WRINKLING IN GRAPHENE OXIDE PAPERS: EFFECT ON YOUNG’S MODULUS

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1 Introduction

Wrinkling is a common phenomenon in many two dimensional membranes. Graphene, a 2D material made of one-atomic thick hexagonal carbon layer, is found to have intrinsic ripples with out-of-plane deformation of about 1 Å due to thermal fluctuation in a 3D space [1]. Graphene oxide (GO) is the oxygenated derivative of graphene covered with hydroxyl and epoxy groups on the basal plane, as well as carboxyl groups at the edges. Functional groups [2] or structural defects [3] on the graphene basal plane modify the electronic structure of the carbon atom from \( sp^2 \)- to \( sp^3 \)- hybridization. Consequently, carbon atoms are deviated from the original plane, causing atomic level corrugation. Large area graphene sheets produced by chemical vapor deposition also contain wrinkles [4]. Many properties of graphene, such as carrier mobility [4], thermal conductivity [5], optical transmittance [6] and wettability [7], are shown to be significantly affected by such atomic and nanometer level wrinkles.

GO can be assembled into GO papers with layered structures by flow-directed filtration of aqueous suspension. They exhibit excellent mechanical properties, with Young’s modulus much higher than those of carbon nanotube bucky papers [8]. Although the individual GO sheets are tightly interlocked with each other in the layered structure of GO papers, subtle undulation - another form of wrinkling on the micro- and macroscopic scales - is always observed on the paper edge [8 - 10]. Despite the common presence of such undulation, relatively little is understood about its detailed structure and the impact on the mechanical properties of GO papers. Unlike the atomic or nanometer level wrinkles in monolayer graphene sheets, the undulation appeared in GO papers normally has much larger amplitudes. This suggests the mechanism behind the formation of wrinkles in GO papers is different from that occurring in the individual graphene sheets. While the source of wrinkling in graphene sheets, such as defects and functionalization, may still present in GO papers, other mechanisms should exist to substantiate the extra amplitude.

Understanding the mechanisms behind the formation of wrinkles in GO papers and their effects on mechanical properties is important in designing the paper-like materials with improved mechanical properties. We report the possible formation mechanisms of the undulation and its effect on Young’s modulus of GO papers using molecular dynamics simulations (MDSs).

2 Simulation details

2.1 Models

The GO paper models were built using stacked monolayer GO sheets with periodic boundary conditions implemented along the short (y-axis) and out-of-plane (z-axis) directions, and with a 100-Å-thick vacuum slab along the loading direction (x-axis) to prevent any interaction between the periodic images. The dimensions of a monolayer GO sheet used to construct GO papers were 5.4 x 2.5 nm in the x- and y-axes, respectively. Three epoxy groups and one hydroxyl group per twelve carbon atoms were randomly distributed on both sides of the graphene basal plane. Five carboxyl groups were attached to each of the GO sheet edges. These functional groups represent the typical chemical
compositions of GO papers studied previously [10]. Three models with different GO sheet stacking arrangements were built, as shown in Fig. 1. The first structure consisted of two monolayer GO sheets of the same size stacking on each other, representing a pure face-to-face interaction case (Fig. 1a). The second one was constructed by duplicating the first structure along the loading direction to introduce edge-to-edge interactions (Fig. 1b). These two structures represent the ordered stacking of GO sheets, in which edges interact only with edges and faces with faces. In the fabrication of GO papers, however, GO sheets are more likely to stack randomly rather than in such ordered structures. The brick-and-mortar arrangement shown in Fig. 1c therefore can better reflect the real structure of GO papers. For all three models, the interlayer distance was kept the same 6 Å according to previous findings [11, 12].

2.2 Simulation methods

MDSs were carried out using the program, Materials Studio (Accelrys). The Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field was used to simulate interatomic interactions. Simulations were carried out using the NPT (with a constant number of atoms, constant pressure and constant temperature) ensemble for equilibration and the NVT (with a constant number of atoms, constant volume and constant temperature) ensemble for the production run. The time step for all the simulations was set at 1 fs, unless otherwise specified. The Verlet algorithm was used for the integration of the Newton’s equation. The atom-based summation with a cut-off distance of 9.5 Å was used for Van der Waals interactions while the Ewald summation was used for electrostatic interactions.

2.3 Calculation of Young’s modulus

After initial minimization, the models were first relaxed by increasing the temperature from 0 to 300 K in a time span of 10 ps at a time step of 0.2 fs. Then, the temperature was kept constant at 300 K for another 40 ps for equilibrium of the structures. The stress-strain curves were obtained after equilibrium by imposing the strain to the structure and calculating the virial stress:

$$\sigma_{ij} = \frac{1}{V} \sum_{\alpha=1}^n \left( \frac{1}{2} m^\alpha \dot{v}_i^\alpha \dot{v}_j^\alpha + \sum_{\beta=1}^n r_{i\beta}^\alpha f_{i\beta}^\alpha \right) \quad (1)$$

where $i, j$ denote the indices in Cartesian coordinate systems; $\alpha$ and $\beta$ are the atomic indices; $m^\alpha$ and $v^\alpha$ are the mass and velocity of atom $\alpha$; $r_{i\beta}^\alpha$ and $f_{i\beta}^\alpha$ are the distance and force between atoms $\alpha$ and $\beta$, respectively; $V$ is the total volume of the system.

3 Results and Discussion

3.1 Formation mechanism of wrinkles in GO papers

Large amplitude of waviness was always observed in GO papers [10]. Apart from the contribution of the wrinkles in individual GO sheets, the interactions between them may play a key role in determining the structure and deformation behavior of GO papers because GO papers consist of numerous GO sheets. Typical structures and out-of-plane displacement profiles corresponding to three stacking structures given in Fig. 1 upon equilibrium at 300 K are shown in Fig. 2. It is found that the third structure (Fig. 2c) consisting of individual GO sheets stacked in the form of brick-and-mortar contained wrinkles with larger amplitude than the first two structures (Figs. 2a and b). In the first two structures, the faces interacted only with faces and the edges interacted only with edges due to the simple stacking, whereas the brick-and-mortar stacking configuration in the third structure introduced the mixed interactions between the faces and edges, causing ‘peak and valley’ undulation to the structure. The out-of-plane displacements reached the maximum when these combined interactions were most vigorous near the GO sheet edges (Figs. 2c). The undulation at the edges of GO sheets with pure edge-to-edge interaction (Fig. 2b) was also higher than that occurring on the basal plane. These observations strongly suggest that the edge-to-edge interactions contributed significantly to the degree of undulation in GO papers. Simple models with two sheets arranged in the edge-to-edge configuration and different degrees of functionalization were built in order to further explore the effect of edge-to-edge interactions on the degree of wrinkling in GO papers, as shown in Figs. 3a, c and e. The three models represent two graphene sheets without functional groups (Fig. 3a), with functional groups only on the basal plane (Fig. 3c) and with functional groups both on the basal plane and edges (Fig. 3e), respectively. Periodic boundary conditions were not applied so that
graphene/GO sheets could displace freely in the out-of-plane direction. The typical structures of the three models obtained after equilibrium are shown in Figs. 3b, d and f, respectively. It can be seen clearly that two graphene or GO sheets with edge-to-edge interactions were not a stable configuration. They all tried to form more stable configurations by minimizing their surface areas: For both the graphene sheets and GO sheets without edge carboxyl groups, they overlapped on top of each other to form more stable face-to-face interactions. The difference was that the surface functional groups on GO sheets hindered the full overlap which otherwise was the case of graphene sheets. In the presence of carboxyl groups at the edges, the GO sheets became seriously buckled in the perpendicular direction because the steric hindrance prevented them from overlapping.

We can concluded from the above observations that neighboring graphene or GO sheets initially placed in the edge-to-edge configuration always tended to form a more stable face-to-face configuration by either overlapping or buckling, depending on the degree of functionalization. This process was thermodynamically favorable due to the inherently lower potential energy of GO sheets in the face-to-face configuration than in the edge-to-edge configuration. Therefore, the appearance of ‘peak and valley’ undulations near the GO edges in the GO paper model (Figs. 2c) was likely due to the buckling of the two GO sheets in favor of the face-to-face interactions.

3.2 Effect of wrinkles on Young’s modulus of GO papers

The stress-strain curves of GO papers without and with wrinkles are shown in Figs. 4a and b, respectively. The stress-strain curve of GO papers without wrinkles was linear, whereas that of GO papers with wrinkles was divided into two regions. The moduli calculated from the two regions were 6.2 and 13.1 GPa respectively, both of which were much lower than the Young’s modulus of GO papers without wrinkles (~31.3 GPa). Such a nonlinear stress-strain curve of GO papers was commonly observed in the previous experimental studies [8, 13]. The significantly lower modulus at low strains than that obtained at higher strains probably arose from the gradual flattening of wrinkles at different length scales. However, no direct evidence was provided showing that the wrinkles in GO papers were indeed flattened upon initial loading and it was also unclear as to what extent the wrinkles affected the deformation behavior of GO papers. To address such issues, we show quantitatively how the Young’s modulus was affected by the wrinkles in GO papers. The total potential energies of GO papers without and with wrinkles are shown as a function of strain in Figs. 4c and d. The total potential energy of GO papers without wrinkles increased parabolically, in agreement with the linear response of the stress-strain curve. For GO papers with wrinkles, two distinct stages can be observed in the change of the total potential energy, corresponding to two regions in the stress-strain curve. The potential energy gradually decreased until the strain reached about 1.6 %, only to give a lower modulus in the stress-strain curve. After the initial loading, the potential energy oscillated to increase at strains beyond 1.6 %, indicating that more energy was needed to deform the GO papers, resulting in a higher modulus in the stress-strain curve.

During the tensile deformation of GO papers with wrinkles, the total potential energy of GO papers is comprised of two components: (i) the potential energy of GO sheets arising from the change in strain energy stored in the wrinkles; and (ii) the potential energy associated with inter-sheet interactions corresponding to the energy change due to the inter-sheet deformation taking place in the form of relative displacement between the adjacent individual GO sheets. The two energy components are plotted together with the total potential energy as a function of strain in Fig. 5. The strain energy stored in wrinkles decreased at an almost constant rate, indicating the continuous flattening of wrinkles over the whole loading stage. The energy associated with the inter-sheet interactions remained negligible until the strain reached about 1.0 %, indicating small or negligible inter-sheet deformation in the initial stage of loading. This means that the deformation in the initial stage arose mainly from the flattening of wrinkles, requiring little energy and thus the much lower modulus. In the second stage, the energy associated with the inter-sheet interactions increased more rapidly, dominating the whole deformation of GO papers. Summing the two energy components, the total potential energy required to deform the GO papers started to pick up at about 1.6 %, resulting in a higher Young’s modulus (Fig. 4b). Noting that the
flattening of wrinkles and the inter-sheet deformation took place simultaneously, the release of strain energy stored in the wrinkles reduced the total energy required for deformation, inevitably leading to a much lower Young’s modulus of GO papers with wrinkles than that without. This observation agrees well with the experimental report [10] that the Young’s modulus of GO papers increased with increasing the size of precursor GO sheets through better structural alignment with less wrinkling.

4 Conclusion

The formation mechanisms of wrinkles and their effects on Young’s modulus of GO papers have been investigated using the MDSs. Major wrinkles or undulations in GO papers are formed due to the interactions between adjacent GO sheets. GO sheets initially placed in the edge-to-edge configuration tend to form a more stable face-to-face configuration by buckling in the presence of edge carboxyl groups, creating ‘peak and valley’ undulations. As a result, two different deformation modes are observed in the structures of GO papers, depending on the applied strain. The Young’s modulus of GO papers is significantly affected by wrinkles. The modulus obtained at high strains of GO papers with wrinkles is only 40% that without wrinkles. This is because the loads on individual GO sheets in GO papers are transferred between adjacent sheets predominantly by shear force, which is often too low to fully straighten the wrinkles before the initiation of the inter-sheet deformation.

Although wrinkles are detrimental to the functional and mechanical properties of GO papers, GO papers without wrinkles cannot be produced in practice. Several implications of the findings in this study can help minimize the effect of wrinkles. They include: (i) the degree of wrinkling can be significantly reduced by minimizing the presence of edges in GO papers; and (ii) wrinkles can be fully flattened if the inter-sheet interactions are improved in GO papers. A few practical methods have been suggested for reducing the degree of wrinkling in GO papers, including the use of large size GO sheets [10] and improved inter-sheet stress transfer by chemical cross-linking of GO sheets [14,15].
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Fig 1. 3D atomistic models and 2D schematics of GO papers with (a) face-to-face interaction; (b) edge-to-edge interaction; and (c) combined interactions.
Fig 2. Structures of GO paper models with different stacking arrangements given in Fig. 1, and the corresponding out-of-plane displacement profiles after equilibrium.

Fig 3. Models with two sheets arranged in the edge-to-edge configuration: (a) two graphene sheets without functional groups; (c) two GO sheets with functional groups on basal plane; and (e) two GO sheets with functional groups both on basal plane and edges. The corresponding structures after equilibrium are shown in b, d and f, respectively.
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Fig. 4. Stress-strain curves of GO paper models (a) without and (b) with wrinkles (solid lines are linear fit of the data); and energy-strain curves of GO paper models (c) without and (d) with wrinkles (solid lines are only guides to the eyes).

Fig. 5. Plots of two energy terms along with the total potential energy as a function of strain. Solid lines are only guides to the eyes.

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