MULTISCALE HOMOGENIZATION METHOD TO PREDICT FILLER SIZE-DEPENDENT THERMOELASTIC PROPERTIES OF POLYMER NANOCOMPOSITES

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1 Introduction

When nano-sized particles are added into a polymer matrix, the arrangement of the polymer chains near the particle is changed and critically immobilized [1]. This structural change is related to the mechanical and thermal properties of nanocomposites and their particle size dependency. Thus, it is important to consider the particle-size effect in the multi-scale modeling of nanocomposites.

In order to describe the particle-size effect, Yang and Cho [2] have suggested a sequential scale bridging method that combines molecular dynamics (MD) simulations and micromechanics model. In the scale bridging method, an additional effective interphase is defined between the particle and matrix. Then, the property of the interphase is obtained with the results of MD simulations. By bridging the MD simulation results to the micromechanics model, repeated MD simulation procedure is replaced by a simple linear algebraic equation to estimate the effective properties of the nanocomposites.

Together with the micromechanics models, the mathematical homogenization method has been efficiently applied to estimate the effective properties of heterogeneous structures. Compared with the micromechanics models, the mathematical homogenization method is more advantageous to consider complicated shape of the heterogeneity and is more rigorous to capture high volume fraction conditions.

The present study utilizes the homogenization method to describe the particle-size effect on the thermoelastic properties of nanocomposites that are obtained from MD simulations. For this task, the thermoelastic properties of the effective interphase that is adopted to describe the particle size effect are numerically obtained using the homogenization method via finite element analysis (FEA). The results are compared with those of the previous results obtained from the micromechanics-based bridging method. Then, using the thermoealstic properties of the interphase, the overall elastic stiffness and coefficient of thermal expansion (CTE) of nanocomposites that has perturbations in radii of the reinforced particles are estimated for stochastic analysis of real nanocomposites.

2 Homogenization theory

2.1 Fundamental formulation

The homogenization method is a numerical tool to describe the mechanical and thermal behaviors of a heterogeneous material using a rigorous mathematical foundation. The main purpose of the homogenization method is to find equivalent macroscopic homogeneous properties of the microscopically heterogeneous structures such as composites. In this method, the displacement field is expressed using the asymptotic expansion as follows:

$$u(X) = u^0(x,y) + \varepsilon u^1(x,y)... \quad (1)$$

$$\varepsilon = x / y \quad (2)$$

where the non-dimensional parameter, ε, represents the ratio of the microscopic representative length to the macroscopic one. Considering the microstructure, the governing equation for thermoelastic problem can be described as follow:

$$\int_{V_X} C_{ijkl}\frac{\partial u_k}{\partial x_l}\frac{\partial \delta u_i}{\partial x_j}d\Omega = \int_{A_t} t_i \delta u_i dA_t \ ... \\ + \int_{V_X} C_{ijkl}\alpha_{kl}(T-T_0)\frac{\partial \delta u_i}{\partial x_j}dV_X \tag{3}$$

After substituting Eq.(1) into Eq. (3), the governing equation is arranged by the power of the parameter ε, as below:

$$O(1/\varepsilon^2)\frac{1}{\varepsilon^2} + O(1/\varepsilon)\frac{1}{\varepsilon} + O(1) = 0 \tag{4}$$

As Eq. (4) is always satisfied regardless of the parameter ε, following equations are easily derived,

$$\int_{V_y} C_{ijml}\frac{\partial \chi_m^{kl}}{\partial y_n}\frac{\partial \delta u_i^1}{\partial y_j}dV_y = \int_{V_y} C_{ijml}\frac{\partial \delta u_i^1}{\partial y_j}dV_y \tag{5}$$

$$\int_{V_y} C_{ijkl}\frac{\partial \phi_k}{\partial y_l}\frac{\partial \delta u_i^1}{\partial y_j}dV_y = \int_{V_y} C_{ijkl}\alpha_{kl}\frac{\partial \delta u_i^1}{\partial y_j}dV_y \tag{6}$$

$$\int_\Omega \mathrm{C}_{ijkl}^H\frac{\partial u_k}{\partial x_l}\frac{\partial \delta u_i}{\partial x_j}d\Omega = \int_{\Gamma_t} t_i \delta u_i^0 d\Gamma \ ... \\ + \int_\Omega \mathrm{C}_{ijkl}^H \alpha_{kl}^H (T-T_0)\frac{\partial \delta u_i^0}{\partial x_j}d\Omega \tag{7}$$

where $\mathbf{C}_{ijkl}^H$ and α_{kl}^H are the homogenized elastic stiffness and thermal expansion coefficient of the nanocomposites and given as:

$$\mathbf{C}_{ijkl}^H = \frac{1}{|Y|}\int_Y (\mathbf{C}_{ijkl} - \mathbf{C}_{ijmn}\frac{\partial \chi_m^{kl}}{\partial y_n})dY \tag{8}$$

$$\alpha_{ij}^H = (C_{ijkl}^H)^{-1}\frac{1}{|Y|}\int_Y C_{pqkl}(\alpha_{kl} - \frac{\partial \phi_k}{\partial y_l})dY \tag{9}$$

2.2 Finite-element discretization

For finite-element discretization, the virtual displacement field is expressed using the shape function as follows:

$$u = [\mathbf{N}]\{u\} \tag{10}$$

and the virtual strain is:

$$\nabla \boldsymbol{\upsilon} = [\mathbf{B}]\{\boldsymbol{\upsilon}\} \tag{11}$$

Due to the periodicity of the base-cell, the tensor, $\boldsymbol{\chi}(\mathbf{x},\mathbf{y})$, has the following symmetry:

$$\chi_{ijk} = \chi_{ikj} \tag{12}$$

and is expressed as:

$$\chi_{ijk} = [\chi_{i11}, \chi_{i22}, \chi_{i33}, \chi_{i12}, \chi_{i23}, \chi_{i13}] \tag{13}$$

By substituting Eq. (13) into Eq. (5) and Eq. (6), the tensor, $\boldsymbol{\chi}$ and ϕ are obtained from:

$$\int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}][\mathbf{B}][\boldsymbol{\chi}]dV_y = \int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}]dV_y \tag{14}$$

$$\int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}][\mathbf{B}][\phi]dV_y = \int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}]\{\alpha\}dV_y \tag{15}$$

which can be expressed as a simple algebraic expression given by:

$$[\mathbf{K}][\boldsymbol{\chi}] = [\mathbf{Q}] \tag{16}$$

$$[\mathbf{K}][\boldsymbol{\phi}] = [\mathbf{P}] \tag{17}$$

where,

$$[\mathbf{K}] = \int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}][\mathbf{B}]dV_y \tag{18}$$

$$[\mathbf{Q}] = \int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}]dV_y \tag{19}$$

and

$$[\mathbf{P}] = \int_{\overline{V_y{}^C}} [\mathbf{B}]^T[\mathbf{C}]\{\alpha\}dV_y \ . \tag{20}$$

In the same manner, Eq. (8) and Eq. (9) can be expressed as shown below.

$$[\mathbf{C}^H] = \frac{1}{vol(V_y{}^C)}\int_{\overline{V_y{}^C}} [\mathbf{C}] - [\mathbf{C}][\mathbf{B}][\boldsymbol{\chi}]dV_y \tag{21}$$

$$\{\alpha^H\} = [\mathbf{C}^H]^{-1}\frac{1}{vol(V_y{}^C)}\int_{\overline{V_y{}^C}} [\mathbf{C}](\{\alpha\} - [\mathbf{B}][\boldsymbol{\phi}])dV_y \tag{22}$$

After substituting the tensor, $\boldsymbol{\chi}$ and ϕ obtained from Eq. (16) and Eq. (17) into Eq. (21) and Eq. (22), the homogenized elastic stiffness tensor and the coefficient of thermal expansion(CTE) of the nanocomposite can be obtained.

3 Characterization of the interfacial properties

In this study, the mechanical and thermal properties of matrix, particle, and nanocomposites are obtained from MD simulations [3]. Then, the thermoelastic properties of the effective interface are numerically obtained from the homogenization method with finite element analysis following the numerical scheme that has ever been demonstrated in our earlier work on the elasticity problem [4].

The estimated thermoelastic properties of the effective interphase obtained from the present multiscale homogenization method are compared with the results obtained from the previous micromechanics-based bridging method [3] in Fig. 1. As the particle radius increases, both the elastic moduli and the shear moduli gradually decreases indicating that the reinforcing effect of larger particle reinforced cases are superior. At the same time, the CTE of the interface gradually increases as the radius of the nanoparticle increases. In all the properties, the results obtained from the present homogenization method and the previous micromechanics-based method agree well each other to reproduce the overall thermoelastic properties of nanocomposites and their particle size dependency.

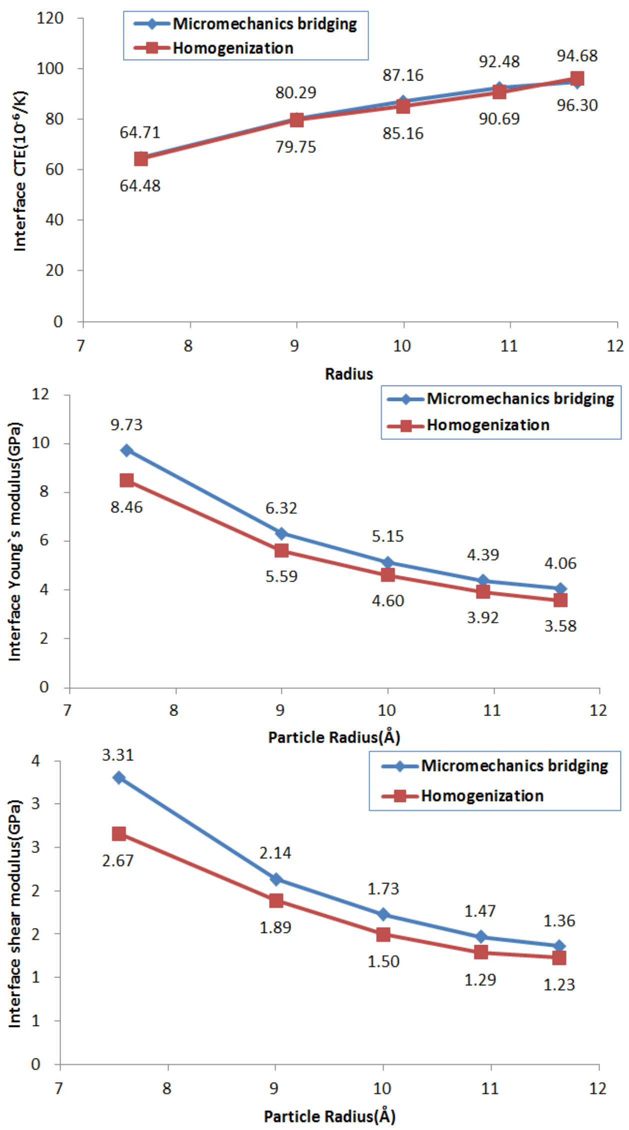

Fig.1. Comparison of the thermoelastic proprieties of effective interphase

4 Estimation of the nanocomposite properties

After obtaining the thermoelastic properties of the interphase, the overall elastic modulus of nanocomposites is reproduced from Eq. (21) and Eq. (22), using the properties of the interface obtained in part 3. For establishing the continuum modeling of nanocomposites, it is convenient and useful to estimate the representative properties of nanocomposites with a simplified periodic distribution of the particles, such as simple cubic arrangement. However, in real nanocomposites, the distribution of the reinforcing particles shows more complicated configurations with randomness.

As has been mentioned in introduction, the present homogenization method is superior to the micromechanics-based approaches in considering complicated shape of the heterogeneity. Thus, the present homogenization method can be extended to stochastic analysis by considering perturbation of particle radius or volume fractions. In this study, in order to consider stochastic variation of the particle radius, one base-cell having 27 nanoparticles is constructed as shown in Figure 2. The radii of the particles are randomly generated within the limit of 20% perturbations from the radius of 10.90Å. The volume fraction of the whole representative volume element (RVE) is fixed to 5.8%. The maximum and minimum radii of the nanoparticle are 12.78Å and 9.07Å, respectively.

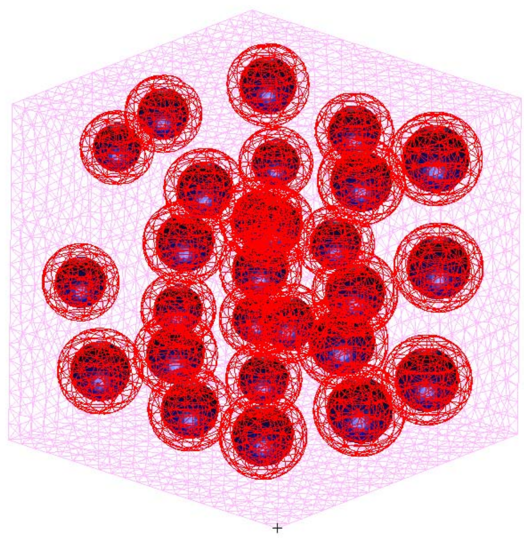

Fig.2. Nanocomposites base-cell composed of 27 nanoparticles with stochastic variations in particle radius.

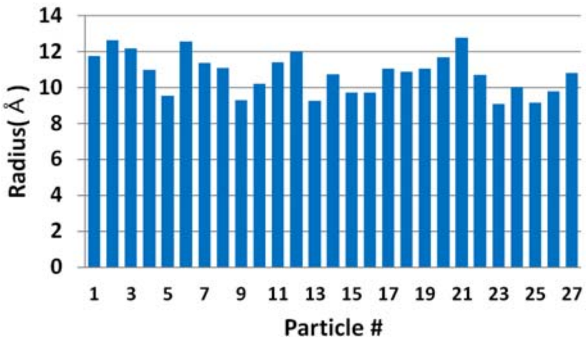

Fig.3. Particle radius distribution of the nanocomposites for stochastic analysis

To obtain the elastic stiffness and the CTE of the interface at various particle radii for stochastic analysis, all the properties of the interface obtained in part 3 were fitted into functions of the particle radius as $E_{int}=3.16+158*\exp(-0.485r_p)$ for the Young's modulus, $G_{int}=1.14+151*\exp(-0.62r_p)$ for the shear modulus and $\alpha_{int}=103.6-586*\exp(-0.36r_p)$ for the CTE of the nanocomposites respectively. From these fitted functions, the thermoelastic properties of each interphase are calculated as shown in Fig. 4.

Using the interphase properties, the properties of the nanocomposites with 27 nanoparticles are calculated and compared with the upper(lower) bounds that are obtained from the same homogenization method of two different base cells which only considers the largest(smallest) single nanoparticle in a base cell. As shown in Table 1, all the properties obtained from the present method lie between the upper and lower bounds meaning that the present multi-scale homogenization method is applicable to stochastic analysis of nanocomposites considering the perturbation in size and position of the nanoparticles.

Table 1. Thermoelastic and mechanical proprieties of the nanocomposites with stochastic variation of the particle radius

Case	CTE (10-6/K)	E (GPa)	G (GPa)
Upper bound (r_p =12.78Å)	95.735	3.622	1.3046
Stochastic approach	94.932	3.6862	1.3242
Lower bound (r_p= 9.071Å)	92.246	3.9127	1.3982

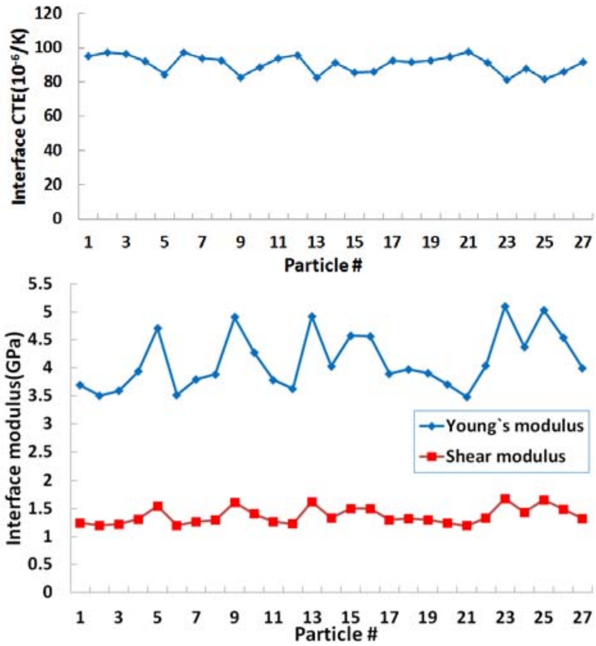

Fig.4. Thermoelastic and mechanical proprieties of the effective interface distribution estimated from the particle radius of each particle

5 Conclusion

In this study, the thermoelastic multiscale homogenization method was proposed to describe the particle size effect on the thermoelastic properties of nanocomposites. An effective interphase was defined to describe the particle size dependency and a fully continuum modeling strategy for the characterization of nanocomposites and a numerical technique to estimate the properties of the effective interphase were proposed and validated. Then, for stochastic analysis of real nanocomposites with randomness in particle size and distribution, the properties of composites including many particles having various radii are calculated and verified.

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