield stress. The equivalent stress σ^*_{eq} is chosen to be a variable elliptic function of the first and second stress invariants (Green, 1972; Besson and Guillemer-Neel, 2003; Chaboche et al., 2006) such that the effects of hydrostatic stresses may be considered to determine the plastic state of the material.

The evolution of the state variables need to be defined for implementation of the CDM formulations. The plastic strain rate is obtained using the normality condition:

$$\dot{\underset{\sim}{\epsilon}}^p = \dot{\lambda}\frac{\partial\phi}{\partial\left(\frac{\rho_0}{\rho}\underset{\sim}{\sigma}\right)} = \frac{\dot{\lambda}}{1-D}\frac{\partial\sigma^*_{eq}}{\partial\underset{\sim}{\sigma}} \tag{6}$$

where the Peric viscoplastic equation (Perić, 1993) is used to calculate the viscoplastic multiplier $\dot{\lambda}$:

$$\dot{\lambda} = \frac{1}{K}\left[\left(\frac{\phi+\sigma_y}{\sigma_y}\right)^{\frac{1}{n}} - 1\right] \tag{7}$$

where K and n are the viscoplastic constants.

Elements of polymer mechanics are included to simulate the process of chain motion, linkage, and entanglement. The evolution of the internal strain in the polymer is controlled by the increase in internal energy due to entanglement of the polymer chains and the subsequent energy release due to the co-operative movement of the polymer chains at release. When polymer chains become entangled an internal strain like quantity, defined by ξ, is produced. Anand and Gurtin (2003) developed equations to describe the evolution of this quantity, which was further simplified by Bouvard et al. (2010) and is presented in Eqs. (8) and (9):

$$\dot{\xi} = h_0\left(1 - \frac{\xi}{\xi^*}\right)\dot{\lambda} \tag{8}$$

$$\dot{\xi}^* = g_0\left(1 - \frac{\xi^*}{\xi_{sat}}\right)\dot{\lambda} \tag{9}$$

The internal strains evolution equation simulates the obstacles to chain movements such as entanglement points. ξ^* is the energy barrier opposing chain movement and as further chains escape the entanglement points, this barrier is lowered resulting in further increased motion of chains. Further details on this procedure can be found in Rai et al. (2016b).

The damage evolution equation is formulated from the MD simulation results of the bond disassociation energy density variation under applied strain. A recently developed hybrid MD simulation framework that utilizes reactive force fields was used to characterize the energy variations caused by successive bond breakages at