Effects of functional groups on the mechanical and wrinkling properties of graphene sheets

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ABSTRACT
The effects of the degree of functionalization, molecular structure and molecular weight of functional groups on the Young's modulus of graphene sheets were investigated through molecular dynamics and molecular mechanics simulations. The dependence of shear modulus, strength and critical wrinkling strain of graphene sheets on the chemical functionalization was also examined. It is found that Young's modulus depends greatly on the degree of functionalization and molecular structure of the functional groups, while the molecular weight of the functional groups plays a minor role in determining Young's modulus. The chemical functionalization also reduces the shear modulus and critical wrinkling strain. The binding energy between the functional groups and the graphene sheets is mainly responsible for these findings.

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1. Introduction
Graphenes have a two dimensional structure and possess unique mechanical, electrical, thermal and optical properties, which are different from those of other carbon allotropes, such as carbon nanotubes (CNTs) and fullerene [1]. Their unique physical properties can have numerous potential applications in areas like nanoelectronics, sensors, transistors, batteries, as well as conducting polymer composites [2–4]. In particular, graphene sheets (GSs) can be good candidates as nanofillers to enhance the mechanical and functional properties, including the electrical and thermal conductivities, of polymer-based composites [5,6]. Thus, many studies have been directed toward developing techniques to prepare GSs [7]. Several approaches have been developed to obtain individual GSs, including chemical vapor deposition (CVD) [8–10], micromechanical exfoliation of graphite [1], epitaxial growth [11] and chemical methods [12,13]. Among the current fabrication methods, only the chemical method can produce GSs in large quantity, in which certain chemical groups are inevitably attached to the GSs during the course of production. In addition, similar to CNT-based composites [14,15], it is necessary to chemically modify the GSs to allow uniform dispersion and enhance the adhesion with the polymers in the composite. Therefore, functionalized GSs appear to be more popular and extensively used than pristine GSs in practical applications [16]. However, the functional groups attached onto the GSs may affect the mechanical and physical properties of the GSs and the resulting composites.

The mechanical properties of pristine graphenes have been recently determined by atomic force microscope nanoindentations [17], showing that they are as strong and stiff as single-wall CNTs. Nevertheless, it may be difficult to show how chemical functionalization affects the mechanical properties of GSs. As a popular numerical approach, molecular dynamics (MD) simulations have been used to predict the properties of GSs under various loading conditions. The buckling, Young’s and shear moduli of GSs have been studied using atomistic simulation methods [18–24]. The effects of large defects and cracks on the mechanical properties of GSs have been investigated based on the coupled quantum mechanics/molecular mechanics (QM/MM) [25]. A theoretical
framework of nonlinear continuum mechanics for GSs and a formula for the elastic bending modulus of GSs have also been developed [26]. Although the mechanical properties of GSs functionalized with hydrogen or methyl have been examined [27,28], the majority of these studies have been focused on pristine GSs or GSs functionalized with only one kind of functional group.

The above literature survey indicates that there is absence of more general evaluation based on different functional groups, and the wrinkling behavior of GSs has not been studied. Resistance to wrinkling is considered one of the most important characteristics of GSs from the viewpoint of transparent conducting films made from graphene. In this work, MD and MM simulations are used to investigate the effects of functional groups on the elastic properties of GSs. The Young moduli of GSs affected by the degree of functionalization, molecular structure and weight of the functional groups are specifically evaluated. The shear modulus and critical wrinkling strain of the functionalized GSs are also studied.

2. Simulation method

The MD and MM simulations are performed using a software (Materials Studio by Accelrys Inc.). The condensed-phase optimized molecular potential for atomistic simulation studies (COMPASS) force field, which has been widely employed for various gas- and condensed-phase properties of many popular organic and inorganic materials [29–31], is used to model the interatomic interactions. In most of the simulations, periodic boundary conditions (PBCs) are not employed. Instead, to avoid the unsaturated boundary effect, hydrogen atoms are added at the edges of the GSs. The length of each C–C bond is 1.42 Å and that for C–H bond is 1.14 Å. The hydrogen atoms and the carbon atoms connecting these hydrogen atoms each has a charge of +0.1268 and −0.1268e, respectively, allowing neutral GSs. The electronic structure of all carbon atoms in the graphene model without functionalization is naturally sp2-hybridized. When a functional group is attached to a carbon atom through a covalent bond, the carbon atom becomes sp3-hybridized. A pristine GS containing 1372 carbon atoms and a GS functionalized with 137 hydroxyl functional groups randomly attached on the surface are shown in Fig. 1. The lengths of these GSs in the x and y directions are $L_x = 58.232\ \text{Å}$ and $L_y = 59.040\ \text{Å}$, respectively. As shown in Fig. 2a, the chiral vector determines the boundary structure of GSs and the two possible symmetric structures are zigzag and armchair GSs. Fig. 2b and c shows the examples of armchair GSs under tensile and shear loadings.

The simulations are carried out in the ($N$, $V$, $T$) ensembles and the time step is 1 fs. The temperature of the simulation system is maintained at 1 K. The Verlet algorithm is used for the integration of Newton’s equations. The cutoff distance for the non-bond interactions, such as the van der Waals and electronic static forces, is 9.5 Å. The Andersen thermostat is used for maintaining the temperature. All the measurements are made after the graphene reaches equilibrium, which is achieved through a minimizer processor, a module in Materials Studio. The energy minimization process enables the atoms in the system to rotate and vibrate such that the total potential of the system reaches the minimum [32].

2.1. Determination of Young’s modulus

To determine Young’s modulus of a graphene, the boundary carbon atoms on the bottom edge of the graphene are secured and a positive displacement $\Delta L$ in the y direction is applied to the carbon atoms on the top edge. The system is then relaxed for 30 ps and the total net force $F$ acting on all the carbon atoms in the y direction is used to compute the tensile stress $\sigma$ through $\sigma = F/A$, where $A = L_xh$ is the cross-sectional area and $h$ is the thickness of the graphene, which is usually taken as 0.34 nm. The tensile strain $\varepsilon$ is determined as $\varepsilon = \Delta L/L_y$, and Young’s modulus, $E$, is defined by

$$E = \frac{\sigma}{\varepsilon} = \frac{FL_y}{A\Delta L}. \quad (1)$$
Eq. (1) can be arranged to express the force $F$ as
$$F = \frac{EAADL}{Ly}; \quad \text{(2)}$$
and the strain energy $U$ is calculated by
$$U = \int FdL = \frac{1}{2}EV\varepsilon^2; \quad \text{(3)}$$
where $V = ALy$ is the volume of the graphene. Therefore, Young’s modulus can be calculated by
$$E = \frac{1}{V} \frac{\partial^2 U}{\partial \varepsilon^2}. \quad \text{(4)}$$

In the simulations, the strain energy $U$ of the graphene is computed as a function of strain $\varepsilon$ by varying $\Delta L$. Young’s modulus is obtained based on Eq. (4) by fitting $U - \varepsilon$ curves [33].

2.2. Validation of simulation method

To validate the numerical approach, Young’s modulus is first determined for pristine GSs, for which experimental measurements are available. Fig. 3a shows the $U - \varepsilon$ curves of zigzag and armchair GSs. By fitting the curves, Young’s modulus of the GS with zero chiral angle (i.e., zigzag mode) is found to be 1.050 TPa, which is in good agreement with nanoindentation measurements (1.0 TPa) [16] and ab initio computations (1.05 TPa) [19], confirming the validity of the simulation method used here to characterize the mechanical properties of GSs.

To further validate the simulation method, the dependence of Young’s modulus on the chirality of GSs is examined. Due to the hexagonal structure of GSs, it is expected that the elastic properties of GSs should be relatively independent of the loading direction and thus Young’s modulus should not be greatly affected by the chirality of GSs. Young’s modulus of GSs with chiral angles varying from $0^\circ$ (zigzag) to $30^\circ$ (armchair) is shown in Fig. 3b. Indeed, the Young modulus changes in a narrow range from 1.050 TPa for the zigzag GS to 1.086 TPa for the armchair GS, which is consistent with our expectation. In the following studies, Young’s modulus is calculated only for zigzag GSs.

3. Results and discussion

3.1. Effect of degree of functionalization on Young’s modulus

As discussed in the Introduction, the electronic structure of a carbon atom in the GS changes from $sp^2$- to $sp^3$-hybridization when a functional group is attached to it. The degree of functionalization $S$ is defined as the ratio of the number of $sp^3$-hybridized carbon atoms to the number of total carbon atoms in the GS. Fig. 4 shows a GS with 10% of the carbon atoms being randomly attached with hydroxyl groups (top panel) and the change in the local structure of a $sp^3$-hybridized
It is interesting to note that the graphene structure is modified such that the carbon atoms with functional groups are lifted from the original graphene plane. The conversion of in-plane sp² hybridization to off-plane sp³-hybridization will have several deteriorating effects, such as (i) destroying the local p bond in GS; (ii) making the sp³ bonds with an off-plane structure much easier to be bent by tension; and thus further weakening the GS. As the degree of functionalization, S, increases, both the number of displaced carbon atoms and the average perpendicular displacement, d, increase (Fig. 5b), resulting in a gradual reduction in Young's modulus. This is why Young's modulus decreases with increasing degree of functionalization.

### 3.2. Effect of molecular structure of functional groups on Young’s modulus

Different functional groups may affect Young's modulus of GSs in different ways. To understand the effect of molecular structure, three functional groups with similar molecular weights (MWs), namely propyl (–C₃H₇, MW = 43), carboxyl (–COOH, MW = 45) and methyl hydroperoxide (–CH₂–O–OH, MW = 47) groups are specifically studied. The Young modulus of GSs containing the three functional groups is shown in Fig. 6a. It is seen that Young's modulus decreases consistently with increasing degree of functionalization and the reduction depends significantly on the type of functional groups. It is interesting to note that Young's modulus becomes increasingly
sensitive to the structure of the functional groups as the degree of functionalization is increased. The –COOH group is shown to most adversely affect Young’s modulus, followed by the –C3H7 and –CH2–O–OH groups.

As discussed above, the functional groups on GS surfaces result in the conversion of carbon bonding from in-plane sp² hybridization to off-plane sp³-hybridization and the decrease of Young’s modulus is due to the local lattice distortion of the GS. The binding energy is a measure of the ability of the functional groups to deform the GS and the degree of distortion is characterized by the average perpendicular displacement, \( d \). The higher the binding energy is, the easier is to deform the GS. To obtain the binding energy, a model system consisting of a GS and a function group was used (PBSs are employed in all the directions). A representative slab supercell is shown in Fig. 6b, where the GS contains 50 carbon atoms and is attached with a –COOH group (S = 2%). The height of the vacuum section is 15 Å, so that the interactions between two neighboring slabs could be ignored [34]. The binding energy, \( U_{\text{bind}} \), is estimated as

\[
U_{\text{bind}} = -(U_{\text{total}} - U_{\text{GS}} - U_{\text{FG}}),
\]

where \( U_{\text{total}} \) is the total potential energy of the functional group and graphene; \( U_{\text{FG}} \) is the energy of the free functional group that is not attached to the graphene; and \( U_{\text{GS}} \) is the energy of the pristine graphene without functional groups.

The binding energy, \( U_{\text{bind}} \), between the functional groups and GS is shown in Fig. 6c. It is found that \( U_{\text{bind}} \) for the –COOH group is much higher than that for the other two groups. The comparison between Fig. 6a and c, indicates that the higher is the binding energy, the more unstable is the GS, and thus the easier is the GS to be deformed.

### 3.3. Effect of MW of functional groups on Young’s modulus

Fig. 6 also suggests that the MW of functional groups may not influence much the Young modulus. To systematically evaluate the effect of MW on Young’s modulus, a further study was performed, where six alkyl functional groups with continuously varying MWs including, –CH3 (MW = 15); –C2H5 (MW = 29); –C3H7 (MW = 43); –C4H9 (MW = 57); –C5H11 (MW = 71); –C6H13 (MW = 85), were used. Fig. 7 presents the Young modulus of functionalized GSs as a function of MW of the functional groups, showing that it remains almost unchanged regardless of MW. This observation is not surprising because the six groups are fundamentally similar in terms of molecular species and degree of interactions with the GS, as confirmed by the constant binding energy, \( U_{\text{bind}} \), which is also shown in Fig. 7. All these groups shared almost the same binding energy, which is the major parameter responsible for the reduction in Young’s modulus (see Fig. 6).

### 3.4. Shear modulus and wrinkling properties of GS

In addition to Young’s modulus, the shear modulus (\( G \)) and the critical wrinkling strain (\( \varepsilon_{\text{crit}} \)) are important mechanical properties in many applications of GSs. The critical wrinkling strain, \( \varepsilon_{\text{crit}} \), is defined as the strain at which wrinkles start to initiate in GSs and estimated from the displacement of carbon atoms on the top side of the GSs. These properties are calculated using similar approach, i.e., based on the stress-strain curves. Fig. 8 shows the shear stress–shear strain curves for the pristine and –OH and –COOH functionalized GSs, and Table 1 summarizes the corresponding shear properties. The presence of the functional groups significantly reduces both the shear modulus and strength, and the MW of the functional groups has only a marginal impact on these shear properties. The reduction in shear modulus due to the functional groups is more significant than that in Young’s modulus: e.g. for the same –COOH group with \( S = 7.5\% \), the shear modulus is reduced by about 45% whereas the reduction in Young’s modulus is only 19%. This is because the wrinkling of GSs is primarily controlled by sudden deformation of the weakest bonds, while Young’s modulus is a measure of the average deformation of GSs. As indicated in Section 2, the functional groups induce the conversion of local carbon bonding from sp² hybridization to much weaker sp³ bonds. Therefore, the shear strength, critical wrinkling strain and shear modulus should be more sensitive to the functionalization.

In Table 1, it is seen that the pristine GSs and the GSs functionalized with 7.5% –OH and –COOH groups, the \( \varepsilon_{\text{crit}} \) values are about 6%, 4.5% and 4%, respectively. Upon wrinkling, there was a sudden drop of shear stress while the average perpendicular displacement, \( d \), greatly increases (see Fig. 8 and

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**Fig. 5** – Effect of degree of functionalization on Young’s modulus of GSs: (a) \( U - \varepsilon \) curves for different S (solid lines represent polynomial fitting); and (b) Young’s modulus and average perpendicular displacement \( d \) as a function of S.

**Table 1** – Young’s and shear moduli of pristine and functionalized GSs.
Table 1). A typical wrinkling of a pristine graphene is schematically illustrated in Fig. 9, along with a map showing the vertical profile perpendicular to the graphene plane. It is worth noting that the wrinkles occur preferentially along

Fig. 6 – Effect of molecular structure of functional groups on Young’s modulus of GSs: (a) Young’s modulus as a function of $S$ for $-\text{CH}_2\text{-O-}$, $-\text{C}_3\text{H}_7$, and $-\text{COOH}$ functionalized GSs; (b) a slab supercell containing a graphene attached with a $-\text{COOH}$ group (50 carbon atoms in the graphene); and (c) binding energy for the three functional groups.

Fig. 7 – Effect of the MW of functional groups on Young’s modulus of GSs ($S = 7.5\%$) and the corresponding binding energy between the functional groups and GSs.
the direction about 30° inclined to the shear direction. The degree of wrinkling is higher at the edge than in the center as indicated by the vertical displacement.

4. Conclusions

The effects of functionalization on the mechanical properties, including Young’s modulus, shear modulus and wrinkling properties of GSs have been evaluated using MD and MM simulations. It is found that the Young modulus is strongly dependent on the degree of functionalization and molecular structure of functional groups. The effect of MW of functional groups on Young’s modulus is unimportant. The chemical functionalization also reduces the shear modulus and critical wrinkling strain. The weakening of the elastic properties of GSs arising from the attached functional groups is associated with the binding energy between the functional groups and GSs as well as the corresponding change in the molecular structure of GSs, which causes the GSs to become unstable. The functionalization also adversely influences the wrinkling resistance of GSs in terms of lowered shear modulus, strength and critical wrinkling strain. The simulation results indicate that although chemical functionalization has been considered an effective way to disperse GSs in various kinds of solvents and polymers, attention should also be paid to the reduction of mechanical properties due to the attachment of functional groups. The implication of this study is tremendously useful in understanding the mechanical behavior of functionalized GSs that are being considered for applications in many emerging areas.

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