
Nonlinear Multi-Scale Finite Element Method to Predict Tensile Behavior of Carbon Nanotube-Reinforced Polymer Composites

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Abstract. The ability of carbon nanotubes (CNTs) to consider as the strongest and stiffest elements in nanoscale composites remains a powerful motivation for the research in this area. This paper describes a finite element (FE) approach for prediction of the mechanical behavior of polypropylene (PP) matrix reinforced with single walled carbon nanotubes (SWCNTs). A representative volume element is proposed for modeling the tensile behavior of aligned CNTs/PP composites. The CNT is modeled with solid elements. Modified Morse potential is used for simulating the mechanical properties of an isolated carbon nanotube. The matrix is modeled as a continuum medium by utilizing an appropriate nonlinear material model. A cohesive zone model is assumed between the nanotube and the matrix with perfect bonding until the interfacial shear stress exceeds the bonding strength. Using the representative volume element, a unidirectional CNT/PP composite was modeled and the results were compared with corresponding rule-of-mixtures predictions. The effect of interfacial shear strength on the tensile behavior of the nanocomposite was also studied. The influence of the SWCNT within the polymer is clearly illustrated and discussed. The results showed that polymer's Young's modulus and tensile strength increase significantly in the presence of carbon nanotubes.

Introduction

Among various nanomaterials, carbon nanotubes (CNTs) have gained widespread attention owing to their superior properties, good chemical stability, and large surface area [1]. CNTs are extremely thin tubes and feature an extremely enviable combination of mechanical, thermal, electrical, and optical properties [2]. Their size, shape, and properties constrain them as prime contenders for exploiting the growth of a potentially revolutionary material for diverse applications. Therefore, in many studies, CNTs have been used as reinforcements in polymer matrix composites [2-5].

One of the issues in CNT reinforced polymer is to obtain the optimum load transfer across the CNT-polymer matrix interface. Many research studies have been done to measure the interfacial strength between CNT and polymer matrix. Since most of the studies are impeded by the technical difficulties involved in the manipulation of the nanotubes, the use of theoretical and computational approach to predict the load transfer ability of the nanocomposites might be implemented [6]. Lau et al. [7] theoretically studied the stress transfer properties between single-/multi-walled nanotubes and polymer matrix. They used local density approximation, elastic shells and conventional fiber pullout models. Lordi and Yao [8] used force-field based molecular mechanics to study the binding energies and sliding friction between the nanotubes and different polymer matrices. They found that helical
polymer conformations play a significant role in the strength of the interface. They suggested that the strength of the interface may result from molecular-level entanglement of the two phases and forced long-range ordering of the polymer. Liao and Li [9] studied the interfacial characteristics of the CNT/polystyrene composite system in the absence of atomic bonds between nanotubes and polymer matrix using molecular mechanics. Results showed that the interfacial shear stress of the nanotube/polystyrene composite system is about 160 MPa, significantly higher than most carbon fiber reinforced polymer composites.

Frankland et al. [10] studied the matrix-nanotube shear strength using molecular dynamics simulations. It was concluded that the shear strength of a polymer/nanotube interface with weak non-bonded interactions could be increased by over an order of magnitude with the introduction of a relatively low density (<1%) of chemical bonds between the nanotube and polymer. Tan et al. [11] studied the effect of van der Waals-based interface forces on the CNT-polystyrene composite. They incorporated a nonlinear cohesive law introduced by Jiang et al. [12] in the micromechanical model of the composite. The results showed that CNTs improve the mechanical behavior of the composite only at small strains. Tserpes et al. [13] proposed a multi-scale representative volume element (RVE) for modeling the tensile behavior of carbon nanotube-reinforced composites. Between the nanotube and the matrix a perfect bonding was assumed until the interfacial shear stress exceeds the corresponding strength which simulated the debonding effect. It was found that the tensile strength significantly increases with increasing interfacial shear strength.

Since computational models usually over-predict the tensile modulus of composites, Bhuiyan et al. [14] built a RVE to investigate the effect of polymer-filler contact properties. While assuming perfect filler–polymer interfacial contact leads to over predicted tensile modulus of the CNT/PP composites by 85% for 5 wt.% CNT/PP composites, more accurate data was obtained by considering the imperfect CNT/PP contact, CNT agglomerates and alignment in the composites.

In this study, a multi-scale RVE for CNT-reinforced composites is proposed to investigate the nonlinear behavior of the composite under tension. Finite element (FE) simulations were performed to simulate the pullout of a single-walled carbon nanotube (SWCNT) from the polypropylene (PP) matrix. The PP resin model was modeled by incorporating three-dimensional solid elements. In this study, the chemical bonding between SWCNTs and the PP was not considered because SWCNTs have less defects and more chemical stability compared to MWCNTs. Only the influences of non-bonded interactions on interfacial stress transfer were studied. A cohesive law for interfaces between the CNT and polymer was established characterized by the van der Waals force.

**Finite Element Modeling**

A cylindrical RVE consisting of CNT, PP matrix and contact interface was modeled using ANSYS software. In the FE modeling, CNTs were assumed as solid structures. A three-dimensional (3D) RVE with the applied boundary conditions, was investigated under uniform extension to determine the tensile behavior of CNT/PP composites. A high order 3D structural solid element with three degrees of freedom per node was used for both matrix and SWCNT. A cohesive zone material model was used at the CNT/PP interface. An optimum mesh density that guarantees a fully converged solution with minimum computational time is determined based on a parametric study.

Perfect bonding was assumed between the phases. The simulated resin was treated as a nonlinear isotropic material. Young's modulus and Poisson’s ratio was inserted according to the experimental data. The Multilinear Isotropic Hardening Material Model was utilized to include nonlinear plasticity of PP and CNT. Isotropic hardening has been adopted. The material properties and dimensions used for the RVE are shown in Table 1. The stress-strain relationship of the composite was calculated as the ratio of the average stress to the applied strain. The average stress generated in the RVE was calculated using the nodal stresses obtained from the FEA by accounting for all phases present in the RVE.
Carbon nanotube. An armchair SWCNT with chiral index of (5,5) was chosen for the model. The CNT properties were obtained from previous study conducted by present authors based on the Modified Morse potential equations [15]. A correlation between inter-atomic molecular potential energies and strain energies of a beam has been established by using equivalence of energies. Figure 2 shows the nonlinear stress-strain curve of armchair (5,5) SWCNT under axial tension.

Polymer Matrix. Since the volume fraction of CNTs is about 5% in the RVE, subsequently, the volume of the polymer matrix is much higher than that of the CNTs at molecular scale. As a reasonable compromise, the surrounding polymer is taken into account as a continuum medium and solid elements are used to construct the thick resin. A higher order 3-D 20-node solid element, SOLID186, was employed for this purpose. The element has three degrees of freedom per node which are translations in x, y and z directions. This element supports nonlinear material behavior and is well suited to model curved boundaries. The simulated resin was treated as an nonlinear isotropic material with Young’s modulus of 0.751 GPa and 0.3 as Poisson’s ratio according to the experimental data.
**Nanotube/matrix interface.** Fundamental to the reinforcing effectiveness are the interfacial characteristics between the nanotube and the matrix. Upon this issue, a considerable number of works have been reported previously [11, 14]. Since CNTs usually agglomerate due to van der Waals force [16], they are extremely difficult to disperse and align in most of the common polymer matrices [17]. Moreover, CNTs usually do not bond well to polymers such that their interaction is the van der Waals force [18], which is much weaker than covalent bonds. This leads to sliding of the CNT in the polymer matrix when subjected to loading.

McCarthy et al. [19] studied the interaction between CNTs and a conjugated polymer to gain a better understanding of the binding. A good wetting between the conjugated polymer and nanotubes has been observed. Wagner et al. [20] reported the stress transfer ability of nanotubes–polymer interfaces of the order of 500 MPa. Schadler et al. [21] studied mechanical behavior of multi-walled carbon nanotube (MWCNTs)/epoxy composites in tension and compression. It was found that the compression modulus is higher than the tensile modulus, indicating that load transfer to the nanotubes in the composite is much higher in compression. Later on, Cooper et al. [22] used a scanning probe microscope tip to measure the interfacial strength of an individual SWCNT ropes and MWCNTs bridging across holes in an epoxy matrix. Based on these experiments, the interfacial shear strength between the MWCNTs and the epoxy matrix were calculated to be in the range of 35–376 MPa, whereas most of SWCNT ropes were fractured instead of being pulled out of the epoxy matrix. Barber et al. [23] also directly measured adhesive interactions between the MWCNT and the polyethylene–butene matrix by performing reproducible nano pullout experiments using atomic force microscopy. The result showed a relatively high interfacial debonding stress of 47 MPa. Wagner [24] used a traditional force balance approach which was modified for a hollow tube. He applied an expanded form of the Kelly–Tyson model to calculate the interfacial strength between the SWCNT and polymer. It was shown that high values of the interfacial strength are attainable.

As the CNTs are represented by solid elements, the interfacial shear stress cannot be computed directly. To overcome this obstacle, an approach described by Tserpes et al. [13] was considered. Figure 3 shows the free-body diagram of the CNT in the RVE. From the FE analysis, the normal stresses $\sigma_1$ and $\sigma_2$ at nodes 1 and 2, respectively, are computed. If constant shear stress $\tau$ along the element is assumed, then the equilibrium formulation can be written as,

$$[\sigma_1-\sigma_2]A = \tau \pi D l$$

where, $D$ is the outer nanotube diameter and $l$ is the CNT length. From Eq. (1) $\tau$ will be computed and compared to the interfacial shear strength (ISS) value. If $\tau \geq$ ISS, the interface has failed leading to load-carrying disability of the specific element, which is modeled by a cohesive material model (CZM). The above procedure was repeated at each load step. In this study a prefect bonding between CNT and Polymer was chosen to show the effect of material nonlinearities.

![Fig. 3. (a) Schematic diagram of the beam representing the nanotube, (b) contact elements representing CNT/PP interface](image-url)
In the RVE proposed here, simulation of nanotube/matrix debonding was incorporated. The debonding refers specifically to separation of the bonded contact. Bilinear material behavior with tractions and separation distances was defined according to [25]. A cohesive zone material has been defined to simulate the traction separation behavior of the CNT/polymer interface by adopting augmented Lagrangian method.

Results and Discussion

As noted previously, it is not impossible to create a strong bond via functionalization methods in a CNT-based composite. Therefore, perfect bonding between CNT and PP was assumed in the model between CNT and polymer. The interface model was adjusted to account the full bonded condition between the CNTs and matrix. The RVEs containing long CNT (100 nm) and short CNT (50 nm) is depicted in Figure 4.

![Section of the FE model for (a) RVE with long CNT and (b) RVE with short CNT](attachment:image)

The nodal displacement and reaction forces were computed for the described boundary conditions. These data were used to calculate the stress-strain relationships of RVEs. Below equations were employed to compute the axial strain ($\varepsilon_x$), axial stress ($\sigma$), Young’s modulus ($E$), ultimate strength ($\sigma_{ult}$) for the RVE.

\[
\varepsilon_x = \frac{\Delta l}{l_0} = \frac{l - l_o}{l_0}
\]

\[
\sigma = \frac{F}{A}
\]

\[
E = \frac{\sigma}{\varepsilon_x}
\]

The volume factor, $\nu_f$ for two RVEs is calculated as 0.033 and 0.016 for long and short CNTs, respectively. Thus, the rule of mixture yielded $E_{mix} = 28.7$ GPa which predicts a significant improvement in the composite mechanical response [26]. However, the calculated value for the more elaborated Halpin-Tsai equation leads to $E_{H-T} = 475$ MPa. This value is closer to the experimental observation. The difference is much obvious in the plots illustrated in Figure 6. The lower values of material constants obtained from FEA, compared with that of the results of rule of mixture and Halpin-Tsai model, suggested that the effect of material nonlinearity caused by both material properties and geometry of the RVE cannot be neglected.

If we consider the rule of mixture for short CNTs, a calculation for $\nu_f = 0.016$, $E_f = 861$ GPa and $E_m = 0.475$ GPa yields $E_{mix} = 0.912$ GPa. While, the extracted value form the RVE was $E_c = 603$ MPa.
To find out the effect of CNT length on the tensile properties of composites, the stress-strain curves for both cases were plotted in Figure 5. The lower value of Young's modulus and ultimate strength ($\sigma_{uts}$) obtained from FEA, compared with that of the rule of mixture, suggests that we cannot neglect the effect of material nonlinearity caused by both material properties and geometry for the composite RVE.

It can be seen that RVE with long CNTs shows several order higher strength comparing to short CNT. This conclusion is in good agreement with reports by Liu et al. [26, 27] and Georgantzinos et al. [28]. However, both of these studies were based on elastic models.

![Stress–strain curves for RVEs obtained from FEA and rule of mixture.](image)

**Fig. 5.** Stress–strain curves for RVEs obtained from FEA and rule of mixture.

**Conclusions**

A finite element model for predicting the tensile behavior of aligned CNT/PP has been proposed. The continuum FE method is employed for building the RVE and performing the analysis while data regarding the behavior of the nanotube are drawn from Morse potential. The interfacial interaction between CNT and polymer was modeled via a cohesive zone model. This model was used to investigation the impact of non-bonded interface in the mechanical properties of the composite.

The simulation results showed a significant enhancement in the stiffness of the polymer owing to the addition of the aligned nanotubes with different length. The prediction of composite’s initial stiffness was compared by the rule-of-mixtures. This study of interfacial bonding between CNT/PP indicated that there could be an effective stress transfer from the PP resin to the CNT at prefect bonding.

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References


