Computational Materials Science 92 (2014) 444–450

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Stiffness prediction of graphene nanoplatelet/epoxy nanocomposites by a combined molecular dynamics–micromechanics method

M.M. Shokrieh [a,*], M. Esmkhani [a], Z. Shokrieh [a], Z. Zhao [b]

[a] Composites Research Laboratory, Center of Excellence in Experimental Solid Mechanics and Dynamics, School of Mechanical Engineering, Iran University of Science and Technology, 16846-13114 Tehran, Iran
[b] School of Chemical Engineering, Shandong University of Technology, 255049 Zibo, Shandong, PR China

ARTICLE INFO

Article history:
Received 1 November 2013
Received in revised form 11 May 2014
Accepted 2 June 2014
Available online 9 July 2014

Keywords:
Micromechanics
Nanocomposites
Molecular dynamics
Graphene nano platelet
Mechanical properties

ABSTRACT

In this research, by a combined molecular dynamics–micromechanics method the stiffness of graphene nanoplatelet/epoxy nanocomposites is predicted. It is assumed that graphene sheets are randomly oriented in the polymer matrix. First, the stiffness of a multilayered graphene nanoplatelet was achieved using the molecular dynamics (*MD*). Then, results obtained by the molecular dynamics were used by the Mori–Tanaka (*MT*) and the Halpin-Tsai (*HT*) micromechanics models to predict nanocomposite stiffness. These combined models are called the *MD–MT* and *MD–HT* models, respectively. The results obtained show that the *MD–MT* model is more compatible with the result of experiments at low filler contents (<0.25 wt.%) in comparison with the *MD–HT* model. While, the *MD–HT* model is more reliable at high filler contents (>0.25 wt.%). Mechanical properties of graphene nanoplatelet/epoxy nanocomposites with several contents of graphene nanoplatelet, *i.e.* 0.05, 0.1, 0.25, 0.5 and 1 wt.% were considered and the optimum graphene content was obtained.

1. Introduction

Graphene nano platelet (*GPL*) is a multilayer of sp2-hybridized carbon atoms arranged in a two-dimensional lattice and has attracted tremendous attention in recent years owing to its exceptional properties [1,2]. The in-plane elastic modulus of pristine, defect-free graphene is approximately 1.1 TPa and is the strongest material that has ever been measured on a micron length scale [2]. The development of a nano level dispersion of graphene particles in a polymer matrix has opened a new and interesting area in materials science in recent years [3]. One possible route to harnessing these properties for applications would be to incorporate graphene nano sheets in a composite material [4].

In order to predict the modulus of nanocomposites, various methods like micromechanics, molecular dynamics and quantum mechanics approaches are available. There are several micromechanics models for the prediction of the elastic properties of nanocomposite materials, based on the geometry, orientation of the filler, elastic properties of the filler and matrix, such as Halpin-Tsai model, Nielsen Model, Mori–Tanaka model, Eshelby model, etc. The Mori–Tanaka (*MT*) method [5–7] is an effective field theory based on the Eshelby's elasticity method for inhomogeneity in an infinite medium and achieves the average internal stress in the matrix of a material containing inclusions with transformation strain. The stiffening effect of graphene sheets dispersed in polymer nanocomposites using the *MT* micromechanics method has been used by some researchers. Ji et al. [8] predicted the effective elastic modulus of graphene sheet-reinforced composites by assuming that all graphene sheets are either aligned or randomly oriented in the polymer matrix while maintaining their platelet-like shape by means of *MT* micromechanics method. Potts et al. [9] investigated thermo-mechanical properties of composites of poly (methyl methacrylate) (*PMMA*) and chemically modified graphene (*CMG*) fillers and applied *MT* theory to quantify dispersion, suggesting platelet aspect ratios greater than 100 at low loadings and a lower quality of dispersion at higher loadings.

The molecular dynamics (*MD*) simulation is a numerical modeling technique for studying molecular behaviors of defined substances and the corresponding bulk material properties in larger scales as continuum using appropriate up-scaling approaches [10,11]. Gao and Hao [12] carried out mechanical properties of monolayer graphene under tensile and compressive loading from quantum mechanics method. They obtained zigzag and armchair graphene Young's moduli equal to 0.6 and 1.1 TPa, respectively. Ito and Okamoto [13] investigated mechanical properties of graphene and graphite containing vacancies under tensile loading using *MD* simulations. They calculated zigzag and armchair pristine

* Corresponding author. Tel.: +98 2177491206.
E-mail address: Shokrieh@iust.ac.ir (M.M. Shokrieh).

http://dx.doi.org/10.1016/j.commatsci.2014.06.002
0927-0256/

graphene Young's moduli as 0.79 and 0.87 TPa, respectively. Although, researchers that use continuum mechanics approach imply isotropic behavior of graphene sheet [14,15]. The basic unit in a molecular dynamics simulation is an atom, with its motion computed over a discrete simulation timespan. Afterward, the determination of the force field is definitely crucial to accurately describe the interactions among atoms and molecules [16]. The *MD* simulation relies greatly on the force interactions among atoms following Newton's second law of the classical mechanics.

A combined molecular dynamics–micromechanics model (called *MD–M* model) was developed by Shokrieh [17] to find the stiffness of randomly distributed graphene embedded in epoxy resin nanocomposites. In the present paper a similar approach is utilized. First, the stiffness of multilayered graphene nanoplatelet embedded in epoxy resin was obtained using the *MD* simulation. Then, results obtained by the molecular dynamics were used by the Mori–Tanaka (*MT*) and the Halpin-Tsai (*HT*) micromechanics models. The combined models are called the *MD–MT* and *MD–HT* models, respectively. Furthermore, an experimental investigation on effects of addition of graphene nanoplatelet nanoparticles on mechanical properties of graphene nanoplatelet/epoxy nanocomposites is presented. The results obtained from the two modeling approaches are compared with the experimental results.

2. Molecular dynamics simulation

The *MD* simulation is useful in calculating mechanical properties of a composite system. The stress components σ_{ij} (both tensile and compressive) can be calculated from Virial theorem [18]:

$$\sigma_{ij} = -\frac{1}{Vol}\left[\left\{\sum_{i=1}^{N} m_i\left(v_i\, v_i^T\right)\right\} + \left(\sum_{i<j} r_{ij}\, f_{ij}^T\right)\right] \tag{1}$$

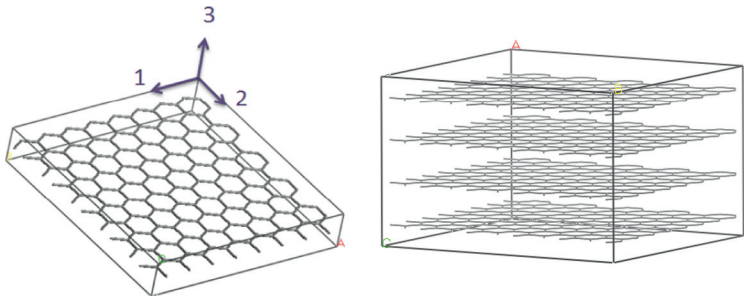
where *Vol* is the volume of the simulation box, m_i is the mass of *i*th atom, v_i is the velocity of *i*th atom, *N* is the total number of atoms, r_{ij} is the distance between *i*th and *j*th atoms and f_{ij}^T is the force exerted on *j*th atom by *i*th atom. Hence, for series of six uniaxial strains $\varepsilon = [\varepsilon_{11}\ \varepsilon_{22}\ \varepsilon_{33}\ \varepsilon_{12}\ \varepsilon_{23}\ \varepsilon_{31}]^T$ the simulation box undergoes tensile and compressive deformations in all six directions. This leads us to calculate the corresponding stress tensors by using Virial expression. Every time, the unit cell is deformed in just one direction, while other strain components are fixed to zero.

The *MD* simulations were conducted using the Material Studio Package provided by Accelrys Inc. [19]. The consistent valence force field (CVFF) is used to specify the molecular interactions. Four different configurations are constructed to predict the Young's modulus of the nano graphene. First, one layer graphene is put into the simulation box and in other configurations the number of graphene layers is increased. Two configurations are shown in Fig. 1. The Cartesian coordinate system is also represented in this Figure. A $19.676 \times 21.300 A^2$ graphene and periodic boundary condition is used, so the bonds at the edge of the nano graphene are broken. Specifically, the introduction of periodic boundaries is equivalent to considering an infinite space-filling array of identical copies of the simulation region. There are two consequences of this periodicity. The first is that an atom that leaves the simulation region through a particular bounding face immediately re-enters the region through the opposite face. The second is that atoms lying within a specified distance of a boundary interact with atoms in an adjacent copy of the system, or equivalently, with atoms near the opposite boundary. Another way of regarding periodic boundaries is to think of mapping the region (topologically, not spatially) onto the equivalent of a torus in four dimensions (a two-dimensional system is mapped onto a torus); then it is obvious that there are no physical boundaries. In this way, it is possible to model systems that are effectively bounded but that are nevertheless spatially homogeneous insofar as boundaries are concerned [20]. The 3-D periodic boundary condition used for graphene sheet provides the capability of modeling of a large graphene sheet and properties in upper scales can be used. Also a 3-D periodic boundary condition can consider the effect of stacking layers in graphene. The distance between each two layers of nano graphene is 3.35 A.

3. Calculation the stiffness of graphene nano-platelets/epoxy composites

3.1. Mori–Tanaka micromechanical model with Hill's parameters (MT-model)

The Mori–Tanaka (*MT*) method [9–11] is an effective field theory based on the Eshelby's elasticity method for inhomogeneity in an infinite medium. Fourth-order tensor relates average inclusion strain to average matrix strain and approximately accounts for fiber interaction effects. The *MT* method calculates the average internal stress in the matrix of a material containing inclusions with transformation of the strain. It is shown that the average stress in the matrix is uniform throughout the material and independent of the position of the domain where the average treatment is carried out. In this method, it is also shown that the actual stress in the matrix is the average stress plus the locally fluctuating stress, the average of which vanishes in the matrix. Average elastic energy is also considered by taking into account the effects of the interaction among the inclusions and of the presence of the free boundary [6]. In this method, to predict the modulus of nanocomposites, the three-dimensional elastic parameters of both polymer matrix and nanofiller are needed. However, graphene platelets are in fact two-dimensional materials and their out-of-plane elastic parameters do not have a well accepted definition in the literature [8]. A graphene sheet, along with bulk graphite, could be regarded as a transversely isotropic material. As shown in Fig. 1, graphene nanoparticles are considered lying in x_1–x_2 plane and normal to x_3-axis, which is the symmetric axis. The elastic behavior



(a) First configuration (b) Fourth configuration

Fig. 1. Coordinate system and nano graphene simulation boxes.