Strain-dependent elastic properties of graphene oxide and its composite

Z.M. Xia[a,b], C.G. Wang[a,b,*], H.F. Tan[a,b]

[a] Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, PR China
[b] National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, PR China

A B S T R A C T

This paper investigates the effect of hydroxyl groups on elastic properties of graphene oxide (GO) and its composites. A strain-dependent pseudo crease model considering the effects of out-of-plane initial strain and geometric configuration is proposed to predict the elastic modulus of GO, combining with a homogenization method. The results show that the elastic modulus of GO varies from 0.214 TPa to 0.463 TPa as tensile strain increases from 0 to 0.07. Further, considering GO as a rectangular inclusion and using the Mori-Tanaka method, the elastic properties of GO composites are predicted by taking aspect ratio and mass fraction of GO into account. Our study provides an effective method to evaluate the effects of functional groups on elastic modulus of GO and to understand the effect of microstructural parameters of GO on elastic properties of GO composites.

1. Introduction

Graphene oxide (GO) is a promising candidate as a component in nanomechanical devices [1] and polymer composites [2–4], due to its outstanding mechanical properties. 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 [5,6]. The atomic level ripples can be induced by the functional groups, which alter many intrinsic physical properties of GO [7–12].

In particular, these ripples strongly perturb the mechanical properties of GO [13] and soften its in-plane stiffness [14,15] compared with the elastic modulus (~1.0 TPa) of pristine graphene [16–18]. By using the molecular dynamics simulations, Shen et al. [19] studies show that the ripples reduce the elastic modulus of GO papers up to 60%. By the first-principles computations, Liu et al. [20] obtained the elastic modulus varies from 380 to 470 GPa for the ordered GO and varies from 290 to 430 GPa for the amorphous GO. Based on atomic force microscopy (AFM) technology, Suk et al. [21] obtained a lower elastic modulus (207.6 ± 23.4 GPa) of monolayer GO, combined with the finite element method. Robinson et al. [22] measured the elastic modulus (185 GPa) of reduced GO films for nanomechanical resonators. Gómez-Navarr et al. [23] measured the elastic modulus (250 GPa) of monolayer chemically derived GO.

The above simulation and experiment studies have shown that the ripples would reduce the mechanical properties of GO. However, how exactly do these ripples affect the mechanical response of GO? In fact, relatively little is known about its detailed influence mechanism. In addition, there is still only limited knowledge about theoretical prediction of effects of GO microstructural parameters on mechanical behavior of GO composites [24]. To address the above issues, here we first study and extract the detailed morphology features of ripple induced by the hydroxyl groups. Based on the characteristics of initial strain and out-of-plane configuration, a pseudo crease model is proposed to predict the elastic modulus of GO, combined a homogenization method. Further, considering GO as a rectangular inclusion, the elastic properties of GO composites are predicted in the Mori-Tanaka micromechanics scheme, and the effects of tensile strain, mass fraction and aspect ratio of GO on the elastic properties of GO composites are discussed.

2. Prediction of the elastic modulus of graphene oxide

Aromatic entities, double bonds and epoxide groups in GO give rise to a nearly flat carbon grid [25,26], only the carbons attached to hydroxyl groups are in a tetrahedral configuration, which makes GO look like a ripple structure [27], as shown in Fig. 1(a). So this paper discusses emphatically the effects of ripple induced by the hydroxyl group on the elastic properties of GO.

The hydroxyl groups almost exist in pairs in GO [27]. Firstly, we use the Materials Studio 8.0 software (MS) to establish the model that a pair of hydroxyl groups are appended on the center of a large enough graphene sheet (GS). By using forcite module in which COMPASS force field and geometry optimization algorithm are chosen, single ripple induced by a pair of hydroxyl groups can be obtained, as shown in Fig. 1(b). The outlines of side section displayed by the purple solid line look like a pseudo crease. During a tensile simulation, the first stage of
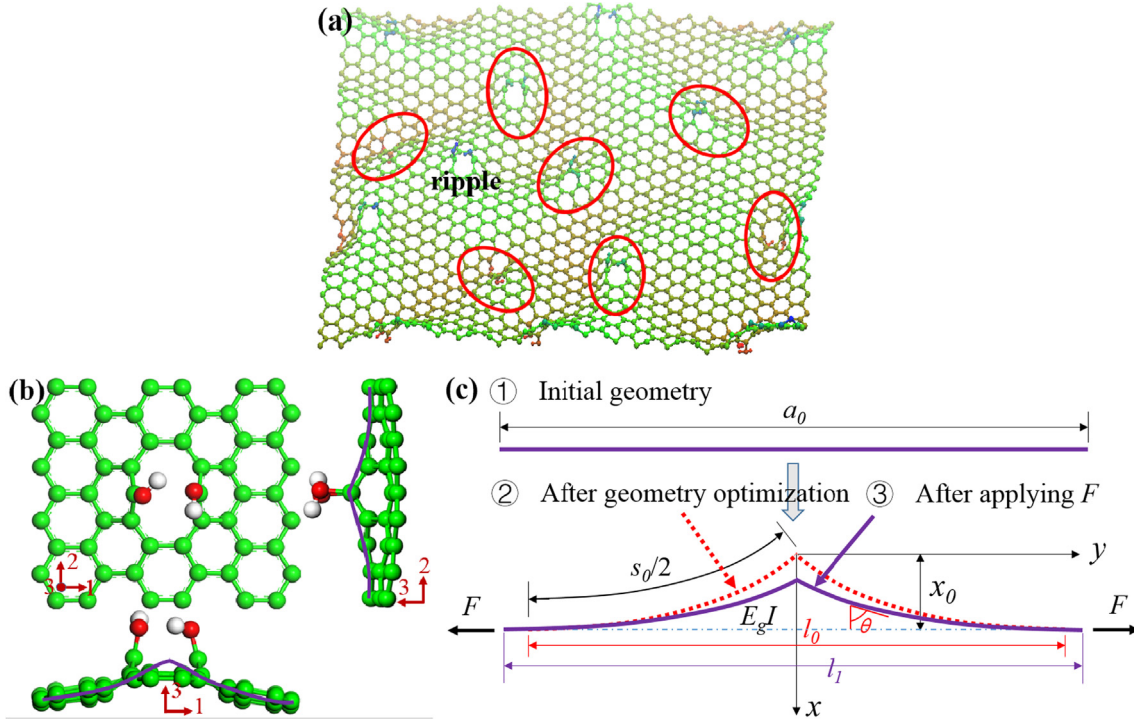
Fig. 1. (a) The ripple configuration of GO; (b) the geometrical morphology of single ripple; (c) the description of the pseudo crease model.

the deformation is the straightening or flattening of ripple and the second stage is the stretching of carbon–carbon bonds [6], which is consistent with unfolding of the macroscopic crease [28].

Based on the above description, a one-dimensional pseudo crease model is proposed, as described in Fig. 1(c). The initial length of the model is a_0, and the length and the arc length after geometry optimization is respectively noted as l_0 and s_0. So the initial strain can be calculated by $\varepsilon_0 = (s_0 - a_0)/a_0$, which can be equivalently considered as the strain caused by a pseudo tensile loading F_0. After applying the external tensile loading F_1, the length of the model changes to l_1. The length variation Δl is obtained by $\Delta l = l_1 - l_0$. In the range of elastic deformation, $\sin\theta = 1 - \frac{F}{2E_gI}(x - x_0)^2$ can be easily deduced when the loading F is applied, where θ and E_gI is the inclined angle between vertical line and tangent line and the bending stiffness of graphene, respectively. Further Δl can be expressed as [29]

$$\Delta l = 2\int_0^{x_0} \sqrt{\frac{1-\sin\theta}{1+\sin\theta}}\, dx = 2(\sqrt{2}-1)\sqrt{\frac{2E_gI}{F}} \tag{1}$$

where $F = F_0 + F_1 = E_g(\varepsilon_0\cos\theta + \varepsilon_e)t$, t and ε_e is respectively the thickness of graphene and the tensile strain generated by the external tensile loading F_1.

The elastic response $E_{pseudo.crease}$ of GO due to the out-of-plane configuration of ripple is

$$E_{pseudo,crease} = \left(\frac{1}{l_0}\frac{\partial \Delta l}{\partial \sigma}\right)^{-1} \tag{2}$$

The existing study has shown that not only out-of-plane configuration but also initial strain can alter the elastic response of graphene [30–33]. When the out-of-plane initial strain exceeds 0.5%, the elastic modulus of graphene reaches 2.06 TPa, considering the thickness 0.34 nm of graphene [30]. The above simulated results show the initial strain indeed exists in the region of ripple. The out-of-plane initial strain along direction 1 and along direction 2 can be calculated as 1.7% and 1.2% respectively, so the elastic modulus of GO after considering out-of-plane initial strain is 2.06 TPa. The elastic modulus of single ripple is further calculated as $(E^{uc})^{-1} = E_g^{-1} + E_{inital,strain}^{-1} + E_{pseudo,crease}^{-1}$ [15]. Substituting Eq. (2) into the

equation, it can be obtained as

$$E^{uc} = \left\{ \frac{1}{E_g} + \frac{1}{E_{inital,strain}} + \frac{\sqrt{2}-1}{\sqrt{6}}\frac{t}{l_0}\sqrt{\frac{1}{E_g^2(\varepsilon_0\cos\theta + \varepsilon_e)^3}} \right\}^{-1} \tag{3}$$

where E_g represents the elastic modulus of pristine graphene, 1.025 TPa.

For determining the elastic modulus of single ripple, the relationship between tensile strain and θ is calculated firstly by using MD simulations, as shown in Fig. 2(a). Substituting the above data into Eq. (3), the strain-dependent elastic modulus of single ripple can be obtained, as shown in Fig. 2(b). As the tensile strain increases from 0 to 0.07, the elastic modulus E_1^{uc} of single ripple along direction 1 increases from 0.232 TPa to 0.603 TPa. The elastic modulus of single ripple along direction 1 is slightly larger than its elastic modulus along direction 2, which shows that the ripple makes the structure non-isotropic. Here we assume the ripple is orthotropic. In addition, the Possion' ratio and shear modulus of single ripple are also calculated as follows, $\nu_{21} = 0.16$, $\nu_{12} = 0.15$, $G_{12} = 0.13$ TPa.

Because the carboatomic ring is a regular hexagon, there are three kinds of possible arrangement directions for hydroxyl groups, as shown in Fig. 3(a). The generated ripple is marked as *a*, *b* and *c* orderly. For obtaining the elastic properties of GO, the strain–stress relationship of each ripple should be transformed into the loading direction using the off-axis formulas. Here the loading direction is assumed along x axis, as shown in Fig. 3(b). The elastic modulus of ripple *a* along direction 1 and along direction 2 is that $E_x^a = E_1^{uc}$ and $E_y^a = E_2^{uc}$. The flexibility matrix S_a under the plane stress state is easily obtained as

$$S_a = \begin{bmatrix} S_{11}^a & S_{12}^a & 0 \\ S_{21}^a & S_{22}^a & 0 \\ 0 & 0 & S_{66}^a \end{bmatrix} \tag{4}$$

where $S_{11}^a = 1/E_x^a$, $S_{22}^a = 1/E_y^a$, $S_{12}^a = \nu_{12}/E_y^a$, $S_{66}^a = 1/G_{12}$.

The strain–stress relationship of ripple *b* needs to be transformed as

$$\begin{bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \end{bmatrix} = T^T S_a T \begin{bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{bmatrix} = S_b \begin{bmatrix} \sigma_x \\ \sigma_y \\ \tau_{xy} \end{bmatrix} \tag{5}$$