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Reinforcing mechanism of graphene at atomic level: Friction, crack surface adhesion and 2D geometry

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ABSTRACT

Owing to its superior mechanical properties, graphene has been used to reinforce and substantially improve the strength of composite materials. Still lacking, however, is a clear understanding of graphene's reinforcing mechanism at the atomic level, especially in relation to its pull-out behavior. By molecular dynamics (MD), it is found that pull-out of graphene, different from that of micro fibers, is not governed by friction only. Rather, the pull-out force is revealed to be governed by a "crack surface adhesion" phenomenon due to unbalanced adhesion at the crack surface when graphene is not functionalized and the crack opening rate is small. Crack surface adhesion produces a constant pull-out force (about 0.2–1 N per meter width) regardless of the embedded length. There is a transition from crack surface adhesion governed pull-out to friction governed pull-out when the crack opening speed, graphene size and degree of functionalization increase. A new model is developed to integrate friction and crack surface adhesion with the 2D geometry of graphene. The new model can be used to predict the crack bridging stress for 2D graphene (or other 2D atomic thin reinforcements). The outcome of this study benefits the understanding and design of new graphene composites.

1. Introduction

Owing to their superior strength and elastic modulus, graphene and its derivatives have been among the best candidates for reinforcing biomaterials [1–3], polymer [4–10], metal [11–14], and ceramic/cementitious materials [15–18]. It has been reported that the elastic modulus of chitosan increased over 200% with the addition of 0.1–0.3 wt% of graphene [1]; the inclusion of 0.7 wt% graphene oxide (GO) increased the tensile strength and Young's modulus of polyvinyl alcohol (PVA) by 76% and 62%, respectively [10]; the tensile strength of aluminum composite reinforced by 0.3 wt% graphene was increased by over 62% [11]; with the addition of 0.8 vol% graphene, the fracture toughness of an alumina ceramic was increased by 40% [15]; the compressive strength and flexural strength of cement increased by 15–33% and 41–59% respectively with the introduction of 0.05 wt% GO [18]. Thus, graphene or graphene-like atomically thin materials (ATMs) have been acknowledged as promising reinforcing materials for generating stronger composites.

A major advantage of using nanosized reinforcements, such as graphene, is that they can distribute more evenly in the matrices, allowing them to arrest crack propagation at earlier stage [17,19–22]. The pull-out of nanometer scale reinforcements during fracture has been one of the major mechanisms for enhancing mechanical properties [23,24]. During pull-out, the interaction between the embedded reinforcement and the matrix, i.e., friction and chemical bonding, consumes energy and resists the widening and propagation of cracks [25,26].

The pull-out process of reinforcement, such as with a one-dimensional (1D) fiber, has often been divided into two stages: the debonding stage and the pull-out stage [25,27]. During debonding, chemical bonds between the fiber and the matrix break, allowing relative movement of the fiber. It has been widely recognized that after debonding, the pull-out of the fiber is governed by friction between the matrix and the fiber [20,23,27–34]. Theoretical models based on friction have been developed to predict the reinforcing effect of microfiber reinforcements [27,28]. In the previous studies of the present authors and colleagues [24,34], it was also demonstrated that the friction-based pull-out model could be extended to nanometer level for multiwall carbon nanotubes with diameter around 10–20 nm. In these friction governed pull-out models, the pull-out force decreased with the embedded

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length of the fiber/CNTs reinforcement, due to the reduced fiber-matrix contact area [24,25,27].

Despite the widely reported and superior reinforcing effect of graphene, investigation of their reinforcing mechanism, such as the forces in pull-out and the effect of their 2D geometry, has still been limited. Due to the sub-nanometer thickness of graphene, existing models and theories describing the pull-out of micro- [27,28] and nanoscale [20,23,29–34] reinforcing materials may not be valid for graphene. It has been found that at nanometer scale, friction also follows Amonton's First Law: being proportional to normal force and being a result of surface roughness, or in other words, asperities [35]. However, some key issues, such as whether the friction governed pull-out mechanism can be directly applied to graphene (with thickness around or below 1 nm and with correspondingly low surface roughness), have rarely been investigated. Furthermore, existing pull-out models or theories used to predict the reinforcing effect have been based on 1D fibers. The 2D geometry of a micro-/nanoreinforcement has rarely been considered. For applications of graphene/ATM-reinforced composites, therefore, it is imperative to clarify the pull-out mechanisms and effects of 2D geometry.

In this study, three steps are taken to understanding the pull-out mechanism of atomically thin graphene. The first step is to evaluate the friction between atomic thin graphene and matrices. On the basis of molecular dynamics (MD) simulation of friction between graphene and various matrices, it is demonstrated that friction between graphene and matrix can be significantly affected by sliding speed and covalent functionalization. The second step is to evaluate another source of pull-out resistance due to the surface energy. Using MD, by coupling and quantifying the energy and forces during the pull-out of graphene, it is suggested that graphene pull-out from various matrices subjects to a constant resistance force (R). The origin of this constant R is the unbalanced adhesion force between the matrix and the graphene at the crack surface. This unbalanced adhesion force is therefore referred as “crack surface adhesion” in this paper.

The third step is to integrate the crack surface adhesion with the 2D geometry of graphene/ATMs. A new theoretical model is developed to describe the pull-out of 2D circular graphene/ATMs with random spatial distribution. Furthermore, a new formulation of the crack bridging stress is established for estimating the reinforcing effect of 2D graphene/ATM. The reinforcing mechanism and model presented here provides better understanding on the effects of size, crack surface adhesion, friction, and surface properties of atomically thin reinforcements, contributing to the optimal design of future graphene/ATM-reinforced composites.

2. Simulation methods

Molecular dynamics (MD) simulations were conducted to quantify the friction and pull-out interactions between graphene sheet and various matrices. Three types of matrix were used, calcium silicate hydrate (C-S-H), aluminum (Al), and polyethylene (PE), that are typical representatives of ceramics/cementitious materials, metals, and polymers, respectively. The atomic interaction was modeled by the COMPASS force field (condensed-phased optimized molecular potential for atomistic simulation studies) [36,37], which is the first *ab initio* force field that was parameterized and validated using condensed-phase properties. This force field has been shown to be applicable in describing the mechanical properties of sp2 carbon [38,39], calcium silicate hydrate (C-S-H) [40–42], metal [43], and polymers [43–45]. The force field has also been used to study interfacial properties and interaction between graphene and polymers [46] or C-S-H [47]. Comparison between first principle and force field computed graphene-aluminum interaction energy shows less than 5% difference [48].

2.1. Friction

A periodic simulation box (49.7 Å × 25.9 Å × 30.8 Å for C-S-H, 88.8 Å × 25.6 Å × 42.5 Å for Al and 42.3 Å × 24.4 Å × 27.0 Å for PE) was created with two layers of matrix materials sandwiching a monolayer graphene (MLG). After geometry optimization, a 100 ps NPT ensemble (a constant number of particles, constant pressure and temperature dynamics simulation) was employed to optimize the shape of the lattice and relax the system. The pressure was set to be the atmospheric pressure. Then the sheet was assigned a speed v_x and a NVE ensemble (a constant number of particles, constant volume, and energy dynamics simulation) was conducted. The speed v_x of all the atoms in the MLG was then extracted under different sliding distances δ. Based on v_x, the loss of global kinetic energy ($\Delta E_{kinetic}$) of the MLG during sliding was computed as

$$\Delta E_{kinetic} = \frac{1}{2} m\left(v_x^2(\delta) - v_x^2(\delta_0)\right) \tag{1}$$

where $v_x(\delta_0)$ is the average speed of all the atoms of the MLG after being assigned an initial speed, $v_x(\delta)$ is the average speed of all the atoms of the MLG after sliding and m is the mass of the MLG.

The friction force f was then calculated as:

$$F = \frac{\Delta E_{kinetic}}{\delta} \tag{2}$$

The interfacial shear strength τ could be given by:

$$\tau = \frac{F}{A} \tag{3}$$

where A is the area of MLG.

In addition, first principle MD was performed to evaluated friction at adhesion sites where graphene and PE matrix were covalently bonded via SiO_4. Using SiO_4 (or silane based compounds) to bond graphene with polymer matrix such as PE is often seem in creating functionalized graphene polymer composites [49]. A small simulation box (9.1 Å × 7.9 Å × 10.7 Å) was created with two layers of PE sandwiching a MLG while one side of graphene forms a covalent bond with SiO_4 which was connected with carbon atoms in PE chains. Either LDA or PBE functional was used to calculate the force on atoms based on density functional theory (DFT). The results from the two functionals show minimum difference (see Fig. S2 in supplementary information) in estimated friction parameters indicating low level of error in the DFT calculation [50]. The molecular structure was optimized and relaxed in a NVT until the temperature is stable. Then a velocity of v_x was applied to the graphene and the movement of the atoms is calculated using newton's second law of motion. To prevent overheating of the system, the temperature of matrix is control at 298 K (via temperature scaling). The friction F and τ was then calculated using Eqs. (2) and (3).

2.2. The pull-out

To describe the pull-out, a sandwiched periodic structure was built with similar style to that for the simulation of friction. Periodic boundary condition was also used. But an isolated MLG sheet (IMLG) was used instead of a continuous MLG sheet. Geometry optimization and a 100 ps NPT ensemble at 298 K with atmospheric pressure were employed to optimize the parameter of the simulation box (lattice) and relax the system. To leave space for the pull-out of the isolated MLG, a vacuum gap was introduced in the pull-