

# Atomistic-Based Continuum Modeling of the Interfacial Properties of Structural Adhesive Bonds

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## ABSTRACT

This work is concerned with the multiscale modeling of nano-reinforced structural adhesive bonds (SABs) that are typically used in the transport industry, with the aerospace sector being the prime target. Specifically, it is our objective to develop the appropriate formulations to allow the atomistic-based continuum modelling of SABs and the development of a representative volume element that accounts for the nonlinear behaviour of its constituents. This model is used to evaluate the load transfer and strengthening mechanism(s) and interfacial properties of the nanofiller and surrounding adhesive. The work is further extended to establish experimentally, the relative merits of the candidate nanofillers upon the mechanical properties of SABs. We experimentally explore the benefits of selected adhesives, interface properties of SABs with a view to identify candidate systems for industrial applications. The experimental results show that the addition of 2.5 wt% of carbon nanotubes (CNTs) into aerospace structural adhesive can lead to as much as a 40% increase in the tensile strength and 30% increase in the interlaminar shear strength.

## 1 INTRODUCTION

Most multiscale modeling techniques adopt either the discrete model or atomistic-based continuum models. In the discrete model, it is common to employ tight binding (TB) for electronic band structure, molecular dynamics (MD) for atomistics and finite element FE (or meshfree) methods for continuum. Unfortunately, most FE/MD multiscale modeling techniques suffer from one or more of the following difficulties: (i) the necessity of meshing traditional FE regions down to the atomic scale, thus leading to physical inconsistency and numerical difficulties, (ii) contamination of the solution due to wave reflection resulting from the improper description of the transition zone, and (iii) the FE/MD combination of energy mismatch and mesh incompatibility leads to erroneous non-physical effects in the transition region. A summary of the different discrete modeling techniques can be viewed in the recent review by Wernik and Meguid [1].

The other multiscale modeling approach is the atomistic-based continuum technique. It has the unique advantage of describing atomic positions, their interactions and their governing interatomic potentials in a continuum framework.

The interatomic potentials (deformation measures) introduced in the model capture the underlying atomistic structure of the different phases considered. Thus, the influence of the nanophase is taken into account via appropriate atomistic constitutive formulations. Consequently, these measures are fundamentally different from those in the classical continuum theory. The strength of atomistic-based continuum techniques lies in their ability to avoid the large number of degrees of freedom encountered in the discrete modeling techniques, whilst at the same time allow for the description of the nonlinear constitutive behaviour of the constituents. A schematic of this approach as it relates to the modeling of CNT structures is depicted in Fig. 1.

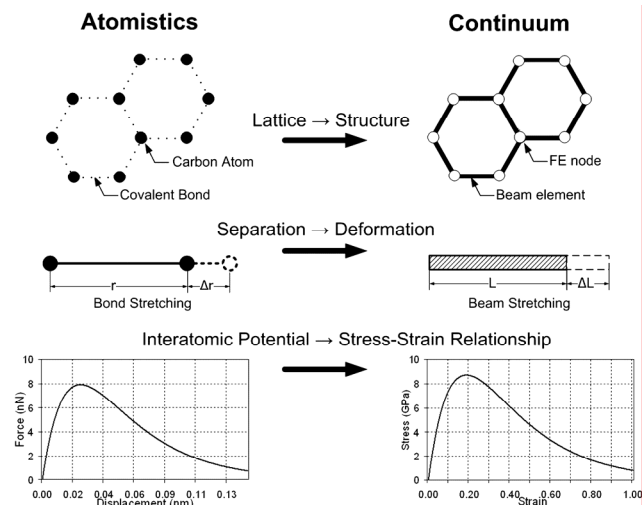


Figure 1: Atomistic-based continuum modeling technique as it relates to CNT structures.

In this paper we describe a novel approach to the development of a nonlinear atomistic-based representative volume element for the study of carbon nanotube reinforced composites.

## 2 ATOMISTIC-BASED CONTINUUM MODEL

A three-dimensional nonlinear representative volume element (RVE) was developed to study the nano-reinforced polymer system. The RVE consists of the carbon nanotube (CNT), the surrounding polymer matrix, and the CNT-polymer interface, as depicted in Fig. 2. Due to the nano-

scale involved in simulating carbon nanotube structures, an atomistic description was incorporated on two levels. First, the carbon-carbon (C-C) covalent bonds in the CNT structure were described using the Modified Morse potential. Secondly, the atomic van der Waals interactions between the atoms in the CNT and the atoms in the polymer matrix were described using the Lennard-Jones potential. This description implies the assumption of a non-bonded interfacial region.

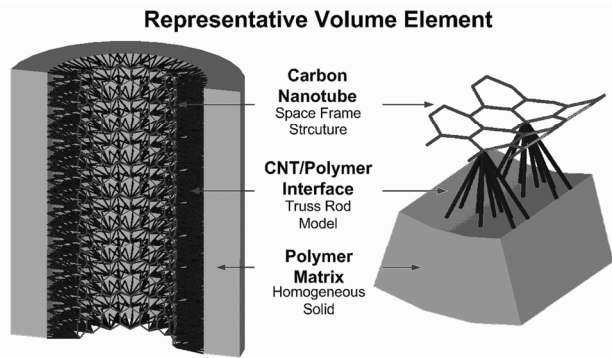


Figure 2: The components used in the development of the representative volume element.

The CNT was modeled as a space-frame structure as depicted in Fig. 3. In the space-frame model, each beam element corresponds to an individual chemical bond in the CNT. As in traditional FE models, nodes were used to connect the beam elements to form the CNT structure. In this case the nodes represent the carbon atoms and their positions are defined by the same atomic coordinates. In this way, the space-frame structure allows the mechanical behavior of the CNT to be accurately modeled in terms of the displacements of the atoms. Figure 3 also illustrates a portion of the hexagonal lattice to demonstrate the connectivity of the beam elements in the continuum representation of the CNT. The Modified Morse interatomic potential was used to derive the material models for the continuum representations of the atomic interactions in the CNT. This potential is well suited for characterizing the behavior of C-C covalent bonding.

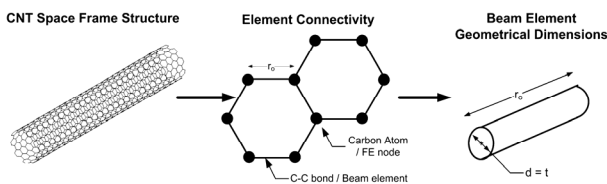


Figure 3: Carbon nanotube space frame structure.

To model the surrounding polymer matrix, a two component-epoxy adhesive (SikaDur330) was used. The stiffness of the epoxy polymer was assumed to be 4.6 GPa and Poisson's ratio was taken to be 0.3. This epoxy adhesive is commonly used in the fabrication of glass reinforced polymer composites (GFRP). The polymer was modeled as a homogeneous solid. The volume of the

polymer was varied in order to investigate the effect of the CNT's volume fraction on the effective mechanical properties of the nano-reinforced polymer system.

In this study, we investigate a non-bonded configuration which implies that only van der Waals interactions are considered. In order to simulate the van der Waals interactions, we have adopted the use of a truss rod model whereby each interaction was represented by one truss rod. Each rod extends out from a carbon atom in the CNT structure to an atom in the polymer matrix. The Lennard-Jones interatomic potential was used to describe the behavior of the van der Waals interactions.

### 3 RESULTS AND DISCUSSION

As an intermediary step in the study of the effective properties of nano-reinforced composites, the nonlinear response of the individual carbon nanotube was investigated. Two carbon nanotube arrangements were studied: the (16,0) zigzag nanotube and the (9,9) armchair nanotube, both having diameters of approximately 1.2 nm and lengths of 10 nm. Two loading conditions were investigated to obtain both tensile and shear properties.

The results show that the zigzag nanotube can withstand a strain of 17%, while the armchair nanotube can withstand a strain of up to 22%. The respective tensile modulus for the armchair and zigzag nanotubes are 944.8 GPa and 920.2 GPa. The overall trend of the stress-strain curves agree well with others in the literature [2,3], and also show that the armchair configuration exhibits higher strength and stiffness when compared to the zigzag configuration. The shear modulus for zigzag and armchair nanotubes was 322.6 GPa and 333.8 GPa, respectively. The present study has predicted shear strengths of 68 GPa and 96 GPa for armchair and zigzag nanotubes, respectively, with corresponding failure strains of approximately 30% and 37%. These values do agree with several quoted values in literature [4,5].

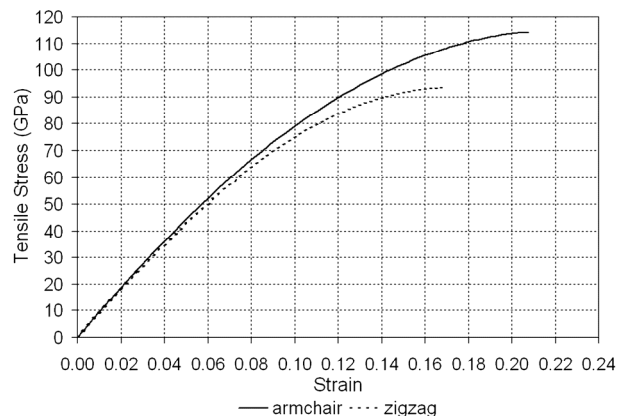


Figure 4: Tensile stress-strain curves for zigzag and armchair nanotubes

The RVE was loaded under tension and torsion to provide the respective properties. For both loading

conditions, the volume of the surrounding polymer was varied to investigate the effect of CNT volume fraction on the mechanical properties. For all cases, the CNT was treated as a continuous fiber in the representative volume element. The RVE stress-strain curves confirm that the armchair nanotube acts as a better reinforcing agent when compared to the zigzag nanotube. For CNT volume fractions ranging from 1% to 10%, we see a 3- to 23-fold increase in the Young's Modulus over that of the pure polymer. This demonstrates the reinforcement capabilities of the carbon nanotubes. However, both zigzag and armchair RVEs show a clear deviation from the traditional continuum rule of mixtures. This proves that this continuum law cannot be used to predict the effective properties of nano-reinforced polymers. In the case of torsional loading we again see the same desirable increase in the shear modulus for volume fractions ranging from 1% to 10%. At 1% we see a 16% decrease in the shear modulus while at 10% there is up to an approximate 8-fold increase.

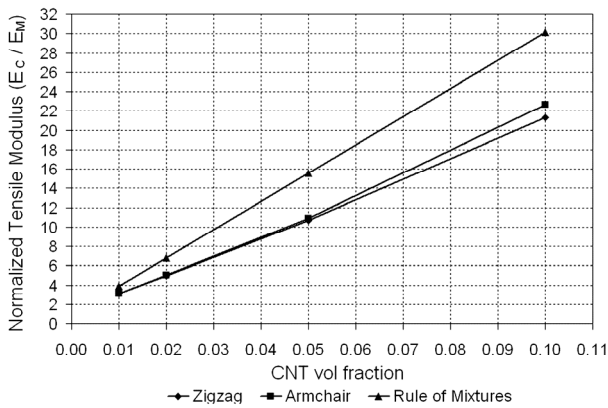


Figure 5: Normalized composite tensile modulus for different CNT volume fractions

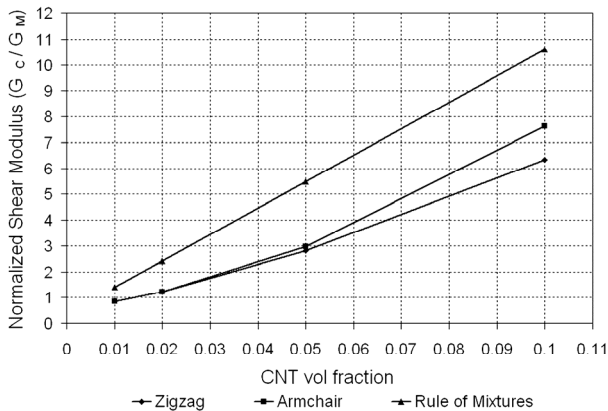


Figure 6: Normalized composite shear modulus for different CNT volume fractions

The measured values of mechanical properties of CNT-based composites reported by various researchers are lower than those predicted by theoretical models. The published experimental results [6-8] have all shown lower improvements in composite stiffness from the addition of

carbon nanotubes. This discrepancy can be attributed to the assumption of a defect-free system in the present analysis as well as the use of perfectly aligned CNT fibers. In comparison, the results of the experimental work would have been hindered by the random orientation of CNTs in the polymer matrix, the inability to ensure defect-free nanotubes, as well as the possible agglomeration of CNTs. In addition, the use of multi-walled carbon nanotubes (MWCNTs) have been shown to perform less efficiently as reinforcing agents when compared with single-walled CNTs.

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