



Elastic moduli of covalently functionalized single layer graphene sheets



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ABSTRACT

Due to their flexibility, large surface area and high specific mechanical properties, single layer graphene sheets (SLGSs) are potential candidates as filler materials for improving mechanical properties of polymers. Their effective utilization as reinforcements requires strong interfacial binding with the matrix surrounding them. The covalent functionalization of SLGSs is an effective technique to enhance this binding. However, covalent bonds introduced by a functional group usually alter the pristine structure of the SLGS that may affect its mechanical properties. Thus it is important to delineate effects of covalent functionalization on elastic moduli of an SLGS. We consider five groups of different polarities, namely, hydrogen (–H), hydroxyl (–OH), carboxyl (–COOH), amine (–NH₂), and fluorine (–F) as model functional groups and investigate their effects on values of Young's modulus and the shear modulus of the SLGS. We use molecular mechanics (MM) simulations with the MM3 potential and the software TINKER to conduct the study. The pristine and the functionalized SLGSs are deformed in simple tension and simple shear, and from curves of the strain energy density of deformation vs. the axial strain and the shear strain, values of Young's modulus and the shear modulus, respectively, are derived. These values are based on the hypothesis that the response of an SLGS is the same as that of an energetically and geometrically equivalent continuum structure of wall thickness 3.4 Å. It is found that functionalization reduces the elastic moduli of the SLGSs which could be due to nearly 120% local strains induced at the functionalized sites of relaxed but unloaded SLGS, and the change in hybridization from sp² to sp³. The decrease in the value of the modulus increases with an increase in the amount of functionalization but is essentially independent of the functionalizing agent. For 10% functionalization, Young's modulus and the shear modulus of the SLGS are found to decrease by about 73% and 42%, respectively. However, the moduli of a fully functionalized SLGS are about the same as those of a 4% functionalized sheet. Even though the moduli of the pristine armchair and zigzag SLGSs are the same, the moduli of functionalized armchair SLGSs are about 20% less than those of the corresponding zigzag SLGSs. The work will help material scientists interested in designing graphene sheet reinforced polymeric composites.

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1. Introduction

A great deal of research has been devoted to investigating mechanical properties of a single layer graphene sheet (SLGS) in the last two decades. Methods used to find values of elastic moduli include ab initio calculations, density functional theory (DFT), molecular mechanics (MM) and molecular dynamics (MD) simulations, continuum theories, and experimental techniques. Many of these approaches hypothesize that the response of an SLGS to an applied load is the same as that of an energetically and geometrically equivalent continuum structure (ECS). Since an SLGS is only an atom thick, it is a challenging task to find the wall thickness of the ECS. In Table 1 we have summarized values of Young's

modulus, E , basal plane stiffness, K , Poisson's ratio, ν , and wall thickness, t , obtained by various investigators using different techniques. Here, K , E and t are related by $K = Et$. We note that of the results reported in Table 1, Kudin et al. [3] and Gupta and Batra [12] have found values of the wall thickness to be 0.893 and 1 Å, respectively. Neek-Amal and Peeters [13] assumed it to be 1 Å and other researchers have taken it to equal 3.4 Å, which is the interlayer separation distance in bulk graphite.

Due to their high elastic moduli and large surface area (theoretical limit = 2630 m²/g) [16], SLGSs are desirable reinforcing materials for improving mechanical properties of polymer based composites. However, in order to effectively utilize SLGSs as reinforcements, it is necessary to achieve their strong interfacial binding with the surrounding matrix. Chemical functionalization involving covalent bonding of functional groups to carbon atoms of the SLGS is an effective method to enhance this binding.

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Table 1
Values of E , K , ν and t for an SLGS reported in the literature.

Author(s)	Method/potential	K (N/m)	E (TPa)	ν	t (Å)
van Lier et al. [1]	Ab initio	~377	1.1		3.4
Liu et al. [2]	Ab initio	~357	1.05	0.186	3.4
Kudin et al. [3]	Ab initio	345	3.86	0.149	0.894
Arroyo and Belytschko [4]	Brenner's 1st generation	236		0.412	
	Brenner's 2nd generation	243		0.397	
Konstantinova et al. [5]	DFT	~420	1.24		3.4
Faccio et al. [6]	DFT	323		0.18	
Klintonberg et al. [7]	DFT	358			
Lee et al. [8]	Nano-indentation (experimental)	340 ± 50			
Reddy et al. [9]	Tersoff–Brenner				
	–Along zigzag	~227	0.669	0.416	3.4
	–Along armchair	~276	0.812	0.465	3.4
Cadelano et al. [10]	Tight binding atomistic simulations	312		0.31	
Jiang et al. [11]	MD with Brenner's 2nd generation potential	318–369	0.95–1.1	0.17	3.35
Gupta and Batra [12]	MM with MM3 potential	340	3.4	0.21	1
Neek-Amal and Peeters [13]	MD with Brenner's bond-order potential		1.3 ± 0.07		1
Neek-Amal and Peeters [14]	MD with Brenner's bond-order potential	164–211	0.49–0.63		3.35
Lajevardipour et al. [15]	Monte Carlo with the valence force field model of Perebeinos and Tersoff	350.42 ± 3.15			

However, the introduction of covalent bonds by functional groups alters the pristine structure of the SLGS that may degrade its mechanical properties. Hence, it is important to determine the effect of covalent functionalization on elastic moduli of SLGSs.

Pei et al. [17,18] investigated mechanical properties of hydrogen (–H) and methyl (–CH₃) functionalized SLGSs using MD simulations with the adaptive intermolecular reactive bond order (AIREBO) potential. They found that Young's modulus of the SLGS decreased by 30% and the tensile strength and the fracture strain dropped by 65% when all atoms of the SLGS were functionalized with hydrogen. For 30% atoms of the SLGS functionalized with the methyl group, the elastic modulus, the tensile strength and the fracture strain were found to decrease by 18%, 43% and 47%, respectively. Zheng et al. [19] used MM and MD simulations and the condensed phase optimized molecular potential for atomistic simulation studies (COMPASS) force field to investigate the effect of chemical functionalization on mechanical properties of an SLGS at 1 K. They found 42.2% reduction in Young's modulus with 16% functionalization with the carboxyl (–COOH) group, and ~41.5% drop in the shear modulus with 7.5% functionalization with the hydroxyl group. Kheirkhah et al. [20] used MD simulations with the AIREBO potential to study shear deformations of –H functionalized SLGSs at 300 K, and found that the shear modulus of the SLGS gradually decreased with an increase in the functionalization to 50% with hydrogen.

The polarity of a functional group covalently bonded to carbon atoms of the SLGS is an important factor in determining binding between the two, and with a matrix material. Here we consider five groups of different polarities, namely, hydrogen (–H), hydroxyl (–OH), carboxyl (–COOH), amine (–NH₂), and fluorine (–F) as model functional groups and determine their effects on elastic moduli of SLGSs for varying percentage of functionalization. We employ MM simulations with the MM3 potential and the freely available software TINKER [21] to perform the study.

2. Molecular mechanics simulations

2.1. Force-field

As in our previous work on single wall carbon nanotubes (SWCNTs) [22] and on SLGSs by Gupta and Batra [12], we use the MM3 potential [23] with higher order expansions and cross-terms to model interatomic interactions. We note that the basal plane stiffness of 340 N/m found using the MM3 potential agrees with that found experimentally [24]. This potential,

given by Eq. (1), is suitable for studying deformations of an SLGS because of similarities between sp² bonds in the hexagonal structure of graphene and the hexagonal structure of aromatic proteins for which the potential was originally developed. For this potential the energy of the system equals the sum of energies due to bonded and non-bonded interactions. The contributions for bonded interactions come from bond stretching (U_s), in-plane angle bending (U_θ), out-of-plane bending (U_γ), torsion (U_ϕ), and cross-interactions including stretch–bend ($U_{s\theta}$), angle–angle ($U_{\theta\theta'}$) and stretch–torsion ($U_{s\phi}$). The non-bonded interactions are van der Waals (U_{vdW}) and dipole–dipole electrostatic ($U_{\mu\mu'}$).

$$U_s = 71.94K_s(r - r_0)^2 \left[1 - 2.55(r - r_0) + \frac{7}{12}(2.55(r - r_0)^2) \right]$$

$$U_\theta = 0.0219K_\theta(\theta - \theta_0)^2 \left[1 - 0.014(\theta - \theta_0) + 5.6(10^{-5})(\theta - \theta_0)^2 - 7.0(10^{-7})(\theta - \theta_0)^3 + 2.2(10^{-8})(\theta - \theta_0)^4 \right]$$

$$U_\gamma = 0.0219K_\gamma\gamma^2 \left[1 - 0.014\gamma + 5.6(10^{-5})\gamma^2 - 7.0(10^{-7})\gamma^3 + 2.2(10^{-8})\gamma^4 \right]$$

$$U_\phi = (V_1/2)(1 + \cos \phi) + (V_2/2)(1 - \cos 2\phi) + (V_3/2)(1 + \cos 3\phi)$$

$$U_{s\theta} = 2.511K_{s\theta}[(r - r_0) + (r' - r'_0)](\theta - \theta_0)$$

$$U_{\theta\theta'} = -0.021914K_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta'_0)$$

$$U_{s\phi} = -5.9975K_{s\phi}(r - r_0)(1 + \cos 3\phi)$$

$$U_{vdW} = \varepsilon \left[-2.25(r_v/r)^6 + 1.84(10^5) \exp\{-12.00(r/r_v)\} \right]$$

$$U_{\mu\mu'} = \frac{14.3928[\mu\mu'(\cos \chi - 3 \cos \alpha \cos \alpha')]}{R^3 D} \quad (1)$$

Parameters r , θ , θ' and ϕ in Eq. (1) are shown in Fig. 1(a). Variables θ and θ' appearing in $U_{\theta\theta'}$ are two bond angles centered at the same atom. If an atom is bonded to three other atoms, the angle between one of the bonds and the plane defined by the three adjacent atoms is represented by γ . Variables r and r' in the expression for $U_{s\theta}$ equal lengths of the two bonds which make angle θ between them. A subscript, 0, on a variable represents its value in the configuration of the minimum potential energy with

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