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A molecular dynamic simulation study of mechanical properties of graphene–polythiophene composite with Reax force field

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ABSTRACT

In this paper, we performed molecular dynamic simulations by Reax force field to study the mechanical properties of graphene–polythiophene nanocomposite. By computing elastic constant, breaking stress, breaking strain and Young's modulus from the stress–strain curve for the nanocomposites, we investigated effects of tension orientation, graphene loading to the polymer, temperature of nanocomposite and defect of graphene on these mechanical characters. It is found that mechanical characters of tension along the zigzag orientation are higher than other directions. Also, by increasing the weight concentration of graphene in composite, the Young's modulus and breaking strain increase. Our results showed that the Young's modulus decreased with increasing temperature. Finally by applying defect on graphene structure, we found that one atom missing defect has lower Young's modulus. Also, by increasing the defects concentration, elastic modulus decreases gradually.

1. Introduction

The ability of understanding of behavior and properties of nanostructures with modeling and simulation is one of the keys in developing of nanotechnology [1–5]. Carbon-based nanostructures have been attracting much attention during the last decade, because of their superior mechanical, electrical and thermal properties [6].

Graphene is one of the most important of these nanomaterials with two-dimensional monolayer structure. It is a two-dimensional nanostructure made of sp2-hybridized carbon atoms arranged in a honeycomb-like lattice with the 1.42 Å inter-atomistic distances between the adjacent carbon atoms. Electronic properties of the graphene like electron transport capacity and electron conductivity and mechanical properties such as the high intrinsic tensile strength and stiffness and also its high thermal conductivity caused it used in many areas of technology [7–9]. All the above properties render graphene as a promising candidate for a new class of polymeric materials, known as graphene–polymer nanocomposites. The benefit of graphene–polymer nanocomposites which are based on the incorporation of graphene in polymer matrices is to modify the electrical, mechanical and thermal properties of the composite system and to use it in various applications [10,11]. One of the interesting aspects of graphene–polymer nanocomposites is that all these improvements can be realized even at low filler loadings in the polymer matrix. For example, Ramanathan et al. [12] by experimental method reported a significant enhancement of the mechanical properties of PMMA, estimating the increase in the Young's modulus of the nanocomposite with the low graphene loading to the PMMA matrix. Also Kim et al. [13] reviewed so many articles to compare the electrical, thermal and mechanical properties of different graphene/polymer nanocomposites. They showed the Young's modulus of these polymers increased with filling of graphene.

Because it is difficult to study of graphene–polymer composite at the molecular level with experimental techniques, simulation approaches are valuable tools and necessary for design and develop of these hybrid nanostructure systems [14]. Molecular dynamics (MD) simulations can provide the structure and the dynamic intercalated molecules details to study of their mechanical and thermal behavior [6,15–19].

Many researchers have simulated graphene–polymer composites using MD techniques to investigate mechanical and thermal properties of the composite. For example, Alkhateb et al. [6] studied the effects of geometrical parameters on mechanical properties of graphite–vinylester nanocomposites and their constituents using MD simulations. They found that exfoliation improves mechanical properties of graphite nanoplatelet vinylester nanocomposites. Rahman et al. [18] studied the mechanical properties of graphene/cellulose (GC) nanocomposites using MD simulations.

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Their results showed a significant improvement in Young's modulus for the GC composites compared to neat cellulose. Awasthi et al. [20] studied the interfacial mechanical behavior of the graphene/polyethylene (PE) using MD simulations. They have examined the force separation behavior between graphene and polymer matrix. Lv et al. [21] have studied the influence of the chemical functionalization of graphene on the interfacial bonding characteristics. They have used two well-known polymers, PE and poly(methyl methacrylate) (PMMA), as polymer matrices to found that the functional groups of the graphene increase the interfacial bonding between the graphene and the polymer. Mansfield and Theodorou [22] investigated the interface between graphite and a glassy polymer and determined that a 10 Å thick interfacial region existed in the polymer that was structurally different from that of the bulk polymer. Also, Chunyu Li et al. [23] used MD simulations to observe the interface of a crosslinked thermoset polymer in the presence of a graphite surface. Wang et al. [24] using molecular dynamics (MD) simulations, studied the effectiveness of hydrogenation, defecting and doping on reducing the graphene–paraffin interfacial thermal resistance. They found that the graphene–paraffin nanocomposites under tensile loading, are lower Young's modulus and smaller tensile strength for the paraffin filled with hydrogenated graphene.

In the present work, MD simulations by Reax force field are used for study of the mechanical properties of graphene–polythiophene (PT) composite. We have chosen this polymer because in our previous works, we studied the mechanical properties of polymer composites which are used in organic solar cell [25,26]. We found that among the P3HT, PT, PFB, PE, TPV, MDMO–PPV and MEH–PPV polymers, the PT polymer showed the strongest interaction with CNT, because of existence a sulfur atom in its backbone. However, despite such practical applications for example in organic solar cell technologies, to the best of our knowledge there is no paper in the literature that studies the mechanical properties of the graphene–PT composite using MD simulation by Reax force field. The MD simulations have done by LAMMPS code with the details of simulation in the corresponding section. The results are organized in the five parts. The first part contains study of Young's modulus of pure graphene by applying a uniaxial tension along the zigzag direction to obtain the results agree well with previous values of experimental and theoretical results. The second part exhibits the effect of directions of tension on the Young's modulus of composites. We applied tension along the zigzag, armchair and $(2n, n)$ directions. In the third part we obtained stress–strain curved for different graphene loadings in the polymer matrix. We used 10%, 15% and 20 wt% graphene as filler in the polymer. The fourth part is calculating of Young's modulus of graphene–PT composites as a function of temperatures to investigating of the effect of temperature on mechanical strength and breaking point. And finally in the fifth part, we study how the graphene defects affected on the composite's mechanical properties.

2. Simulation model

In this research, equilibrated MD simulations were performed using the LAMMPS (Large Scale Atomic/Molecular Massively Parallel Simulator) software package [27] by Reax force field. The Reax force field is used for metallic and organic materials [28–31] and it includes both covalent interactions, includes Coulomb and Vander Walls interactions, via bond-orders and noncovalent interaction [32]. The bond-order is computed from the distances between atoms and their positions that are updated in molecular dynamics simulation in every step, thus allowing creation and breaking of chemical bonds. The other interactions such as angle, torsion and out-of-plane are computed from bond-orders. The total potential energy in Reax force field is computed as the sum of various terms including:

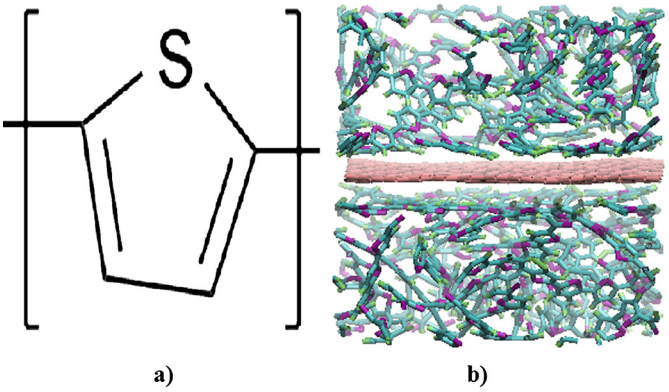

Fig. 1. a) The structure of PT chains and b) graphene–PT composite with 12 PT chains.

$$E_{total} = E_{bond} + E_{over} + E_{val} + E_{tors} + E_{VdWaals} + E_{Coulomb} \quad (1)$$

where E_{bond}, E_{over}, E_{val}, E_{tors}, $E_{vdWaals}$, and $E_{Coulomb}$ are the energies corresponding to bond, over coordination, angle, torsion, Vander Walls, and Coulomb interaction, respectively. Each term has several parameters, these parameters are fitted into experimental or quantum mechanics data. We used Mattsson parameters for fitting the parameters of Reax FF interaction terms, which is a general-purpose hydrocarbon parameterization [33].

At the first part of simulation section, we optimized the geometry of pure graphene to obtain its mechanical properties. This part of simulation, which is tested and validated in many articles [34–36], enables us to test the accuracy of our results. The second part is constructing the graphene–PT composites with different defects and graphene weight concentrations.

2.1. Simulations of graphene

For the first step, MD simulations are carried out on the graphene with 416 atoms and dimension around 32×34 Å^2. The zigzag and armchair directions, which are oriented along the X and Y axes, respectively.

Prior to applying the stress, the system is fully relaxed at room temperature of 300 K using the Nose–Hoover algorithm [37,38] under NPT ensemble with the periodic boundary conditions in the in-plane directions. Then, the uniaxial tensile loading is applied along the armchair, zigzag and $(2n, n)$ direction at a strain rate of 1.0% ps^{-1}.

To obtain the stress–strain relations during tensile loading, the virial stress σ_{IJ} is calculated according to the equation

$$\sigma_{IJ} = \frac{\sum_k^N m_k v_{k_I} v_{k_J}}{V} + \frac{\sum_k^N r_{k_I} f_{k_J}}{V} \quad (2)$$

where N is the number of atoms in the system, V is the system volume, v_{k_I} is the ith component of the velocity of atom k, r_{k_I} is the ith component of the position of atom k and f_{k_J} is the jth component of the force applied on atom k. The volume of the graphene sheet is obtained by assuming the thickness of graphene as 3.4 Å.

2.2. Simulations of graphene–polythiophene composites

An amorphous PT is constructed of PT chains which each chain has 142 atoms contain 20 monomers (Fig. 1). Simulations are carried out for 10 (25 PT chains), 15 (17 PT chains) and 20% (12 PT