# A study on the tailoring of interfacial shear strength between graphene and polymer by addressing defects in graphene

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## ABSTRACT

A molecular dynamics simulation study on the interfacial strengthening between defected graphene and polypropylene matrix is implemented. As intrinsic defects in single layer graphene, oxidation, Thrower-Stone-Wales(TSW) defect, and Adatom defect are considered. On the transversely isotropic nanocomposites unit cell embedding different defected graphene, transversely isotropic stress-strain relations are predicted from quasi-static tensile and shearing simulation. At the same time, the degradation of graphene by the addressed defects is studied to elucidate the degradative feature of the defects. Since all the defects considered in this study is found to decrease tensile and shear properties of graphene, tensile behavior of graphene reinforced nanocomposites is degraded according to the density of each defect. In shearing of nanocomposites which involved face-to-face interfacial sliding of graphene and polymer, however, it is found that the defected graphenes show better interfacial load transfer,thus, enhaced shear moduli. To establish structure-to-property relationship of defected graphene reinforced composites, surface roughness induced by the addressed defect is calculated and correlated with the shear moduli of nanocomposites.

## 1. INTRODUCTION

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Graphene has become one of the most promising nanostructured materials for its excellent physical properties with transparency [Geim et al.;2007]. During the manufacture process of the graphene such as growth from catalyst or exfoliation method, however, several intrinsic defects such as oxidation, void, Thrower-Stone-Wales (TSW) defect, adatom defect are inevitably formed. Since the defects degrade the properties of graphene and transparency, removal of the defects is a critical issue for the application of graphene to transparent conducting films and electrodes. Moreover, when graphene is used as reinforcements in polymer matrix, degradation of the graphene by the defects results in the degradation of nanocomposites.

In the application of graphene to polymer composites, however, the existence of the defect needs to be understood from a different point of view. In the design of graphene reinforced polymer composites, load transfer between graphene and host matrix at the materials' interface is one of the most important design issues. In general, interfacial adhesion strength between defect-free graphene and typical engineering polymers is known to be poor without proper surface functionalization of graphene or direct covalent grafting between the graphene and polymer. In recent study on the effect of several intrinsic defect in carbon nanotube on the interfacial load transfer between nanotube and polymer, it has been revealed that both TSW and adatom defect can promote interfacial load transfer between the CNT and polymer[Yang et al.; 2015]. Since carbon nanotube and graphene have the same $sp^2$ carbon structure, the same mechanism can be applied to the graphene reinforced polymer composites. According to the quantum simulation and molecular simulation studies on the application of the defect in graphene to the supercapacitors [Pak et al.; 2014], a positive aspect of the defect in improving the charge capacitance has been revealed. Since the removal of defects in nanotube and graphene has been a burdensome process for the application of the defect, possibilities of the defect engineering can be an innovative way to reduce the cost for the manufacture and to improve the performance of the applications.

In this study, we reveal the possibility of graphene defect engineering to tailor the interfacial properties of graphene/polyethylene (PE) nanocomposites using molecular dynamics simulations. On the transversely isotropic unit cell structures of nanocomposites including arbitrarily defected graphene and amorphous polymer matrix, the stress-strain relations are derived from tensile and shearing simulations according to the density of defects. In addition, mode I and II decohesion tests are implemented to develop interfacial cohesive law according to the defects.

## 2. MOLECULAR MODELING AND SIMULATIONS

Details on the construction of graphene nanocomposites unit cell structure embedding different number and types of defects in graphene and ensemble simulation procedures to derive stress-strain curve of nanocomposites are as follows. All the ensemble simulations including production runs have been implemented using an open molecular simulation program, LAMMPS, together with a commercial molecular modeling and simulation package, *Material Studio version 5.5* for modeling initial structures [Plimpton; 1995]. To describe inter-and intra-atomic interactions in the nanocomposites system, two different potential libraries are used; REBO potential for

graphene and defects, and CVFF potential for matrix polymer PE and non-bond interaction between graphene and PE, respectively.

### 2.1 Unit cell preparation

The transversely isotropic molecular unit cell of nanocomposites and the planar molecular structure of graphene and defects are shown in Fig. 1. The adatom defect is an interstitial one formed by a covalently bonded extra carbon. The optimized configuration of the adatom defect is not planar and a spike is formed after the formation of adatom defect as shown in Fig. On the other hand, the TSW defect does not involve a interstitial process of carbon atoms and the $sp^2$ conjugation is not brokene. The molecular structure of local TSW defect can be made by changing the four adjacent hexagonal structures into two pentagonal and two heptagonal structures as shown in Fig. 1.
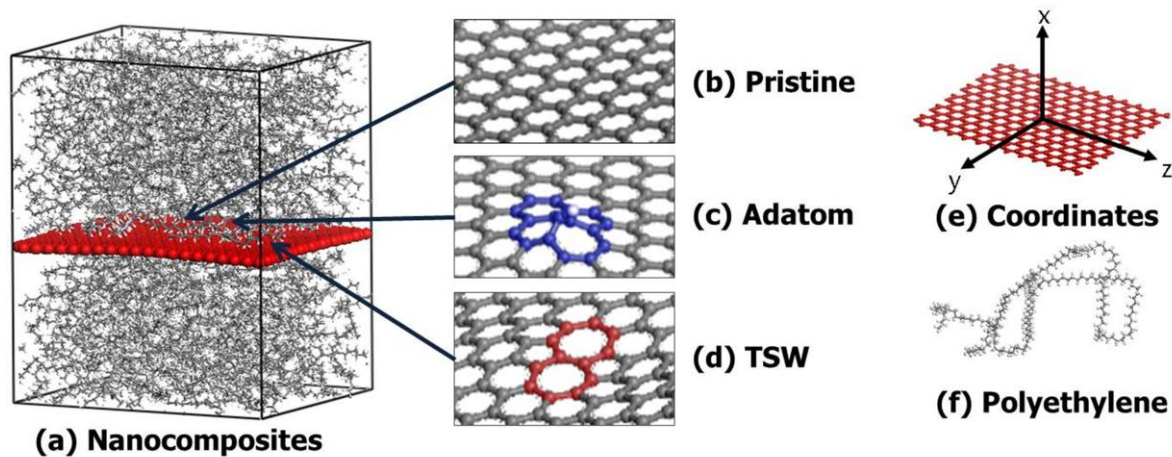


Fig.1 Molecular structure of nanocomposites unit cell and structural defects in graphene

In each intrinsic defect, 0(pristine), 5, 10 defects are considered. The unit cell construction process is as follows. First, a pure amorphous PE matrix structure is constructed using a finite number of $C_{100}H_{202}$ PE chains with periodic boundary conditions. The unit cell was then optimized to its minimum potential energy state using the conjugate gradient method. At the same time, single layer graphene in a periodic cell box is prepared and laminated together with the PE unit cell structure with a sequence of PE-graphene-PE. Then, total potential energy is minimized using the conjugate gradient method. According to the defect density, finite numbers of defects are formed in the graphene followed by a potential energy minimization process. Finally, all the unit cell structures are equilibrated at 200K and 1atm using the isothermal-isobaric (NPT) ensemble simulations using Nosé-Hoover extended Hamiltonian method for 3000 pico-seconds(ps).

### 2.1 Production run to obtain stress-strain curves

The stress-strain curves of nanocomposites in uniaxial tension and shearing deformations are predicted by applying a constant true strain rate of 200micron/sec to each unit cells. In uniaxial tension, according to the prescribed strain rate, finite affine

deformation is applied to one edge of the unit cell. The virial stress at each loading step is then used to draw stress-strain curves. In shearing simulation, a continuous change of the tilting angle corresponding to the given strain rate is applied to the unit cell without volume change. Since the volume change is not involved in shearing simulation, the isothermal (NVT) ensemble simulation is used. To achieve computational accuracy, all the tensile and shearing simulations are implemented three times with a different initial random number seeds to assign velocity of individual atoms. The stress-strain curves are then averaged over the three different simulation results.

## 3. RESULT AND DISCUSSIONS

The transversely isotropic stress strain curves of nanocomposites embedding the TSW defects are depicted in Fig.2. In longitudinal tension, both the elastic modulus and magnitude of the stress in nanocomposites are degraded by the adatom and TSW defects. This is related with the boundary condition of nanoconposites and degradation of the graphene itself by the adatom and TSW defects. When the TSW defects exists, tensile modulus of graphene itself is degraded. Since the periodic boundary condition is applied to the unit cell shown in Fig. 1, the graphene inside the unit cell experience the
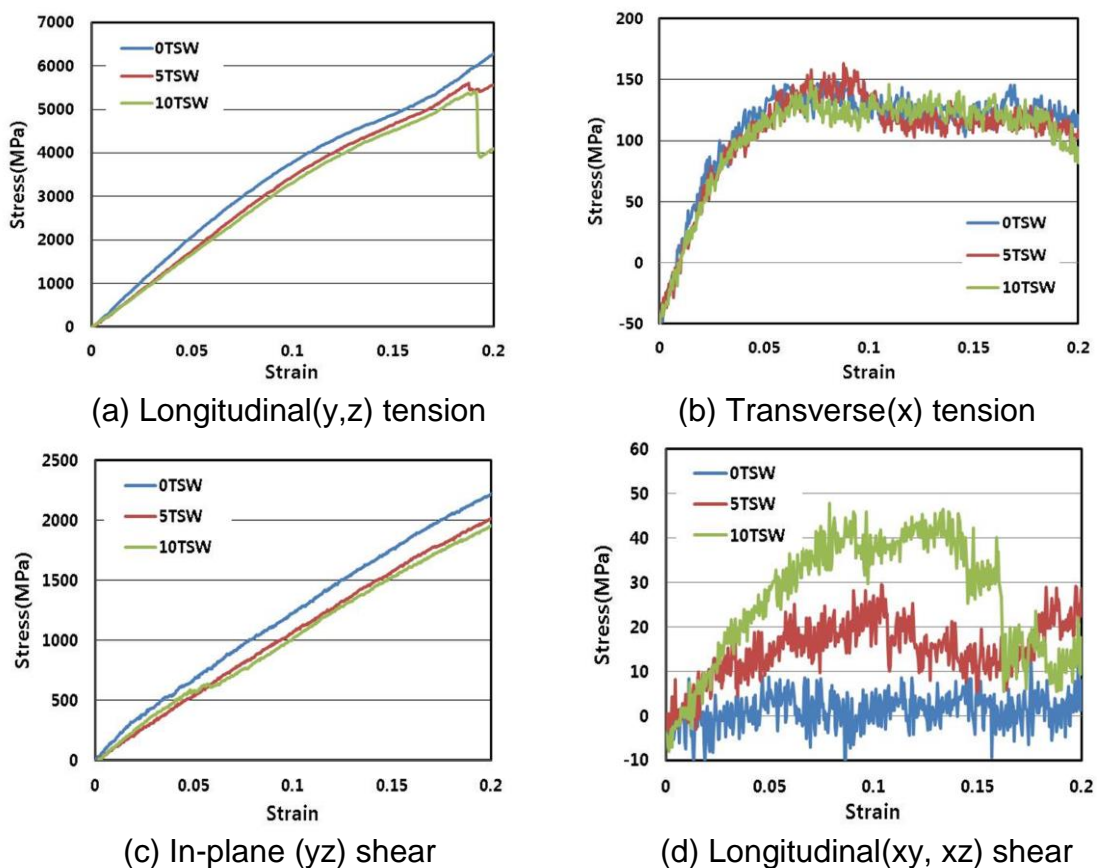


(a) Longitudinal(y,z) tension

(b) Transverse(x) tension

(c) In-plane (yz) shear

(d) Longitudinal(xy, xz) shear

Fig.2 The stress-strain curves of nanocomstes embedding TSW defects

same amount of longitudinal strain to the loading directions. Therefore, graphene takes most of the stress inside the nanocomposites and the behavior of nanocomposites is degraded by the defect.

In transverse tension, however, the difference in the magnitude of the stress is not as mush high as in the case of longitudinal tension and the PE matrix takes most of the stress in tension. At the materials' interface between $sp_2$ carbon and engineering polymer, intrinsic adhesion strength is not enough strong to assume that the interface is perfectly bonded [Yang et al.; 2013]. In transversely loading of the unit cell shown in Fig.1, therefore, load transfer from PE matrix to graphene is not enough. Moreover, the fact that the graphene is a single layer structure consists of only one atom layer to the through the direction makes it difficult to define and measure the through the thickness stress and strain of graphene.

In in-plane shearing where wrinkling of graphene can be involved, the magnitude of the stress steeply increases and a clear degradation the stress-strain relation is observed. Similar to the longitudinal tension of nanocomposites, the graphene takes most of the shear stress in in-plane shear deformation of the nanocomposites with the full periodic boundary condition of the unit cell structure shown in Fig. 1. In the above three deformation loading condition, it is found that both adatom and TSW defects in graphene degrades the overall mechanical behavior of nanocomposites.

In longitudinal shearing of nanocomposites where a face-to-face shearing between the graphene and PE matrix occurs, however, an unexpected shear stress-shear strain relation is observed. When the graphene is pristine, the magnitude of the shear stress in nanocomposites does not increase as the shear strain increases. This means that the interfacial shear load transfer from matrix to graphene and vice versa is poor and interfacial sliding occurs when the unit cell experience shear deformation. As the number of TSW defect increases, however, the magnitude of the shear stress increases even up to 40MPa with 10 TSW defects. In the TSW defect, no change in $sp_2$ carbon conjugation is involved and the CVFF force field applied to describe the non-bond interaction between graphene and PE matrix provides the same van der Wales potential parameters of the same $sp_2$ carbon atoms. Therefore, the fact that the shear stress-shear strain relation in longitudinal shearing is improved by the TSW defect is attributed to other structural factors which might have affected the movement of PE molecules right in the vicinity of the TSW defected graphene.

## 4. CONCLUSIONS

In this study, the effect of structural defects in graphene on the mechanical and interfacial behavior of graphene reinforced PE composites was studied through molecular dynamics simulations. Even if TSW defect degrades the properties of graphene, interfacial shear stress transfer capability is improved by the TSW defect. Therefore, a remarkable enhancement in shear stress-shear strain relation could be attained by addressing the TSW defect. Since we have considered an infinite graphene inside a PE matrix by considering the unit cell shown in Fig. 1 with periodic boundary condition, further exploration of the mechanical test of nanocomposites with different boundary condition needs to be performed. In the near feature, equivalent micromechanical constitutive models will be developed to handle the same problem in continuum scale.

## ACKNOWLEDGEMENT

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