EFFECTS OF GRAPHENE MASS FRACTION AND ASPECT RATIO ON ELASTIC PROPERTIES OF GRAPHENE-BASED COMPOSITES

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ABSTRACT

Graphene-based nanocomposites have attracted tremendous research interest over the past decade due to the unique mechanical properties of graphene as the reinforcement plays an important role in these applications. First, this paper presents an equivalent discrete model (a pseudo-beam model) to accurately predict the elastic properties of graphene, including the Young's modulus and Poisson's ratio. A pseudo-beam with modified internal bending moment and variable stiffness is used to represent the C-C bond. By calculating the deformation strain energies of unit cell, the parameter equivalence relationships between C-C bond and pseudo-beam are established. Further, the pseudo-beam model is deduced based on the above energies equivalence combining Castigliano second theorem. By choosing the appropriate force field constants, the Young's modulus and Poisson's ratio of graphene are calculated compared with the open literatures, which verifies the availability and accuracy of the pseudo-beam model. Then, considering that graphene is regarded as a rectangular inclusion, the averaged Eshelby's tensor for a rectangular shape in different aspect ratios is obtained, which parameters can be determined by the properties of graphene predicted based on the above model. Further, the elastic properties of graphene-based composites are predicted based on the Mori–Tanaka micro-mechanics scheme. The effects of aspect ratio and mass fraction of graphene on the elastic properties of graphene-based composites are discussed. Our work can guide the designer to accurately evaluate the elastic properties of graphene-based composites for further applications.

1 INTRODUCTION

Determining the fundamental mechanical properties of graphene sheet (GS) accurately is required for their further applications [1]. Several attempts have been employed, including experiments, theoretical models and computational simulations. Considering the difficulty of exact experimental measurements limited by testing technology and the time-consuming of computational simulations, an efficient theoretical model is expected to accurately predict the mechanical properties of GS.

Currently one class of equivalent discrete model (EDM) is considered as a very efficient and promising technology. The basic idea of EDM is to establish the link between chemical potentials of covalent bond and strain energies of beam, pioneered by [2]. Based on this model, several modified models have been further presented [3-6]. The core of the above efforts is to capture a more accurate energy equivalent relationship between C-C covalent bond and beam element by adjusting beam parameters.

But in the above modification models, the bending strain energy of beam is obtained using pure bending theory regardless of the real load conditions in the process of energy equivalence, which is impractical obviously. Based on this standpoint, a pseudo-beam model is presented, in which the strain energies of beam are calculated according to the real load conditions and a kind of variable stiffness beam is also introduced, which has been successfully applied [7].

As an interesting reinforcement-graphene sheet, the graphene-based composites are widely studied and applied [8]. However, currently for determining its elastic properties, the research on the Eshelby's tensor for the GS considering its real geometrical morphology is relative few. Here combining the irreducible decomposition of the Eshelby's tensor by [9, 10] with a rectangular aspect ratio, the reinforcement GS as a rectangular inclusion is introduced to determine the elastic properties of graphene-based composites in the Mori-Tanaka micro-mechanics scheme.

The paper is structured as follows. In Section 2, a pseudo-beam model is presented to obtain the elastic properties of GS based on deformation strain energies of unit cell. In Section 3, the effective elastic moduli of graphene-based composites are obtained based on the Eshelby's tensor for a rectangular inclusion. In Section 4, the effects of aspect ratio and mass fraction of graphene on the elastic properties of Graphene-based composites are discussed. Finally, the paper ends up with some concluding remarks in Section 5.

2 A PSEUDO-BEAM MODEL ON ELASTIC PROPERTIES OF GRAPHENE

2.1 A pseudo-beam model

In this section, a pseudo-beam is proposed to represent the C-C bond. For clarity of the paper, the parameter symbols of model are defined ahead. The unit cell is chosen as shown in Fig.1a, including beam *a*, beam *b*, and beam *c*. The axial elongation, torsion angle variation and beam included angle variation of three beams are marked as Δr_a, Δr_b, Δr_c, $\Delta\tau_a$, $\Delta\tau_b$, $\Delta\tau_c$, and $\Delta\theta_{ab}$, $\Delta\theta_{bc}$, $\Delta\theta_{ca}$ respectively. It can be obtained that $\Delta r_a = 4\Delta r_b = 4\Delta r_c$, $\Delta\tau_a = 4\Delta\tau_b = 4\Delta\tau_c$, $\Delta\theta_{bc} = 2\Delta\theta_{ab} = 2\Delta\theta_{ca}$. The variable stiffness beam consists of one long beam (LB) and two short beams (SB). As stated, $E_1A_1 = E_2A_2$, $G_1J_1 = G_2J_2$ and one assumption is made that the bending stiffness of LB is n times as big as one of SB, $E_1I_1 = nE_2I_2$. The length of LB, L_1, is r times as long as one of the whole beam, L =0.142nm. The subscript 1 represents LB and 2 represents SB.

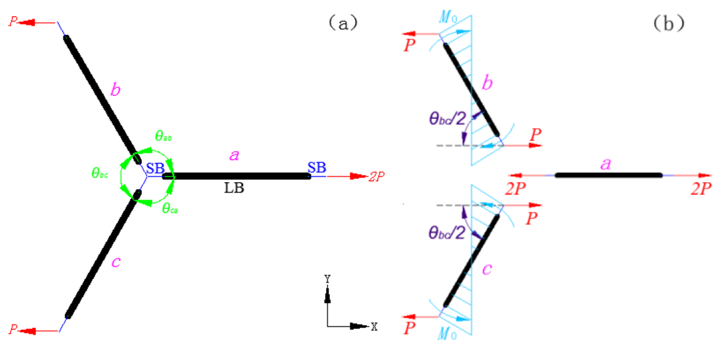


Figure 1: (a) The description of unit cell model, (b) The free-body diagram of unit cell

The total strain energy of unit cell is the sum of strain energies due to axial, torsion and bending deformation. Each strain energy is as follow in sequence.

$$U_A^{uc} = \frac{9}{16}\frac{E_1A_1}{L}\left(\Delta r_a\right)^2 \quad U_T^{uc} = \frac{9}{16}\frac{G_1J_1}{L}\left(\Delta\tau_a\right)^2 \quad U_B^{uc} = \frac{3}{2}\frac{E_1I_1}{L\left[r^3+n(1-r^3)\right]}\left(\Delta\theta_{bc}\right)^2 \tag{1}$$

From the point of molecular mechanics, the dominant contributions to the total chemical potential energy of unit cell are calculated by summing up the respective contributions from three C-C bonds. The energies of unit cell due to bond stretch interaction, combined dihedral angle and out-of-plane torsion, bond angle variation can be obtained as in sequence.

$$U_r^{uc} = \frac{9}{16}k_r(\Delta r_a)^2 \quad U_\tau^{uc} = \frac{9}{16}k_\tau(\Delta\tau_a)^2 \quad U_\theta^{uc} = \frac{3}{4}k_\theta(\Delta\theta_{bc})^2 \tag{2}$$

where k_r, k_τ and k_θ are respectively the force constants related to bond stretching, torsional and bending stiffness.

Using energy equivalence, the relationship between the pseudo-beam parameters and molecular mechanics force field constants can be established as

$$\frac{E_1A_1}{L}=k_r \qquad \frac{2E_1I_1}{[r^3+n(1-r^3)]L}=k_\theta \qquad \frac{G_1J_1}{L}=k_\tau \tag{3}$$

Further the beam parameters E_1, G_1, D_1 can be deduced.

$$E_1=\frac{2}{[r^3+n(1-r^3)]}\frac{k_r^2L}{4\pi k_\theta} \qquad G_1=\frac{4}{[r^3+n(1-r^3)]^2}\frac{k_r^2k_\tau L}{8\pi k_\theta^2} \qquad D_1=\sqrt{\frac{[r^3+n(1-r^3)]}{2}}4\sqrt{\frac{k_\theta}{k_r}} \tag{4}$$

where $r^3+n(1-r^3)$ are called the bending modified coefficient.

According to the front stiffness relationship between LB and SB, E_2, G_2, D_2 can be obtained further. Based on this, the bridge between pseudo-beam properties and C-C bond force field constants is established.

2.2 Young's modulus and Poisson's ratio of GS

Based on the above analysis, the Young's modulus and Poisson's ratio of graphene is further deduced. Here the armchair GS is taken for example. Considering the force and moment in the unit cell shown in Fig. 1b, the strain energy U_r^a due to the axial deformation of beam *a* and the strain energy due to the axial and bending deformation of beam *b* can be deduced as

$$U_r^a=\frac{(2P)^2L}{2E_1A_1} \qquad U_r^b=\frac{\left(P\cos(\theta_{bc}/2)\right)^2L}{2E_1A_1} \qquad U_\theta^b=\frac{\left(P\sin(\theta_{bc}/2)\right)^2L^3}{24E_1I_1}\left[r^3+n\left(1-r^3\right)\right] \tag{5}$$

The axial deflections Δ_r^a and the horizontal deflections due to axial deformation Δ_r^b and bending deformation δ_θ^b of beam *b* can be obtained using Castigliano' second theorem as

$$\Delta_r^a=\frac{2PL}{E_1A_1} \qquad \Delta_r^b\cos(\theta_{bc}/2)=\frac{P\cos^2(\theta_{bc}/2)L}{E_1A_1} \qquad \delta_\theta^b\sin(\theta_{bc}/2)=\frac{P\sin^2(\theta_{bc}/2)L^3[r^3+n(1-r^3)]}{12E_1I_1} \tag{6}$$

The horizontal and vertical strains of the structure can be calculated as

$$\varepsilon_x=\frac{\Delta_r^a+\Delta_r^b\cos(\theta_{bc}/2)+\delta_\theta^b\sin(\theta_{bc}/2)}{L(1+\cos(\theta_{bc}/2))} \qquad \varepsilon_y=\frac{\Delta_r^b\sin(\theta_{bc}/2)-\delta_\theta^b\cos(\theta_{bc}/2)}{L\sin(\theta_{bc}/2)} \tag{7}$$

Using the results in Eq. (3) and substituting $\theta_{bc}/2=\pi/3$, the Young's modulus and Poisson's ratio of graphene are obtained as follows.

$$E_g=\frac{P}{tL\sin(\theta_{bc}/2)\varepsilon_x}=\frac{8\sqrt{3}}{t}\frac{k_rk_\theta}{k_rL^2+18k_\theta} \qquad \upsilon_g=-\frac{\varepsilon_y}{\varepsilon_x}=\frac{k_rL^2-6k_\theta}{k_rL^2+18k_\theta} \tag{8}$$

where *t* is the thickness of graphene. Similarly, the Young's modulus and Poisson's ratio of zigzag GS can be deduced, which are same as the results of armchair GS.

Assuming that the GS is transverse isotropic, for the case of in-plane stress, it can easily obtain the following relationship between the stress and strain.

$$\begin{Bmatrix}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{Bmatrix}=\frac{E_g}{1-\upsilon_g^2}\begin{bmatrix}1 & \upsilon_g & 0\\ \upsilon_g & 1 & 0\\ 0 & 0 & \left(1-\upsilon_g\right)/2\end{bmatrix}\begin{Bmatrix}\varepsilon_x\\ \varepsilon_y\\ \gamma_{xy}\end{Bmatrix} \tag{9}$$

For simplifying the writing, the above equation can be rewrited to $\boldsymbol{\sigma}_g=\mathbf{L}_g\boldsymbol{\varepsilon}_g$.

Herein, the thickness *t* is assumed to equal with the interlayer spacing of graphite (0.34nm) in the majority of the studies. Meanwhile, taking the commonly used force constants [11-12] as: $k_r/2=469$ kcal/mol/nm^2, $k_\theta/2=63$ kcal/mol/rad^2. Then the elastic constants of GS can be obtained using Eq. (8). The Young's modulus E_g is 0.805TPa and the Poisson's ratio υ_g is 0.273. Table 1 compares the present prediction along with data from the open literatures. Substituting these two values into Eq. (9), the stiffness tensor $\mathbf{L}_\mathrm{g}$ can be further determined.

Reference	E_g (TPa)	υ_g
Present study	0.805	0.273
Refer. [2]	1.03	0.066
Refer. [6]	0.804	0.273
Refer. [13]	0.833	0.357
Refer. [14]	0.725	0.397

Table 1: Comparison of elastic properties of GS by the proposed model and other open results.

3 ELASTIC PROPERTIES OF GRAPHENE-BASED COMPOSITES

3.1 Eshelby's tensor for the rectangular GS

For two-dimensional isotropic material, the averaged Eshelby's tensor for an arbitrary inclusion shape is expressed

$$\mathbf{S}{=}\mathbf{S}_0{+}\mathbf{S}_\mathrm{e} \tag{10}$$

where $\mathbf{S}_0$ and $\mathbf{S}_\mathrm{e}$ represents the Eshelby's tensor of an unit circle and the Eshelby's tensor of intersection parts between the inclusion boundaries and the unit circle respectively. Their specific expressions are as follows by [9].

$$\mathbf{S}_0=\frac{1}{8(1-\upsilon)}\begin{bmatrix}5-4\upsilon & 4\upsilon-1 & 0\\ 4\upsilon-1 & 5-4\upsilon & 0\\ 0 & 0 & 3-4\upsilon\end{bmatrix} \tag{11}$$

$$\mathbf{S}_w=\frac{1}{(1-\upsilon)}\begin{bmatrix}(1-\upsilon)p_2+p_4 & \upsilon p_2-p_4 & \frac{(1-2\upsilon)}{2}q_2+q_4\\ -\upsilon p_2-p_4 & -(1-\upsilon)p_2+p_4 & \frac{(1-2\upsilon)}{2}q_2-q_4\\ \frac{1}{2}q_2+q_4 & \frac{1}{2}q_2-q_4 & -p_4\end{bmatrix} \tag{12}$$

Considering a rectangular inclusion of size ($2a\times 2b$) with $a\geq b$ and $a^2{+}b^2{=}1$, the sides are set to be parallel to the orthonormal basis vectors respectively, the expressions about p_2, q_2, p_4, q_4 can be obtained as follows. $p_2=\frac{2}{\pi}\left(\arctan\eta-\frac{\pi}{4}\right)-\frac{1}{2\pi\eta}\ln\left(1+\eta^2\right)+\frac{1}{2\pi}\ln\left(\frac{1+\eta^2}{\eta^2}\right)$, $p_4=-\frac{1}{8}+\frac{1}{4\pi\eta}\ln\left(1+\eta^2\right)+\frac{\eta}{4\pi}\ln\left(\frac{1+\eta^2}{\eta^2}\right)$, $q_2{=}0$ and $q_4{=}0$ [15]. Substituting the elastic constants of GS, the Eshelby's tensor $\mathbf{S}_0$ and $\mathbf{S}_\mathrm{e}$ can be determined for different aspect ratio η, $\eta{=}b/a$.

3.2 Elastic modulus of graphene-based composites

Assuming that the GS inclusions are ideally distributed in the polymer matrix, the Mori-Tanaka micro-mechanics is used to predict the elastic moduli of graphene-based composites. According to the Eshelby's equivalent inclusion theory, the averaged strain $\boldsymbol{\varepsilon}_g$ of the GS inclusion is obtained as

$$\boldsymbol{\varepsilon}_g{=}\mathbf{A}_g\boldsymbol{\varepsilon}_m \tag{13}$$

where $\mathbf{A}_g$ is the strain concentration tensor expressed by

$$\mathbf{A}_g=\left[\mathbf{I}+\mathbf{S}\mathbf{L}_m^{-1}\left(\mathbf{L}_g-\mathbf{L}_m\right)\right]^{-1} \tag{14}$$

where $\mathbf{I}$ and $\mathbf{S}$ represent the identity tensor and the Eshelby's tensor, respectively. The averaged stress $\bar{\boldsymbol{\sigma}}$ and strain tensor $\bar{\boldsymbol{\varepsilon}}$ of graphene-based composites are obtained by

$$\bar{\boldsymbol{\sigma}} = V_g\boldsymbol{\sigma}_g + V_m\boldsymbol{\sigma}_m \qquad \bar{\boldsymbol{\varepsilon}} = V_g\boldsymbol{\varepsilon}_g + V_m\boldsymbol{\varepsilon}_m \tag{15}$$

where V_g and V_m represent the identity tensor and the Eshelby's tensor, respectively.

Substituting Eq. (13) and $\boldsymbol{\sigma}_m = \mathbf{L}_m\boldsymbol{\varepsilon}_m$ into Eq. (15), we can obtain

$$\bar{\boldsymbol{\sigma}} = \left(V_g\mathbf{L}_g\mathbf{A}_g + V_m\mathbf{L}_m\right)\boldsymbol{\varepsilon}_m \tag{16}$$

The relationship between the stress and the strain for the homogenised graphene-based composites can be defined as

$$\bar{\boldsymbol{\sigma}} = \mathbf{L}\bar{\boldsymbol{\varepsilon}} = \mathbf{L}\left(V_g\mathbf{A}_g + V_m\mathbf{I}\right)\boldsymbol{\varepsilon}_m \tag{17}$$

So it can be easily obtained that

$$\mathbf{L} = \left(V_g\mathbf{L}_g\mathbf{A}_g + V_m\mathbf{L}_m\right)\left(V_g\mathbf{A}_g + V_m\mathbf{I}\right)^{-1} \tag{18}$$

where $V_g = \dfrac{\rho_m M_g}{\rho_g M_m + \rho_m M_g}$, $V_m = \dfrac{\rho_g M_m}{\rho_g M_m + \rho_m M_g}$, $\left(\rho_{c,g,m}\right)$ denotes the density of composites, graphene, and matrix, respectively.

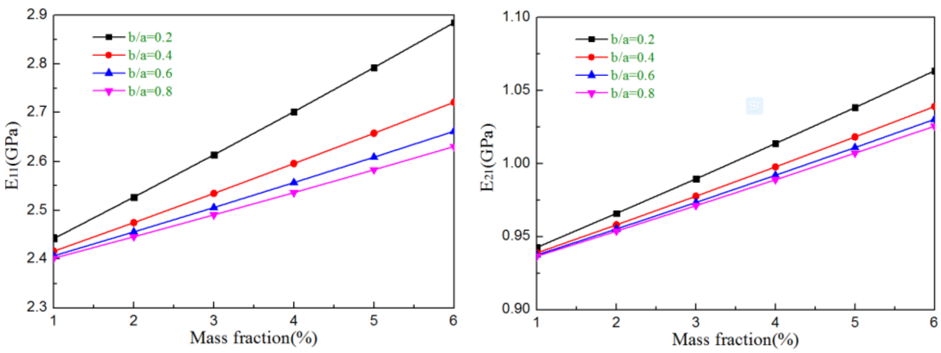
4 RESUTLS AND DISCUSSION

Here the material properties of GS and polymer are listed in Table 2.

Properties		GS	Polymer matrix
E	[TPa]	0.805	0.002
υ	–	0.273	0.39
ρ	[g/cm^3]	1.06	1.13

Table 2: Material properties of GS and polymer.

Using the data in Table 2, the stiffness tensor $\mathbf{L}$ of graphene-based composites can be calculated for different mass fractions and aspect ratios. The relationship between the components of the stiffness tensor and the mass fractions are shown in Fig. 2. From Fig. 2, it can be easily obtained that the components, including E_{11}, E_{22}, E_{12} and E_{21}, increase with the increase of the mass fraction. The components E_{11} and E_{21} decrease with the increase of the aspect ratios η. However the components E_{12} and E_{22} increase with the increase of the aspect ratios η. Whilst, the anisotropic degree can be obtained. With the increase of the aspect ratios η, the material properties trend to the isotropic behaviour. It is easy to understand that the inclusion trends to square as the aspect ratios η varies from 0.2 to 0.8.



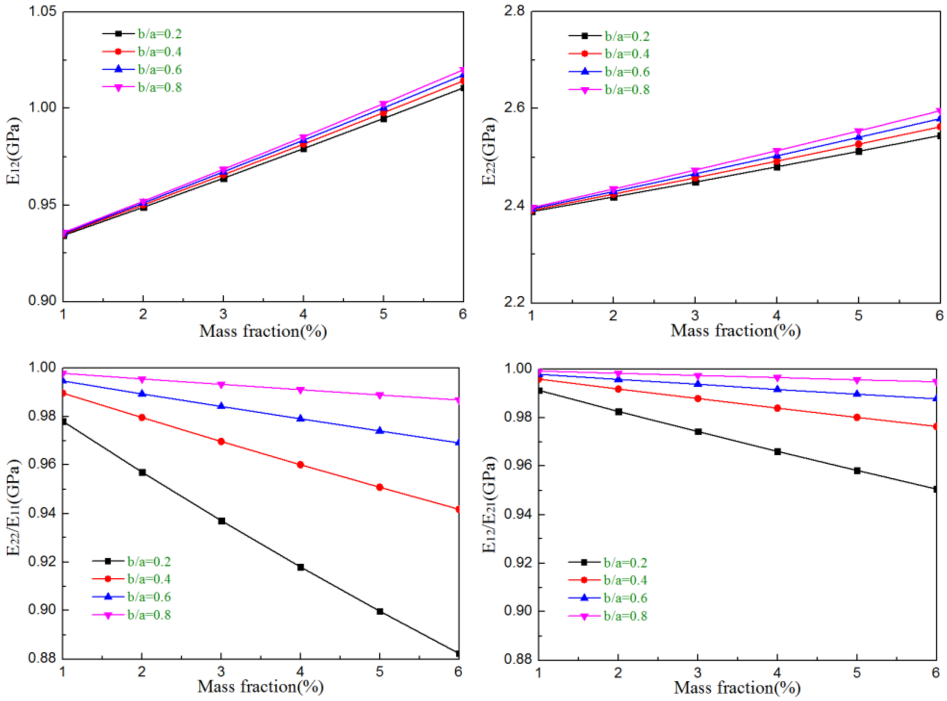


Figure 2: The influence of mass fractions on different components of stiffness tensor E

5 CONCLUSION

A pseudo-beam model is proposed to accurately predict the elastic properties of GS. In the model, the C-C bond is represented by a variable stiffness and modified internal bending moment pseudo-beam. Using the deformation energy equivalence of unit cell and combing the Castigliano' second theorem, the Young's modulus and Poisson's ratio of GS are deduced. By choosing the proper force field constants, the Young's modulus and Poisson's ratio of GS is predicted as 0.805TPa and 0.273 respectively. To determine the elastic properties of graphene-based composites, GS are considered as the rectangular inclusion and the irreducible decomposition of the Eshelby's tensor for a rectangular inclusion shape is used. In the scheme of the Mori-Tanaka micro-mechanics, the effective stiffness tensor are obtained for different mass fractions and aspect ratios. The results show that the stiffness tensor is enhanced with the increase of mass fractions and the degree of anisotropy is decreased with the increase of the aspect ratio. This study may help to further understand how to establish the relationship of relative accurate energy equivalence in the process of determining the elastic properties of GS. Also it may offer a guide on the influence of the GS on the elastic properties of the graphene-based composites.

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