Interfacial strengthening between graphene and polymer through Stone-Thrower-Wales defects: *Ab initio* and molecular dynamics simulations

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ABSTRACT

In this study, we revealed the interfacial strengthening mechanism between a Stone- Thrower-Wales (STW) defective single layer graphene and polypropylene (PP), through a density functional theory (DFT) simulation and atomistic molecular dynamics simulations. In quantum mechanical simulation, the adhesion energy of propylene monomer on STW defective graphene is calculated with van der Waals interaction. An improved adsorption characteristic of propylene to the STW defective graphene is clearly observed, compared with a pristine counterpart. For deeper understanding of the adsorption, the electronic structure calculation and geometrical analysis of the adsorbed structures are also performed. In molecular dynamics simulation, three transversely isotropic nanocomposite unit cell structures consisting of PP and single layer graphene having a different number of STW defects are constructed. The stress-strain curves of nanocomposites according to the density of STW defects are obtained from uniaxial tension and shear tests. Since the properties of graphene itself are degraded by the STW defects, the overall stress-strain characteristics of nanocomposites involving the deformation of graphene are degraded by the addressed STW defects. However, in longitudinal shearing, where interfacial shearing between graphene and PP is involved, the STW defect can critically improve the shear load bearing capability. The increased interfacial shear load transfer is mostly attributed to the rippling of graphene at the STW defective sites, and the resultant surface roughness of graphene.

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1. Introduction

Together with carbon nanotube [1] and fullerene [2], graphene has become one of the most important nanostructured materials to be categorized as nanocarbon structure [3,4]. The fascinating physical properties of graphene, such as ultra-high elastic stiffness (~1 TPa, [5]) and strength (~120 GPa, [5]), as well as its thermal and electronic properties [6,7], have resulted in proposals for a variety of applications, including soft electronics [8], electrochemical sensors [9], hydrogen storage carrier [10], and structural multifunctional composites [11]. In most of the applications of graphene for which good electron transport capability is required, the achievement of high quality defect-free graphene is still the most challengeable task in bottom-up manufacture of graphene, such as the chemical vapor deposition (CVD) process [12]. On the other hand, in solution-based approaches, representatively Hummer's method [13,14], cost effectiveness, as well as high throughput of exfoliated graphene solution that is readily available from market or laboratory, are major concerns, rather than extremely high purity. Nonetheless, the reduction and desirable purification of graphene is also an important issue in solution-based approaches for graphene. Therefore, the growth method or solution-based methods are selected according to the applications, and the requirement of the impurity of graphene.

In general, several intrinsic defects remain after the manufacturing process of graphene, such as the Stone-Thrower-Wales (STW) defect [15,16], vacancies [17], oxidations [18], doping [19], and grain boundaries [20]. With the help of current quantum chemistry, some designed defects, such as inverse STW (ISTW) defects are demonstrated, and theoretically studied as a

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new building block of graphene. When such intrinsic defects are initiated, the change in sp^2 chemical bond order alters electronic properties of the graphene in detail, and degrades important physical properties. However, the interpretations of graphene or other nanocarbon defects have found negative, as well as positive aspects. Since the electron distribution of defective carbon sites is altered, the chemical reactivity and cohesive strength of the defective carbon can also be altered. For example, in our previous works on STW defective carbon nanotube (CNT) reinforced nanocomposites [21,22], an improved interfacial bond strength between the defective CNT and surrounding polymer could be demonstrated by a molecular dynamics (MD) simulation. On the application of the graphene to the electrodes for electric double layer capacitors, it has been confirmed that the defects in graphene such as STW defect, vacancies and doping can enhance the quantum capacitance [23,24]. Using the quantum mechanics calculations as well as experimental measurement of carbon nanosheets, a new possibility of the vacancy defect that it can substantially improve the electrical conductivity of graphene [25] has been demonstrated. Since the graphene can easily be self-doped to alter the electronic properties, various attempts to engineer the graphene by incorporating the designed defects to attain new functionalities have been made by theoretical studies [26,27]. Moreover, recent works on the experimental introduction of extended defects of graphene [28], and on the reversible defect engineering of CNT using scanning tunneling microscopy [29], have improved the realization of defect engineering of nanocarbon structures. More information on the role of well-known structural defects in graphene are well summarized in Ref. [30].

When graphene is used as a multifunctional reinforcing filler inside a polymer matrix, the defect can also be taken advantage of, because interfacial strengthening between the graphene and matrix is involved. In this study, we only focus on the topological STW defect in tailoring the interface properties. Recalling the rule of mixtures for composites, it is undoubtedly conjectured that the STW defective graphene degrades the overall properties of composites, since the properties of the reinforcement phase are primarily degraded. However, considering the two-dimensional structure of graphene and the interfacial load transfer mechanism of penny-shaped inclusion, an improved interfacial shear load transfer can be accomplished by the enhanced reactivity or cohesive energy between the STW defective graphene and polymer. Therefore, it is essential for the design of graphene reinforced polymer composites to tackle the two rival effects of the degradation of graphene, and the improvement of interfacial strength. To the authors' best knowledge, however, a systematic research incorporating extreme scale computer simulation on this arguable issue of graphene has never been performed yet.

To reveal the physics behind the positive and negative aspects of the STW defects, and to correlate the defective structure with the macroscopic properties, computational studies capable of describing the charge redistribution of defective carbon, geometrical distortion, and rippling of graphene embedding designed defects are of primary importance. In this respect, both quantum mechanical calculations and molecular dynamics simulations can be effectively used. Using quantum mechanics approaches, the electronic structure of defective graphene is calculated within density functional theory. The physical non-bonding interaction can be described with van der Waals formalism, and the resultant cohesive strength between the defective sites and other species of atoms constituting the polymer matrix is accurately quantified. Moreover, the optimum physisorption sites on the defects on top of the carbon, such as carbon-carbon bridge, penta- or hepta-hole, can be determined in detail [23]. Therefore, material interface level characterization of between the STW defect and polymer chain,

and the screening of defect-to-polymer type combination, are readily available using the DFT simulation.

For the representative volume element (RVE) level modeling and prediction of composites properties according to the STW defects, molecular level simulation is rather more useful than the quantum level approach for its ability to consider rather larger molecular systems than quantum simulations, as has been demonstrated in many literatures [21,22,31,32]. However, in regard to the chemical reactivity of carbons in defects, existing classical potential models, such as the consistent valence force field (CVFF) [33] and polymer consistent force field (PCFF) [34], do not distinguish the van der Wales potential parameter of carbon atoms in octagonal or pentagonal ring, from that of carbons in hexagonal ring. Therefore, the classical potential models cannot describe the intrinsic adhesion characteristics of the STW defects to the typical engineering polymers. Nonetheless, local geometry changes of defective sites, such as out-of-plane distortion and rippling, which are described by DFT simulation [35], can also be described by MD simulations. In interfacial load transfer between an inclusion and a rigid polymer, the surface roughness of the inclusion plays a very important role. Therefore, the effect of geometrical change by the STW defect on the mechanical properties of graphene reinforced nanocomposites can be readily studied within the classical MD simulations.

In this study, the interfacial strengthening mechanism between STW defective graphene and polypropylene (PP) matrix is examined by DFT simulation and MD simulations, respectively. The DFT simulation focuses on the intrinsic binding energy between the STW defect and PP monomer and dimer. The detailed adhesive energy and distance according to the adsorption site of PP monomer in the STW defect, and the charge difference of the adsorbed molecular structure are analyzed to evaluate the intrinsic adhesive nature of the STW defect with the PP monomer. In MD simulations, transversely isotropic nanocomposites unit cell structure is considered, and the stress-strain curves are obtained from tensile and shear tests according to the number of STW defects. To correlate the change in surface distortion and the resultant shear moduli of nanocomposites, the mean arithmetic surface roughness is analyzed according to the density of the STW defect.

2. Density functional theory

To investigate the STW defective single layer graphene-PP chain, density functional theory calculations are performed using the Vienna Ab initio Simulation Package (VASP) [36,37]. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) are used for comparison. The local and semi local density functional theory calculations are unable to correctly describe the van der Waals interaction resulting from dynamical correlations between fluctuating charge distribution. Therefore, the DFT-D2 method of Grimme is added to the conventional Kohn-Sham DFT energy [38,39]. We use the projector augmented wave (PAW) method with a plane wave basis set [40,41]. The polypropylenes are linear, saturated hydrocarbon chains absent of branches, with the general formula $(C_3H_6)n$, where n is the number of monomers in one chain. In this work, we analyze the adsorption of propylene monomer and several short polymers ($0 < n < 15$) on graphene and STW defective graphene. The migration energy barriers of polypropylene monomer are calculated using the climbing-image nudged elastic band (NEB) method on the tangential direction of graphene [42].

2.1. Model configuration and structure relaxation

The STW defect on graphene or CNT is formed by a 90° rotation of two neighboring carbon atoms in a hexagonal ring. As a