Molecular dynamics simulation to enhance the mechanical and tribological properties of polyimide composites by graphene reinforcement

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Abstract. Background: Polyimide is one of the organic polymer materials with the best comprehensive performance. It has outstanding mechanical properties, excellent thermal stability and excellent corrosion resistance, but pure polyimide has high coefficient of friction and wear rate. By combining graphene with polyimide, the mechanical properties of the composite are significantly reformatived, and the friction coefficient and wear rate can be reduced. Objective: The molecular models were developed to study the mechanical and tribological properties of graphene as a reinforced material. Methods: In this paper, the mechanical properties and friction and wear mechanism of materials are studied by molecular dynamics method from the microscopic point of view. The Young's modulus and hardness of composites were calculated using the strain constant method. Results: Molecular dynamics simulation results expressed that the Young's modulus and hardness of polymer composites benefited by approximately 115% and 42%, respectively, after the addition of the graphene-reinforced material. The average friction coefficient and wear rate of polymer composites fall by 35% and 48%, respectively. Through the calculation and statistics of the micro-information in the process of friction simulation, the internal mechanism of various situations is revealed in the atomic dimension. Conclusions: Graphene can adsorb on the surface of polymer chain segment, a strong polymer matrix, through van der Waals and electrostatic forces and can effectively resist external loading.

Keywords: Polyimide composites; Graphene; Molecular dynamics; Sliding friction

1. Introduction
The excellent mechanical, thermal, and self-lubricating properties and corrosion resistance of polymer composites make them one of attractive anti-friction media [1]. Many studies conducted to improve the tribological performance of composites by adding new fibre fillers. Many studies have investigated carbon fibre- [2] and carbon nanotube-reinforced polymer composites. In 2004, professors at the university of Manchester, England, Konstantion Novaselov and Andre Geim for the first time used the mechanical peel isolated graphene obtained from graphite [3]. Graphene is a monolayer carbon atoms
with the sp² hybridisation of a two-dimensional hexagonal grid structure [4] and due to its unique structure, outstanding electrical, mechanical, thermal properties, such as nanofillers, is used to improve the tribological performance of high polymer materials that exhibit considerable potential.

Li et al. studied the graphene-enhanced mechanical and tribological properties butadiene rubber composites by using the molecular dynamics (MD) method and found that after the addition of graphene, the Young's modulus, shear modulus, and matrix surface hardness of the composites increased by 150%, 27.6%, and 35%, respectively, on average. Li et al. exploited a three-layer molecular model to explore the tribological properties of carbon nanotubes (CNTs)/polymer composites by using CNTs as reinforcing materials through MD simulations. Liu et al. conducted the MD simulation of graphene/polyethylene composites and reported the mechanism for the improvement of their mechanical properties. The strength of the interaction between the polymer chain and graphene was investigated. Toughness increased as the volume fraction of the graphene sheets increases. Therefore, in this study, we investigated the mechanical and fricological properties of graphene/polymer composites, that is, layer models is iron atoms, is placed on top nanorods and substrates, and graphene/polymer composites were then fabricated as the core to further determine the friction coefficient. Improving mechanism for the frictional properties of graphene/polymer composites are obtained.

2. Modelling

A visualiser modelling module was used to complete the model. To study the mechanical properties of graphene as a reinforcing material, first, the molecular models of pure polyimide and graphene/polyimide composites were constructed through random copolymer functions [Fig. 1 (a) and (b)]. In the modelling process, first, unit and empty unit cells with a size of 5 × 5 × 5 nm³ that contained monolayer graphene were constructed. Graphene with a size of 3.45 × 3.3nm was functionalised using hydrogen to achieve better mechanical properties [Fig. 1 (d)] [5,6].

![Fig. 1. Molecular conformations of (a) pure polyimide and (b) graphene/polyimide composites. (c) Interface region between graphene and polyimide. (d) Edge-functionalised graphene by hydrogen atoms. White, grey, blue, and red colours represent polyimide chains; graphene is denoted by the yellow colour.](image)

Fig. 2 (a) and (b) shows the molecular formula of the synthetic route of polyimide in the experiment and a repeatability unit that forms the molecular chain of polyimide, respectively.
Fig. 2. (a) Synthesis and molecular formula of polyimide. (b) Polyimide molecular chain. White, blue, grey, and red colours represent hydrogen, nitrogen, carbon, and oxygen atoms, respectively.

Finally, 27 molecular chains were filled unit at 0.6 g/cm³. For packaging, the cell packaging task was used in Accelrys materials studio (MS) software. The molecules in cells were constructed by following the Monte Carlo simulations by minimising the close contact between atoms while maintaining the true distribution of twist angles. After the initial construction of the amorphous molecular model, the total energy obtained in the two molecular systems was considerably high and the configuration was unstable. To achieve local minimum energy configuration, further optimisation was required. The condensed matter optimised molecular potential atomic simulation study force field, which is the first ab initio force field capable of simultaneously and accurately predicting a wide range of molecules and polymers, was used in subsequent MD simulations. The mechanical properties of graphene and polymers are suitable for this force field [7-8]. Simultaneously, an amorphous cell and a forcite module in MS software was used. The theories of Andersen and Berendsen were employed to control system temperature and pressure. Ewald and Lennard–Jones methods were used to calculate electrostatic interactions and interatomic van der Waals forces, respectively. The MD toddler was set to 1 fs. The cutoff radius of molecular potential energy was set to 1.25 nm. To obtain the global minimum energy configuration, the conjugate gradient method was used for geometric optimisation, and the convergence condition was 0.0001 kcal/mol. To more accurately calculate the results, the molecular system should be further optimised to achieve the global minimum energy configuration. Therefore, the aforementioned two molecular models were initially simulated under a constant pressure ensemble of 5 ps. The simulated pressure and temperature were set to room temperature (298 K) and 1 atmosphere (101 KPa), respectively. After geometric optimisation, the well-balanced molecular systems of pure polyimide and graphene/polyimide composites were obtained. These simulation processes eliminated the internal stress and unreasonable configuration of polyimide. To further balance the molecular system, five-cycle annealing was performed with constant volume and temperature (NVT ensemble) ranging from 150 K to 600 K at 200 ps per cycle. In the annealing process, the molecular system was completely relaxed through a cycle of high and low temperatures and system configurations tended to be reasonable. In the two models, the MD equilibrium of NVT ensemble at room temperature 298 K and 2 ns was performed again.

To explore the mechanical properties of the two materials, initially, MD tensile simulations were conducted to calculate their elastic modulus and then the constant strain method was used to obtain their stress-strain behaviour. Two cubes were continuously stretched with a strain rate of 0.001%, and the
system was stretched by continuously expanding the unit size along the z-axis of the model. After each expansion of the lattice size, the molecular system was simulated with 10 ps NVT (298 K) integration MD. Surface hardness is a crucial performance index for polymer materials; thus, the nano surface indentation method was used to study the influence of graphene on polyimide matrix, when hardness was increased to develop the atomic model of an iron pin, and the pin was placed in the above the two models [Fig. 3]. Subsequently, different radial pressure was applied to the iron pin, and the recorded depth was compared.

**Fig. 3.** Configurations of molecular models: initial structure of (a) pure polyimide and (b) graphene/polyimide composites. Pink and yellow colours represent iron atoms and graphene sheets, respectively.

Further investigate the improved frictional properties of graphene as a reinforcing material, two other models were constructed [Fig. 4 (a) and (b)].

**Fig. 4.** Friction configurations of pure polyimide and nano-graphene/polyimide composites

To apply friction, the layer structure was withstand shear load by moving the upper nanorod for 5000 ps at 298 K, and at a normal pressure of 20 kcal/mol/Å under a loading of 0.13 Gpa. During the MD simulation, the sliding force and atomic locus of iron nanorods and polyimides were calculated and recorded, and the friction coefficient and wear loss were investigated. The worn polymer molecules were identified because the molecules were removed from the polymer matrix. Subsequently, the wear rate was calculated using the ratio of the number of the worn molecules to the total number of molecules in the polymer matrix.
3. Results and discussions

3.1 Calculations of Young’s modulus
The mechanical properties of polymer materials affect their tribological behaviour. First, the MD method was employed to simulate the enhancement of the Young's modulus of polymer composites with graphene as the reinforcing material. Two molecular models of the pure polyimide matrix and graphene/polyimide composite were constructed [Fig. 1 (a) and (b)]. Subsequently, isothermal and isobaric equilibria were obtained and geometric optimisation was performed to obtain the global minimum energy configuration. After equilibria were achieved, a series of small tensile strains (isotropic) of 0.001% was applied to the molecular model along the X-axis. The tensile strain was realised by uniformly expanding the simulation unit size in the loading direction and readjusting the atomic coordinates. The stress along the X-axis was calculated by following the definition of virial stress. Finally, the strain–stress curves of the pure polyimide matrix and graphene/polyimide composites were obtained [Fig. 5].

![Stress–strain curves of the pure polyimide matrix and graphene/polyimide composites under a tensile load.](image)

The stress of both the pure polyimide matrix and graphene/polyimide composite material exhibited a virtual linear increase of 0–0.13 and 0–0.28 GPa as the strain increased from 0 to 0.58 (Fig. 5). Therefore, the Young's modulus of the polyimide matrix can be increased by 115% by introducing graphene as a reinforcing agent. Moreover, the experimental results confirmed the feasibility of graphene to enhance the Young's modulus of the polyimide matrix. The increase in the Young's modulus of graphene to the polyimide matrix can be explained as follows: Adsorption between the polymer chain and graphene was obtained using van der Waals interaction energy. Because adsorption on graphene surface involves van der Waals force and static electricity, graphene can form a space between the polymer and matrix reinforcing interface [Fig. 1 (c)]. The polymer chain was adsorbed through van der Waals and electrostatic forces around graphene; thus, the space interface exhibited an enhanced interface system. When an external force was applied to the system, the reinforcing interface prevented polymer chain segment caused by graphene surface spalling; therefore, related to the pure polyimide substrate, during the stretching of graphene/polyimide matrix, a higher tensile force must be provided to achieve the same strain. Thus, a higher modulus of elasticity was obtained. The high elastic modulus can reduce potential cracks in the tensile process of the system, thereby further improving the strength of the material and enhancing the service life of composites.

3.2 Hardness calculations
The iron pin was placed above the two molecular models, the two-layered polymer matrix was subjected to loads of top iron nanorods. The atomic bar of the iron pin was pressed to the surface of the two molecular systems with a radial pressure of 10, 20, and 30 kcal/mol/Å. Subsequently, the
indentation depth for each pressing was recorded (Table 1).

**Table 1** Depths of the indentations of pure polyimide and graphene/polyimide composites under different impact loadings.

| Impact Loading (kcal/mol/Å) | Pure PI (Depth of indentation) | Graphene/PI (Depth of indentation) | Decrease (%) |
|-----------------------------|-------------------------------|-----------------------------------|--------------|
| 10                          | 0.0054 Å                     | 0.0022 Å                         | 59%          |
| 20                          | 0.0261 Å                     | 0.0161 Å                         | 38%          |
| 30                          | 0.1325 Å                     | 0.0928 Å                         | 30%          |

The indentation depths of pure polyimide and graphene/polyimide with an increase in the radial pressure of iron pin atom rod (from 10 to 30 kcal/mol/Å) increased from 0.0054 to 0.1325 Å and from 0.0022 to 0.0928 Å, and according to calculations, the indentation depth of graphene/polyimide was smaller than that of pure polyimide by an average of 42% (Table 1). This finding indicated that the surface hardness of polyimide can be improved by 42% by using graphene as the reinforcing material. This phenomenon can be interpreted as: after joining graphene, van der Waals and electrostatic forces formed in the polymer matrix between graphene and the interface enhanced. When the material matrix was radially compressed and graphene was gradually compressed the distance between the polymer chain changed. When compressed to a certain range, the graphene surface provided reverse repulsion, and the repulsive force was larger than repulsion between polymer chains. The polymer chain continued to come close to the graphene surface to improve the surface hardness of the polyimide substrate. Moreover, studies have shown that the introduction of graphene improves the hardness of polymer matrix [9]. By improving the hardness of polymer composites, better load transfer and viscosity reduction can be achieved. According to a study, while improving the polymer matrix hardness, the internal stress transfer capacity and viscosity of the matrix increased and decreased, respectively. Therefore, when the material is subjected to friction and wear, the increase in hardness can substantially reduce the stress concentration, reduce the occurrence of adhesive wear, and improve the service life of the material.

3.3 **Discussions of tribological properties**

To study the tribological properties of polyimide composites reinforced with graphene, the friction coefficient and wear rate of the pure polyimide matrix and graphene/polyimide composite were calculated using the MD equilibrium process introduced in the three-layer structure and model section [Fig. 4 (a) and (b)]. During simulations, the molecules reduced from the model lattice were identified as polymer molecules worn away from the polymer matrix. The wear rate was given by the ratio of the number of the worn molecules to the total number of molecules in the polymer matrix. The friction coefficient and wear rate were 0.196 and 31.4% and 0.374 and 43.5%, respectively, for the graphene/polyimide composite and pure polyimide matrix, respectively. After the introduction of graphene, the friction coefficient and wear rate were reduced by 35% and 48%, respectively. To explore the mechanism of improving the tribological properties of polyimide composite materials, the atomic concentration distribution curves obtained along the thickness of the two materials were extracted (Fig. 6).
In the direction of the substrate thickness at 5 and 68 Å, atomic concentration peak related to pure polyimide appeared; in the thickness direction delay matrix at 22 Å, a peak related to the atomic concentration of graphene/polyimide composites appeared, and the concentration of the pure polyimide substrate near two was approximately 8% higher than that of composite materials (Fig. 6). Simultaneously, at a distance of approximately 40 along the substrate thickness direction, the average relative atomic concentration of the graphene/polyimide substrate was 40% higher than that of the pure polyimide matrix, and this data showed that the pure polyimide substrate, in the friction process, attached to the surface of iron atoms layer, leading to more wear, and because of a lack of the graphene reinforcing effect, the occurrence of friction of the molecular chains of polyimide layers with pair of iron atoms increased, forming a large area of the polymer adsorption membrane. This finding is consistent with the experimental literature. By contrast, due to the van der Waals force and electrostatic adsorption on the graphene surface, more polyimide molecular chains concentrated in the matrix and fewer molecular chains interacted with the iron atomic layer, thereby maintaining the matrix integrity and improving the tribological properties of the polyimide matrix. To further explore the tribological characteristics of graphene-enhanced polyimide matrix, the distribution of atomic temperature and velocity along the matrix thickness observed during MD friction simulation was calculated and extracted (Fig. 7).

For the pure polyimide matrix, in the direction where substrate thickness was approximately 13 Å, which is a place for the polyimide substrate metal layer of the friction interface with iron atoms, the peak temperature value was 308 K; by contrast, for the graphene/polyimide matrix, peak temperature on the friction interface was 211 K, and the contrast data showed that the addition of graphene as the reinforcing material can effectively reduce the friction interface temperature by approximately 30%.
(Fig. 7). This phenomenon is consistent with the results presented in Fig. 6 for atom concentration distribution. The higher interaction of polyimide chains with friction layer with iron atoms led to higher interface friction temperature, and this temperature can not only easily destroy the viscoelastic properties of polymers but also simultaneously easily cause adhesion wear, resulting in the reduced service life. This result is in a strong agreement with the aforementioned discussions [Fig. 8 (a) and (b)], which shows better wear resistance.

![Fig. 8. (a) and (b) Two composites during friction simulations.](image)

4. Conclusions
MD simulations were employed to confirm that graphene enhances the mechanical properties, friction, and wear characteristics of the polyimide matrix and prolongs the service life of composite materials. To construct a graphene/polyimide nanocomposite amorphous model, the Young's modulus of composites was simulated, and hardness, friction coefficient, and wear rate revealed that reinforcement with graphene materials enhances the mechanical properties of the microscopic mechanism of polyimide matrix. The results showed the increase of approximately 115% and 42% in the Young's modulus and hardness of polyimide composites were obtained after reinforcement with graphene sheets. Furthermore, the average friction coefficient and wear rate of polyimide composites were reduced by 35% and 48%, respectively, because of graphene reinforcement. According to the atomic concentration within the matrix, during the simulation of microscopic information such as atomic temperature calculation and statistics provided the graphene-reinforced system based on the microscopic mechanism of the mechanical properties of polyimide polymer matrix. Graphene can adsorb on the surface of polymer chain segment, a strong polymer matrix, through van der Waals and electrostatic forces and can effectively resist external loading.

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