Multiscale Modeling on Polymer Nanocomposites Considering Percolated Interphase

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Keywords: Multiscale modeling, Molecular dynamics simulation, Polymer nanocomposites, Multiscale homogenization, Interphase percolation

Abstract

In this study, a multiscale homogenization modeling of polymer nanocomposites is conducted. The fundamental physics about mechanical behavior has not been established in view of nanoparticle/nanoparticle interaction and nanoparticle/polymer interaction when the fillers are agglomerated. In this study, molecular statics/dynamics approach is employed in order to characterize these kinds of fundamental physics. The interphase characteristics are investigated in continuum-based homogenization modeling. The elastic constants of polymer nanocomposites are decreased when the distance of nanoparticles are less than 1 nm. This is because the characteristics of interaction between polymer and nanoparticles are reduced as the polymer chains are difficult to be entangled in the vicinity of nanoparticles due to repulsive potential energy of nanoparticles. The degree of nanoparticle/polymer interaction is reflected in the elastic constants of effective interphase.

1. Introduction

Polymer nanocomposites are widely employed in industrial fields due to their weight advantage and multifunctionality. As the filler size decreases to nanometer scale, the physical properties of nanocomposites show a dramatic filler-size dependency due to surface area to volume ratio. The molecular chains are entangled in the vicinity of the reinforced nanoparticles due to high interaction between polymer matrix and fillers. Entangled molecular chains are condensed and crystallized like a unique phase, which is well-known as the interphase. There are many studies about interphase characteristics. Linear elastic properties, thermal properties and electrical properties of interphase are characterized in many literatures [1-2].

However, in real manufacturing procedure, there is agglomeration phenomenon due to van der Waals interaction between nanoparticles. Therefore, the reinforced fillers are not well-dispersed in polymer matrix and some clusters of nanoparticles are formed [3]. In many literatures, agglomeration of nanoparticles occurs to weakened mechanical behavior. However, this kind of phenomenon is almost not investigated in molecular viewpoint. In this study, the distance effect of nanoparticles is investigated. In order to investigate distance effect of nanoparticles, 6 molecular models are employed in this study. Elastic properties such as Young's modulus and shear modulus of polymer nanocomposites are predicted. In this study,

particle-particle interaction and particle-polymer interaction behaviors are investigated by multiscale bridging method.

2. Molecular dynamics simulation

2.1. Unit cell modeling & unit cell configuration

In every molecular modeling, Material Studio 5.5 was employed. Silicon carbide (SiC) nanoparticles are embedded in cross-linked epoxy matrix as shown in Figure 1. In order to investigate size effect of nanoparticles, 6 molecular models are employed. Every molecular models satisfy 3% of volume fraction, and particle radius is 1.8 nm. Unit cell size is 93.3817(Å)×46.6908(Å)×46.6908(Å). Periodic boundary condition is imposed on unit cell.

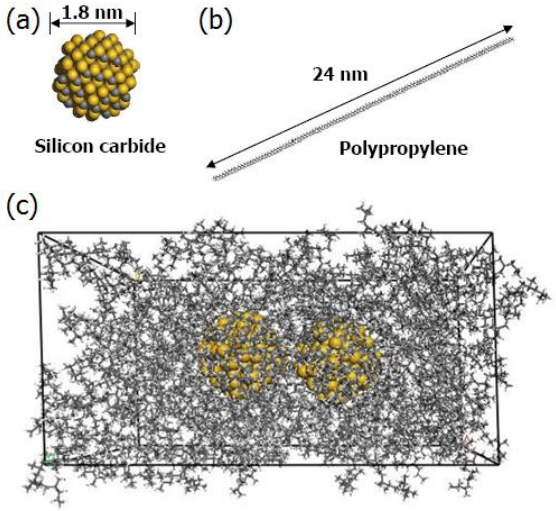

Figure 1. Molecular models: (a) Silicon carbide spherical filler, (b) Polyprophylene, and (c) Nanocomposites unit cell.

2.2. Parrinello-Rahman fluctuation analysis & elastic properties of nanocomposites

In order to obtain elastic properties of nanocomposites, Parrinello-Rahman fluctuation analysis is employed. After energy minimization of unit cell, NVT ensemble simulation is conducted in order to adjust absolute temperature at 200K which is lower than glass transition temperature. After NVT ensemble simulation, NPT ensemble simulation is conducted in order to adjust pressure at 1 atm. And finally, NσT ensemble simulation is conducted. Under constant external stress condition, elastic properties of nanocomposites of unit cell are computed by Parrinello-Rahman fluctuation analysis.

$$C_{ijkl} = \frac{kT}{\langle V \rangle} \left\langle \delta\varepsilon_{ij} \delta\varepsilon_{kl} \right\rangle^{-1} \tag{1}$$

where k, T, V and $\langle \cdot \rangle$ are Boltzmann constant, absolute temperature, volume of unit cell and ensemble average, respectively.

3. Multiscale analysis

3.1. Review of multiscale homogenization theory

The multiscale homogenization method is a numerical technique to describe deformation behavior of heterogeneous solid materials when microscopic structures are repeated by periodicity of unit cell. In order to describe heterogeneous solids, two-scale coordinates such as macroscopic coordinate **x** and microscopic coordinate **y** are introduced. Displacement fields are expanded asymptotically by scale parameter ε as follows:

$$\mathbf{u}(\mathbf{x},\mathbf{y}) = \mathbf{u}_0 + \mathbf{u}_1\varepsilon + \mathbf{u}_2\varepsilon^2 + \cdots \tag{2}$$

Then, constitutive equation of linear elastic problem could be represented by following form:

$$\sigma_{ij}(\mathbf{x},\mathbf{y}) = C_{ijkl}(\mathbf{y})u_{k,l} \tag{3}$$

where $u_{k,l} = \frac{d}{dX_l}u_k = \left(\frac{d}{dx_l} + \frac{d}{dy_l}\right)\left(u_k^0 + u_k^1\varepsilon + u_k^2\varepsilon^2 + \cdots\right) = \varepsilon^{-1}\left(\frac{du_k^0}{dy_l}\right) + \varepsilon^0\left(\frac{du_k^0}{dx_l} + \frac{du_k^1}{dy_l}\right) + \varepsilon^1\left(\frac{du_k^1}{dx_l} + \frac{du_k^2}{dy_l}\right) + \cdots.$

By introducing Eq. (3) into equilibrium equation of linear elastic problem, equations could be drawn as follows:

$$\frac{\partial\sigma_{ij}}{\partial x_j} + f_i = 0 \tag{4-1}$$

$$\varepsilon^{-2} : \frac{\partial\sigma_{ij}^{(0)}}{\partial y_j} = 0 \tag{4-2}$$

$$\varepsilon^{-1} : \frac{\partial\sigma_{ij}^{(0)}}{\partial x_j} + \frac{\partial\sigma_{ij}^{(1)}}{\partial y_j} = 0 \tag{4-3}$$

$$\varepsilon^{0} : \frac{\partial\sigma_{ij}^{(1)}}{\partial x_j} + \frac{\partial\sigma_{ij}^{(2)}}{\partial y_j} + f_i = 0 \tag{4-4}$$

$$\varepsilon^{s-1} : \frac{\partial\sigma_{ij}^{(s)}}{\partial x_j} + \frac{\partial\sigma_{ij}^{(s+1)}}{\partial y_j} = 0 \tag{4-5}$$

where Eq. (4-3) and Eq. (4-4) mean the microscopic equilibrium equation and the macroscopic equilibrium equation, respectively. Characteristic variable χ which means microscopic displacement fields under the macroscopic unit cell strain is introduced in order to solve Eq. (4-3) as follows:

$$u_i^{(1)}(\mathbf{x},\mathbf{y}) = -\chi_i^{kl}(\mathbf{y})\frac{\partial u_k^{(0)}}{\partial x_l}(\mathbf{x}) \tag{5}$$

By introducing Eq. (5) into Eq. (4-3), the microscopic equilibrium equation could be represented by the following form:

$$\frac{\partial}{\partial y_i}\left(C_{ijkl} - C_{ijmn}\frac{\partial\chi_m^{kl}}{\partial y_n}\right) = 0 \tag{6}$$

Then, homogenized elastic stiffness tensor could be following form:

$$C_{ijkl}^H = \frac{1}{|Y|}\int_Y C_{ijkl}(\mathbf{y}) - C_{ijmn}(\mathbf{y})\frac{\partial\chi_m^{kl}}{\partial y_n}dy \tag{7}$$

3.2. Characterization of effective interphase

A three-phase continuum model with matrix, particle and interphase is introduced in order to reflect interface effect, i.e., particle-polymer interaction. Elastic properties of interphase are

computed by iterative inverse algorithm as shown in Figure 2. Interphase thickness is 7 Å. Purpose of the proposed algorithm is to find elastic properties of interphase such that the elastic properties of nanocomposites are satisfied with those of three-phase continuum model.

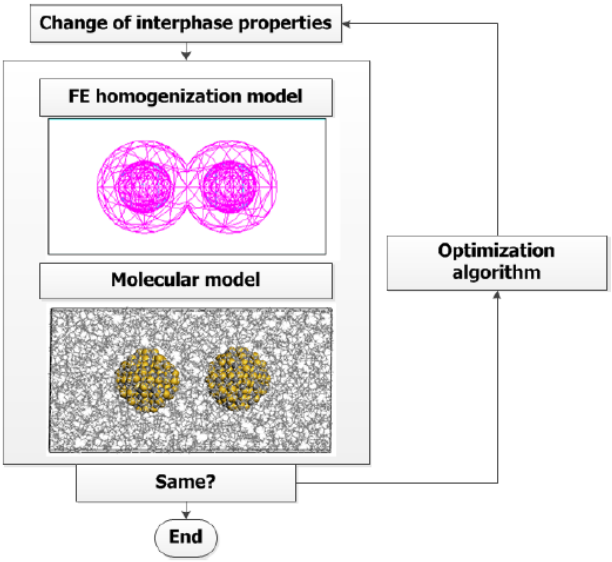

Figure 2. Flowchart of the numerical estimation of the elastic modulus of the interphase using the multiscale homogenization method.

3.3. Multiscale modeling of particle-particle interaction

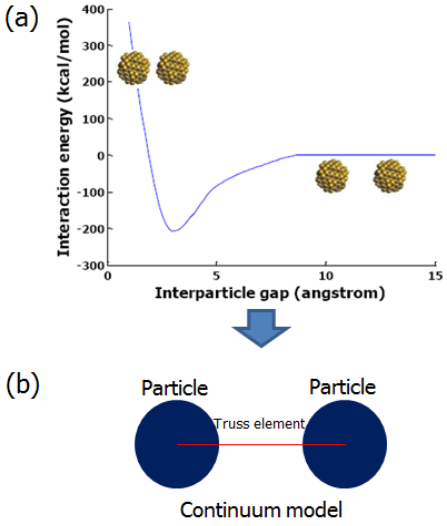

Figure 3. Multiscale modelling considering non-bond interaction between nanoparticles: (a) nonbond interaction energy with respect to interparticle gap, and (b) schematics of multiscale modelling.

As distance between nanoparticles decreases, the non-bond interaction energy is changed as shown in Figure 3. Non-bond interaction energy is composed of van der Waals potential energy and electrostatic potential energy. Figure 3 shows high gradient change of interaction energy as the nanoparticles distance decreases. In order to reflect interaction characteristics of nanoparticles, simple spring element are introduced in continuum modeling as follows:

$$k_{ij}(r_{ij}) = \frac{\partial^2 \Phi(r_{ij})}{\partial r_{ij}^2} \text{ where } \Phi = \Phi_{vdW} + \Phi_{elec} \tag{8}$$

where Φ_{vdW} and Φ_{elec} are van der Waals energy and electrostatic energy, respectively.

4. Simulation results

4.1. Elastic properties of nanocomposites with respect to nanoparticle gap

Figure 4 shows elastic properties of nanocomposites computed by molecular dynamics simulation. As the nanoparticle distance decreases, Young's modulus and shear modulus of nanocomposites decrease. This results show importance of well-dispersion of nanoparticles in polymer matrix.

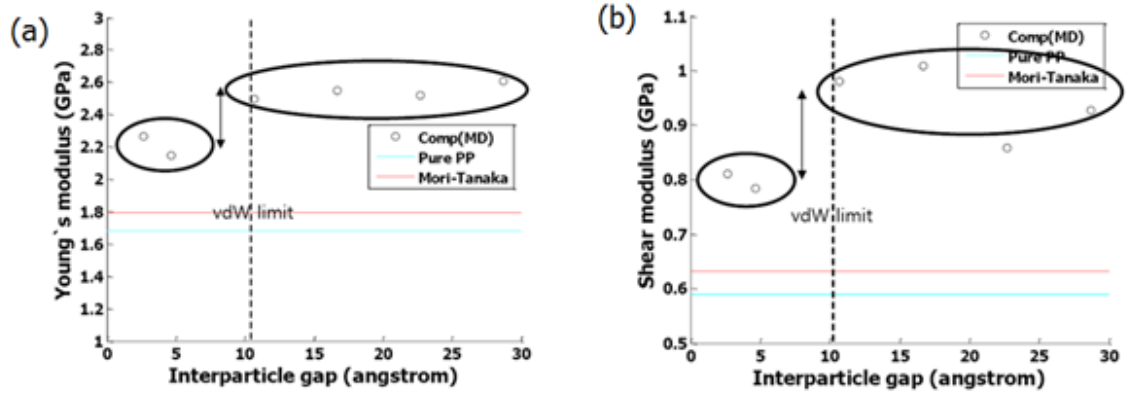

Figure 4. Elastic constants of polymer nanocomposites with respect to interparticle gap estimated by molecular dynamics simulation: (a) Young's moduli and (b) shear moduli.

4.2. Elastic properties of interphase with respect to nanoparticle gap

Figure 5 shows the effective interphase elastic properties which are predicted from the proposed numerical algorithm in Figure 2. As the nanoparticle gap decreases, the effective interphase elastic properties decrease. If the nanoparticle gap is higher than 2.5 nm, the interphase characteristics are not changed.

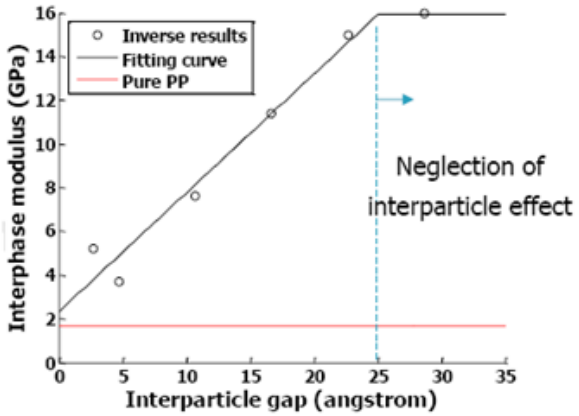

Figure 5. Effective elastic properties of interphase with respect to interparticle gap.

4.3. Effect of particle-particle interaction behavior in view of mechanical behavior

Figure 6 shows the influence of interaction energy between nanoparticles in view of elastic behavior. Interaction force is reflected on the continuum model by truss element. In small interparticle gap, there is only 2% error of Young's modulus between with spring model and without spring model. From this result, particle-polymer interaction behavior is more dominant than that of particle-particle interaction.

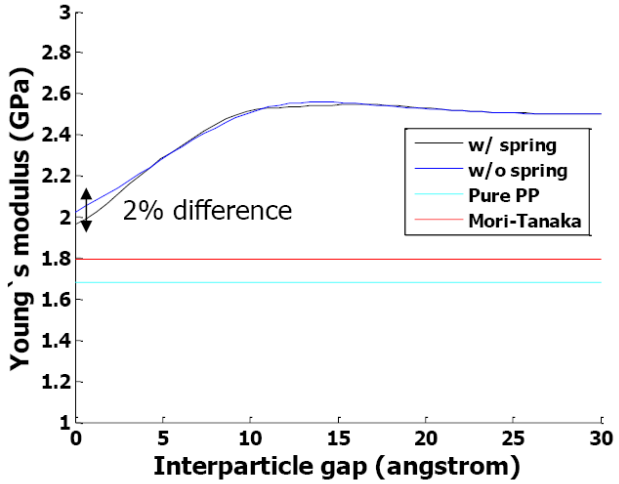

Figure 6. Influence of interaction energy between nanoparticles about homogenized elastic constants of polymer nanocomposites.

5. Conclusion

In this study, elastic behavior of polymer nanocomposites about various interparticle gap are investigated. As the gap of nanoparticles decrease, the overall behavior of nanocomposites is weakened. As shown in simulation results, particle-polymer interaction is more dominant than that of particle-polymer interaction. The proposed multiscale modeling could be applied to do optimal design and reliability-based design of polymer nanocomposites.

References

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