Review Article

Challenges of the Modeling Methods for Investigating the Interaction between the CNT and the Surrounding Polymer

Roham Rafiee,[1] Timon Rabczuk,[2] Reza Pourazizi,[1] Junhua Zhao,[2] and Yancheng Zhang[2]

[1] *Composites Research Laboratory, Faculty of New Sciences and Technologies, University of Tehran, Tehran 1439955941, Iran*
[2] *Institute of Structural Mechanics, Bauhaus University Weimar, Marienstraße 15, 99423 Weimar, Germany*

Correspondence should be addressed to Roham Rafiee; roham.rafiee@ut.ac.ir

The interaction between the carbon nanotubes (CNT) and the polymer is a key factor for determining the mechanical, thermal, and electrical properties of the CNT/polymer nanocomposite. However, it is difficult to measure experimentally the interfacial bonding properties between the CNT and the surrounding polymer. Therefore, computational modeling is used to predict the interaction properties. Different scale models, from atomistic to continuum, are critically reviewed addressing the advantages, the disadvantages, and the future challenges. Various methods of improvement for measuring the interaction properties are described. Finally, it is concluded that the semicontinuum modeling may be the best candidate for modeling the interaction between the CNT and the polymer.

1. Introduction

Predicting the mechanical properties and modeling the mechanical behavior of the CNT Reinforced Polymer (CNTRPs) have attracted the great attention of many researchers [1–5], especially considering their rapid development in various industries such as automotive industry, aerospace, packaging, and wind turbines. Therefore, over the past two decades, extensive studies have been executed to predict the mechanical properties of CNTRPs.

Different factors affect the performance of CNTRPs. The main governing issue which characterizes the efficiency of CNT reinforcement at nano-/microscale can be attributed to the load transfer mechanism from the matrix to the CNTs. As a result, prior to understanding the mechanical behavior of CNTRP at macrolevel, the corresponding physical performance has to be addressed. For this purpose, a proper simulation technique, which captures the required details sufficiently and reasonably, needs to be employed in accordance with the investigated scale.

Interfacial bonding in the interphase region between the embedded CNT and its surrounding polymer is a crucial issue for the load transferring and reinforcement phenomena. The atomic structure of carbon nanotubes consisting of sp^2 hybridized carbons hinders the formation of strong covalent bonds with the surrounding polymer matrix. Although functionalization can improve the load transfer of the interphase by providing covalent cross-links between the carbon atoms of CNTs and the molecules of polymer, this procedure has a main drawback in providing defects in the structure of carbon nanotubes due to formation of sp^3 hybridized sites. It can significantly reduce the beneficial properties of carbon nanotubes. Therefore, CNTs naturally interact with the polymer chains of the matrix just through weakly nonbonded van der Waals (vdW) and electrostatic forces. Mechanical interlocking, which is useful to improve the adhesion between the fiber and the matrix in fibrous composites, is not pertinent to CNTRPs due to the smooth surface of the CNTs.

Up to now, various methods have been employed to investigate the interaction behavior between the CNT and the surrounding polymer, including experimental studies, atomistic modeling, and continuum modeling. Through systematically studying the shortcomings and advantages of all the available methods from the literature, the objective of this review is to find the best solution for evaluating the interaction behavior between the CNT and the polymer matrix. On one side, the accuracy must be guaranteed; on the other side, the method should be simple and have minimal computational costs.

This paper aims to review recently developed modeling techniques to study the interaction between CNT and surrounding polymer. The organization of the paper is as follows: Section 2 is a brief explanation of challenges imposed to the experimental studies at the scale of Nano. Section 3 discusses performed theoretical studies for investigating interaction between CNT and polymer. This section includes two main groups of available modeling techniques as atomistic modeling Section 3.1 and continuum modeling Section 3.2. Molecular dynamics, coarse grain simulation, and density functional theory are reviewed in Sections 3.1.1, 3.1.2, and 3.1.3, respectively. Then, associated obstacles and shortcomings of atomistic modeling are presented in Section 3.1.4 which are the main reasons encouraging researchers to employ continuum modeling approaches. Categorized under continuum modeling group, Sections 3.2.1 and 3.2.2 present analytical and numerical modeling techniques. Finally, Section 4 concludes the review by highlighting pros and cons of available methods.

2. Experimental Studies

The performed experimental studies for characterizing the interaction between CNT and surrounding polymer can be divided into three main categories.

Some researchers have performed experiments on CNT-polymer bulk composites at the macroscale and observed the enhancements in mechanical properties (like elastic modulus and tensile strength) and tried to correlate the experimental results and phenomena with continuum theories like micromechanics of composites or Kelly Tyson shear lag model [1–5, 32, 33].

Other researchers have used the spectroscopy techniques. Spectroscopy is a powerful technique for characterizing the properties of the CNT. This technique includes Raman spectroscopy, Fourier Transform infrared spectroscopy (FTIR), and X-ray scattering. The main principle of this method is that by straining the CNT/polymer, the C–C bonds will vibrate, and this will affect the peaks in the Raman spectrum. Therefore, Raman spectroscopy can determine the characteristics of CNTs such as the diameters and the level of dispersion in the matrix [34–38].

In situ TEM (Transmission Electron Microscopy) straining has also been used to understand the mechanics, fracture, and failure processes of the interface. In these techniques, the CNT-polymer composite (an electron-transparent thin specimen) is strained inside a TEM and simultaneously imaged to get real-time and spatially resolved (1 nm) information [39, 40].

Rahmat and Hubert [41] and also Desai and Haque [42] have conducted a comprehensive review on the experimental methods.

Generally, an experimental study at the scale of nano is a challenging task due to the following reasons:

(i) the lack of proper direct measuring techniques at the nanometer scale;

(ii) tremendous limitations on the specimen size;

(iii) an uncertainty in the data obtained from indirect measurements;

(iv) inadequate preparation techniques of test specimens and the lack of control over the alignment and distribution of nanotubes.

Therefore researchers have a tendency to employ theoretical methods for predicting properties of CNT-reinforced composites. Moreover, it is not possible to measure the interfacial bonding properties between CNT and surrounding polymer through direct measurement, and this would be another source of error.

3. Theoretical Studies

In this category of studies, the interaction between the CNT and the surrounding polymer which plays a key factor in transferring the load from the matrix to the CNT is examined using theoretical and computer models. Up to now, the employed theoretical studies to simulate the interaction and measure the mechanical properties of the interaction are mainly divided into two major groups: atomistic modeling and continuum modeling.

3.1. Atomistic Modeling. Atomistic modeling is accomplished using molecular dynamic (MD) simulation, density functional theory (DFT), or coarse grain (CG) simulation. These techniques are widely used to resolve the relevant fracture problems on different scales.

3.1.1. Molecular Dynamics. The MD method solves Newton's equations of motion for a molecular system [43], which provides the methodology for detailed microscopic modeling on the molecular scale [44]. For the nanocomposite interaction studies, MD has shown strong potential, due to its accuracy, flexibility, and various force fields [10, 13, 45, 46]. Xu and Buehler [10] adopted the AIREBO potential to simulate the mechanical behavior of the CNT-based nanocomposite. In the work of Zhang et al. [13], the UA (united atom) potential is adopted to address the similar problem of the nanocomposites. Moreover, the coarse-grained potential is also employed to study the interaction among particle-particle and particle-polymer [45, 46].

Additionally, the comparable sizes of nanotubes and polymer chains make MD a great candidate to simulate nanocomposites without sacrificing the accuracy of the results, especially with the rapid development of high-performance supercomputers.

The MD simulations can also investigate the effects of various parameters and types of interaction on mechanical properties like elastic moduli, interfacial shear strength, and bonding energy.

The interface properties of CNT/polymer were widely investigated based on MD simulation from the available literatures [6, 8–10, 12, 13]. Referring to the nonbonded CNT/polymer interaction, Chen et al. [9] performed MD simulation of single polymer molecular with CNT, and they found that armchair single-walled carbon nanotubes

(SWNTs) present the strongest adhesion. Liao and Li [6] and Rahmat and Hubert [12] studied the noncovalent interaction between the CNTs and the matrix; the shear strength and the binding energy of the composite interfaces were given in their research. Wong et al. [8] found that the locally nonuniformed distribution of CNT-induced mechanical interlocking leads to high interfacial shear stress. The MD simulation also showed that the mismatch of the coefficients of thermal expansions between CNT and polymer matrix also promotes the stress transfer ability. Xu and Buehler [10] have studied the thermal resistance of the two interacting CNTs, with and without polymer, which shows that the thermal resistance of the CNT junctions can be significantly improved through altering the number of polymer molecules. Recently, Zhang et al. [13] have studied the effects of the dispersion of polymer-wrapped two neighbouring SWNTs on nanoengineering load transfer. They found that dispersion angle of the polymer wrapped SWNTs dominates the load transfer. Besides, the self-repairing function of the system is found due to the nonbond interaction between the polymer and the SWNTs.

Frankland et al. [7] modeled a single armchair CNT by MD and found that the shear strength increases 10 times just by forming less than 1% cross-links between the CNT and the polymer. Through the MD simulation, Chowdhury and Okabe [47] also investigated the influence of the chemical cross-links at the interface and found that forming a few cross-links between the CNT and the polymer, the shear strength increases from 310 MPa to 1630 MPa. Liu et al. [11] obtained the shear strength by pullout test of SWNT from covalent bonded polymer with an MD simulation. They found that the increased interface shear strength can either enhance or reduce the damping stability of the composite. Other researchers like Kuang, Tsai, and Odegard adopted MD methods to study the properties of the nanocomposites and interface between the CNT and the polymer [48–50].

However, the large number of particles and the short time steps involved in MD simulations call for powerful computational facilities, which are typically provided through parallel computing. The simulation time may be shortened by employing typical modeling strategies, such as adopting periodic boundary conditions [51] and reducing the cutoff distance assumption [52]. A more detailed discussion can be found in the Table 1.

3.1.2. Coarse Grain Simulation. A coarse grain (CG) approach is used to develop the tools for investigating the material properties. It is also used to study the underlying mechanical behavior typically required for material design that systematically integrates characteristic chemical responses. The CG models provide efficient means to simulate and investigate systems in which the desired behavior, property, or response is inherently at the mesoscale—those that are both inaccessible to full atomistic representations and inapplicable to continuum theory. The CG techniques are developed to map atomistic systems onto systems with coarser resolution. Therefore, a developed CG model can only reflect the behavior included in their governing potentials and associated parameters, and consequently, the source

of such parameters typically determines the accuracy and utility of the CG model [53, 54]. It is emphasized that not all systems will benefit from a coarse-grain representation, and prudent consideration must be given regarding the system characterization and the intent of the simulations. Typical motivations for a CG approach include the following:

(1) inaccessible time scale and length scale for phenomenon or behavior via full atomistic representation;

(2) focus on bulk properties and/or mechanical behavior rather than on molecular structure and/or chemical interactions;

(3) desire for a direct simplified analysis of simulation results and system behavior.

In the past decade, various CG molecular dynamics methods were extensively used to study the thermomechanical properties of polymers, proteins, lipids, and biomaterials [53–56].

Müller-Plathe's group reported many interesting properties of different polymers (e.g., thermal conductivity, chain stiffness) by the CG MD simulations [57–59], in which the CG potentials were developed and their parameters were provided based on the reverse-mapping procedure by validating from full-atom MD simulations. Kremer's group developed two kinds of CG potentials for polystyrene, and the thermodynamical and the chemical properties were studied by CG MD simulations [60, 61]. Theodoru and Fermeglia investigated the multiscale modeling for polymer systems using CG MD and full-atom MD methods as well as Monte Carlo (MC) method [62, 63]. Nielsen et al. [64] calculated surface tension in bulk PE by CG MD simulations, which considerably reduces the amount of numerical computing required in the MD simulations. Recently, Zhao et al. [65] have developed a more accurate CG potential to study the thermomechanical properties (such as bulk density, glass transition temperature, expansion coefficient, Young's moduli, and yield stress) of bulk polyethylene (PE). The size-dependent mechanical properties of compressive stress-strain curves for PE particles have also been obtained by the CG MD method [66].

As it can be seen, all aforementioned studies are performed on pure polymer. The main reason for this is that the first step in studying interaction between CNT and surrounding polymer using CG MD is constructing a reasonable model for the chain of polymer. Therefore, numerous studies have been conducted on pure polymer.

Buehler's group developed the various CG MD potentials to characterize the nanoindentation of single- and double-carbon nanotubes (CNTs) buckypaper [67]. Based on the CG model, the mechanical properties of CNT networks were obtained, and the microstructural evolution and failure mechanism were discussed [68]. Afterwards, the viscoelasticity of the CNTs networks was reported by the CG MD simulations [69].

However, all the previous CG models are used in polymers and CNTs, respectively, while the CNT reinforced polymer composites are scarcely studied by CG MD simulations since the Lennard-Jones (LJ) potentials between CG beads of polymers and CNTs are not obtained yet. Nevertheless,

TABLE 1: Conducted molecular dynamics modeling of interaction between the CNT and the polymer.

Researcher(s)	Year	Reinforcement	Matrix	Simulation size	Simulation setup	Conclusion	Shortcomings/ advantages
Liao and Li [6]	2001	SWNT and DWNT	One chain of 2 to 80 mer polystyrene	20 Å long CNT	Pullout without cross-link between CNTs and matrix	Full-atom and nonbond interaction. Pullout shear strength of 160 MPa	More accurate while limited to small size
Frankland et al. [7]	2002	53 Å long (10, 10) SWNT	178 chains of 42 mer polyethylene	53 Å long SWNT	Pullout for both crystalline and amorphous polymer	An order of magnitude increase in shear strength with less than 1% cross-link between SWNT polymer	Close to the actual situation, limited to small scale
Wong et al. [8]	2003	SWNT	Epoxy, polystyrene	31 Å long CNT	Ununiformed SWNT with two different diameters.	Local nonuniformity of CNT and mismatch of the coefficients of thermal expansions lead to high interfacial shear stress	New aspect for analyzing the enhanced effect
Chen et al. [9]	2008	49.19 Å long (10, 10) SWNT	One chain of 10 mer polyphenylacetylene	49.19 Å CNT with Single polymer chain	SWNTs with different chirality	Strongest adhesion for armchair-type SWNT	Clear analysis but the size is too small
Xu and Buehler [10]	2009	(10, 10) SWNT	Polyethylene, various chain lengths	25 to 75 nm long CNT	Overlapped SWNTs with or without polymers	The thermal resistance of CNT junctions can be significantly improved through modifying the molecular structure at the interface	New idea with full-atom analysis, heavy calculations
Liu et al. [11]	2011	(10, 10) SWNT	EPON 862 and EPI-CURE curing agent	4.6 nm × 4.6 nm × 6.3 nm	SWNT pullout test is preformed by MD method, then the shear strength is applied to a micromechanical damping model	The increased interface shear strength can either enhance or reduce the damping stability of the composite	Useful method to determine the parameters for multiscale hierarchical model
Rahmat and Hubert [12]	2012	52.69 Å (10, 0) SWNT	9 Chains of 32 mer PMMA	Varied	Introduction and pullout test with optimized simulation phases	Interfacial binding energy of 0.39 kcal/mol Å^2 for no covalent interaction	Common MD simulation.
Zhang et al. [13]	2013	59.03 Å long armchair (5, 5)	Chain length of 20, 40, 60	59.03 Å long SWNT	Varying the dispersion angle of two neighbouring SWNTs	Dispersion angle of polymer wrapped SWNTs dominates the load transfer	United atom (UA) method, can apply to large scale

this issue will likely be addressed soon, since studies in this direction show high potential and important applications.

Because the CG models normally lose more detailed information among the beads (such as dihedral and improper information), accurate quantitative nonlinear mechanical properties of materials cannot be accurately given in the CG MD simulations.

3.1.3. *Density Functional Theory.* Density functional theory (DFT) studies the electronic structure of atomic scale systems based on quantum mechanics. The DFT models commonly use approximations, such as local density approximation (LDA), in which only the value of the electronic density at each point in the space is considered compared to the MD simulation.

Ab initio simulations use DFT and are able to converge to the accurate solution. However, these simulations are computationally expensive and grow in size with the power 3–7 of the number of basic functions. Therefore, the ab initio simulations are fairly small in size and use various techniques to reduce the computational costs. For example, during some stages of the simulation, only some part of the system may be optimized, or atomic relaxation may not be allowed and molecules may be considered to be rigid.

Ab initio models have studied various types of nanotube-polymer interaction including van der Waals and chemical functionalization. The results of these models are typically presented in the form of local density of state for the nanotube and the nanocomposite, band structures, charge density contours, and binding energy as a function of distance [70, 71]. In the work of Kim et al. [70], the encapsulation energy of a single (C_2H_2) molecule into the nanotube and the formation energy of (C_2H_2) @ CNT are calculated. In the work of Mylvaganam and Zhang [71], the possible ways of functionalizing CNTs are investigated with the aid of the density functional theory. Using the methoxy radical and the secondary butyl anion as initiators and their reactions with ethylene and epoxide, this leads to polyethylene- and polyepoxide-grafted nanotubes.

Most of DFT models are based on static or zero Kelvin structures and are still limited to small systems. Hence, when using DFT models, the strength of these models (accurate prediction of atomic structure) along with the inevitably expensive computations should be considered.

3.1.4. The Challenges of Atomistic Modeling. As it has been stated, atomic modeling has the accuracy and high flexibility to observe effects of various parameters on the mechanical properties of the nanocomposites and the interphase between the CNT and the polymer. But a lot of limiting factors are affecting these methods. For example, most of the published papers that have used these methods are using SWCNTs with a length less than 10 nm. In addition, the number of polymer chains considered is less than 100.

This is because atomistic modeling methods are not able to handle a large number of atoms due to increasing computational costs. Also the formulas used in these methods often have high complexity. Due to these limitations, continuum models have been used to overcome the aforementioned difficulties.

3.2. Continuum Modeling. Continuum modeling of CNT and surrounding polymer interactions is accomplished either analytically or numerically.

3.2.1. Analytical Modeling. In studies by analytical methods to model interphase between the carbon nanotube and the polymer, most of the researchers have tried to use the existing microscale rules in the field composites. These rules known as micromechanics rules cannot be directly applied to the nanoscale due to assumptions which are no longer valid. These involve the uniform distribution of fibers in polymer and perfect bonding between CNT and polymer, as well as considering reinforcement phase as a continuum medium

which is applicable to fibers. In other words, direct use of micromechanics equations for CNTRP will simply neglect the lattice structure of CNT and consider CNT as a solid fiber. Moreover, micromechanics equations assume perfect bonding between the reinforcing agents and the surrounding polymer. This is not pertinent to the interphase between the CNT and the surrounding polymer, which interact through nonbonded van der Waals (vdW) forces.

Some researchers have proposed that a material region between CNT and surrounding polymer should be considered, but the way to treat the properties of this specific material region remains to be determined. The associated properties are selected between matrix and CNT Young's modulus without any experimental basis. Actually, at the scale of nano, there is no material region for interphase between CNT and polymer, but instead, the region is a molecular interaction space. Some others suggested some corrective factors in order to reflect the imperfection bonding between CNT and polymer, but these factors are also obtained on the basis of curve-fitting data.

Actually, CNTs interact with the surrounding polymer through vdW forces. This will cause the CNT to slide in the polymer matrix when subjected to axial loading. Therefore, the assumption of perfect bonding between CNT and polymer is not valid. Thus, some researchers try to incorporate vdW interactions between CNT and polymer in their modeling methods. Cohesive zone models have been widely used in the continuum study of interface debonding and sliding in composites. A cohesive zone model assumes a relation between the normal (and shear) traction(s) and the opening (and sliding) displacement(s). When implemented in the finite element method, the cohesive zone model is capable of simulating interface debonding and sliding. The existing cohesive models are all phenomenological, because it is difficult to obtain directly the cohesive laws for interfaces. Jiang et al. [14] have developed the cohesive zone model for the interface between the CNT and the polymer. They have calculated the total energy of all the atoms by integrating over the volume and by differentiation from the movement of the plates in the vertical and in the tangential direction. Finally, they report the relation between the normal (and shear) traction(s) and the opening (and sliding) displacement(s) across the interface in terms of the area density of CNT and the volume density of polymer, as well as the parameters in the vdW force.

Assuming an interface which contains vdW interactions, Tan et al. [15] have attempted to calculate the relationship between the stress and the strain in nanocomposites. In this regard, the rules set by Jiang have helped to describe the relationship between the stress and the strain at the interface.

Seidel and Lagoudas [16] tried to evaluate the effect of an interphase on the mechanical properties of nanocomposites. They have considered interphase as a physical environment and assumed elastic modulus of this area 0.1 to 10 times the elastic modulus of the matrix. Then, the effects of interphase properties on nanocomposites were examined using a concentric cylinder model.

The Shear-Lag model was also employed by some other researchers to study the interaction between CNT and

Table 2: Conducted analytical modeling of interaction between CNT and polymer.

Researcher(s)	Year	Interface or interphase	Type of interaction	Thickness	Interphase modulus	Method of modeling
Jiang et al. [14]	2006	Interface	vdW	N/A	N/A	Cohesive energy
Tan et al. [15]	2007	Interface	vdW	N/A	Imperfection coefficient	Elasticity
Seidel and Lagoudas [16]	2006	Interphase	Perfect	$0.5 \times R_{NT}$ to $4 \times R_{NT}$	$0.1 \times E_m$ to $10 \times E_m$	Composite cylinders micromechanics
Tsai and Lu [17]	2009	Interphase	Perfect	0.01 nm	G_{int} = 0.13, 0.286, 4.2, 370 GPa	Elasticity (shear lag)
Nairn [18]	2011	Interface or interphase	Imperfect	N/A	Imperfection coefficient	Shear lag (elasticity)
Shokrieh and Mahdavi [19]	2011	Interphase	vdW	0.17 nm	Function of l_{NT} and R_{NT}	Equivalent fiber (elasticity)
Barai and Weng [20]	2011	Interface	Perfect	N/A	Imperfection coefficient	Elasticity

polymer [17, 18]. This model is usually used for long fiber composites at microscale, and it is not suitable for CNT reinforced composites wherein the effective scale is nano. This model has been basically developed for continuum reinforcing agent, and it could not be applied to the lattice structure of CNT. Tsai and Lu [17] took into account the interphase as a physical environment. They used different values for the shear modulus of interphase and investigated the effect of interphase on load transfer efficiency in the CNTs reinforced nanocomposites using the conventional shear lag model. Nairn [18] considered the effect of the interphase by a coefficient varying between zero and infinity in the formula for calculating the modulus of the nanocomposite.

Shokrieh and Mahdavi [19] considered a virtual material region for the interphase. They have obtained the properties of an equivalent fiber using the elasticity approach when the interactions are assumed to be vdW. The obtained results were in a very good agreement with the developed multiscale FE modeling by Shokrieh and Rafiee [29].

Barai and Weng [20] studied the mechanical properties of carbon nanotube with elasticity equations. They fit an imperfect factor to their equations and investigated the effect of the interphase by changing this ratio. It was reported that when the imperfection at the interface increases, the effective Young's modulus of the composite decreases and those CNTs with very weak interfaces will behave like voids. It should be pointed out that since Barai and Weng [20] have considered perfect bonding between CNT and polymer, they are addressing higher stress transferability from matrix to CNT in contrast to what has been reported by Tan et al. [15] through weak vdW interactions.

An overview of conducted analytical modeling to study the interaction between the CNT and the surrounding polymer is summarized in Table 2.

As it can be understood from the literature survey, different values have been considered for the modulus and also for the thickness of interphase. In some investigations, the influence of the interphase region has just been simulated using some correction factor to reflect the imperfection.

3.2.2. Numerical Modeling. Several researchers have used numerical modeling employing the finite element analysis to study the interaction between the CNT and the surrounding polymer. Some investigators considered an intermediate region between the CNT and the polymer as a separate phase and used various elements like link, truss, rod, beam, and spring with different properties describing the molecular interaction between the CNT atoms and the surrounding polymer chains. Some others have ignored this region in the modeling and simply assumed a perfect bonding between nanotube and the polymer [21, 22]. However, since it is well known that perfect bonding between the nanotubes and the resin is not a valid assumption, these studies will not be reviewed in this report.

Haque and Ramasetty [21] obtained shear and axial stresses at the interface without considering interphase using the equilibrium and the elastic equations.

Wan and his coworkers [27] calculated the properties of the RVE of CNTRP considering interphase with the thickness of 1.357 nm. The modulus of interphase has been varied between 0.3 and 10 times the elastic modulus of the matrix. They considered the interphase as an isotropic material with constant properties.

Li and Chou [23] consider the vdW interactions between the nanotube and the inner surface of the surrounding polymeric matrix and used nonlinear truss elements to simulate vdW interactions. They considered the thickness of this region as 0.17 nm and achieved the properties of the elements using Lennard-Jones potential.

Pourakbar and his coworkers [24] have studied the effect of functionalized nanotube on the properties of a RVE. They modeled covalent bonds between the nanotubes and the resin with beam elements and used properties that were derived from molecular mechanics approach. They found out that by increasing the population of covalent bonds at the interphase, the stress transferability from matrix to CNT is increased and it will converge to the results achieved from the rule of mixture, even though the rule of mixture is not valid at nanoscale.

TABLE 3: Finite element modeling of CNT and polymer interaction.

Researcher(s)	Year	Interface or interphase	Type of interaction	Thickness	E_{int} and G_{int}	Element
Haque and Ramasetty [21]	2005	Interface	Perfect	N/A	N/A	N/A
Wan et al. [27]	2005	Interphase	Perfect	1.357 nm	$10 \times E_m$ and $0.3 \times E_m$	N/A
Li and Chou [23]	2006	Interphase	vdW	0.17 nm	Derived from LJ potential	Truss rod
Pourakbar et al. [24]	2008	Interphase	Functionalized	1.522 nm	From MD	Beam
Giannopoulos et al. [25]	2009	Interphase	vdW	0.17 nm	Parametric	Joint element
Montazeri and Naghdabadi [26]	2009	Interphase	vdW	0.34 nm	Derived from LJ potential	Spring
Kulkarni et al. [22]	2010	Interface	Perfect	0	Different value	Interface element
Needleman et al. [28]	2010	Interphase and interface	Perfect	Variable	Linearly between E_m and E_n	N/A
Shokrieh and Rafiee [29]	2010	Interphase	vdW	0.17 nm	Derived from LJ potential	Nonlinear spring
Ayatollahi et al. [30]	2011	Interphase	Perfect	0.15 nm	1, 5, 10 and 15 GPa	Solid
Wernik and Meguid [31]	2011	Interphase	vdW	0.38 nm	Derived from LJ potential	Truss rod

Giannopoulos et al. [25] considered the modulus of interphase as a function of the matrix and CNT's modulus. In their work, joint elements were used to simulate the interphase between the CNT and the matrix in radial direction along the nanotube. The results reveal a high dependence of the longitudinal modulus of the nanocomposites on the stiffness of the interfacial region. The high stiffness values of the joint elements (perfect bonding between the CNT and matrix) lead to the similar results obtained by the rule of mixture. In contrast, when the nanotube is very softly bonded to the matrix, no substantial enhancement in mechanical properties is observed.

Montazeri and Naghdabadi [26] have used one-dimensional spring elements to model the interphase. They have achieved the associated properties of the spring elements from Lennard-Jones potential.

Kulkarni et al. [22] have studied the properties of the RVE by considering the interface and the force region between the nanotubes and the resin. They have used interface elements in the modeling and used varied strength and investigated the effect of that on the properties of RVE. They reported that the modulus of the nanocomposite increases with increasing interface strength. The rate of increase in the modulus of the nanocomposite becomes smaller, as the interface strength increases.

Needleman and his coworkers [28] calculated the properties of RVEs. They have simulated the interphase with a variable thickness and nonlinear properties between nanotubes and the resin. They considered a perfect bonding between the nanotubes and the resin and investigated the influence of interphase strength on the properties of investigated RVE.

Shokrieh and Rafiee [29] proposed a model for interphase where bonds between nanotubes and the resin would be updated when the applied strain evolves. Consequently, the model is called Adaptive vdW Interaction (AVI). They have used nonlinear spring elements capturing vdW interactions. In other words, when the applied strain is increased, the instantaneous status of each vdW bond is updated in accordance with the governing equation of the vdW interaction. They have observed that the rule of mixture will overestimate the results. This stems from this fact that the rule of mixture considers perfect bonding between CNT and polymer. The results demonstrate the importance of considering vdW based interphase.

Wernik and Meguid [31] offered the same model as Shokrieh and Rafiee's model for interphase. The only difference was that they used truss elements instead of spring elements for interphase. They reported the same trend reported by Shokrieh and Rafiee in comparison with the rule of mixture.

Ayatollahi et al. [30] obtained properties of RVE considering interphase with 3 times the thickness of the carbon nanotube and different elastic moduli as 0.2, 2, and 20 GPa. They investigated the effect of the interphase on the properties of the RVE with different values of elasticity modulus of the interphase. They found out that generally, by increasing the modulus of interphase, the load transfer between CNT and polymer will be improved and the modulus of nanocomposites will be increased.

An overview of the finite element modeling studies on the interphase region between the CNT and the polymer is presented in Table 3.

It can be seen from Table 3 that those who have assumed the interactions between CNT and surrounding polymer take place through force environment also used interface to simulate the interaction between CNT and polymer. They have observed that increasing the interface strength leads to convergence of the modulus of nanocomposite to that obtained by the rule of mixtures, since they are addressing perfect bonding between CNT and polymer.

On the other side, when the interaction between CNT and surrounding polymer is treated as a physical environment, an interphase between CNT and surrounding polymer is modeled. The modeling of interphase appears either in the form of intermediate material region between CNT and polymer or in the form of connection links between CNT and polymer capturing by spring, truss, or beam elements. The former is called continuum modeling of interphase, while the latter is called semicontinuum modeling of the interphase region.

4. Conclusion

The modeling of interface/interphase region between the CNT and the polymer is reviewed in this scientific review. The theoretical studies are divided into two main groups: atomistic modeling and continuum modeling.

Atomistic modeling can well capture the shear strength and bonding energy of the interface between the CNT and the surrounding polymer matrix in nanoscale. Moreover, the obtained properties can be upscaled to the macroscale model. The united atom (UA) and coarse grain (CG) methods are promising solutions to extend the simulation to microscale. However, the beads-incorporated simulation still requires a huge amount of calculation and is limited to small length scale compared to the continuum model. Moreover, obtaining the accurate nonlinear mechanical properties is one of the limitations of using the CG method. As a consequence, continuum modeling is used by different researchers to overcome mentioned difficulties. But the degree to which the continuum modeling can truly predict the actual behavior of CNT at nanoscale has to be carefully studied.

Continuum modeling can be done either analytically or numerically. The analytical modeling of the continuum model usually considers simply perfect bonding between the CNT and the surrounding polymer and tries to capture the influence of the imperfect bonding between the CNT and the polymer by introducing some correction factor in the micromechanics rules.

The numerical continuum modeling which takes place using FEM is divided into three main groups. The first group takes into account the force interaction between CNT and polymer through interface without considering any distinct material region. In this group, the researchers usually replace CNT with a continuum medium for sake of simplicity, and thus their results approach the values reported by rule of mixture. It is worth mentioning that the basic assumptions of the rule of mixture are not valid for the case of CNT. Micromechanics consider continuum medium for the reinforcing agent, which is not pertinent to the case of CNT, and also it assumes perfect bonding between CNT and surrounding polymer when instead CNT naturally interacts with the polymer through weak vdW interactions.

The second group considers an intermediate material region between the CNT and the polymer as a continuum medium and uses different values for the properties of this distinct region. Both the thickness and the mechanical properties of this region are under question in this category of study, as the selection has no experimental basis. Almost all studies selected Young's modulus of the interphase region as a varying parameter between Young's modulus of resin and CNT.

The first two groups can be also found in the field of analytical modeling as well.

The third group uses different elements consisting of joint, bar, truss, spring, and beam to construct the interaction between the CNT and the surrounding polymer. The properties of these elements are obtained from molecular space, and therefore equivalent structural members are employed. Due to the specific fact that a continuum region has not been considered for the interphase region and actually continuum elements are used for the purpose of molecular interaction, this group of study is also called as semicontinuum modeling. Instead of considering a continuum material region, just vdW interactions or covalent bonds between CNT and surrounding polymer are simulated using continuum elements. The former is the natural interaction between CNT and polymer in the absence of chemical functionalization, while the latter captures functionalized CNT. Semicontinuum modeling has received more interest among researchers in the recent years.
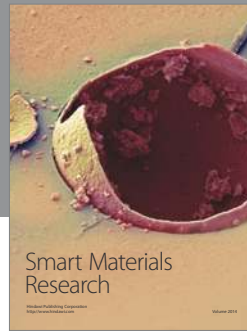
It can be concluded that despite the fact that atomistic modeling can provide an accurate result on local properties and interactions between CNT and polymer, it is computationally intensive, and it is limited to very short time and small length scales. However, continuum modeling can be considered as a reasonable compromise in modeling, while it is focusing on global behavior rather than local one. Among developed continuum modeling, the more preferred approach is semicontinuum modeling, wherein CNT is treated as a lattice structure, and the interactions between CNT and surrounding polymer are replaced by continuum elements.

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