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**Research Article**

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# Molecular dynamic simulation of the mechanical properties of PI/$SiO_2$ nanocomposite based on materials studio

**Yuzhen Mo[1], Hui Zhang[1] and Jiachu Xu[1,2*]**

[1]*Department of Mechanics and Civil Engineering, Jinan University, Guangzhou, China*
[2]*Key Lab of Disaster Forecast and Control in Engineering, Ministry of Education, Jinan University, Guangzhou, China*

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**ABSTRACT**

*The initial unit cell models of PI/$SiO_2$Nanocomposite and pure polyimide were built by Materials Studio, the stiffness matrix and mechanical parameters such as Young modulus, shear modulus, bulk modulus and Poisson ratio of the unit cells were achieved after molecular dynamic (MD) optimizations and calculations. Finally, the mechanical properties of pure polyimide and the PI/$SiO_2$ nanocomposite with 5vol.% and 10vol.% nanosilica were compared. The result shows that the mechanical properties of polyimide can be remarkably reinforced by being filled with a low volume faction of silica-nanoparticle.*

**Keywords:** Polyimide, nanocomposite, Mechanical Properties, Materials Studio.

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## INTRODUCTION

With excellent mechanical properties, good dielectric properties, reliable thermal performance and electricity performance, polyimide has been widely applied. Since our requirement on material become higher, we are concerned about how to improve their performance in all aspects and the approach of fillingwith nanoparticles into polymer to improve the performance is given more and more attention by the researchers. Since Nandi et al [1,2]applied the SOL-GEL process to prepare the hybrid materials of polyimide and silica nanoparticles in the 1990s firstly, the research about the enhancement and toughening effect of nanoparticle on polymer matrix compositeis achievedprofound realizations through experiments during more than 20 years.Nandi observed that $SiO_2$ particles with the average radius of 1~1.5nm were uniformly dispersed in polyimide matrix, and the prepared model still remain transparent when the mass fraction of $SiO_2$ was up to 32% by SEM.Comparing with pure PI, the glass transition temperature (Tg) and thermal decomposition(Td) of the composite material increased by 10℃ and 30 ℃respectively.

Nanosilica is generated through the hydrolysis of silicon or the chloride of organic silicon at high temperature. There is the super tiny powder with hydroxyl groups on the surface. With the high chemical purity, good dispersion, larger specific area than that of common particles, nanosilica has become the most productive nanoparticle which has already realized the industrialization production. It plays an important role in the research in the application of nanocomposite. Therefore, strengthening the properties of PI by filling withnanosilica has become an important direction of research on polymer based nanocomposite.

In recent years, the MD simulation has already been applied in the study of materials in a certain scale with the rapid advancement of computer technology. Therefore, the MD simulation becomes an important method to predict the mechanical properties of polymeric materials.DaanFrenkel and BerendSmit[3] have done a detailed summary of the physical knowledge involved in MD, introducing some applications and algorithms.

Materials Science simulation software named Materials Studio, developed by American Accelrys is widely applied in the pharmaceutical, petrochemical, automotive, aerospace industrials and educational research department. The software is a comprehensive application of a variety of advanced simulation ideas and methods, such as quantum mechanics (QM), molecular dynamics (MD), Monte Carlo (MC) and dissipative particle dynamics (DPD) etc., the 3D molecular modeling and configuration optimization can be easily realized with it. Materials Studio using the Microsoft standard user interface, the appropriate parameter settings and the results analyzed can be achieved by each control panel.

**Simulation Process of Mechanical Properties on Materials Studio**

The steps of model construction and calculation process of molecular dynamics are as follows:

1. To build the crystal model of nanoparticle

Import the model from the material database, select File| Import | Examples |Documents |3D Modelfrom the menu bar to get the model required.Then select Build| Build Nanostructure| Nanoclusterfrom the menu bar，set the shape and particle size, click Build button and the nanocluster required model is obtained.

2.To build the polymer chain

Sketch a fragment or open a 3D atomistic document containing one., set Head Atom and Tail Atom from the menu bar as Build | Build Polymers | Repeat Unit to get the repeated unit , select Build | Build Polymers | Homopolymer to set the chain length and the tacticity, obtain the model of the polymer chain.

3.Geometry Optimization

In molecular dynamics simulation, the structure which is not optimized will obtain erroneous results in the subsequent simulation. Select Modules| Forcite| Calculation to open the Calculation dialog, Geometry Optimization is selected in the Task dropdown list to optimize the initial cell model so as to obtain the stable low-energy structure cell. The Smart algorithm is usually chosen for the simulation, and the simulation time should be adjusted to the size of the structure.The results of the geometry optimization include the files of the density curve, energy, convergence, cell size diagram and the results file.

4.To build the nanocomposite unit cell model

The Amorphous Cell module is used to construct the periodic structure model of complex amorphous materials. Select Build | Build Crystal to open the Build Crystal dialog, set the size to get a periodic empty cell model, then copy and paste the particle cell model to this empty cell, make the body centroid of the cell coincide with the body centroid of the nanoparticle, set the fractional coordinates of the particle centroid as (0.5,0.5,0.5). When the cell model of nanocomposite is build, select Modules| Amorphous Cell| Calculation to open the Calculation dialog, Packing option is chosen in Task dropdown list, the COMPASS option is selected from the force field tab, set the relevant parameters, and “pack in isosurface enclosed volume” is selected, the encapsulation of nanoparticles and polymer can be done. The files of Calculation results will display the detailed information of each parameter set, such as the number of themolecular chains packaged into the cell and the final energy value of the cell model of composites

5.Calculation of Molecular Dynamics

To obtain the true density of material, the Molecular Dynamics Simulation is necessary. The cell density gradually increases under external pressure, and the system can be further compressed by increasing the pressure via NPT simulation. Select Modules| Forcite| Calculation to open the Dynamics dialog. The NPT option is selected from the More tab. Generally, the NPT simulation is more than once, but the appropriate densityalso can be obtained by increasing the pressure via NPT simulation just for once.

6.Mechanical Properties Simulation

Select Modules| Forcite| Calculation to open the Mechanical Properties dialog. Generally the last 10 frames of the stable structures are calculated. The appropriate precision is set and other parameters are kept the default values.The relevant information of the initial parameters, the stiffness matrix and flexibility matrix of thecomposite, bulk modulus and shear modulus which are calculated via Reuss，Voigt and Hill formula respectively, the stress along X ,Y and Z direction which aresetby initial parameters and Lame constants are obtained from the Calculation results files.

In microscopic view, the nano-particle reinforced Polymer Matrix composite is considered as the anisotropic material, while close to isotropic material on macro-level. So it can be assumed that the material is close to isotropic. For isotropic material, the stress-strain relations can be completely described by two Lame constants $\lambda$ and $\mu$, which can be expressed as:

$$\lambda = \frac{1}{3}(C_{11} + C_{22} + C_{33}) - \frac{2}{3}(C_{44} + C_{55} + C_{66}), \quad \mu = \frac{1}{3}(C_{44} + C_{55} + C_{66}). \tag{1}$$

The common elastic parameters such as elastic modulus E, Poisson ratio $\nu$, bulk modulus K and shear modulus G can be expressed by the Lame constants:

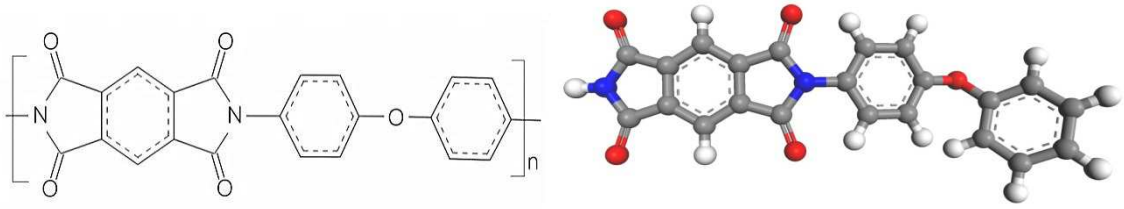
$$E = \mu\left(\frac{3\lambda + 2\mu}{\lambda + \mu}\right), \quad \nu = \frac{\lambda}{2(\lambda + \mu)}, \quad K = \lambda + \frac{2}{3}\mu, \quad G = \mu. \tag{2}$$

## EXPERIMENTAL SECTION

### Molecular Model of PI Single-chain

Make PMDA - ODA polyimide as basic material, its molecular structure is shown in Fig.1(a).

The ball-and-stick model of PI repeat unit is built by Materials Studio software, the Geometry Optimization model is shown in Fig. 1(b).



**（a）The molecular structure of polyimide （b）The ball-and-stick model of PI repeat unit**

**Fig.1 The structure of PMDA - ODA polyimide**

With PI repeat unit, the corresponding polymer chain is established with an appropriate degree of polymerization. Previous studies [4,5]proved that polymer built with 10 to 15 repeating units can meet the accuracy requirements. The paper chooses 15 as single-chain polymerization degree after simulation verification and comprehensive consideration.

The polyimide chain considered is composed of a total of fifteen unit monomers. The PI unit starts with Geometry Optimization via Smart method using the Forcite Module of Materials Studio 6.1. The optimized PI structure is shown in Fig.2.

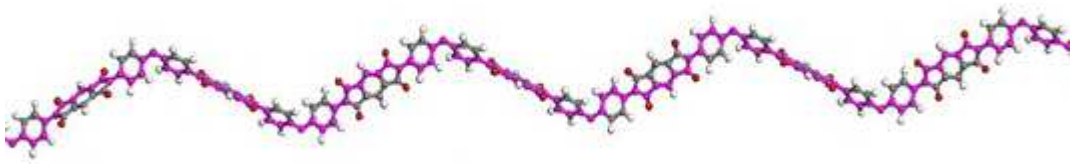
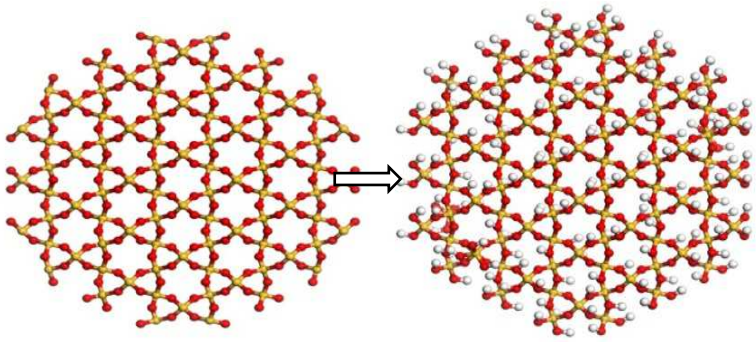


**Fig.2 Molecular model of PI single-chain after Geometry Optimization**

### Silica Nanoparticle Model

The Silica crystals model was imported from the material database, the model started with Geometry Optimization via Smart method using the Forcite Module. Then Sphere was selectedfrom the Shape dropdown list from the Build Nanocluster dialog. The radius of the particleswas set to 1nm. Click the Build button to construct a nanocluster .Then a silicon nanoparticle with manyunsaturated bonds on Si and Oon the surface was obtained which is shown in Fig.3(a). Then open the Atom Selection dialog,theunsaturated bonds on Si atoms were selected, combinedthese unsaturated bonds with O, then all of the unsaturated bonds were selected, clicked the Adjust Hydrogen button to simulate the real process of oxidation . SiO2-nanoparticle without unsaturated bonds is shown inFig.3(b).



**（a）$SiO_2$-nanoparticle with unsaturated bonds（b）$SiO_2$-nanoparticle without unsaturated bonds**
**Fig.3$SiO_2$-nanoparticle model**

**Unit Cell Model of PI/SiO2 Nanocomposite**

Actually the true density of material is 1.3 to 1.4 g/cm$^3$.As the polyimide molecules have aromatic rings, ring spearing and catenation resulting in the excessive energy of system may occur during the cell construction process. Thus, the cell construction started with a small target density of 0.1 g/cm$^3$. The initial model is shown in Fig.5(a). It was necessary to optimize the structure withGeometry Optimization via Conjugate Gradient Method with an execution step of 1000 in order to obtain the state of low potential for further processing.

After the initial unit cellwas prepared, 100ps of isothermal-isobaric ensemble referred to as NPT ensemble simulation at 0.15GPa with a time integration step of 1fs, a temperature of 298K at room temperature was performed. The system has been compressed by increasing the pressure to increase the densityvia NPT simulation just for once in this paper. When the density was close to the experimental value, enough time of isothermal ensemble referred to as NVT ensemble simulation was performed to balance the system .Curve of the cell density varies with time after simulation is shown in Fig.4.

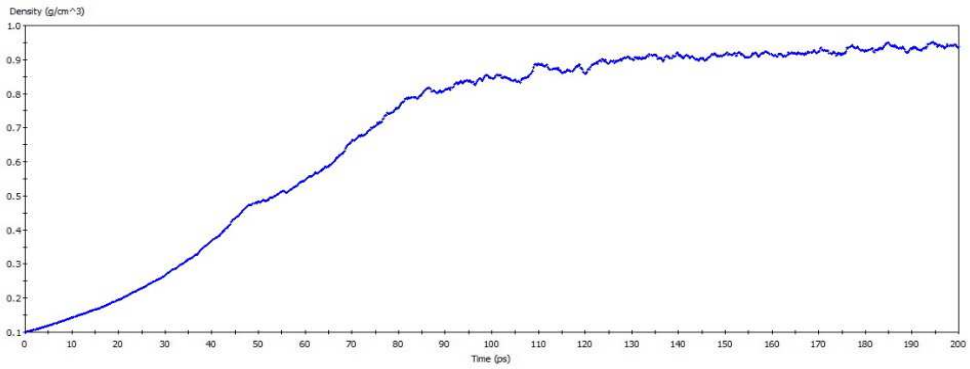
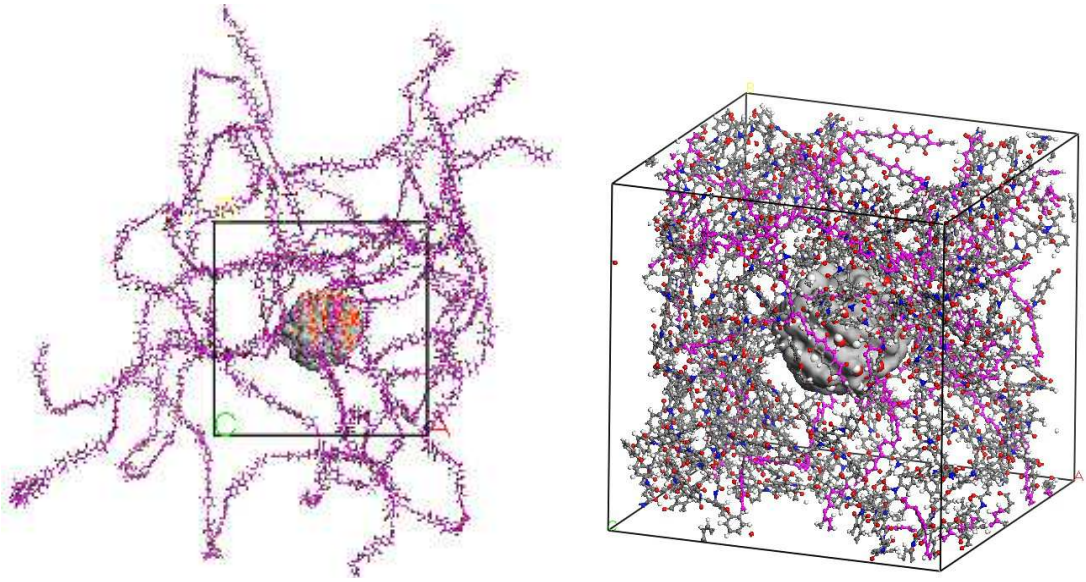



**Fig.4Curve of the cell density varies with time under 0.15GPa**

Through observation, the temperature fluctuated around 298K in a small scale and the energy gradually converged in the NPT calculation process, which indicated that the system dynamics simulation have reached equilibrium. Finally the length of unit cell was about 4.6nm and the density was about 1.4g/cm$^3$. The final model is shown in Fig.5(b).

**Mechanical Simulation of Unit Cell Model of PI/$SiO_2$**

The mechanical properties of the system can be calculated via Forcite module. After the calculation, the elastic stiffness matrix of unit cell can be obtained. In the establishment of the unit cell model with AC module, several polymer chains in cell are distributed randomly which satisfies the initial density requirement, thus the mechanical properties along X, Y and Z directions are usually not consistent. For PI/$SiO_2$,the phenomenon of nanoparticles centroid deviates from the unit cell body-centered position also affects the results.The stiffness matrix of the PI/$SiO_2$model with 5vol.%nanosilica is shown in Table1.



**(a) The initial low-density model of PI/$SiO_2$ (b) The final PI/$SiO_2$ model**
**Fig.5 Unit Cell Model of P I/$SiO_2$**

**Table 1 The elastic stiffness matrix of PI/$SiO_2$ unit cell**

| $C_{ij}$(GPa) | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| 1 | 7.9983 | 5.2554 | 5.0818 | -0.2721 | -0.0463 | -0.0004 |
| 2 | 5.2554 | 8.5265 | 5.2051 | -0.0262 | 0.1415 | -0.0384 |
| 3 | 5.0818 | 5.2051 | 7.7790 | 0.1407 | -0.2449 | -0.1216 |
| 4 | -0.2721 | -0.0262 | 0.1407 | 1.4889 | 0.0580 | 0.3349 |
| 5 | -0.0463 | 0.1415 | -0.2449 | 0.0580 | 1.8760 | -0.0937 |
| 6 | -0.0004 | -0.0384 | -0.1216 | 0.3349 | -0.0937 | 1.6321 |

It can be seen from Table 1 that the value of $C_{ij}(i = 1,2,3; j = 4,5,6)$is close to zero, which indicates that the polymer model simulated by molecular dynamics is not extreme anisotropic material. The values of $C_{11}, C_{22}, C_{33}$, $C_{12}, C_{13}, C_{23}$ and$C_{44}, C_{55}, C_{66}$are similar which indicate that the model is close to the isotropic material. So it can be assumed that the material is isotropic. The Lame constants are obtained by using formula (1):

$$\lambda = 4.7700 \text{ GPa} \quad , \quad \mu = 1.6656 \text{ GPa}$$

According to formula(2) ,the elastic modulus E, Poisson ratio ν, bulk modulus K and shear modulus G are

$$E = 4.56 \text{ GPa}, \qquad \nu = 0.37, \qquad K = 5.88\text{GPa}, \qquad G = 1.6656 \text{ Gpa}$$

## RESULTS AND DISCUSSION

### Comparison and Analyses on the Mechanical Properties

In order to study the reinforcing effects of nanosilica on mechanical properties of polyimide nanocomposite, another unit cell modelof the PI/$SiO_2$nanocompositein which the volume fraction of nanosilica was 10% and the unit cell model of pure polyimide were also simulated independently,then their properties were compared. The results are shown in Table 2.

**Table 2 The mechanical properties of the pure PI and PI/$SiO_2$nanocomposite**

| | | PI/$SiO_2$ | |
|---|---|---|---|
| property | pure PI | 5% vol.$SiO_2$ | 10% vol.$SiO_2$ |
| **E(GPa)** | 4.23 | 4.56 | 4.87 |
| **G(GPa)** | 1.28 | 1.67 | 1.75 |
| **K(GPa)** | 5.63 | 5.88 | 7.50 |
| **ν(GPa)** | 0.39 | 0.37 | 0.39 |

According to the Table 2, the values show that when polyimide is filled with about 5vol.% nanosilica,Young modulus, shear modulus and bulk modulus are improved by 8%, 30% and 4% respectively,when compared to pure

PI, with no change in Poisson's ratio basically ; when the volume fraction of nanosilica reaches to 10%, Young modulus ,shear modulus and bulk modulus are improved by 15%, 37% and 33% respectively. These data adequately demonstrate that the mechanical properties of material can be reinforced by being filled with nanoparticle.

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