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Thermo-mechanical properties of a piezoelectric polyimide carbon nanotube composite: Assessment of composite theories

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ABSTRACT

In this work, we have characterized the thermomechanical properties of carbon nanotube based piezoelectric polymer nanocomposite using a hybrid force field for all atomistic molecular dynamic simulations. In addition, applicability of some of the well-known micromechanics composite theory in estimating carbon nanotube based polymer nanocomposite properties were assessed. We found that the primary reason for the strengthening effect of a nanocomposite with incorporation of a nanotube is the carbon–carbon bond and angle strength. The orientation of the nanotube in the polymer matrix is key to its reinforcement effect on a nanocomposite. We also observed that a perfect axial orientation does result in improving the axial modulus, but in the radial direction any strengthening for such a unidirectional composite does not seem possible without any bonding at the interface between the filler and the matrix material. The self-consistent field theory was found to be the closest with the atomistic simulation results for predicting mechanical properties of a polymer nanocomposite. The Halpin–Tsai model also demonstrated reasonable capability in predicting the strengthening effect. Mori–Tanaka model, however, underestimated the strengthening effect of carbon nanotube on the polymer matrix. It was also found that the existing composite theories are better at estimating low weight percentage nanotube strengthening effect.

1. Introduction

Engineering polymer nanocomposite materials at the atomistic level, suited for different advanced applications has made them lucrative to both researchers and industry [1–5]. However, the lack of understanding of the physics at nanoscale, have limited our ability to optimally exploit the possibilities and understand the limitations of nano-reinforced materials. Models capable of capturing composite properties with reasonable accuracy can significantly help successful implementation of engineering applications using nanocomposites and its optimal design. As we illustrated below, in various studies, existing composite theories have been extended and applied to understand their effectiveness in establishing structure–property relationship for characterizing polymer nanocomposites.

Mechanical properties of carbon nanotube and its polymer nanocomposites have been investigated using finite element analysis [6–10], micromechanics model with emphasis on failure [10] and reinforcement mechanism [11], models based on continuum mechanics [8,12], cohesive zone model with incorporation of details related to the interface of the nanocomposite [9], shear lag model to understand effect of electro-thermo-mechanical loadings [13], finite difference model [14], neural network model to estimate transverse elastic modulus of unidirectional composite [15], progressive fracture model [16], Krenchel model [17,40], rule of mixture model [17] and Kelly–Tyson model [39]. Among the micromechanics models, Halpin–Tsai [17,18,35] and Mori Tanaka model [19,29] are two of the well known models. Other models [20] include implementing a combination of 3D voxel based model representation of material structures and Voigt–Reuss method of material property estimation. Quaresimin et al. [21] classified various approaches for assessment of nanocomposite mechanical properties into molecular models, nanostructured models and micromechanics models. However no model till date has emerged as a widely accepted approach in designing nanocomposite materials. Through their review Quaresimin et al. [21] assessed that molecular modeling method is the most effective way of reasonably predicting mechanical properties of nanocomposites. Rahmat et al. [22] also noted the effectiveness and accuracy of

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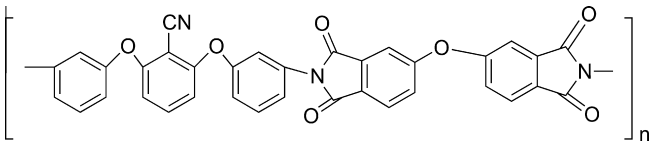

Fig. 1. $(\beta - CN)APB/ODPA$ monomer.

using molecular dynamics in capturing the interaction between the polymer matrix and its nanofiller. Hence, experimental studies and simulation of nanocomposite materials at an atomistic level are still the best way for estimating its properties through capturing the behavior at the interface and explain different structure property relationships observed for nanocomposites.

By comparing results to a fully atomistic model, this study attempts to assess the degree of effectiveness of three well received micromechanics models in characterizing a single walled carbon nanotube polymer nanocomposite of a piezoelectric polyimide matrix. Specifically, we have compared our results against rule of mixture, Mori Tanaka, Halpin Tsai and Self Consistent theory. In addition the study looks into thermal softening of nanocomposites, effect of implementing stress perpendicular to nanotube axial direction in a nanocomposite and change in glass transition behavior of nanocomposite owing to the presence of nanotube through atomistic simulation.

2. Material and methods

2.1. System

The nanocomposite system studied in this work consists of infinitely long single walled (10, 10) carbon nanotube with unidirectional alignment (z direction), inside an amorphous piezoelectric polymer matrix. The matrix is a piezoelectric polyimide substituted with nitrile dipole known as $\beta - CN)APB/ODPA$ polyimide (Fig. 1).

2.2. Model building

A modified approach of building amorphous polymer samples [23,24] was used to build the nanocomposite samples. An amorphous polymer sample with a very low density was built with Cerius$^{2.0}$ or Materials Studio with sufficient space in the unit cell to incorporate the infinitely long nanotube along the desired axial direction. The carbon nanotubes were then placed and bonded across the periodic boundaries of the unit cell [25]. For efficient use of resources, the nanotube was treated as a rigid rod, ignoring energies resulting from bond and angle vibration in the equilibration stage. Owing to the infinite length of the nanotube, the unit cells were only compressed in two directions. Subsequent to unit cell compression, the charges at the interface were updated through implementation of charge equilibration technique [26]. The built sample then went through temperature annealing within each compression cycle and was followed by isothermal–isobaric (NPT) molecular dynamics simulation to attain an equilibrated state. Fig. 2 illustrates such a sample nanocomposite as viewed in a molecular dynamics simulation environment.

A representative volume element, that is, a zoomed out version of Fig. 2, the polymer nanocomposite sample in its unit cell is shown in Fig. 3.

To overcome the structural biasness in sample distribution resulting from exploration of limited phase space by a single nanocomposite sample, in this work we have built eight different nanocomposite samples with varying weight percentage of nanotube ranging from 2.18% to 18.7%. For convenience, the eight samples constructed are defined below, which are referred throughout the article with the names as given below in Table 1. The corresponding pristine polyimide is prefixed by the word 'pristine'.

2.3. Force field

The interfacial interaction between the polymer and the nanotube was incorporated through van der Waals and coulombic interaction. A force field consisting of hybrid potentials for various energy components was defined to describe the components of the Hamiltonian for the heterogeneous nanocomposite system. A specially developed force field for nanotube, derived from first principle energy calculation of graphite [27], as implemented in another work by the authors [25], was used to describe the energetic of the carbon nanotube. The total energy of the carbon nanotube was defined as:

$$E = E_B + E_A + E_I + E_{VDW} + E_C$$

where E is the total energy of the system; E_B the energy due to bond stretching (two body); E_A the energy due to angle bending (three body); E_I the energy due to out of plane configuration or dihedral (two body); E_{VDW} the energy due to van der Waals interaction; E_C is the energy due to Coulomb interaction.

The energetic due to torsion was assumed to be insignificant and was neglected. The contribution of different components of the total energy were calculated as follows:

van der Waals interaction:

$$E_{vdw} = D_{vdw}(\rho^{-12} - \rho^{-6}) \quad \text{where} : \rho = r/r_v$$

where r_v is the separation energy at minimum energy between the two atoms.

Bond stretch energy:

$$E_{bond} = D_b(\mu - 1)^2 \quad \text{where } \mu = e^{-[r-r_b]}$$

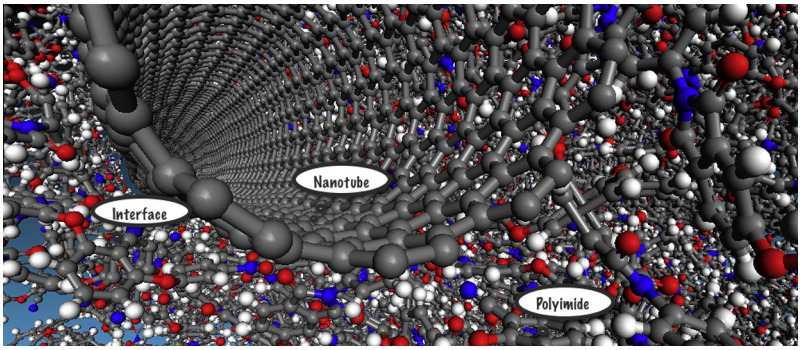

Fig. 2. A cartoon of polymer nanocomposite.