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A novel combined molecular dynamics–micromechanics method for modeling of stiffness of graphene/epoxy nanocomposites with randomly distributed graphene

M.M. Shokrieh [a,*], Z. Shokrieh [a], S.M. Hashemianzadeh [b]

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

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ABSTRACT

In this paper, by combining molecular dynamics and micromechanics methods, a new approach for prediction of the stiffness of the nanocomposites with randomly distributed nanoparticles in the macro level is presented. The molecular dynamics method is used to model the stiffness of the graphene/epoxy nanocomposites containing one layer of an aligned nano graphene embedded in epoxy resin. By considering the large sizes of the length and width of the nano graphene in comparison with its thickness and the shortcomings of the available hardware and software for simulation purposes, a new approach for modeling is also developed. This new approach, by using the moduli of different graphene sheets with different sizes embedded in a representative volume element, can predict the moduli of a real size graphene embedded in the matrix along the longitudinal, transverse and normal directions in the nano-scale. In order to consider the effect of the random distribution of graphene sheets in epoxy resin, a micromechanical approach is used. The results obtained by the molecular dynamics method are used by the micromechanics approach and the stiffness of graphene/epoxy nanocomposites with randomly distributed graphene in the macro-scale is predicted. An experimental program is conducted to evaluate the capability of the model. The result of the modeling is in a very good agreement with the experimental data.

1. Introduction

Development of composite materials and structures as well as the emergence of a new branch of science called nanotechnology, led to the creation of a new generation of composite materials that are known as nanocomposites. In general, a nanocomposite material is a structure that the repeated distances between different constituent phases are in nanometer level [1]. Graphene as a nano reinforcement, due to its extraordinary mechanical properties has become a fascinating subject for researchers. Many researches [2–6] have been performed on modeling of graphene sheet to characterize its properties. When small amounts of these carbon thin plates are properly combined with the polymer, physical properties of the polymer increasingly improved [7]. One of the methods for prediction of nanocomposite properties is the random multiscale modeling approach. Using this concept, Shokrieh and Rafiee [8] examined the mechanical properties of nanocomposites containing carbon nanotubes and resin. To identify local behaviors of nanocomposites in nano scale, using an atomic modeling is necessary and inevitable. Due to limitations of the computational hardware features, modeling approaches are limited to very few numbers of atoms and they does not have the ability to deal with networks containing large number of atoms. For this reason, most of atomic modeling researches have been done on the modeling of pure polymer or graphene, separately. For example, Gao and Hao [9] determined the mechanical properties such as the stiffness of monolayer graphene under tensile and compressive loadings by a quantum molecular dynamics technique. Yan et al. [10] investigated the effect of defects on the fracture strength of graphene by molecular dynamics (MD). Odegard et al. [11] studied molecular modeling of epoxy resin and measured mechanical properties such as stiffness and shear modulus by considering the percentage of crosslinking of polymer chains. Some studies are also performed on nanocomposites containing graphene. Awasthi et al. [12] modeled the interfacial behavior between one layer of graphene and polymer using the MD. Rahman and Haque [13] using MD simulation, measured the strength and stiffness of the graphene epoxy

* Corresponding author. Telefax: +98 21 7720 8127.
E-mail address: shokrieh@iust.ac.ir (M.M. Shokrieh).

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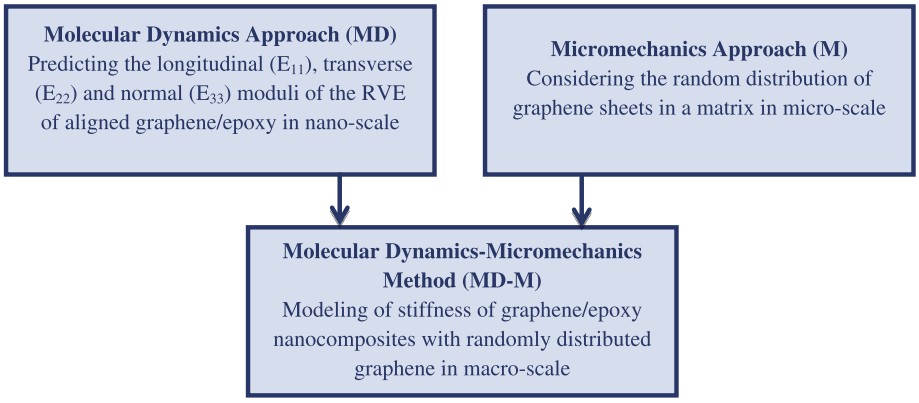

Fig. 1. The concept of the combined molecular dynamics and micromechanics methods.

nanocomposites. Because of the above-mentioned limitations, these simulation techniques available in the literature have been performed by assuming just a few layers of graphene with limited sheet dimensions. Therefore, these approaches cannot simulate a real physical problem and a new approach for simulation of such complicated phenomenon is needed. Moreover, a comprehensive survey shows that the most of researches on the modeling of nanocomposites are limited to aligned nanoparticles embedded in the polymer [13–16]. However, to the best knowledge of the present authors there is no any approach to model the modulus of nanocomposites with randomly distributed graphene nanoparticles.

In the present research, a graphene epoxy nanocomposite is simulated by considering the representative volume element (RVE) concept. The moduli of graphene/epoxy nanocomposites with a randomly distribution of nano graphene in the resin are measured by combining the MD and micromechanics called MD–M method. Finally, to validate the results of the modeling, experiments have been conducted and results are compared. The results of the comparison between the modeling and experiments indicate the good capability of the proposed model in the present research.

2. Modeling philosophy

The present model is a combination of molecular dynamics (MD) and micromechanics (M) methods, called as MD–M (Fig. 1). The model is able to predict the stiffness of nanocomposites reinforced with nanoparticles, such as graphene nano platelets. As shown in Fig. 1, in the first step, using the MD approach the model predicts the longitudinal (E_{11}), transverse (E_{22}) and normal (E_{33}) moduli of the RVE of graphene/epoxy nanocomposites with aligned distributed graphene particles in epoxy in the nano-scale. In this scale, bonding length, diameter, atomic interactions and configuration of the graphene sheet are considered. In the next step, the results obtained by the MD method are used by the micromechanics approach and the stiffness of graphene/epoxy nanocomposites with randomly distributed graphene in epoxy in the macro-scale is predicted.

3. Principles of MD simulation

The MD simulation is a numerical modeling technique to study the molecular behavior of a material that eventually bulk properties of the material can be obtained in large scales [17,18]. The first step in the modeling process is creating the atomic structure of the desired molecule. This includes a precise definition of the element type, partial charge of atoms, connecting bonds, atoms locations and their boundary conditions. An atom is the basic unit in a complicated atomic model that its motion is computed during simulation time intervals. Determination of the force field is definitely crucial to accurately describe the interactions among atoms and molecules. Despite of existing of various force fields like CVFF[1], CHARMM[2], COMPASS[3], PCFF[4], etc., a suitable force field should be selected which take into account all major bonded and non-bonded interactions including ionic bonds, covalent bonds, hydrogen bonds, metallic bonds, Columbic interaction and Van der Waals forces.

For the MD computations, constructed atomistic system should attain an admissible energy state. With predefining initial positions of all atoms, the total potential energy of the entire system (U) is calculated and should be minimized. This energy is summation of energy of all atoms obtained by the defined force field. The total potential energy of the entire system is minimized by varying the atomic positions. In the theory, this minimal energy, which indicates the thermodynamics equilibrium state, is the most preferable molecular configuration for operations on the system.

The MD simulation relies on the force interactions between atoms following Newton's second law of the classical mechanics [19]. The force F_i acting on an atom is expressed as:

$$F_i = m_i a_i \tag{1}$$

where m_i and a_i are the mass and acceleration of the atom, respectively. Moreover, F_i includes all the interactions among other nearby atoms and can be expressed as:

$$F_i = \sum_{j=1,2,\ldots,n;\, j\neq i} \left(\frac{-\partial U}{\partial r_{ij}}\right) \tag{2}$$

where r_{ij} is the distance between atoms i and j. Once F_i is computed, the acceleration of atom i can be resolved to predict its sequential velocity and position by an appropriate numerical integration scheme in the time domain. In this research, Material Studio package provided by Accelrys Inc. [20] is used for the MD simulation.

The MD simulation can be used to calculate mechanical properties of a system such as stiffness. The constructed energy-minimized structure is subjected to twelve deformations; three pairs in uniaxial tension/compression and three pairs involving pure shear. Each of these deformations corresponds to setting one of the components of the strain vector to some small value of strain (for example 0.001) while keeping all other components fixed at zero. The stress tensor obtained analytically using the virial Eq. [21] is as follows:

[1] Consistent Valance Force Field.
[2] Chemistry at Harvard Molecular Mechanics.
[3] Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies.
[4] Polymer Consistent Force Field.