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Molecular dynamics and atomistic based continuum studies of the interfacial behavior of nanoreinforced epoxy

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ABSTRACT

In this study, we investigate the interfacial mechanical characteristics of carbon nanotube (CNT) reinforced epoxy composite using molecular dynamics (MD) simulations. The second-generation polymer consistent force field (PCFF) is used in the MD simulations. In particular, we compare MD results with those obtained by atomistic-based continuum (ABC) multiscale modeling technique, which makes use of the appropriate constitutive relations derived solely from interatomic potentials. The results of our comparative investigation suggest that (i) the ABC multiscale model and MD simulation provides almost identical predictions for the interfacial properties of the nanocomposite for smaller diameter of CNTs, (ii) the ABC model slightly over predict the interfacial properties of the nanocomposite for larger diameter of CNTs, and (iii) the MD simulations represents the real nanocomposite structure with the minimum assumptions compared to that of the ABC multiscale model but with much greater computer requirements and limited length scale.

1. Introduction

In view of their remarkable mechanical, thermal and electrical properties (Ebbesen et al., 1996; Teacy et al., 1996; Yakobson et al., 1996; Berber et al., 2000; Che et al., 2000), carbon nanotubes (CNTs; Iijima, 1991) have been the subject of intense research. The exceptional properties of CNTs have shown great promise for a wide variety of applications, such as nanotransistors, semiconductors, hydrogen storage devices, structural materials, molecular sensors, field-emission based displays, fuel cells, and as the ideal reinforcements for advanced nanocomposites (Endo et al., 2004; Bekyarova et al., 2007; Schmidt et al., 2007; Vaysse et al., 2009; Bao et al., 2012; Kundalwal and Ray, 2012). It is found that a few weight percentages of CNTs can significantly improve the interfacial and mechanical properties of CNT-based composites. The elastic properties of CNT-based composites are governed by the characteristics of the reinforcing CNT–polymer matrix interface. The great aspect ratio of CNTs lend themselves to greatly improved transferability of load at the interface, when compared with conventional microfibers. However, the degree of interfacial adhesion between the CNTs and polymeric based matrices also becomes a key parameter affecting the mechanical properties of the resulting nanocomposite. CNT pull-out tests have been recognized as the standard method for evaluating the interfacial mechanical characteristics of the nanocomposites. For example, interfacial shear strength (ISS) as high as 500 MPa has been observed by Wagner et al. (1998) in their fragmentation tests in urethane–CNT composites. Cooper et al. (2002) demonstrated that the ISS between a multi-walled CNT and epoxy matrix is in the range of 35–376 MPa using a scanning probe microscope setup to pull-out a CNT from the epoxy matrix. Barber et al. (2003) utilized an atomic force microscope to directly

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pull-out a multi-walled CNT from a polyethylene–butene matrix and observed an average interfacial stress of 47 MPa.

A number of analytical and numerical techniques at different time and length scales have also been proposed by researchers to study the interfacial mechanical characteristics of CNT-reinforced composites. At the coarser end of the length scale, continuum mechanics concepts have been used in characterizing the CNT behavior. For instance, He et al. (2012) developed an analytical pull-out model to investigate the mechanical properties of CNT-reinforced composites. Chen et al. (2009a,b) proposed an analytical curved-fiber pull-out model for the nanocomposites, and found that fibers with more curvature and longer embedded length need higher debonding initiation force. They also validated their analytical results with those of finite element pull-out results. Pan et al. (2013) investigated the interfacial effects on the viscoelastic characteristics of CNT-reinforced polymer composite. In these continuum-based approaches, a CNT is modeled as a continuous shell with a fixed wall thickness and material properties. However, the only way of distinguishing between CNTs of different chirality (that is, zigzag, armchair, chiral) is through the radius of the shell. The disadvantages of this approach are that the CNT is drastically oversimplified, it cannot be used to study the effect of defects, and the atomic structure of the CNT has been ignored.

The ABC multiscale modeling technique (Yakobson et al., 1996; Pantano et al., 2004; Meguid and coworkers, 2010, 2012, 2014) has been used to predict the mechanical behavior of CNTs, the elastic as well as the interfacial mechanical properties of CNT-reinforced polymer composites. It has the unique advantage of describing the atomic-property relations of the structure in a continuum framework. In this case, the continuum constitutive models are derived purely from atomistic principles. The deformation measures are introduced in the model to capture the underlying atomistic structure of the different phases under consideration. As a result, the significance of these measures is fundamentally different from those in the classical continuum theory. For example, in the case of CNT systems, it is important to consider the atomic bonding and interaction between the carbon atoms in the CNT lattice. This is typically carried out at the atomistic scale by using appropriate interatomic potentials. This leads to an atomistic constitutive law between the force and the displacement. The strength of ABC techniques lies in their ability to avoid the large number of degrees of freedom typically encountered in coupled atomistic discrete modeling techniques. In the literature, except the study by Wernik et al. (2012) and Wernik and Meguid (2014), there is no work reported on the determination of interfacial properties of CNT-based composite by using the ABC technique. In their study, the effects of CNT embedded length, number of van der Waals (vdW) interactions, thickness of the interface, CNT diameter and Lennard–Jones (LJ) cut-off distance on the ISS are investigated and discussed.

MD simulation is a powerful modeling technique, which may reduce the need for costly and extensive experiments. In fact, it may provide accurate physical insight into material systems where realistic and controlled experiments are not feasible. MD simulations by Frankland et al. (2002) have shown that the ISS of a CNT–polyethylene system is on the order of 2 MPa, when only vdW interactions were considered. The MD model of Xu et al. (2002) predicts an ISS of approximately 138 MPa when considering non-bonded interactions between a CNT and the epoxy matrix. Using MD simulations, Zheng et al. (2009) reported the ISS of 33 MPa and 575 MPa for the cases involving pristine non-bonded CNTs and phenyl functionalized CNTs in a polyethylene matrix, respectively. Furthermore, classical MD and molecular mechanic simulations have been shown to play an important role in determining the ISS of the nanocomposite as well as the constitutive relations of CNTs under different loading conditions (Yu et al., 2000; Liao and Li, 2001; Demczyk et al., 2002; Gou et al., 2005; Cao and Chen, 2006, 2007).

Evidently, a number of experimental, analytical and numerical works has been reported by researchers to investigate the complexities of the CNT–polymer interface. However, correlation between these results is often difficult due to significant differences in the materials, processing techniques, procedures, adopted simulation techniques and the way the pull-out problem is formulated in the numerical investigations. Several fundamental differences between numerical simulations are worthy of investigation. To our knowledge, among continuum-molecular pull-out models, a newly developed ABC technique is the first which has successfully described the atomic-property relations of the nanocomposite in a continuum framework. In comparison to other, more established MD methods, this recent technique is distinguished by its simplicity and versatility. Therefore, we compare the present MD results with those obtained by the ABC technique. Specifically, the effect of different types of single-walled armchair CNTs on the interfacial mechanical properties of the nanocomposite is considered to present the comparative results.

2. Descriptions of ABC technique and MD simulations

2.1. Atomistic-based continuum technique

In this section, we describe the basic approach adopted in simulating CNT pull-out tests by using the ABC technique to investigate the interfacial properties of CNT-reinforced polymer composites. Only vdW interactions are considered between the atoms in the CNT and the polymer assuming a non-bonded system. The vdW interactions are simulated using the LJ potential, while the CNT behavior is described using modified Morse potential. The problem is formulated by using a representative volume element (RVE), which consists of the reinforcing CNT, the surrounding polymer matrix, and the CNT/polymer interface as depicted in Fig. 1(a). Fig. 1(b) shows a schematic of the pull-out process, where 'x' is the pullout distance and 'L' is the embedded length of a CNT. The idea behind the ABC technique is to incorporate atomistic interatomic potentials into a continuum framework. In this way, the interatomic potentials are introduced in the model to capture the underlying atomistic behavior of the different