



Molecular dynamics simulation on interfacial mechanical properties of polymer nanocomposites with wrinkled graphene



Feng Liu ^{a,b}, Ning Hu ^{b,c,d,*}, Huiming Ning ^c, Yaolu Liu ^c, Yuan Li ^e, Liangke Wu ^c

^a State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, Hunan University, Changsha 410082, China

^b Department of Engineering Mechanics, College of Mechanical and Vehicle Engineering, Hunan University, Changsha 410082, China

^c College of Aerospace Engineering, Chongqing University, Chongqing 400044, China

^d Department of Mechanical Engineering, Chiba University, Chiba City 263-8522, Japan

^e Department of Nanomechanics, Tohoku University, Sendai 980-8579, Japan

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ABSTRACT

Interfacial mechanical properties between nanofiller and matrix in various nanocomposites are extremely important for the load transfer capability between the nanofiller and the matrix. In this study, molecular dynamics (MD) simulations were carried out to investigate the interfacial mechanical properties of polyethylene (PE) and poly (methyl methacrylate) (PMMA) polymer nanocomposites reinforced by graphene. The influences of graphene wrinkles, matrix type, polymer chain length, and pull-out velocity of graphene sheet (GR) on the interfacial mechanical properties were systematically explored. The results show that compared with a flat GR, a wrinkled GR can effectively enhance the interfacial mechanical properties. The pull-out velocity of wrinkled GR has a great impact on the interfacial mechanical properties of both the GR/PE and GR/PMMA nanocomposites. The influence of the polymer molecule chain length on the interfacial mechanical properties is small in the GR/PE system, but very significant in the GR/PMMA system.

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1. Introduction

Graphene is an advanced 2-dimensional material due to its sp^2 -hybridized carbon systems and unique honeycomb structure. Since a single graphene sheet was fabricated in 2004 [1], it has attracted tremendous attention from both academic and engineering communities, and many previous studies on the graphene sheet show that it has extraordinarily outstanding mechanical and electrical properties [2–5]. For instance, Lee et al. [6] measured the elastic properties and intrinsic breaking strength of graphene membranes by using nanoindentation in an atomic force microscope. Their experimental results show that the Young's modulus is 1.0 TPa and the intrinsic breaking strength is 130 GPa. Liu [7] also obtained the similar mechanical properties by using density functional perturbation theory. Besides the above stated outstanding mechanical properties, compared with carbon nanotubes (CNTs), graphene has a much larger specific surface area, leading to larger bonding surface with polymer matrix. Therefore, it is

usually used as filler to enhance the mechanical properties of polymer materials.

To date, a large number of theoretical and experimental studies have demonstrated that addition of small amounts of graphene sheets can dramatically improve polymer matrix's mechanical properties [8–12] and thermal properties [13]. For instance, as pointed out in Rafiee et al. [9], by adding 0.1 wt.% graphene to fabricate a nanocomposite, its strength and the stiffness are the same as those of a nanocomposite using 1.0 wt.% CNTs. Rafiee et al. [10], Montazeri and Rafii-Tabar [11] found that, in the perspective of mechanical properties, polymer-based nanocomposites with graphene sheets are superior to those with CNTs. Moreover, as for resistance of fatigue crack propagation, an increase of around two orders of magnitude was observed in the nanocomposites reinforced by graphene compared with pristine polymers [12]. Based on MD simulations, Mortazavi et al. [13] found that the thermal conductivity of single layer graphene decreased by around 30% in epoxy matrix for two different hardener chemicals. In order to investigate the thermal properties of graphene epoxy nanocomposites by a multiscale approach, they further developed the finite element (FE) based representative volume elements (RVE) based on the MD results and investigated the thermal conductivity at

* Corresponding author at: College of Aerospace Engineering, Chongqing University, Chongqing 400044, China. Tel.: +86 23 65102527; fax: +86 23 65102421.

E-mail addresses: ninghu@cqu.edu.cn, huning888@hotmail.com (N. Hu).

microscale. Their computational results agreed well with the experimental results.

In the field of theoretical and numerical modeling, many research results were obtained to date [11,14–17], some of which focused on the interfacial properties [16,17] between graphene and polymer matrix by taking graphene sheet as a perfect flat plane. However, at room temperature, single-layer graphene sheets, which have no multilayer π -stacking to favor a flat structure and to increase reaction activation barriers, tend to react with H atoms more easily compared with double-layer graphene sheets [18]. In fact, many experimental observations have demonstrated that graphene sheets are not flat, but with a wrinkled morphology. For instance, for the first time, Meyer et al. [19] found that suspended graphene sheets are not perfectly flat, and their surface normal varies by several degrees and out-of-plane deformation can reach 1 nm to form wrinkles. They concluded that free-standing graphene tends to be corrugated due to the instability of its molecular structure. Monte Carlo simulations also indicated that free-standing graphene can produce energetically stable ripples [20]. Wrinkles have significant effect on the graphene's electronic [21,22] and mechanical properties [23,24] when graphene is used as substrate material [25]. Fasolino et al. [20] found that the ripples of graphene sheets appear spontaneously owing to thermal fluctuation. Xu et al. [26] also observed wrinkled graphene sheets and found that, besides thermal fluctuation, long-range attraction among atoms is another reason to cause wrinkles. Graphene prepared by reduction of graphene oxides were also found to possess wrinkles [27,28].

In spite of piles of experimental evidences as stated in above, unfortunately, few works have systematically explored the influence of graphene wrinkles on the interfacial mechanical properties between graphene and polymer matrix, e.g., Ebrahimi et al. [29]. Therefore, the purpose of the present work is to investigate the interfacial mechanical properties of nanocomposites with wrinkled graphene sheets. Pull-out simulations of graphene sheet (GR) from polymer matrix were carried out using molecular dynamics (MD). The influences of wrinkles of GR, polymer matrix type, polymer chain length and pull-out velocity of GR on the interfacial mechanical properties were systematically studied.

2. Force-field

In general, the total potential energy of a molecular system includes the following terms [30]:

$$E_{\text{total}} = E_{\text{valence}} + E_{\text{cross-term}} + E_{\text{nonbond}} \quad (1)$$

where

$$E_{\text{valence}} = E_{\text{bond}} + E_{\text{angle}} + E_{\text{torsion}} + E_{\text{oop}} + E_{\text{UB}} \quad (2)$$

$$\begin{aligned} E_{\text{cross-term}} = & E_{\text{bond-bond}} + E_{\text{angle-angle}} + E_{\text{bond-bond}} + E_{\text{bond-angle}} \\ & + E_{\text{end-bond-torsion}} + E_{\text{middle-bond-torsion}} + E_{\text{angle-torsion}} \\ & + E_{\text{angle-angle-torsion}} \end{aligned} \quad (3)$$

$$E_{\text{nonbond}} = E_{\text{vdw}} + E_{\text{Coulomb}} + E_{\text{H-bond}} \quad (4)$$

In this work, the ab initio polymer consistent force field (PCFF) [31,32] based on CFF91 with additional parameters specified for polymer materials was used to simulate the atomistic interactions of the current nanocomposites systems as it can effectively model the interfacial atomistic interactions between matrix and graphene, e.g., between graphene and PE [16,33]. In fact, the PCFF and COMPASS (Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies) force fields have the same

functional form. Moreover, the PCFF force field uses different expressions for various components of the potential energy as follows [34–36]:

$$E_{\text{bond}} = \sum_b \left[k_2(b - b_0)^2 + k_3(b - b_0)^3 + k_4(b - b_0)^4 \right] \quad (5)$$

$$E_{\text{angle}} = \sum_{\theta} \left[H_2(\theta - \theta_0)^2 + H_3(\theta - \theta_0)^3 + H_4(\theta - \theta_0)^4 \right] \quad (6)$$

$$\begin{aligned} E_{\text{torsion}} = & \sum_{\phi} \left[V_1 [1 - \cos(\phi - \phi_1^0)] + V_2 [1 - \cos(2\phi - \phi_2^0)] \right. \\ & \left. + V_3 [1 - \cos(3\phi - \phi_3^0)] \right] \end{aligned} \quad (7)$$

$$E_{\text{oop}} = \sum_{\chi} k_{\chi} \chi^2 \quad (8)$$

$$E_{\text{bond-bond}} = \sum_{b,b'} F_{bb'}(b - b_0)(b' - b'_0) \quad (9)$$

$$E_{\text{angle-angle}} = \sum_{\theta,\theta'} F_{\theta\theta'}(\theta - \theta_0)(\theta' - \theta'_0) \quad (10)$$

$$E_{\text{bond-angle}} = \sum_{b,\theta} F_{b\theta}(b - b_0)(\theta - \theta_0) \quad (11)$$

$$E_{\text{end-bond-torsion}} = \sum_{b,\phi} F_{b\phi}(b - b_0)[V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] \quad (12)$$

$$E_{\text{middle-bond-torsion}} = \sum_{b',\phi} F_{b'\phi}(b' - b'_0)(b' - b'_0)[F_1 \cos \phi + F_2 \cos 2\phi + F_3 \cos 3\phi] \quad (13)$$

$$E_{\text{angle-torsion}} = \sum_{\theta,\phi} F_{\theta\phi}(\theta - \theta_0)[V_1 \cos \phi + V_2 \cos 2\phi + V_3 \cos 3\phi] \quad (14)$$

$$E_{\text{angle-angle-torsion}} = \sum_{\theta,\theta',\phi} k_{\theta\theta'\phi}(\theta - \theta_0)(\theta' - \theta'_0)\cos\phi \quad (15)$$

$$E_{\text{Coulomb}} = \sum_{ij} \frac{q_i q_j}{\epsilon r_{ij}} \quad (16)$$

$$E_{\text{vdw}} = \sum_{ij} \epsilon_{ij} \left[\left(\frac{\sigma}{r_{ij}} \right)^9 - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] \quad (17)$$

where q is the atomic charge, ϵ the dielectric constant, r_{ij} the $i - j$ atomic separation distance, b and b' the lengths of two adjacent bonds, θ the two-bond angle, ϕ the dihedral torsion angle, and χ is the out-of-plane angle. The parameters b_0 , k_i ($i = 2-4$), H_i ($i = 2-4$), ϕ_i^0 ($i = 1-3$), V_i ($i = 1-3$), $F_{bb'}$, b'_0 , $F_{\theta\theta'}$, θ'_0 , $F_{b\theta}$, $F_{b\phi}$, $F_{b'\theta}$, F_i ($i = 1-3$), $F_{\theta\phi}$, $K_{\phi\theta\theta'}$, A_{ij} and B_{ij} are fitted from quantum mechanics calculations.

3. Molecule models

First, the atomistic models of the present nanocomposites with graphene were constructed using Materials Studio. We used polyethylene (PE) and poly (methyl methacrylate) (PMMA) as matrices since they can represent the main features of a large class of polymer materials. Moreover, their structures are comparatively very simple, leading to effective reduction of computational cost. The molecular models of PE and PMMA with 10 repeat unit chain lengths are shown in Fig. 1 [37,38]. To explore the influence of

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