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Molecular dynamics based simulations to study failure morphology of hydroxyl and epoxide functionalised graphene

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ABSTRACT

In this article, molecular dynamics based simulations were performed to study the effects of functional groups such as hydroxyl and epoxide on the mechanical strength and failure morphology of graphene oxide. Reactive force field potential was used to capture the interatomic interactions between carbon, oxygen and hydrogen atoms. In contrast to previous observations, atomistic simulations predicted a transition in the failure morphology of hydroxyl functionalised graphene from brittle to ductile as a function of its spatial distribution on graphene. This transition in failure morphology from brittle to ductile was gradual in nature and was observed at lower percentage coverage of graphene in the range of 25–50%. Failure morphologies depict that hydroxyl groups tend to boost the ductility through chains and elongated rings formation at lower percentage coverage. Also, the electrostatic charge redistribution and epoxide to ether transformation were found to be the decisive mechanisms behind the ductile response shown by hydroxyl and epoxide groups, respectively.

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1. Introduction

One of the most fascinating 2D nano-material that has spellbound the research community, due to its exemplary mechanical and thermal properties is graphene [1]. Graphene, a sp^2 hybridized allotrope of carbon possessing a honeycomb lattice structure, attracts many diversified applications in the field of microelectronics [2,3], biotechnology [4,5], desalination membrane [6], reinforcing nanocomposites [7,8] and hydrogen storage [9]. Graphene oxide (GO) is a chemical derivative of graphene, and is also known for its superior reinforcing capabilities for nanocomposites [10]. GO is the most utilised raw material to synthesize graphene on a massive scale via mechanical exfoliation and chemical modification [11]. GO holds the same atomically thin structural framework as graphene, but contains additional functional groups such as hydroxyl, epoxide and carboxyl [12]. The sp^3 hybridised C—O bond in GO nanosheet turns GO into an insulator, thus, found applications in microelectronics [13,14]. In addition to this, GO has also find applications in removing radioactive substances from water [15], energy storage sector [16], nano-reinforcement in polymer based composites [17,18], nonporous separation membrane [19], gas permeation [20], electromagnetic shielding [21], supercapacitors [22,23], hydrogen gas barrier [24,25], biomedical [26], clean energy devices [27], biomedical [28], nanomedicine [29], biotechnology [30], fluorescence and sensing [31] applications.

Accurate atomistic structure of GO was reported by Lerf-Klinowski, by using non-periodic and non-stochiometric model, which was further validated by using experimental means [32–35]. Dyer et al. [35] defined GO structure as a function of oxidation level. Lahaye et al. [36] in their density functional based calculations had predicted a fully oxidized GO has around 50 percent coverage of functional groups and an ideal composition of $C_8O_2(OH)_2$ or $C_6O_1(OH)_2$. Earlier, researchers have varied the range of oxidation (C:O ratio) from 4:1 to 2:1, although the chemical reduction can provide a ratio upto 12:1 and even higher [11]. Suk et al. [37] employed atomic force microscopy (AFM) in conjunction with finite element method (FEM) to estimate Young's modulus of 207.6 ± 23.4 GPa and a prestress of 76.8 ± 19.9 MPa for a monolayer of GO nanosheet. Gomez-Navarro and his team [38] used AFM based nano-indentation techniques for estimating modulus of elasticity of chemically reduced monolayer of GO as 250 GPa. Kang et al. [39] coupled nanoindentation technique on a dynamic contact module (DCM) system and calculated the mechanical properties of free-standing GO. Recently in 2017, Gao et al. [40] discussed the effects of strain characterization and gripping effects on stress-strain behavior of GO. Paci et al. [41] predicted the decrement in intrinsic mechanical properties of GO as compared to pristine graphene via monte-carlo scheme and molecular dynamics

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(MD) simulations. In 2012, Liu et al. [42] predicted the mechanical properties for ordered and amorphous GO nanosheets.

Due to the complex atomistic level structure of GO, conflicting trends have been predicted or reported about its failure mechanism and morphologies. Cao et al. [43] observed a brittle fracture in GO nanosheets, containing carbon-to-oxygen ratio of 4:1 with 20% hydroxyl functionalisation, whereas, Wei et al. [44] predicted a ductile failure for 70% oxidized graphene sheet. Thereby to eradicate this discrepancy, Meng et al. [10] and Soler-Crespo et al. [45] proposed that the epoxide and hydroxyl groups were the main source for ductile and brittle failure, respectively.

So far, researchers have studied the effect of functionalisation with respect to percentage coverage over graphene, but literature is almost mute on the effects of spatial distribution of hydroxyl and epoxide functional groups on the graphene. Herein this article, the authors have studied the effects of these groups separately as well as altogether on the mechanical properties of GO. Overall simulations were performed in three stages, initially, separate simulations were performed with each of the functional groups, and later on the best configurations with respect to failure morphology and mechanical strength were simulated altogether to study the mechanical behavior of GO nanosheets. Spatial distribution of these functional groups can help in altering the hydrogen bonding and stress distribution over the carbon atoms of graphene sheets, which can be further explored for tailoring the failure morphology of GO.

2. Modeling details

In this article, all the MD simulations were performed in an open source code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) package [46]. Success of any MD based simulation depends on the type of interatomic potential used for capturing the bond dynamics. So far, researchers have employed different types of potentials to simulate the mechanical behavior of graphene, AIREBO and Tersoff are commonly used for graphene. But these two potentials are incapable of capturing the bond dynamics between carbon, and oxygen atoms, that limits its application in simulating GO nanosheets. On the other hand, reactive force field (ReaxFF) based interatomic potential are considered as more accurate, and capable of capturing the bond dynamics between carbon, oxygen and hydrogen atoms [13,19,47,48,49]. In this work, ReaxFF parameters proposed by Chenoweth et al. [50] has been used to estimate interatomic forces acting between carbon, oxygen and hydrogen atoms. In addition to these advantages, ReaxFF is also capable of capturing electrostatic energy component as illustrated in Eq. (1), which helps in performing charge equilibration after desired number of integration steps. Mathematically, the total energy of atomistic system (E_{system}) specified by ReaxFF is in accordance with Eq. (1):

$$E_{system} = E_{bond} + E_{over} + E_{angle} + E_{tors} + E_{vdWaals} + E_{coulomb} + E_{specific} \quad (1)$$

where E_{bond} describes the energy contribution due to bond formation between atoms; E_{over} is an energy penalty that prevents the over coordination of atoms; E_{angle} and E_{tors} report the energies associated with three-body valence angle strain and four-body torsional angles; $E_{vdWaals}$ and $E_{coulomb}$ are the van der Waals and Coulomb interaction energies; $E_{specific}$ is for system specific terms that encompasses lone-pair, hydrogen-binding and conjugate bonds corrections. For further elaborated discussion on ReaxFF formulation and expressions, researchers are referred to the work of Senftle et al. [51].

In all simulations performed either with pristine or functionalised graphene, size of nano-sheet was kept constant at 60 Å, for both in plane directions. Simulations with the opted ReaxFF parameters can be performed in a range of temperatures, starting as low as 1 K to room temperature. But, in order to minimize the thermal disturbances and for neglecting entropic contribution to formation energy, the temperature of simulation box was kept fixed at 1 K with an integration time step of 0.25 fs. Any further reduction in temperature of the simulation box, generates weird results with respect to stress-strain response and failure stresses. In plane periodic boundaries were imposed over the nanosheet to avoid edge effects. Equilibration as well as simulation under uni-axial tensile loading was performed under the influence of NPT (number of atoms, pressure and temperature constant) ensemble, where Noose-Hover thermostat and barostat were used for controlling and maintaining the desired temperature and pressure, respectively [52]. During relaxation under NPT ensemble, pressure in all the directions, whereas in tensile deformation, pressure along the direction transverse to loading was maintained at zero. System was relaxed for a time period of 12.5 ps, such that the potential energy reaches a minimum value as illustrated in Fig. 1.

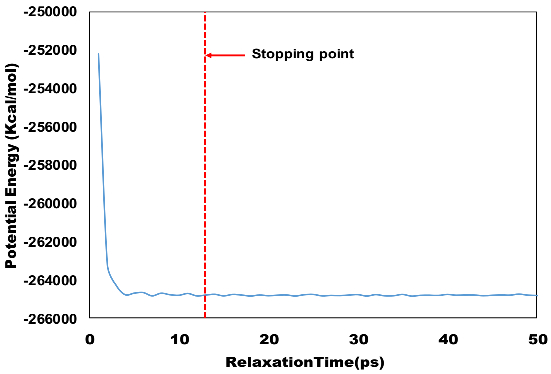

Fig. 1. Potential energy trend with respect to relaxation time.

After relaxing the structure, the GO sheet was subjected to a tensile deformation either along x-direction (zigzag-ZZ) or y-direction (armchair-AC) with a strain rate of 10^{-3} ps^{-1}. An optimum value of strain rate and integration time steps were used in all the simulations. The choice of these parameters was based on our previous research work and data from the literature [10,13,48,53]. It has been established that strain rate in the range of 10^8 s^{-1} to 10^{10} s^{-1} has negligible impact on the mechanical and fracture behavior of graphene and GO. To keep the computational cost in control, MD simulations are usually run at these high strain rates. In our simulations, strain rate was kept at 10^9 s^{-1} (10^{-3} ps^{-1}). In each simulation, charge equilibration was performed after every 10 integration steps. Considering the ReaxFF parameters, near neighbour and hydrogen bonding cut-off distances were kept fixed at 4.5 Å and 6 Å, respectively. The atomic virial stresses [54] were predicted using the formulation given in Eq. (2):

$$\sigma_{ij}^{\alpha} = \frac{1}{\varphi^{\alpha}}\left(\frac{1}{2}m^{\alpha}v_i^{\alpha}v_j^{\alpha} + \sum_{\beta=1,n} r_{\alpha\beta}^{j} f_{\alpha\beta}^{i}\right) \quad (2)$$

where m^{α} and υ^{α} are the mass and velocity of atom α; $r_{\alpha\beta}$ is the distance between atoms α and β; φ^{α} is the atomic volume of system; i and j stand for indices in Cartesian coordinate system; α and β being the atomic indices.

3. Results and discussion

Initially, simulations were performed at 300 K with pristine graphene to validate the potential parameters proposed by

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