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Mechanical properties of polymer near graphite sheet

Jing-Suei Gao, Sung-Chiun Shiu and Jia-Lin Tsai

Abstract

This study aims to investigate the local mechanical properties of polyimide near graphite sheet in the graphite/polyimide nanocomposites. In order to understand the influence of graphite on the molecular configuration, the corresponding density and order parameter of the polyimide near the graphite/polyimide interface were evaluated using molecular dynamics simulation. In addition, the local mechanical properties of polyimide polymer were characterized through the calculation of the local stress distribution of the polyimide subjected to a uniform strain deformation. Results illustrated that in the vicinity of the graphite sheet, the polyimide chains are not only adsorbed compactly toward the graphite sheet but they are also oriented along the graphite surface. Moreover, it is found that the modulus of polyimide near the graphite/polyimide interface is higher than that in other regions. The phenomena clearly illustrated that the mechanical properties of polyimide close to the interface are affected dramatically by the graphite sheet.

Keywords

Nanocomposites, mechanical properties, graphite sheet, molecular dynamics simulation

Introduction

Because of high strength and stiffness, graphite sheets were employed as reinforcements to enhance the mechanical and thermal properties of composites. Experimental results illustrated that with the addition of a small amount of graphite (around 5%), the mechanical properties of nanocomposites can be improved remarkably.^{1,2} In conventional micromechanics model, the nanocomposites were treated as a continuum solid, consisting of a reinforcement phase (graphite) and a matrix phase (polymer), and the corresponding improvement in mechanical properties were attributed to the introduction of the stiff reinforcement. In addition, during the modeling, the mechanical properties of the matrix are usually assumed to be homogeneous and not affected by the presence of reinforcement. In general, the mechanical properties of the matrix near the interface may not be noteworthy in traditional composites. Nevertheless, for the nanocomposites, because of the high specific surface area of the nano-reinforcement, the interfacial area between the nano-reinforcement and surrounding matrix is becoming relatively large. The mechanical properties of the polymer matrix in the interfacial area would play an

important role in the responses of nanocomposites. As a result, understanding the local mechanical properties of the polymer may facilitate the characterization of the nanocomposites' mechanical properties with accuracy. Recently, a micromechanical model with an effective interface was proposed to model the properties of the particulate nanocomposites.^{3–5} In their modeling, the local mechanical properties of matrix as well as the interfacial adhesion were lumped together and represented by an effective interface with assumed material properties. In fact, the material properties of effective interface should be presumable if the morphology as well as the mechanical properties of polymer in terms of different intra-molecular interactions near the interface can be fully elucidated. Based on the effective-interface micromechanical model, it is revealed that as the particle size decreases,

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the corresponding moduli of nanocomposites increase, which is coincided with the experimental observation.⁶ Without taking interface effect into account, the phenomena cannot be characterized properly by micromechanical model.

The local configurations of polymer near the interface have been explored by several researchers.^{7–11} Wei et al.⁷ scrutinized the local structure of polyethylene (PE) in nanotubes reinforced composites using MD simulation. Results depicted that the PE molecular structures near the nanotube/PE interface are very different from the bulk PE in both density and chain orientation. They indicated that the well-oriented molecular chains and dense molecular structure enhance the load transfer efficiency between the carbon nanotube (CNT) and polymer matrix, resulting in the improved modulus of CNT composites. However, such improvement in modulus is lessening at high temperatures, which could be due to the increased thermal fluctuation making the interfacial structures less organized.⁸ Cho and Sun⁹ investigated the elastic behavior of particulate nanocomposites, indicating that there is a higher density polymer layer formed around the nanoparticles, which may induce a higher elastic modulus of the nanocomposites. A high density layer of polymer was also observed near the surface of nanoparticles by Yu et al.,¹⁰ who characterized the mechanical properties of alumina/epoxy nanocomposites. This highly adsorption layer was regarded as a different phase from the bulk polymer in their modeling. Papakonstantopoulos et al.¹¹ examined the mechanical properties of particulate nanocomposites with three different atomistic interactions between the particle and polymer, that is, neutral, attractive, and repulsive. It was found that for neutral and attractive fillers, an interface layer of polymer near the particle was formed, but no obvious interface layer was observed in the repulsive interaction. In light of the foregoing investigations, it seems that there is an interface layer existing near the nano-reinforcement, however, the detail configuration as well as the mechanical properties of the interface layer is not well elucidated. In this study, the local mechanical properties of polyimide in the vicinity of graphite were examined from MD simulation by evaluating the order parameter of molecular chains as well as the density distribution. Moreover, by applying a constant-strain deformation on the graphite/polyimide molecular model, the differentiation of the local mechanical properties of the polyimide can be extracted directly from the calculation of local stress distribution. The qualitative estimation of the local mechanical properties of polyimide will be useful in developing micromechanics model of nanocomposites with the consideration of interface as functionally graded layer.

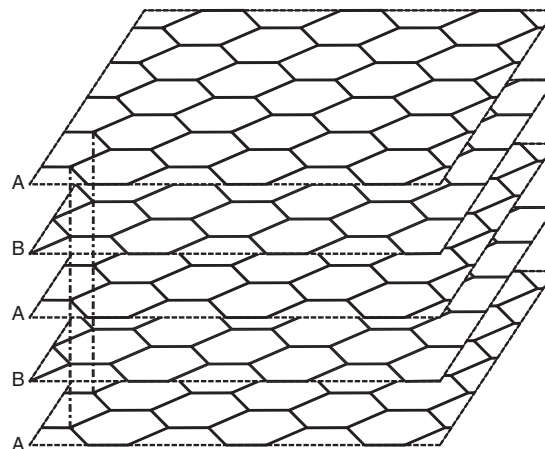


Figure 1. Graphite stacked in the form of A-B sequence.

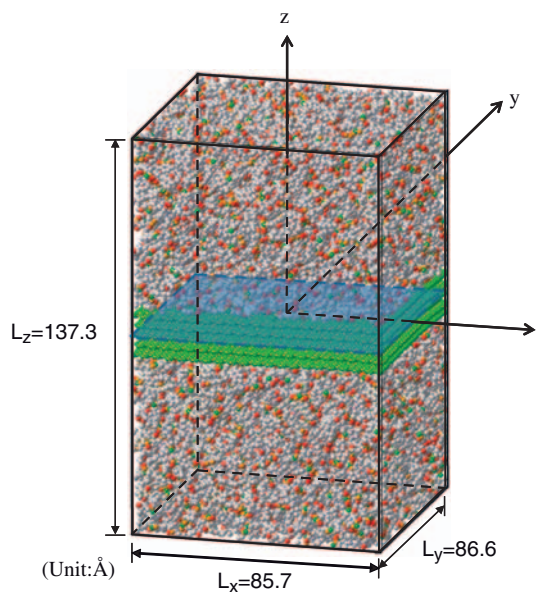


Figure 2. Molecular structure of graphite/polyimide nanocomposite.

Construction of graphite/polyimide nanocomposite model

In order to explore the mechanical properties and morphologies of polyimide near reinforcement, the molecular model of nanocomposites were constructed at the beginning. The molecular model basically consists of a 5-layer graphite sheet (stacked along the z direction in A-B sequence; see Figure 1) and 12 polymer chains exposed randomly on each side of the graphite sheet as shown in Figure 2. Each polyimide chain consists of 50 monomer units, and the total atom number in 1 polymer chain is 3002. Figure 3 illustrates the polyimide monomer unit. The reason to build up the simulation cell of graphite/polyimide nanocomposites in

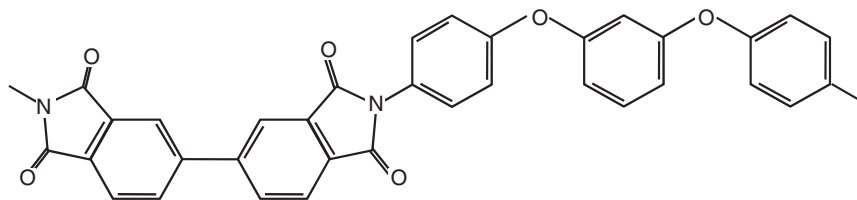


Figure 3. Polyimide monomer unit.

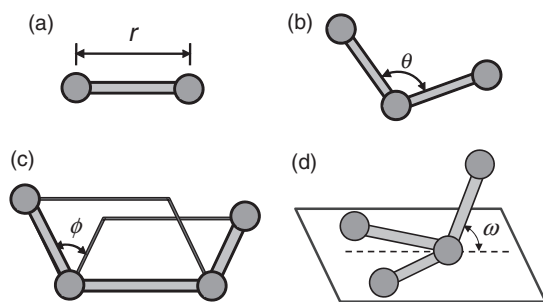


Figure 4. Schematic of bond potential: (a) bond stretching, (b) bond angle bending, (c) dihedral angle torsion, and (d) inversion.

such an arrangement is that graphite sheet is a plan structure and the morphology and mechanical properties of polymer near the interface can be easily examined through uniform strain loading condition. This is also the reason why we adopted graphite sheet as reinforcement in nanocomposites instead of other reinforcements, such as nanoparticles, carbon nanotubes. Because of the periodicity, this model can also be regarded as the nanocomposites that contain a graphite sheet extended infinitely in both x and y directions. Only the mechanical properties of polyimide varied along the z axis would be examined in this study.

Potential function

In the MD simulations, the atomistic interactions between the atoms are described using potential function. In general, there are two kinds of potential functions considered for the graphite/polyimide nanocomposites system: one is the bonded potential, such as the covalent bond, and the other is the non-bonded potential such as van der Waals force. Among the atomistic interactions, the covalent bond between two neighboring carbon atoms that provides the building block of the primary structure of the graphite may play an essential role in the mechanical responses. Such bonded interaction can be described using the potential energy that consists of bond stretching, bond angle bending, torsion, and inversion as illustrated in Figure 4.¹² Therefore, the total potential energy of the

graphite contributed from the covalent bond can be given as

$$U_{\text{graphite}} = \sum U_r + \sum U_\theta + \sum U_\phi + \sum U_\omega \quad (1)$$

where U_r is a bond stretching potential; U_θ is a bond angle bending potential; U_ϕ is a dihedral angle torsional potential; and U_ω is an inversion potential. The explicit form for the bond stretching and bond angle bending can be approximated in terms of elastic springs as¹³

$$U_r = \frac{1}{2} k_r (r - r_0)^2 \quad (2)$$

$$U_\theta = \frac{1}{2} k_\theta (\theta - \theta_0)^2 \quad (3)$$

where k_r and k_θ are the bond stretching force constant and angle bending force constant, respectively. The constants $k_r = 93800 \frac{\text{kcal}}{\text{mole} \cdot \text{nm}^2}$ and $k_\theta = 126 \frac{\text{kcal}}{\text{mole} \cdot \text{rad}^2}$ selected from the AMBER force field for carbon-carbon atomic interaction¹⁴ was employed in our molecular simulation. The parameters r_0 and θ_0 represent bond length and bond angle in equilibrium position, which are assumed to be 1.42 Å and 120°, respectively, for the graphite atomistic structures. The explicit form for the dihedral torsional potential together with the inversion potential is expressed as¹⁵

$$U_\tau = U_\phi + U_\omega = A[1 - \cos(m(\phi - \delta))] \quad (4)$$

where δ represents the dihedral torsion angle, which is equal to 180°, and the parameter A and m in equation (4) are equal to 2.505 kcal/mole and 2, respectively. In addition to the bonded interaction, the non-bonded interaction between the carbon atoms was regarded as the van der Waals force, which can be characterized using the Lennard-Jones (L-J) potential as

$$U_{\text{vdW}} = 4u \left[\left(\frac{r_0}{r_{ij}} \right)^{12} - \left(\frac{r_0}{r_{ij}} \right)^6 \right] \quad (5)$$

where r_{ij} is the distance between the non-bonded pair of atoms. For the hexagonal graphite, the parameters

$u = 0.0556$ kcal/mole and $r_0 = 3.40$ Å suggested in the literature¹⁶ were adopted in the modeling. Moreover, the cutoff distance for the van der Waals force is assigned to be 10 Å, which means that beyond this distance, there are no more van der Waals interactions taking place.

For the polyimide polymer, the Dreiding force field¹⁷ was employed to describe the covalent bonding as well as the non-bonding interaction among the molecular chains. In addition, the atomistic interaction between the polyimide molecular and the graphite were modeled using the L-J potential in which the corresponding parameters were obtained directly from the combining rule.¹⁸ Three different intensities of the atomistic interactions between the graphite and the surrounding polyimide, that is, normal, strong and weak, are individually considered in the L-J potential. The strong interaction assumed the strength to be five times of the normal one while the weak interaction is only 0.2 times of the normal interaction. It is noted that the strong or weak interactions are used to differentiate from the normal one, and thus these should be regarded as relative interactions with respect to the normal interaction.

Molecular dynamics (MD) simulation

The MD simulations for graphite/polyimide nanocomposites were conducted using a DL-POLY package.¹⁹ A five-layer graphite sheet was positioned in the middle of simulation cell at the beginning and 12 polyimide chains were placed randomly on each side of the graphite sheet. Afterward, the polymer chains naturally diffused in NVT ensemble at 1000 K for 600 ps as shown in Figure 5 where the polymer chains naturally adhered to the graphite interface. In this stage, the large volume size of simulation cell and high temperature were specified in order that the molecular can have enough space and kinetic energy for free diffusion and interaction. In addition, the graphite atoms were frozen, which designates that the carbon atoms on graphite were fixed at their original position during the simulation. The equilibrated molecular structure with minimized energy was then accomplished by sequentially performing the NPT ensembles in the MD simulation. It is noted that NVT ensemble stands for the volume and temperature being fixed during the simulation, and the NPT ensemble represents that the pressure and temperature remain constant during the simulation. Subsequently, the NPT ensemble was performed at 0 atm in order to achieve the stress-free state, and at the same time, the corresponding temperature was gradually cooled down from 1000 K to 0 K. In fact, there were three sub-steps introduced during the cooling process. In the first sub-step, the temperature was

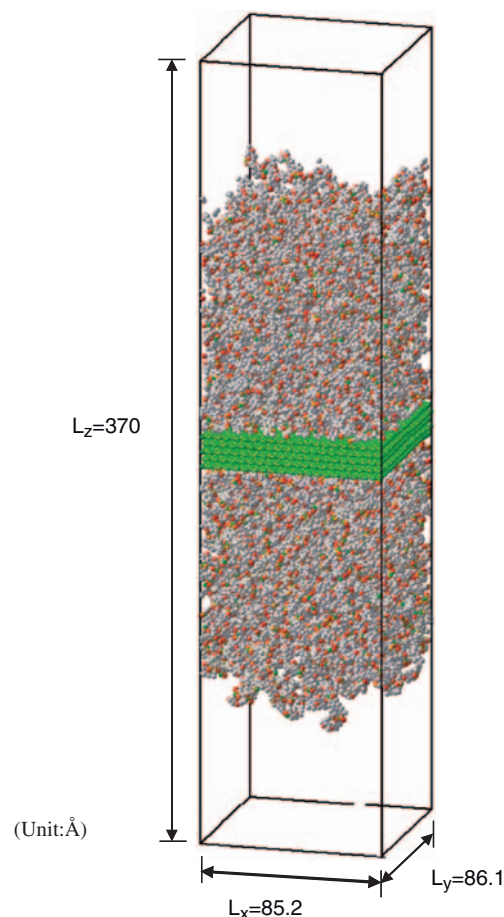


Figure 5. Molecular structure of graphite/polyimide nanocomposite in NVT ensemble at 1000 K.

designated at 600 K, and the simulation time was 400 ps. During this sub-step, the atoms of the graphite layer remained frozen at their original positions. In the second and third sub-steps, the target temperatures were 300 K and 0 K, respectively, and the simulation time in each sub-step was 400 ps. It is noted that the frozen atoms of graphite were released during the last two sub-steps so that the entire nanocomposites system could be equilibrated at 0 K under a stress-free condition. During the simulation, the total potential energy variation was examined, and when the quantity fluctuated around a certain mean value for a while, the system was considered to be in equilibrium. Figures 6 and 7 demonstrate the potential energy history of the nanocomposites as well as the temperature variation during the third sub-step in the NPT ensemble, respectively. It is evident that the potential energy attains a stable condition after 10 ps; concurrently, the temperature is approaching 0 K. Based on the observations, it was suggested that the molecular structure of nanocomposites is in the equilibrium condition and suitable for the characterization of the morphology as well as the

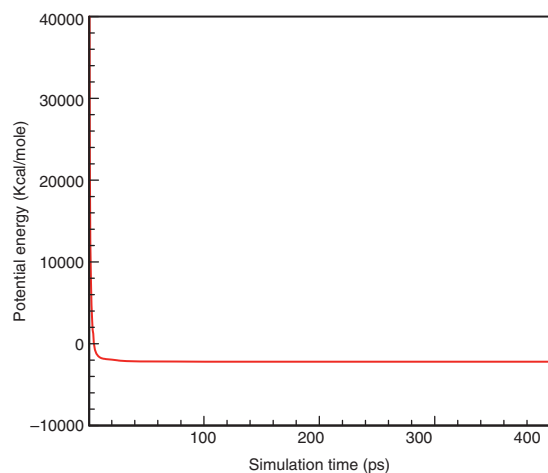


Figure 6. Potential energy history in the third sub-step of NPT ensemble.

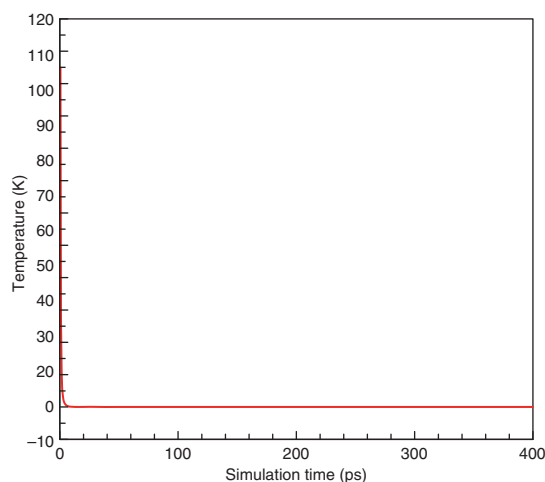


Figure 7. Temperature variation in the third sub-step of NPT ensemble.

mechanical properties. The dimension of the simulation cell under equilibrium condition along x, y, and z directions are $L_x = 85.7 \text{ \AA}$, $L_y = 86.6 \text{ \AA}$, and $L_z = 137.3 \text{ \AA}$ as illustrated in Figure 2.

Examination of molecular configuration of polyimide

In order to understand the effect of graphite on the molecular configuration of polyimide, the variation of density and the order parameter of polyimide chains were examined from the graphite/polyimide interface. This can be done by partitioning the polyimide from $z = z_0$ along the z axis into several small regions as shown in Figure 8. It is noted that the position $z = z_0$ denotes the graphite/polyimide interface, and the

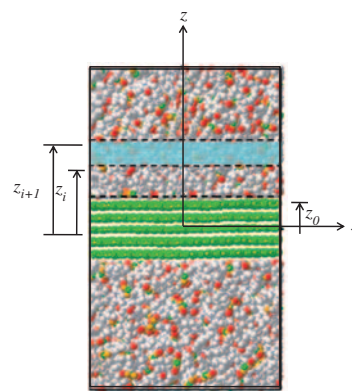


Figure 8. Partitioning the polyimide from $z = z_0$ along z axis into several small regions.

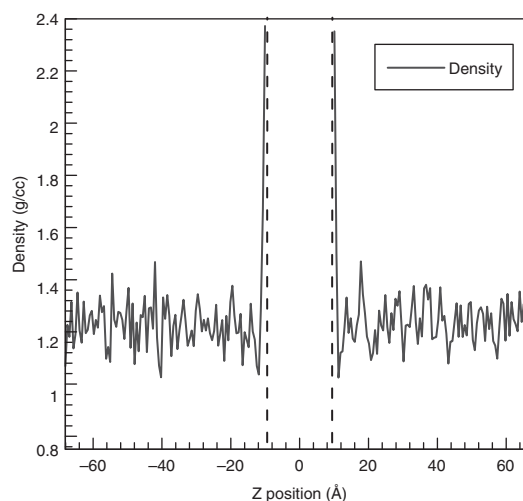


Figure 9. Density distribution of polyimide with normal graphite/polyimide interaction.

partition size $\Delta z = z_{i+1} - z_i$ is around $1 \text{ \AA}$ for the thickness of each small region. In each small region, the total atom mass and the corresponding volume were calculated, and then the density was measured as the mass divided by the associated volume. Thus, the density distribution measured from the interface along the z axis can be evaluated as shown in Figure 9. It can be seen that the density near the graphite/polyimide interface is higher and then rapidly decreases to the bulk value as the location is little away from the interface. Apparently, the district with higher density is restricted within the range of $2 \text{ \AA}$, and the maximum value of density is around 2.5 g/cc , corresponding to the bulk value of 1.27 g/cc . It is noted that the dash line shown in the Figure 9 indicates the location where $z = z_0$. In addition, the density distributions on both sides of the graphite are quite similar, demonstrating that the high

polyimide density always occurs near the graphite surfaces. The density distribution influenced by the extent of the atomistic interaction between the graphite and polyimide are illustrated in Figure 10 where three different degrees of interaction were considered. When the interaction is stronger, the polyimide density near the interface is getting higher as compared to the other cases. On the other hand, for the weaker interaction, it can be seen that the polyimide density is basically not influenced by the graphite.

The effect of graphite on the orientation of polyimide chains was also investigated by measuring the directions of the sub-vectors connecting the carbon atom and nitrogen atom defined in the monomer unit of polyimide as shown in Figure 11. The reason to choose the two sub-vectors as a measure index is that the molecular backbones corresponding to the sub-vectors are rigid so that during the formation of nanocomposite molecular structures, the relative bending deformation can be prohibited. The order parameter of the polyimide was calculated as²⁰

$$f = \frac{1}{2} (3 \langle \cos^2 \phi \rangle - 1) \quad (6)$$

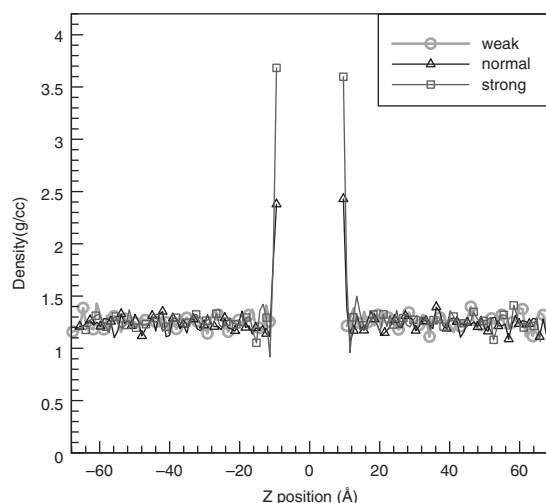


Figure 10. Effect of graphite/polyimide interaction on the density distribution of polyimide.

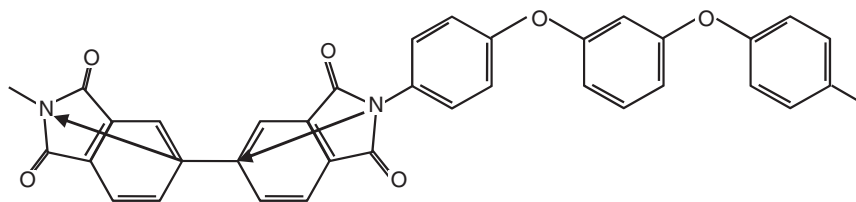


Figure 11. Schematic of the C-N sub-vectors defined in the polyimide monomer unit.

where ϕ is the angle of the sub-vectors with respect to the reference vector, which is perpendicular to the interface as shown in Figure 12, and $\langle \rangle$ denotes the average of all sub-vectors calculated within a designated small region. It should be noted that when $f = 1$, it means that the orientation of polyimide chains are parallel to the reference vector, and when $f = -0.5$, it indicates that the chains are perpendicular to the reference vector while $f = 0$ demonstrates that the chains are randomly distributed. Figure 13 shows the order parameter distribution of the polyimide polymer along the z axis. Apparently, the order parameter in the vicinity of the graphite/polyimide interface is close to -0.5 , which implies most of the polyimide chains are flattened down parallel to the graphite surface. As the location is away from the interface, the corresponding value approaches 0, and the polyimide chains begin to distribute randomly. The influence of the atomistic interaction between the graphite and polyimide on the order parameter of polyimide chains is shown in Figure 14. When the interaction is strong, the polyimide chains are also aligned on the graphite surface. On the other hand, when the atomistic interaction is weaker, no obvious polymer alignment was observed near the interface. According to the forgoing comparison, it is perceptible that the presence of graphite sheet may have a significant effect on the polymer density as well as the molecular orientation, especially in the immediate vicinity of the interfacial region. Moreover, the effect of interface layer is more appreciable, as the interaction is

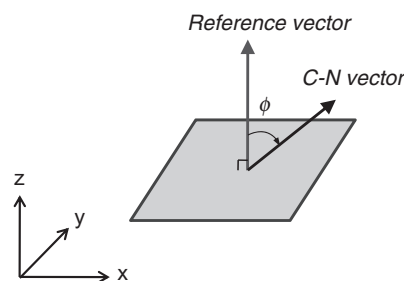


Figure 12. The sub-vectors with respect to the graphite surface normal vector (reference vector).

getting stronger. Therefore, it is required to account for the interface layer in the micromechanical model in order to characterize the mechanical properties of graphite/polyimide nanocomposites with accuracy.

Evaluation of local mechanical properties of polyimide

In addition to the molecular morphology, the local mechanical properties of polyimide in the immediate vicinity of the interfacial region were investigated in the following section. The design of the graphite/polyimide molecular structure shown in Figure 2 makes it possible to explore the local mechanical properties of polyimide directly from the calculation of the local stress distribution of the nanocomposites under uniform strain deformation.

Local stress formulation

The local stress distribution of polyimide in the molecular model was determined based on the Hardy stress formulation,²¹ the explicit form of which is written as

$$\sigma(\mathbf{r}, t) = - \left\{ \sum_{\alpha=1}^N m^{\alpha} (\mathbf{v}^{\alpha} - \mathbf{v}) \otimes (\mathbf{v}^{\alpha} - \mathbf{v}) \Psi(\mathbf{r}^{\alpha} - \mathbf{r}) + \frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta \neq \alpha}^N \mathbf{r}^{\alpha\beta} \otimes \mathbf{F}^{\alpha\beta} B^{\alpha\beta}(\mathbf{r}) \right\} \quad (7)$$

where m^{α} , $\mathbf{v}^{\alpha}$, and $\mathbf{r}^{\alpha}$ represent the mass, velocity, and position of atom α , respectively; $\mathbf{v}$ and Ψ stand for the velocity field and localization function. In addition, $\mathbf{r}^{\alpha\beta} = \mathbf{r}^{\alpha} - \mathbf{r}^{\beta}$, $\mathbf{r}^{\alpha}$, and $\mathbf{r}^{\beta}$ represent the position of α and

β atoms, respectively. $\mathbf{F}^{\alpha\beta}$ denotes the force of between α and β atoms, and $B^{\alpha\beta}(\mathbf{r})$ is the bond function. When the localization function ψ is selected as a Gaussian function

$$\Psi(\mathbf{r}^{\alpha} - \mathbf{r}) = \begin{cases} \frac{1}{(\sqrt{\pi}h)^3} \exp\left[-\frac{(\mathbf{r}^{\alpha} - \mathbf{r})^2}{h^2}\right], & |\mathbf{r}^{\alpha} - \mathbf{r}| \leq r_c \\ 0, & |\mathbf{r}^{\alpha} - \mathbf{r}| > r_c \end{cases} \quad (8)$$

the bond function $B^{\alpha\beta}(\mathbf{r})$ in equation (7) can be expressed as

$$B^{\alpha\beta}(\mathbf{r}) = \int_0^1 \Psi(\lambda \mathbf{r}^{\alpha\beta} + \mathbf{r}^{\beta} - \mathbf{r}) d\lambda \quad (9)$$

where h is the smoothing length and r_c is the cutoff distance. In this study, the smoothing length is 3.2, and the cutoff distance r_c is equal to 10 Å. If the deformation is simulated at a temperature of zero degree, the first term of equation (7) can be neglected, and the Hardy stress formulation can be further deduced as

$$\sigma(\mathbf{r}, t) = -\frac{1}{2} \sum_{\alpha=1}^N \sum_{\beta \neq \alpha}^N \mathbf{r}^{\alpha\beta} \otimes \mathbf{F}^{\alpha\beta} B^{\alpha\beta}(\mathbf{r}) \quad (10)$$

Uniaxial loading on the simulation cell

By applying a uniaxial loading on the simulation cell with a periodic boundary condition, a uniform strain deformation can be generated in the simulation cell. The deformation process in the z and x directions is illustrated in Figures 15 and 16, respectively. Subsequently, the corresponding mechanical properties of the polyimide can be qualitatively evaluated by calculating the local stress field of the polyimide associated with the uniform deformation. In the MD simulation, the uniaxial loading was applied on the simulation cell by conducting the modified NPT ensemble²² with a time increment of 1 fs for 400 ps, from which the deformed configuration of molecular graphite/polyimide nanocomposites was obtained. Afterward, the Hardy stress formulation given in equation (10) was adopted to calculate the ‘local’ stress of polyimide. The purpose of applying loading in z direction (shown in Figure 15) is to validate if the Hardy formulation is capable of evaluating the stress variation in the nanocomposites. It is well known that when the nanocomposites are subjected to the loading in the z direction, as shown in Figure 15, because of equilibrium, the stress component σ_{zz} should be uniform all the way through the z axis. The local stress distribution along z direction with respect to the applied loading of

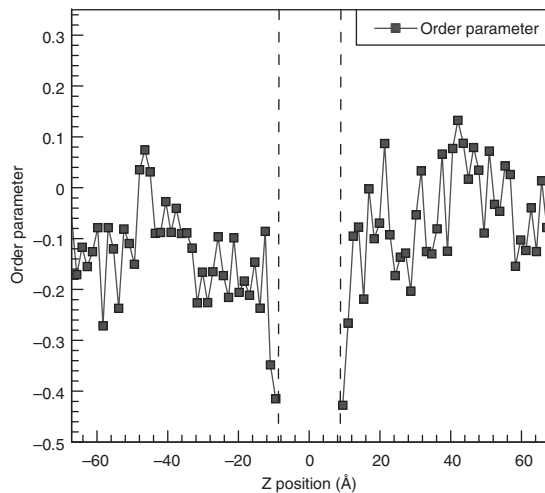


Figure 13. Order parameter of polyimide with normal graphite/polyimide interaction.

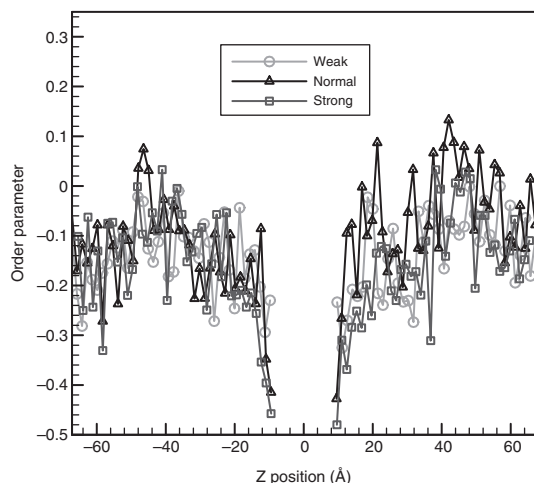


Figure 14. Effect of graphite/polyimide interactions on the order parameter of polyimide.

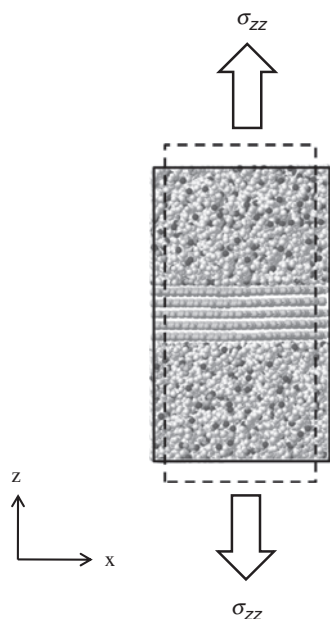


Figure 15. Deformed configuration of graphite/polyimide nanocomposites subjected to axial loading in z direction.

10 MPa is shown in Figure 17. It is revealed that the local stress σ_{zz} in both graphite and polyimide phases are almost the same, which coincides with the applied loading of 10 MPa. It is noted that the strain of the simulation cell associated with the applied loading of 10 MPa is around 1.29×10^{-3} . According to the foregoing examination, it is validated that the Hardy stress formulation is able to describe the local stress distribution of the nanocomposite molecular structure subjected to uniaxial loading.

Basically, the differentiation of the mechanical properties for the polyimide in the nanocomposites cannot

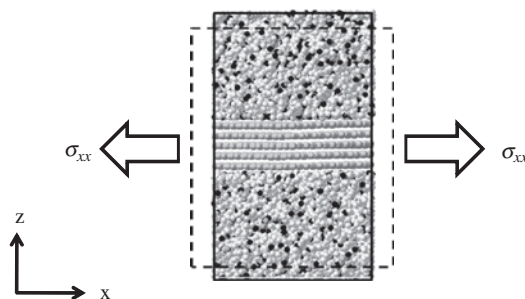


Figure 16. Deformed configuration of graphite/polyimide nanocomposites subjected to axial loading in x direction.

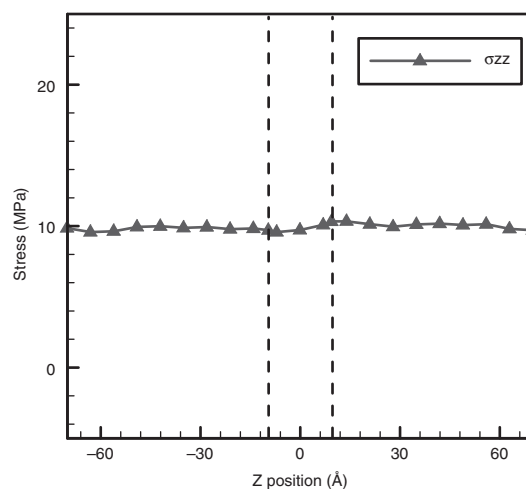


Figure 17. Stress distribution of polyimide and graphite with the applied loading of $\sigma_{zz} = 10$ MPa.

be distinguished by performing the uniaxial loading in the z direction. Instead, it can be differentiated simply by performing the loading in either x or y directions. This concept originated from the micromechanical model of laminated composite structures subjected to constant strain loading in either the x or y direction.²³ When 'average' tensile stress of 10 MPa was applied on the simulation cell in the x direction, because of the periodic boundary condition, the uniform strain is prevailing in the x direction as shown in Figure 16, and the difference of the material properties can be characterized directly from the calculation of the corresponding stress component of σ_{xx} . The stress distribution of polyimide along the z axis is illustrated in Figure 18. It is shown that the stress component σ_{xx} demonstrates the maximum value near the graphite/polyimide interface and then decreases dramatically as the position is little away from the interface. Because the simulation cell is under uniform strain condition, the stress distribution is used as an indication of the variation of material properties. Thus, based on the stress distribution, we

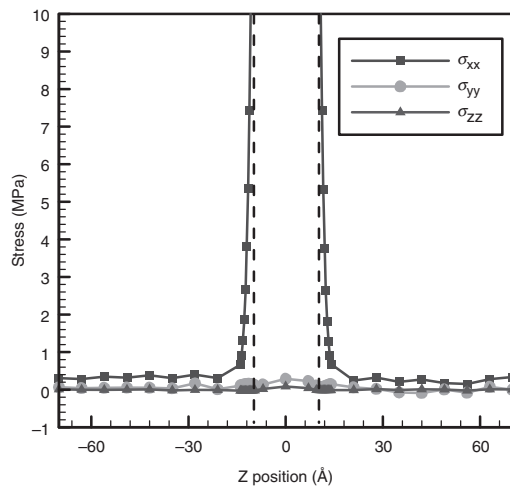


Figure 18. Stress distribution of polyimide with the applied average loading of $\sigma_{xx} = 10$ MPa.

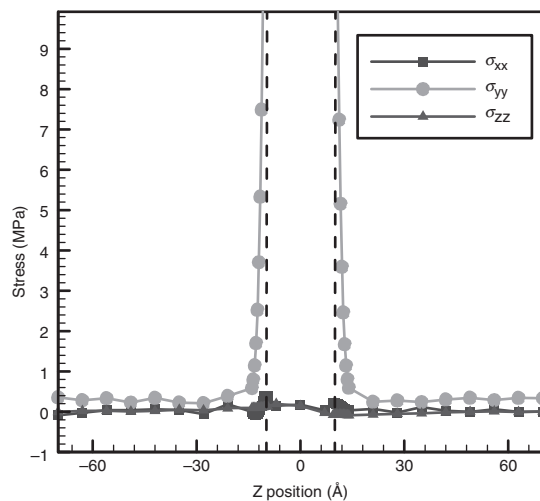


Figure 19. Stress distribution of polyimide with the applied average loading of $\sigma_{yy} = 10$ MPa.

can infer that the stiffness of polyimide in the interface layer is higher as compared to that in other regions. In addition, since the simulation cell is subjected to the deformation in x direction, it can be seen that the stress components rather than σ_{xx} in Figure 18 are relatively low. Similarly, when the deformation is applied in the y direction, the local stress component σ_{yy} of the polyimide near the interface also raise dramatically as shown in Figure 19. The existence of a interface layer with higher modulus adsorbed in the vicinity of interface can be deduced again by the stress distribution of σ_{yy} . This adsorption layer of polyimide is responsible for the improvement of mechanical behavior in nanocomposites either by the enhancement of the polyimide's stiffness or by the feasibility of the load transfer efficiency from polyimide matrix to the

graphite. The influence of the adsorption layer on the load transfer efficiency as well as the mechanical properties of nanocomposites will be explored in the near future.

Conclusions

The density distribution, order parameter, and mechanical properties of polyimide in terms of the distance measured from the graphite/polyimide interface in nanocomposites were investigated using MD simulation. Observing the molecular configuration reveals that in the vicinity of the interface, the polyimide density is high (about twice of bulk value) and the molecular chain are orderly stacked parallel to the graphite surface. On the other hand, at the distance away from the interface, the molecular chains are displaced randomly and the corresponding density is the same as the bulk value. Apparently, there is an interface layer of polyimide formed near the graphite/polyimide interface. In addition, from the calculation of stress distribution in the simulation cell under uniform-strain deformation, it was depicted that this interface layer of polyimide also exhibits higher moduli than bulk polyimide. The influence of the interface layer on the load transfer efficiency between the polyimide and graphite sheet as well as the mechanical properties of nanocomposites will be explored in our further study.

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Conflict of Interest

None declared.

References

1. Cho J, Chen JY and Daniel IM. Mechanical enhancement of carbon fiber/epoxy composites by graphite nanoplatelet reinforcement. *Scr Mater* 2007; 56: 685–688.
2. Yu AP, Ramesh P, Itkis ME, et al. Graphite nanoplatelet-epoxy composite thermal interface materials. *J Phys Chem C* 2007; 111: 7565–7569.
3. Odegard GM, Clancy TC and Gates TC. Modeling of the mechanical properties of nanoparticle/polymer composites. *Polymer* 2005; 46: 553–562.
4. Yang S and Cho M. Scale bridging method to characterize mechanical properties of nanoparticle/polymer nanocomposites. *Appl Phys Lett* 2008; 93: 043111.
5. Yang S and Cho M. A scale-bridging method for nanoparticulate polymer nanocomposites and their non-dilute concentration effect. *Appl Phys Lett* 2009; 94: 223104.
6. Fu SY, Feng XQ, Lauke B, et al. Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate polymer composites. *Composites Part B* 2008; 39: 933–961.

7. Wei CY, Srivastava D and Cho K. Structural ordering in nanotube polymer composites. *Nano Lett* 2004; 4: 1949–1952.
8. Wei CY. Adhesion and reinforcement in carbon nanotube polymer composite. *Appl Phys Lett* 2006; 88: 093108.
9. Cho J and Sun CT. A molecular dynamics simulation study of inclusion size effect on polymeric nanocomposites. *Comput Mater Sci* 2007; 41: 54–62.
10. Yu S, Yang S and Cho M. Multi-scale modeling of cross-linked epoxy nanocomposites. *Polymer* 2009; 50: 945–952.
11. Papakonstantopoulos GJ, Yoshimoto K, Doxastakis M, et al. Local mechanical properties of polymeric nanocomposites. *Phys Rev E* 2005; 72: 031801.
12. Rappe AK and Casewit CJ. *Molecular mechanics across chemistry*. Sausalito, CA: University Science Books, 1997.
13. Li C and Chou TW. A structural mechanics approach for the analysis of carbon nanotubes. *Int J Solids Struct* 2003; 40: 2487–2499.
14. Cornell WD, Cieplak P, Bayly CI, et al. A second generation force field for the simulation of proteins, nucleic acids and organic molecules. *J Am Chem Soc* 1995; 117: 5179–5197.
15. Tsai JL, Tzeng SH and Chiu YT. Characterizing elastic properties of carbon nanotubes/polyimide nanocomposites using multi-scale simulation. *Composites Part B* 2010; 41: 106–115.
16. Battezzati L, Pisani C and Ricca F. Equilibrium conformation and surface motion of hydrocarbon molecules physisorbed on graphit. *J Chem Soc* 1975; 71: 1629–1639.
17. Mayo SL, Olafson BD and Goddard III WA. DREIDING: A Generic Force Field for Molecular Simulations. *J Phys Chem* 1990; 94: 8897–8909.
18. Allen MP and Tildesley DJ. *Computer simulation of liquids*. Oxford: Oxford University Press, 1989.
19. Smith W, Yong CW and Rodger PM. DL_POLY: application to molecular simulation. *Molecular Simulation* 2002; 28: 385–471.
20. Rigby D and Roe RJ. Molecular dynamics simulation of polymer liquid and glass. II. Short range order and orientation correlation. *J Chem Phys* 1988; 89: 5280–5290.
21. Hardy RJ. Formulas for determining local properties in molecular-dynamics simulations: shock waves. *J Chem Phys* 1982; 76: 622–628.
22. Melchionna S, Ciccotti G and Holian BL. Hoover NPT dynamics for systems varying in shape and size. *Mol Phys* 1993; 78: 533–544.
23. Sun CT and Li S. Three-dimensional effective elastic constants for thick laminates. *J Compos Mater* 1988; 22: 629–639.