Hierarchical Multiscale Modeling on Polymer Nanocomposites Considering Hyperelastic Behavior

M. Cho [a*], H. Shin[a], W. Kim[a], S. Yang[b], S. Yu[c], S. Chang[a], and J. Choi[a]

[a]*School of Mechanical and Aerospace Engineering, Seoul National University, Seoul 151-742, South Korea*
[b]*Department of Mechanical Engineering, Dong-A University, Busan 604-714, South Korea*
[c]*Division of Mechanical Engineering, Kyungnam University, Changwon 631-701, South Korea*
**mhcho@snu.ac.kr*

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Abstract

In this study, a hierarchical multiscale modeling approach to characterize the hyperelastic behavior of polymer nanocomposites is proposed. Molecular dynamics simulation and a continuum nonlinear two-scale homogenization method are merged into the proposed multiscale modeling. The characterization of the condensed interphase zone between silica nanoparticle and polymer matrix are conducted.

Nonlinear mechanical behavior of polymer nanocomposites was identified by molecular dynamics simulation. Uniaxial tensile simulations are employed through NPT ensemble simulation. Stress-strain relationship of Nylon6 is fitted by generalized Mooney-Rivlin model in this study. The hyperelastic behavior of effective interphase is quantified by iterative inverse algorithm based on the nonlinear two-scale homogenization method.

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, nonlinear elastic behavior is not handled in many other studies. In this study, the nonlinear elastic characteristics of effective interphase are considered.

In order to obtain stress-strain curve of polymer and polymer nanocomposites, uniaxial tensions for every axis are conducted. Generalized Mooney-Rivlin model is employed to describe the hyperelastic behavior of Nylon6 polymer matrix. NPT ensemble simulations are employed to obtain stress-strain curve. Interphase properties are obtained from iterative inverse algorithm based on the molecular dynamics simulation and multiscale homogenization. Firstly, linear elastic properties of interphase are determined by Parrinello-Rahman fluctuation analysis and asymptotic homogenization method of linear problem. By reflecting the result of linear elastic properties of interphase, other hyperelastic parameters are defined by the proposed iterative inverse algorithm.

2. Molecular dynamics simulation

2.1. Molecular modeling of Silica/Nylon6 nanocomposites

In every molecular modeling, Material Studio 5.5 was employed. The silica nanoparticles are trimmed from bulk α-quartz structure. All of free radicals of the surface atoms are firstly treated by oxygen atoms in order to describe the oxidation process. In order to construct unit cell of pure Nylon6 and Nylon6 composites, amorphous cell construction module which is implemented in Material Studio 5.5 was used. In every modeling and simulation procedure, CVFF forcefield is applied and room temperature is imposed. Unit cell composition is given in Table 1.

Volume fraction (%)	Cell size (Å)	# of polymer chains	Particle radius (Å)
1.8	44.27	7	7.2
2.2	41.41	9	7.2
2.8	38.215	11	7.2
Matrix	39.520	8	-

Table 1. Unit cell configuration of Nylon6 pure matrix and Nylon6/Silica nanocomposites.

In order to investigate volume fraction effect of the nanoparticle, three types of unit cells are constructed for various volume fraction of nanoparticle under same particle radius condition.

2.2. Molecular simulation of Silica/Nylon6 nanocomposites

In order to fit hyperelastic parameters, NVT ensemble simulation is more convenient than NPT ensemble simulation because stretch is necessary in order to obtain hyperelastic parameters. However, NVT ensemble simulation is not appropriate for obtaining elastic modulus of polymer materials. Therefore, in this study, NPT ensemble simulation was employed. NPT ensemble simulation shows Poisson's effect, that is, deformation of other axis occurs when the uniaxial tension or compression is imposed. Authors employed LAMMPS in order to conduct NPT ensemble simulation.

Firstly, energy minimization process is conducted in every unit cell by conjugate gradient method. After energy minimization process, Nose-Hoover NPT ensemble simulation is conducted by LAMMPS. In NPT equilibration process, constant strain rate of 10^8/sec is imposed. In this study, uniaxial tensile simulations are conducted.

In order to impose external strain to a unit cell in uniaxial tension process, a predefined strain rate is imposed along the loading direction. The imposed unit cell strain at final state is 0.15 which shows clear nonlinear behavior of hyperelasticity. Internal stress state of unit cell is computed by the virial theorem. In NPT simulation, the pressure along the loading direction is not defined at any pressure to maintain the external strain while pressure tensor terms perpendicular to the loading direction are kept at 1atm.

3. Multiscale modeling and results

3.1. Hyperelastic modeling of Nylon6 polymer

In this study, Nylon6 polymer is fitted by generalized Mooney-Rivlin hyperelastic model. Generalized Mooney-Rivlin model is as follows:

$$\psi = C_{10}(J_1 - 3) + C_{01}(J_2 - 3) + C_{11}(J_1 - 3)(J_2 - 3) + D_1(J - 1)^2 + D_2(J - 1)^4 \tag{1}$$

where $J_1 = I_1 I_3^{-1/3}$, $J_2 = I_2 I_3^{-2/3}$ and I_1, I_2, I_3 are invariants of Cauchy-Green tensor. In order to obtain hyperelastic parameters, least square method of stress-strain curve is used as shown in Figure 1 and Eq. (2). Nominal strain and 2nd P-K stress are used in every stress-strain relationship in this study. Hyperelastic parameters are listed in Table 2.

$$\begin{bmatrix} 2\dfrac{\partial (J_1 - 3)}{\partial C_{ij}} & \cdots & 2\dfrac{\partial (J - 1)^4}{\partial C_{ij}} \end{bmatrix} \begin{Bmatrix} C_{10} \\ \vdots \\ D_2 \end{Bmatrix} = S_{ij}^{ref} \tag{2}$$

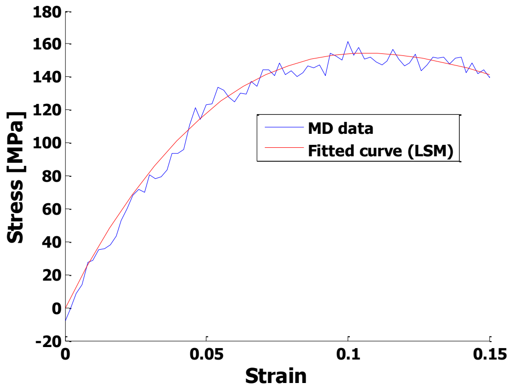

Figure 1. Stress-strain curve of molecular dynamics results and fitted generalized Mooney-Rivlin model. (2nd P-K stress and nominal strain).

Hyperelastic parameters	Nylon6
C_{10}	-2743.24
C_{01}	3336.33
C_{11}	408.13
D_1	2531.24
D_2	-1203895.24

Table 2. Mooney-Rivlin parameters of Nylon6 which is fitted by uniaxial tension results of molecular dynamics.

3.2. Characterization of effective interphase

In order to characterize effective interphase, finite element models are constructed under the identical conditions of unit cell configurations (Table 1). Hyperelastic properties of polymer matrix are determined by hyperelastic parameters of Part 3.1. In this study, effective interphase is assumed to follow Mooney-Rivlin hyperelastic model. Firstly, linear elastic modulus of interphase at zero state of unit cell strain is evaluated by asymptotic homogenization of linear problem. By reflecting the linear elastic modulus of interphase, other hyperelastic parameters are determined by least square method of stress between finite element homogenization method and molecular dynamics simulation results. In order to volume fraction effect on interphase, authors constructed three types of unit cells for various volume fraction. However, in this paper, only one type of unit cell of 2.8% is computed. In future work, the other types of unit cells will be also considered in order to investigate volume fraction effect.

3.2.1. Review of two-scale homogenization theory

In order to describe a heterogeneous continuum body with periodic microstructures, two-scale homogenization method is widely used. Macroscopic scale and microscopic scale are denoted by **x** and **y**. The scale parameter ε is defined as **y**=**x**/ε. By taking the limit ($\varepsilon \to 0$), the microscopic boundary value problem for a unit cell could be represented by the following variational form [3]:

$$\int_Y \nabla_{\mathbf{y}} \delta \mathbf{u}^1 : \boldsymbol{\sigma}(\mathbf{x},\mathbf{y}) dV_y = 0, \ \forall \delta \mathbf{u}^1 \tag{3}$$

where $\boldsymbol{\sigma}(\mathbf{x},\mathbf{y})$ is the microscopic stress. The microscopic stress could be expressed as follows:

$$\boldsymbol{\sigma}(\mathbf{x},\mathbf{y}) = \frac{\partial W(\mathbf{y},\boldsymbol{\varepsilon})}{\partial \boldsymbol{\varepsilon}}, \ \boldsymbol{\varepsilon}(\mathbf{x},\mathbf{y}) = sym(\nabla_{\mathbf{x}} \mathbf{u}^0(\mathbf{x}) + \nabla_{\mathbf{y}} \mathbf{u}^1(\mathbf{x},\mathbf{y})) \tag{4}$$

where $\mathbf{u}^0(\mathbf{x})$ and $\mathbf{u}^1(\mathbf{x},\mathbf{y})$ are macroscopic displacement and microscopic displacement, respectively. In order to obtain microscopic displacement field $\mathbf{u}^1(\mathbf{x},\mathbf{y})$, periodic boundary condition is imposed when Eq. (3) is solved. Macroscopic stress and macroscopic strain are defined as follows:

$$\boldsymbol{\Sigma}(\mathbf{x}) = \frac{1}{|Y|}\int_Y \boldsymbol{\sigma}(\mathbf{x},\mathbf{y}) dV_y, \ \mathbf{E}(\mathbf{x}) = \frac{1}{|Y|}\int_Y \boldsymbol{\varepsilon}(\mathbf{x},\mathbf{y}) dV_y = \nabla_{\mathbf{x}} \mathbf{u}^0(\mathbf{x}) \tag{5}$$

Then, the macroscopic tangent moduli could be computed by following equation:

$$\mathbf{C}^H_{\text{tangent}} = \frac{\partial \boldsymbol{\Sigma}}{\partial \mathbf{E}} \tag{6}$$

3.2.2. Linear elastic properties of effective interphase

Specific flowchart of iterative inverse algorithm is listed in Figure 2. The proposed numerical algorithm is to obtain the elastic moduli of effective interphase such that the homogenized elastic moduli of unit cell have same value with molecular dynamics simulation results. As shown in Table 3, effective interphase has high moduli than those of pure polymer matrix part because effective interphase is condensed and crystallized polymer phase in the vicinity of nanoparticles.

Linear elastic properties	**Interphase**	**Nylon6**	**Silica**
E [GPa]	5.75	3.15	104
G [GPa]	2.05	1.13	37

Table 3. Linear elastic properties of interphase obtained from the multiscale bridging method.

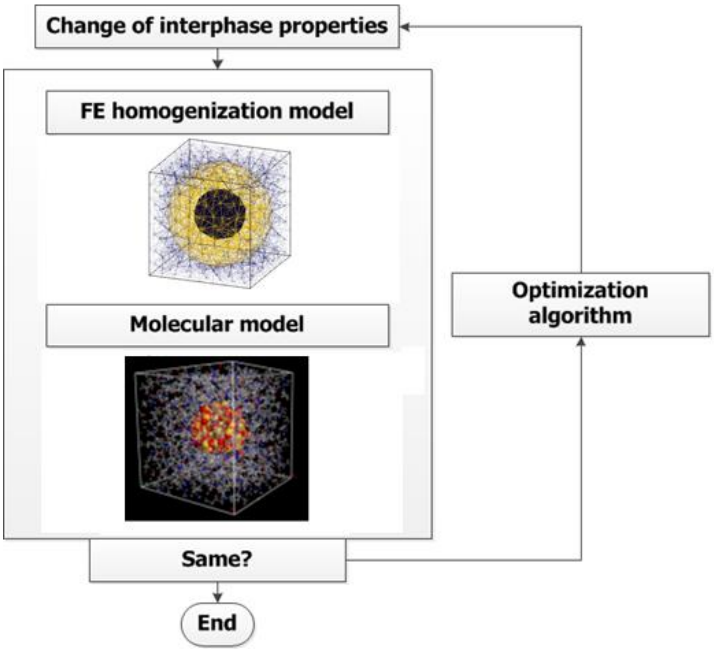

Figure 2. Flowchart of iterative inverse algorithm to obtain linear elastic properties of interphase.

3.2.3. Hyperelastic behavior of effective interphase

In order to describe interphase, Mooney-Rivlin model is employed. Coefficients of Mooney-Rivlin model follow the following rules:

$$\psi = C_{10}(J_1 - 3) + C_{01}(J_2 - 3) + D_1(J-1)^2 \quad (7)$$

$$C_{10} + C_{01} = G/2, \; D_1 = K/2 \quad (8)$$

From Eq. (8), D_1 is determined, however, C_{10} and C_{01} are not determined due to less constraint. As the C_{10} decreases, the material shows less hardening behavior in uniaxial tension problem. In order to minimize least square value of stress difference between continuum model and molecular model, minimization problem is constructed as follows:

$$\min \frac{\left\| \boldsymbol{\sigma}_{Homog.}\left((C_{10})_{\text{int}}, (C_{01})_{\text{int}} \right) - \boldsymbol{\sigma}_{MD} \right\|}{\left\| \boldsymbol{\sigma}_{MD} \right\|} \quad s.t. \; (C_{10})_{\text{int}} + (C_{01})_{\text{int}} = 1.025 \quad (9)$$

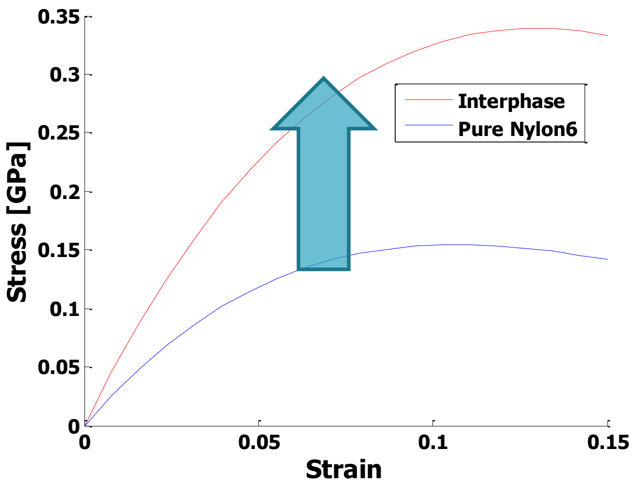

Figure 3. Stress-strain curve of interphase and pure Nylon6.

Figure 3 shows the interface effect explicitly. Interphase zone shows higher mechanical properties than the pure nylon6 matrix phase. Condensed characteristics of interphase zone influence the modulus of interphase. In figure 4, the various elastic models (Linear elastic model, Neo-Hookean model, Mooney-Rivlin model) are compared. Mooney-Rivlin hyperelastic model is the most proper in three types of models. However, Mooney-Rivlin model is also not converged to minimal points because arc length-based formulation is not used in this study. Finite element formulation should be based on the arc length method in order to reflect softening behavior of interphase. In future work, stress-strain curve of interphase will be estimated more properly.

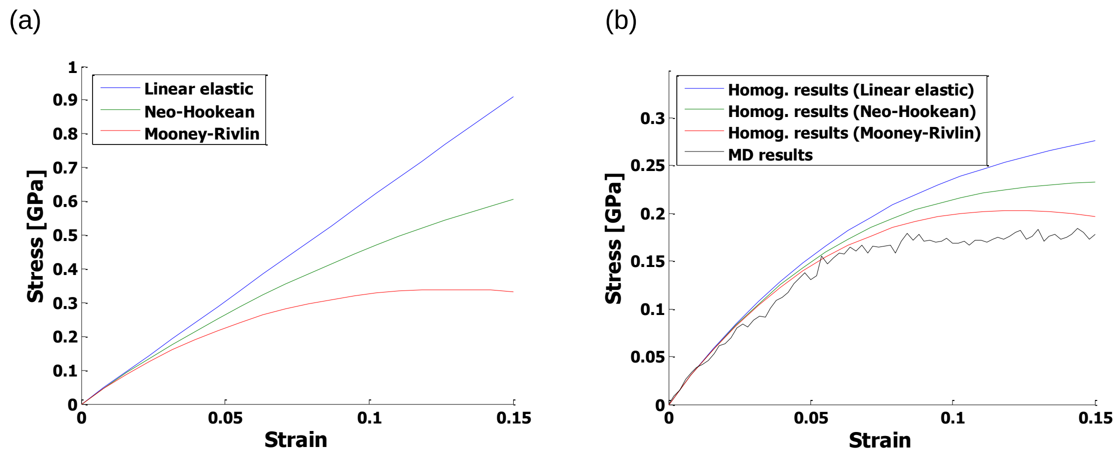

Figure 4. Stress-strain curve for various interphase model: (a) Interphase, and (b) Nanocomposites.

4. Conclusion

In this study, a nonlinear multiscale framework to obtain hyperelastic parameters of interphase is proposed. From the molecular dynamics simulation, polymer materials and polymer nanocomposites show the hyperelastic behavior of generalized mooney-rivlin. From the proposed multiscale framework, it is found that interphase follows Mooney-Rivlin solid model. Interphase shows higher hyperelastic properties than pure Nylon6, that is, interface effect is reflected in interphase model. In future work, volume fraction effect of nanoparticles will be investigated.

References

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