



# CHARACTERIZING MECHANICAL PROPERTIES OF PARTICULATE NANOCOMPOSITES USING MULTI-SCALE SIMULATION

Jia-Lin Tsai, Shi-Hua Tzeng

Department of Mechanical Engineering, National Chiao Tung University  
Hsinchu, Taiwan, 300

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## Abstract

*This research aims to characterize the mechanical properties of the silica nanocomposites using multi-scale simulation. The molecular structures of the nanocomposites were established through molecular dynamic (MD) simulation, from which the non-bonded gap as well as the non-bonded energy between the nano-sized inclusion and the surrounding matrix was evaluated. It was postulated that the normalized non-bonded energy (non-bonded energy divided by surface area of the inclusion) is correlated with the degree of interfacial interaction. Based on the MD simulation, a continuous micromechanical model including silica particles, matrix and effective interphase was developed, in which the dimension of the effective interphase was assumed equal to the non-bonded gap and the corresponding elastic stiffness was calculated from the normalized non-bonded energy. The results calculated from the continuous micromechanical model demonstrate good agreements with those obtained directly from MD simulation.*

## 1 Introduction

With the extensive applications of polymer and its composites, the demanding on the high stiffness and strength of the materials is increasing. In order to improve mechanical properties, spherical particles have been used as reinforcement in polymeric materials for many years. In general, these composite materials mostly were reinforced with micron-sized inclusions. However, recently, with the advance of the nanotechnology as well as the processing techniques, various types of nano particles have been developed and then dispersed into conventional polymeric material to form the

nanocomposites. The corresponding mechanical behaviors of the nanocomposites have been investigated by many researchers using either finite element method (FEM) analysis or molecular dynamic (MD) simulation [1-3].

Odegard et al. conducted molecular simulation to characterize the interface interaction between the nanoparticles and surrounding polyimide matrix with various particle surface treatment and particle sizes [1]. A micromechanical model with effective interphase was proposed to model the properties of the nanocomposites. Results demonstrated that when the particle sizes increase, the modulus of the nanocomposites increase accordingly. However, in their analysis, the thickness of the effective interface as well as its properties was not specified clearly. Cannillo et al. [2] modeled the silica particles filled in the PCL (poly-caprolactone) matrix using a FEM model. By introducing a third phase, namely the interphase, around the particle in the micromechanics analysis, they predicted the mechanical properties of the nanocomposites with various amount of particle loading. In their analysis, it was hypothesized that the dimension of the interphase is the same as the average particle radius, and the modulus of the interphase is set equal to the average value of the modulus of the particles and matrix. Avella et al. [3] adopted the same manner with the interphase of about 100 nm to model the PCL/silica nanocomposites. Since nano-inclusion provide a very high specific surface area as compared to the micro-particle, the interphase thickness as well as the modulus may expect to play an important role in the nanocomposites overall behaviors [4, 5]. Moreover, the other behaviors such as the crack propagation are also influenced by the nanoparticles as well as their interfacial adhesion to the surrounding polymers [6]. Therefore, a more

complete model including the interfacial effect is required to describe the properties of the nanocomposites with accuracy. In particular, the thickness of the effective interphase layer and the properties has to be determined properly [7].

In this study, the effective interphase dimension and the corresponding properties were evaluated from the MD simulation. In addition, the effect of the molecular chain number as well as the number of chain unit on the mechanical properties of polyimide was also investigated. The behaviors of the nanocomposites were characterized using the continuum mechanical model by including the silica inclusion, surrounding matrix and the effective interphase.

## 2 Generation of Molecular Structures

The molecular structure of silica/polyimide nanocomposites suitable for molecular dynamic simulation was constructed at the beginning. A representative volume element (RVE) as shown in Fig.1 with periodicity boundary conditions containing a spherical silica particle embedded in the amorphous polyimide molecular chains was constructed to represent the particulate nanocomposites. In the above molecular model, the particles were assumed to disperse regularly and homogeneously within the polyimide matrix. To generate the spherical nano-particle as shown in Fig.1, a  $\alpha$  type silica crystal was created initially and then all Si and O atoms with the radius measured from the sphere center greater than a certain value were discarded. While, the polyimide polymer was generated by several molecular chains depending on the size of the RVE. Fig.2 illustrates a unit of polyimide monomer. It should be noted that the mechanical properties of polyimide is relied on the number of polyimide monomer unit each chain contains as well as the total polyimide chain number. Table 1 demonstrates the modulus of the polyimide calculated from MD simulation with various molecular chain structures. In the study, the polyimide molecular structures with seven molecular chains and each one containing 10 repeated unit was employed to construct the silica/polyimide nanocomposites because its modulus value is quite close to the experimental data. Moreover, the initial dimensions of the RVE were adjusted such that the density of the polyimide is close to the experimentally measured value,  $1.31 \text{ g/cm}^3$  [8]. There are three different particulate sizes, i.e. 6.56, 8.47 and 10.85 Å in radius, were considered in the simulation.

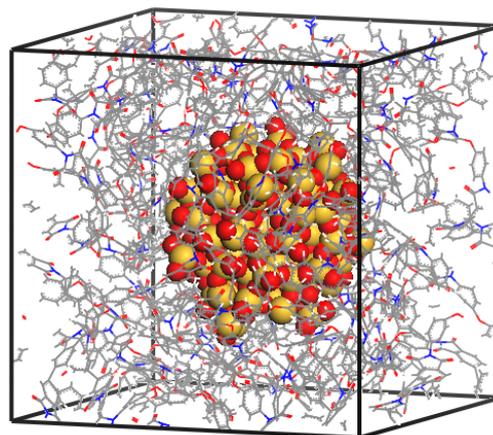


Fig. 1. Representative volume element of the particulate nanocomposites.

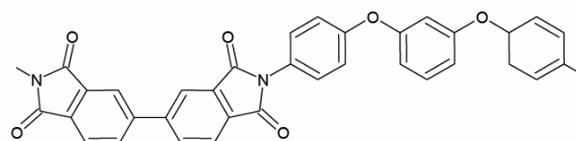


Fig. 2. Schematic of polyimide monomer unit.

Table 1. Comparison of mechanical properties of polyimide with various molecular chain configurations

	PI-1	PI-2	PI-3	PI-4
No. of unit in PI chain	5	10	12	35
No. of chain in PI model	14	7	10	2
Density (g/cc)	1.33	1.31	1.31	1.31
Young's modulus (GPa)	3.043	3.67	3.95	4.53

Subsequently, the force field used for describing the atom/molecular interactions needed to be specified in the MD simulation. In this study, the compass force field derived based on ab initio calculation was selected to characterize the silica

particles and the polyimide polymer as well as their reciprocal interactions. Having consolidated coverage of organic and inorganic materials, the compass force field is applicable for treating the non-bonded interaction between the silica and the polyimide polymers [9]. It is noted that for the inorganic materials, the parameterization and validation of the compass force field were conducted based on the energy minimization at zero temperature resulting in that the temperature effect were not taken into account in their corroboration. As a result, in the following MD simulation, the molecular structure of the nanocomposites and their associated properties were equilibrated and calculated at zero temperature condition.

The MD simulations were conducted using Material Studio package [9]. During the simulation, the NVT and NPT ensembles were employed sequentially in the MD simulation. Here, the purpose of the NVT ensemble conducted at 1500 K for 80 ps was to supply enough kinetic energy on the molecular atoms such that homogeneous molecular structure within the RVE can be achieved. The NPT process was designated to 0 atm such that the RVE with traction-free boundary conditions can be satisfied. Since the compass force field employed for the inorganic materials is validated only at zero temperature, the temperature in the NPT ensemble was eventually set at 0 K.

### 3. Non-Bonded Gap and Non-Bonded Energy

Based on MD simulation, it was found that there is clear gap with relatively lower molecular density existing between the silica particle and the surrounding polyimide matrix. This gap was referred as the non-bonded gap because it is caused by the non-bonded force field between the nano-particle and the polymeric matrix. The non-bonded gap between the silica particle and the polyimide matrix within the unit volume is introduced as

$$r_{nonbonded} = r_{PI}^{min} - r_{SiO_2}^{max} \quad (1)$$

where  $r_{SiO_2}^{max}$  is the maximum radial distance for the silica atoms within a certain volume element and  $r_{PI}^{min}$  is the minimum radial distance. Table 2 indicates the non-bonded gap calculated from the nanocomposites with three different particle sizes. It was found that basically, the non-bonded gap increases as the particle size increases. However, in this regard, the dependence of non-bonded gap on the particle size is not significant.

Table 2. Non-bonded gap calculated based on three different particle radius.

Nanocomposites	PI-SiO <sub>2</sub>	PI-SiO <sub>2</sub>	PI-SiO <sub>2</sub>
Particle radius (Å)	6.56	8.47	10.85
Non-bonded gap(Å)	4.14	4.35	4.55

In addition to the non-bonded gap, the non-bonding energy between the nano-particle and the polyimide matrix was also estimated from the MD simulation. In the compass force field, the non-bonded interaction consists of the electrostatic and van der Waals interactions which are modeled by the Coulomb function and Lennard-Jones function, respectively. Moreover, the total non-bonded energy within the nanocomposites is contributed not only by the interaction between the nano-particle and the polyimide but also by the silica nano-particle itself as well as the polyimide molecular chains. Thus, the non-bonded energy between the silica and polyimide interface is calculated by subtracting the non-bonded energy of the particle and polymer from the total non-bonded energy and written as

$$U_{PI-silica} = U_{total} - U_{silica} - U_{PI} \quad (2)$$

where  $U_{total}$  is the total non-bonded energy obtained from the overall nanocomposites.  $U_{silica}$  and  $U_{PI}$  stand for the non-bonded energy of silica particle and polyimide molecular chain, respectively. The non-bonded energy of the polyimide molecular chain was evaluated in the RVE when the nano-particle was removed and only the molecular structures of the polyimide matrix were left. In the similar manner, the non-bonded energy of silica was calculated. Therefore, with Eq. 2, the non-bonded energy between the nano-particles and the polyimide were determined. It is worthy to mention that the non-bonded energy provides an indication regarding the extent of interaction between the particle and the surrounding matrix. If the non-bond interaction can be further employed to represent the characteristics of an equivalent interphase with the dimension equal to the non-bond gap, it is possible that the mechanical properties of the nanocomposites could be described directly by a continuum micromechanical model.

To achieve the purpose, the degree of interaction between the particle and the matrix is characterized in terms of the normalized non-bonded energy which is defined as the non-bonded energy divided by the surface area of the spherical particle. Subsequently, the normalized non-bonded energy was assumed to be associated with the non-bonded gap in the form of

$$U(r) = \frac{1}{2}kr^2 \quad (3)$$

where  $r$  is the non-bonded gap and  $k$  is the parameter to be determined. Based on the normalized non-bonded energy, the corresponding normalized interaction force was obtained by differentiating the energy with respect to the distance as

$$F(r) = -\frac{\partial U}{\partial r} = -kr \quad (4)$$

The negative sign of the force in Eq. 4 represents the attractive interaction. On the other hand, Eqs. 3 and 4 can also be interpreted as the strain energy of a unit element with length equal to the non-bond gap,  $r$ , and cross section equal to one when it is subjected to the applied loading " $kr$ ". Therefore, from the 1-D elasticity, the strain energy of the unit element is represented as

$$U = \frac{\sigma^2}{2E}r \quad (5)$$

where  $E$  is the Young's modulus of the equivalent unit element, and  $\sigma$  is equal to " $kr$ " which is the loading applied on the unit area (so called stress). From the hypothesis that the strain energy of the unit element is equivalent to the normalized energy given in Eq 3, the modulus of the equivalent unit element is yielded as

$$E = kr = \frac{2U(r)}{r} \quad (6)$$

It is noted that in the above calculation, only the strain energy caused by axial loading was considered to illustrate the normalized strain energy of the nanocomposites obtained from the MD simulation. As a result, once the non-bonded gap as well as the normalized non-bonded energy was calculated, the elastic modulus of the equivalent interphase can be determined by means of Eq. 6. Fig.3 demonstrates

the normalized non-bonded energy of the nanocomposites calculated with different particle sizes. It shows that as the particle size decreases, the corresponding normalized non-bonded energy increases and the interaction is intensified.

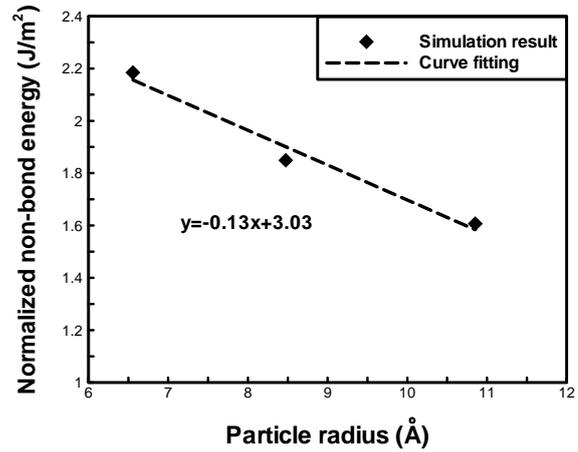


Fig. 3. Particle size effect on the normalized non-bonded energy of silica/polyimide nanocomposites.

In view of the forgoing, the non-bonded interaction between the reinforced particle and the surrounding matrix can be replicated appropriately by a continuum equivalent interphase. With the mechanical properties of the interphase in combination with the properties of spherical particle and surround polymer, the mechanical properties of the nanocomposites can be predicted using the continuum micromechanical model. It is noted in the following analysis, the Poisson's ratio of the interphase is assumed to be 0.3.

#### 4 Continuum Micromechanical Model

When the mechanical properties of the particle, interphase and matrix as well as the corresponding geometric parameters were determined, the behaviors of the nanocomposites can be depicted using the micromechanical model with multiphase particles [10, 11]. It should be note that, there are three ingredients were considered in the effective interphase model which is different from conventional Mori-Tanaka micromechanical model [12] in which only two phases were included in the analysis. The explicit formulation of the effective interphase model is written as [11]

$$C^* = C^m + [(v_r + v_\Omega)\{C^r - C^m\}A_r^{di} + v_\Omega \{C^\Omega - C^r\}A_\Omega^{di}] / [v_m I + (v_r + v_\Omega)\{A_r^{di}\}J^{-1}] \quad (7)$$

where  $C^*$  denoted the stiffness matrix for the nanocomposites.  $C^\Omega$ ,  $C^\Gamma$  and  $C^m$  represent the stiffness of the domain of  $\Omega$  (inclusion),  $\Gamma$  (interphase) and  $m$  (matrix), respectively. The detail derivation and expression for Eq. 7 can be found elsewhere [10, 11]. In the above micromechanical model, all three phases are assumed to be perfectly bonded together, although in reality, there is a non-bonded gap existing between the spherical particle and the surrounding matrix. The interaction between the non-bonded gaps was modeled as an effective interphase the corresponding properties of which were derived from the normalized non-bonded energy calculated using molecular simulation as described early. As a result, with the properties of the inclusion, matrix and the effective interphase, the associated behavior of the nanocomposites could be predicted from Eq. 7.

### 5 Elastic Constants of Molecular Structures

In addition to the micromechanical analysis discussed previously, the mechanical properties of the equilibrated molecular configuration of nanocomposites can also be predicted using the molecular simulation [13]. By applying a small amount of strain component on the RVE, while the other strain components are remaining at zero, the deformed state of the molecular structure was produced. Once the equilibrium condition was accomplished in the deformed state, the associated stress was then calculated from the virial theorem [14] and the stiffness matrix  $C_{ij}$  of the nanocomposites was measured as the derivative of the stress associated with the corresponding strain component

$$C_{ij} = \frac{\Delta\sigma_i}{\Delta\varepsilon_j} \quad (8)$$

where the stress components  $\sigma_{ij}$  is expressed as

$$\sigma_{ij} = -\frac{1}{V_0} \left( \sum_{i < j} r_{ij} f_{ij}^T \right) \quad (9)$$

In Eq. 9,  $r_{ij}$  and  $f_{ij}$  denotes the atomic distance and the corresponding interaction force between any two atoms within the cut-off distance.  $V_0$  represents the total volume of the RVE. It is noted that in Eq. 9, because the model was simulated at 0 K, the temperature effect was neglected in the stress computation.

Table 3. Comparison of the modulus of the silica/polyimide nanocomposites calculated using effective interphase model, MD simulation and Mori-Tanaka model

Nanocomposites	PI-SiO <sub>2</sub>	PI-SiO <sub>2</sub>	PI-SiO <sub>2</sub>
Particle radius (Å)	6.56	8.47	10.85
Volume fraction (%)	3.87	4.75	5.08
Young's modulus (GPa) (MD simulation)	4.52	4.34	4.37
Young's modulus (GPa) (Effective interphase model)	4.52	4.46	4.32
Young's modulus (GPa) (Mori-Tanaka model)	3.97	4.04	4.07

### 6 Results and Discussions

The modulus of the nanocomposites with three different sizes of nano-particles calculated from the molecular simulation and the effective interphase model were illustrated in Table 3. For the sake of comparison, the results calculated from the Mori-Tanaka model were also included in the Table 3. It was revealed that the modulus obtained using the effective interphase model is quite close to those obtained directly from the molecular simulation. However, the results calculated using Mori-Tanaka model deviate from the molecular simulation and the Mori-Tanaka results seem under-estimate the associate values. In addition, molecular simulation results indicate that when the particle sizes decrease, the corresponding modulus of the nanocomposites may increase if the particle volume fraction is remaining the same. In the molecular simulation, it is pretty difficult to generate the molecular models with the same inclusion volume fraction since the volume fraction always varies and deviate from the initially setup value. As can be seen from the Table 3, all three cases have different particle volume fraction after the molecular simulation even though they are the same initially. Apparently, although the nanocomposites containing larger particles have the highest volume fraction, its modulus is almost the same as or even lower than the others with lower volume fraction of small particles.

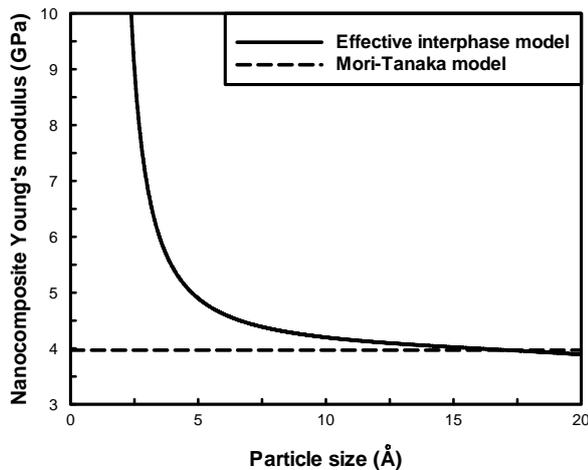


Fig. 4. Particulate size effect on the elastic modulus of silica/polyimide nanocomposites characterized using effective interphase model.

In light of the fact that the small particle having more specific area can effectively enhance the stiffness of the nanocomposites, the applicability of the continuum micromechanical model to characterize the size dependent behaviors of the nanocomposites was examined. From our present simulations, the non-bonded gap varies between 4.2 to 4.5 Å, and thus for simplicity, it was assumed that the non-bonded gap is not influenced appreciably by the particle size and its value is set equal to 4.3 Å for the following calculation. In addition, for the normalized non-bonded energy, since it is directly correlated to the extent of the non-bonded interaction, its relationship to the particle size was described using a linear polynomial as shown in Fig.3. With the properties of the normalized non-bonded energy and non-bonded gap, the modulus of the nanocomposites with various inclusion sizes was predicted using the continuum model. Fig.4 shows the predictions of the nanocomposites with volume fraction 4.2%. It can be seen that as the particle size increase, the modulus of the nanocomposites decreases accordingly. Moreover, the prediction will approach to the results of Mori-Tanaka model as the particle size continues to increase. This tendency is similar to the results provided by Adrian et al. who performed the investigation on the size effect on elastic properties of buckyball/polyethylene nanocomposites system using MD simulation [15].

## 7 Conclusions

The mechanical behaviors of nanocomposites were characterized successfully using the MD simulation in conjunction with the continuum micromechanical model. From MD simulation, the non-bonded gap as well as the non-bonded energy was obtained, based on which the effective interphase was introduced to represent the intensity of the interfacial interaction. With the properties of interphase, the mechanical properties of the nanocomposites were predicted using three-phase micromechanical model. Results demonstrate that the Young's modulus obtained from the micromechanical model is quite close to those directly calculated from MD simulation.

## 8 Acknowledgments

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