

Multiscale approach to predict the effective elastic behavior of nanoparticle-reinforced polymer composites

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Abstract. A multiscale modeling scheme that addresses the influence of the nanoparticle size in nanocomposites consisting of nano-sized spherical particles embedded in a polymer matrix is presented. A micromechanics-based constitutive model for nanoparticle-reinforced polymer composites is derived by incorporating the Eshelby tensor considering the interface effects (Duan *et al.* 2005a) into the ensemble-volume average method (Ju and Chen 1994). A numerical investigation is carried out to validate the proposed micromechanics-based constitutive model, and a parametric study on the interface moduli is conducted to investigate the effect of interface moduli on the overall behavior of the composites. In addition, molecular dynamics (MD) simulations are performed to determine the mechanical properties of the nanoparticles and polymer. Finally, the overall elastic moduli of the nanoparticle-reinforced polymer composites are estimated using the proposed multiscale approach combining the ensemble-volume average method and the MD simulation. The predictive capability of the proposed multiscale approach has been demonstrated through the multiscale numerical simulations.

Keywords: multiscale modeling; molecular dynamics; micromechanics-based constitutive model; nanoparticles; polymer composites.

1. Introduction

Nanocomposites are a novel class of composite materials in which one of the constituents has dimensions that range between 1 and 100 nm. Generally, nano-sized reinforcements have the properties of a high specific surface area, a high surface energy, and a large number of atom surface defects in comparison with conventional reinforcements (Cho *et al.* 2006). Recently, nanoparticle (e.g. nanosphere, nanotube, clay platelet) reinforced polymer materials have received tremendous attention in both scientific and industrial fields due to their extraordinary enhanced physical, chemical, and mechanical properties (Adnan *et al.* 2007, Zeng *et al.* 2008). To facilitate the development of nanostructured polymer composite materials with the aforementioned advantages, constitutive relationships must be developed to predict the bulk mechanics properties of the

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materials as a function of the molecular structure of the polymer and reinforcement (Odegard *et al.* 2005). When the size of the reinforcements in the composites decreases to the nanometer scale, the ratio of their surface area to the volume increases critically, thus enabling unusual mechanical properties that differ from those of their macro-sized counterparts (Cho *et al.* 2006, Chen *et al.* 2007). Therefore, conventional continuum and/or micromechanics cannot accurately predict the behavior of nanocomposites.

Numerous studies of nanoparticle-reinforced composites have been carried out to predict their overall behavior. Previous analyses of nanoparticle-reinforced composites can be broadly classified into two types: 1) a top-to-bottom approach, which extends the classical continuum and/or micromechanics taking into account the surface and size effects and 2) a bottom-up approach based on molecular dynamics (MD) simulation (Guz and Guz 2006, Scocchi *et al.* 2007). In a top-to-bottom approach, Gurtin and Murdoch (1975a, 1975b) developed the surface elasticity theory for isotropic materials based on a number of rational principles of mechanics to consider the surface effects. Gurtin and Murdoch's generic surface model has been successfully applied by many researchers to various problems, such as elastic solids with nanoinclusions or nanocavities (Miller and Shenoy 2000, Sharma *et al.* 2003, Yang 2004, Duan *et al.* 2005a, 2005b, Li *et al.* 2006), determinations of the yield strength of nanowires (Zhang *et al.* 2008), assessments of crack-tip stresses (Wang *et al.* 2008), and analyses of the elastic behavior of homogeneous ultra-thin films (Lim and He 2004). Dingreville *et al.* (2005) proposed the overall elastic behavior of nano-sized structural elements incorporating the surface free energy into the continuum theory of mechanics. In addition, Boutaleb *et al.* (2009) proposed a micromechanical analytical model for nanocomposites consisting of silica nanoparticles embedded in a polymer matrix taking into account an interphase corresponding to a perturbed region of the polymer matrix around the nanoparticles. In the other approach (the bottom-up approach), Adnan *et al.* (2007) investigated the effect of the nanoparticle size on the elastic properties of nano-sized buckminsterfullerene bucky-ball embedded polyethylene (PE) matrix nanocomposites using MD simulations.

In spite of a variety of studies of nanoparticle-reinforced composites, most focused on one method (the top-to-bottom approach or the bottom-up approach), with the result being discrete modeling or a failure to reflect the nature of the nano-sized composite materials accurately. An alternative to conventional analysis is multiscale modeling and simulation strategies that provide seamless coupling among various length and time scales (Zeng *et al.* 2008). Multiscale modeling and simulation play an important role in modern research associated with nano-sized materials, which depends on a fundamental understanding of their hierarchical structures and behaviors (Glotzer and Paul 2002, Fermeglia and Priol 2007, Rojek and Oñate 2008, Zeng *et al.* 2008, Zhao and Aluru 2008). Recently, Odegard *et al.* (2005) used MD simulation initially to calculate the properties of nanoparticles and a polymer, subsequently applying classical micromechanics to estimate the bulk modulus of nanocomposites using the values of each constituent calculated from the MD simulation. However, it appears that the direct use of micromechanics for nanoparticle composites is inappropriate if failing to take into account the effects associated with the significant size difference between a nanoparticle and a conventional particle.

In the present study, a multiscale modeling scheme is presented to address the influence of the nanoparticle size in nanocomposites consisting of nano-sized spherical particles embedded in a polymer matrix. A micromechanics-based constitutive model for nanoparticle-reinforced polymer composites is derived by incorporating the Eshelby tensor considering the interface effects (Duan *et al.* 2005a) into the ensemble-volume average method (Ju and Chen 1994). In order to validate the

proposed micromechanics-based constitutive model, a numerical investigation is carried out, and a parametric study on the interface moduli is also conducted to investigate the effect of interface moduli on the overall behavior of the nanocomposites. In addition, MD simulations are performed to determine the mechanical properties of the nanoparticles and polymer. Finally, the overall elastic moduli of the nanoparticle-reinforced polymer composites are estimated using the proposed multiscale approach combining the ensemble-volume average method and the MD simulation.

2. Micromechanics-based constitutive model of nanoparticle-reinforced polymer composites

2.1 Recapitulation of the Eshelby tensor for a nano-sized particle

The summary of the Eshelby tensor for nano-sized particle is repeated here for completeness of the proposed constitutive model for the multiscale modeling scheme. The position-dependent Eshelby tensor (Duan *et al.* 2005a) with interface stress is adopted to model nano-sized particles and is incorporated into the framework using the ensemble-volume average method. The formulation of the Eshelby tensor for nano-sized particle was systematically derived by Duan *et al.* (2005a). It can be expressed as

$$\mathbf{S}(\mathbf{r}) = \tilde{\mathbf{S}}(r) \cdot \mathbf{E}^T \quad (1)$$

with

$$\tilde{\mathbf{S}}(r) = [S_1(r) \ S_2(r) \ S_3(r) \ S_4(r) \ S_5(r) \ S_6(r)] \quad (2)$$

$$\mathbf{E} = [\mathbf{E}^1 \ \mathbf{E}^2 \ \mathbf{E}^3 \ \mathbf{E}^4 \ \mathbf{E}^5 \ \mathbf{E}^6] \quad (3)$$

where $\mathbf{r}(=r\mathbf{n})$ denotes the position vector of arbitrary point, $\mathbf{n}$ signifies the unit vector, and r is the distance from the center of the spherical inhomogeneity. In addition, a fourth-order tensor $\tilde{\mathbf{S}}(r)$ with the components $S_1(r), \dots, S_6(r)$ and the transversely isotropic tensor $\mathbf{E}$ introduced by Walpole (1981) can be found in Duan *et al.* (2005a).

Here, the Eshelby tensor in Eq. (1) depends on the size of the spherical inhomogeneity through the non-dimensional parameters (e.g. κ_s^r and μ_s^r) and can be finally expressed in the classical form without an interface effect by letting the non-dimensional parameters be zero (Duan *et al.* 2005a). Details of the Eshelby tensor for nano-sized inhomogeneity can be found in Duan *et al.* (2005a).

2.2 Effective elastic moduli of nanocomposites

To obtain the effective properties of randomly distributed nanoparticle-reinforced composites, the ensemble-volume average method (Ju and Chen 1994) is adopted in the present study. Let us start by considering a nanocomposite consisting of a matrix (phase 0) and a randomly distributed nanoparticle (phase 1). Following Ju and Chen (1994), the effective elastic stiffness tensor $\mathbf{C}_*$ for the (two-phase) nanocomposite can be written as

$$\mathbf{C}_* = \mathbf{C}_0 \cdot [\mathbf{I} + \phi_1(\bar{\mathbf{S}} + \mathbf{A}_1)^{-1} \cdot \{\mathbf{I} - \phi_1\bar{\mathbf{S}} \cdot (\bar{\mathbf{S}} + \mathbf{A}_1)^{-1}\}^{-1}] \quad (4)$$

where the subscripts 0 and 1 signify the phase of the matrix and the nanoparticle, respectively. ϕ_1 is the volume fraction of the nanoparticle, $\mathbf{I}$ signifies the fourth-rank identity tensor, the fourth-rank tensor $\mathbf{A}_1$ is $\mathbf{A}_1 = [\mathbf{C}_1 - \mathbf{C}_0]^{-1}$. $\mathbf{C}_0$, and $\mathbf{C}_q$ ($q = 0, 1$) denotes the elasticity tensor of the q -phase (cf. Liang *et al.* 2006, Lee and Pyo 2007).

In the present study, volume integration is carried out to obtain the volume-averaged Eshelby tensor $\bar{\mathbf{S}}$ for a spherical nano-inhomogeneity. After performing volume integration, the volume-averaged Eshelby tensor $\bar{\mathbf{S}}$ can be finally expressed as follows

$$\bar{\mathbf{S}} = \frac{1}{V} \int_V \tilde{\mathbf{S}}(r) \cdot \mathbf{E}^T dV = \xi_1 \delta_{ij} \delta_{kl} + \xi_2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad (5)$$

with

$$\xi_1 = \Lambda_3 - \Lambda_2 - \frac{21}{5} \Lambda_1, \quad \xi_2 = \frac{1}{2} + \frac{3}{2} \Lambda_2 + \frac{63}{10} \Lambda_1 \quad (6)$$

where the components Λ_i ($i = 1, 2, 3$) can be expressed as (cf. Duan *et al.* 2005a)

$$\begin{aligned} \Lambda_1 &= \frac{2\Gamma(4-5\nu_0)(\kappa_s^r + 2\mu_s^r)}{3\eta_1}, \quad \Lambda_2 = \frac{\eta_2}{3\eta_1} \\ \Lambda_3 &= -\frac{(1-2\nu_0)(2+\kappa_s^r)}{3[\Gamma(1+\nu_1) + (1-2\nu_1)(2+\kappa_s^r)]} \end{aligned} \quad (7)$$

with

$$\begin{aligned} \eta_1 &= -2\Gamma^2(7+5\nu_1)(4-5\nu_0) + 7\Gamma(-39-20\kappa_s^r-16\mu_s^r) + 35\nu_0\Gamma(9+5\kappa_s^r+4\mu_s^r) \\ &+ \nu_1\Gamma(285+188\kappa_s^r+16\mu_s^r) - 5\nu_0\nu_1\Gamma(75+47\kappa_s^r+4\mu_s^r) - 4(7-10\nu_1)(7+11\mu_s^r) \\ &+ 4(7-10\nu_1)[- \kappa_s^r(5+4\mu_s^r) + \nu_0(5+4\kappa_s^r+13\mu_s^r+5\kappa_s^r\mu_s^r)] \end{aligned} \quad (8)$$

$$\begin{aligned} \eta_2 &= 4(7-10\nu_1)[7+11\mu_s^r + \kappa_s^r(5+4\mu_s^r) - \nu_0(5+4\kappa_s^r+13\mu_s^r+5\kappa_s^r\mu_s^r)] \\ &+ 7\Gamma(7-5\nu_0+5\nu_0\kappa_s^r-4\kappa_s^r) + \nu_1\Gamma(35+4\kappa_s^r+48\mu_s^r) - 5\nu_0\nu_1\Gamma(5+\kappa_s^r+12\mu_s^r) \end{aligned} \quad (9)$$

in which $\Gamma = \mu_1 / \mu_2$, with ν_0 , ν_1 , μ_0 , and μ_1 being the Poisson's ratio and shear moduli of the matrix and nanoparticle, respectively. $\kappa_s^r = \kappa_s / (R\mu_0)$ and $\mu_s^r = \mu_s / (R\mu_0)$ are two non-dimensional parameters, and $\kappa_s = 2(\mu_s + \lambda_s)$. R denotes the radius of a spherical nanoparticle. In addition, λ_s and μ_s are the interface moduli, which are intrinsic physical properties of the interface. They can be obtained either by experiments or by atomistic simulations (Duan *et al.* 2005b).

From the volume-averaged Eshelby tensor in Eq. (5), the effective elastic stiffness tensor $\mathbf{C}^*$ for the (two-phase) nanocomposite in Eq. (4) can be rephrased as

$$\mathbf{C}^* = \lambda^* \delta_{ij} \delta_{kl} + \mu^* (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \quad (10)$$

with

$$\lambda^* = (3\zeta_1 + 2\zeta_2)\lambda_0 + 2\zeta_1\mu_0, \quad \mu^* = 2\zeta_2\mu_0 \quad (11)$$

where λ_0 and μ_0 are the Lamé constants of the matrix. In addition, the parameters ζ_1 and ζ_2 are

expressed as follows

$$\zeta_1 = \frac{\gamma_1 + 2\gamma_2(3\gamma_1 + 2\gamma_2)\xi_1}{(1 - 4\gamma_2\xi_2)[1 - (3\gamma_1 + 2\gamma_2)(3\xi_1 + 2\xi_2)]}, \quad \zeta_2 = \frac{1}{2} + \frac{\gamma_2}{1 - 4\gamma_2\xi_2} \quad (12)$$

with

$$\gamma_1 = -\frac{1}{2} \cdot \frac{\kappa_1 - \kappa_0}{(\kappa_1 - \kappa_0)(3\xi_1 + 2\xi_2) + \kappa_0} \phi_1, \quad \gamma_2 = \frac{\mu_1 - \mu_0}{2\mu_0 + \xi_2(\mu_1 - \mu_0)} \phi_1 \quad (13)$$

3. Effective elastic moduli of nanoparticle-reinforced polymer composites considering nanoparticle size-dependency

The effective elastic moduli of nanoparticle-reinforced polymer composites are predicted using the proposed micromechanics-based constitutive model. A comparison between the present predictions and experiments on a silica (SiO_2) nanoparticle-reinforced poly (ether-ether-ketone) (PEEK) matrix composite conducted by Kuo *et al.* (2005) is made to assess the predictive capability of the proposed micromechanics-based constitutive model. The material properties of the nanoparticle-reinforced polymer composites used in the simulation are as follows (Kuo *et al.* 2005, Odegard *et al.* 2005): $E_0 = 4.1$ GPa, $\nu_0 = 0.356$ for the PEEK matrix; $E_1 = 88.7$ GPa, and $\nu_0 = 0.082$ for the SiO_2 nanoparticle. The size of the SiO_2 nanoparticle in the composite is 15 nm, which is identical to that used in Kuo *et al.* (2005). In Fig. 1, the effective Young's moduli predicted from the proposed micromechanics-based constitutive model are compared with those obtained by Kuo *et al.* (2005). Fig. 1 shows that the present predictions are in a good quantitative agreement with the experimental data (Kuo *et al.* 2005).

A parametric study of the interface moduli is also conducted to investigate the effect of interface moduli on the overall behavior of the composites. The interface moduli based on Duan *et al.*

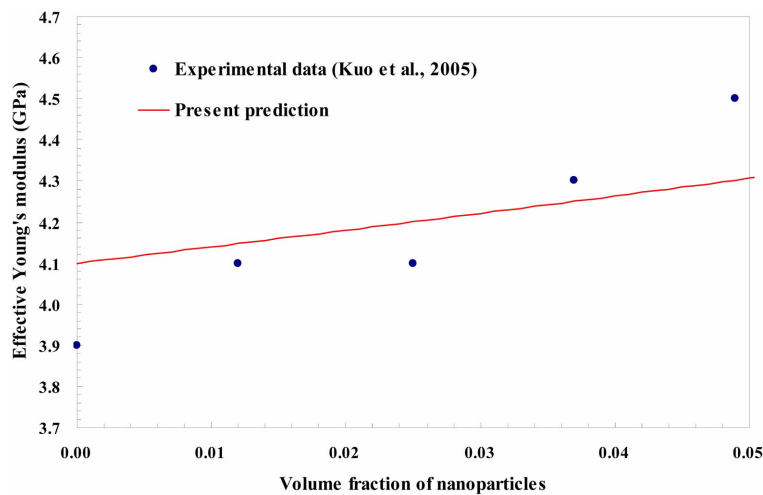


Fig. 1 Comparison between the present prediction and the experimental data (Kuo *et al.* 2005) according to the volume fraction of nanoparticles

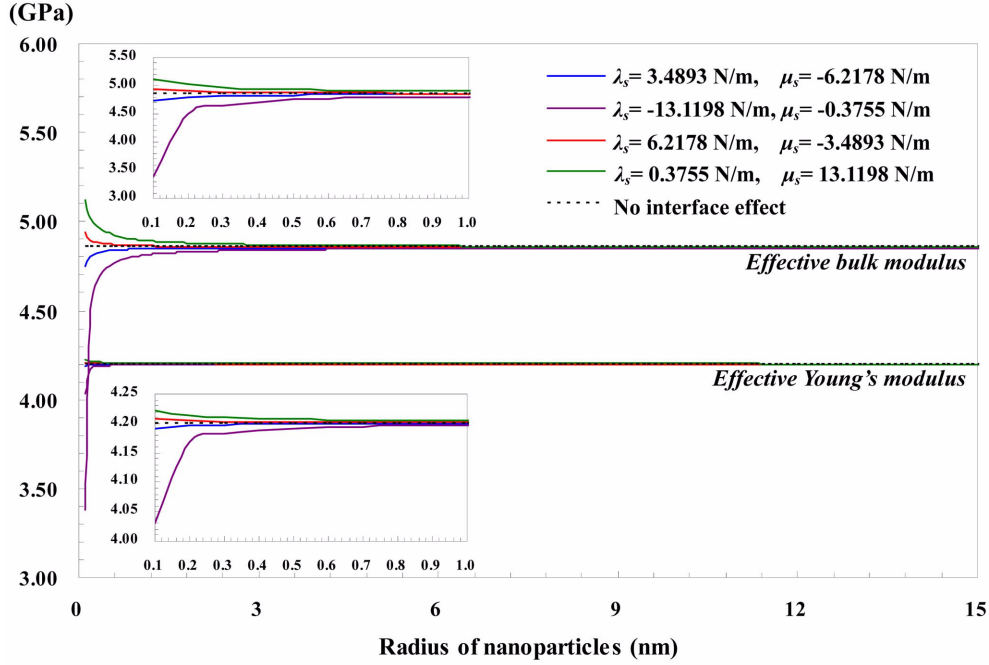


Fig. 2 Effective Young's modulus and bulk modulus of a SiO_2 nanoparticle-reinforced PEEK matrix composite with various interface moduli

(2005a), where the surface properties were taken from Miller and Shenoy (2000) and Sharma *et al.* (2003) and stress concentration as a function of surface properties was investigated, are used as the parameters in the parametric study. Fig. 2 shows the effective Young's modulus and bulk modulus of a SiO_2 nanoparticle-reinforced PEEK matrix composite with various interface moduli. This figure shows that the effective Young's modulus and bulk modulus asymptotically converge at a certain value as the nanoparticle size increases, finally reaching a state in which no interface moduli effect can be observed (cf. Duan *et al.* (2005a)). It is also clear from the figure that, due to strong interface effect at small length scale, the size of nanoparticles affects the mechanical moduli of nanoparticle-reinforced polymer composites. The influence of interface moduli begins to diminish when the size of nanoparticle exceeds 3 nm.

4. Multiscale numerical simulations

Multiscale numerical simulations on nanoparticle-reinforced polymer composites are carried out to illustrate the potential of the proposed multiscale modeling.

4.1 Molecular dynamics (MD) simulation

As the first step of the present multiscale numerical simulations, MD simulations on SiO_2 nanoparticle-reinforced polymer composites are carried out using the MD code Materials Studio 4.3 (Accelrys Inc.) in an effort to determine the elastic properties of the polymer matrix and the SiO_2

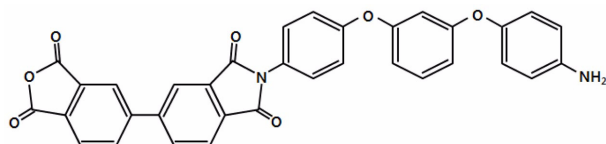


Fig. 3 The schematic description of 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA) and 1,3-bis (4-aminophenoxy) benzene (APB) monomers (cf. Srinivas *et al.* (1997), Hergenrother *et al.* (2002), and Odegard *et al.* (2005))

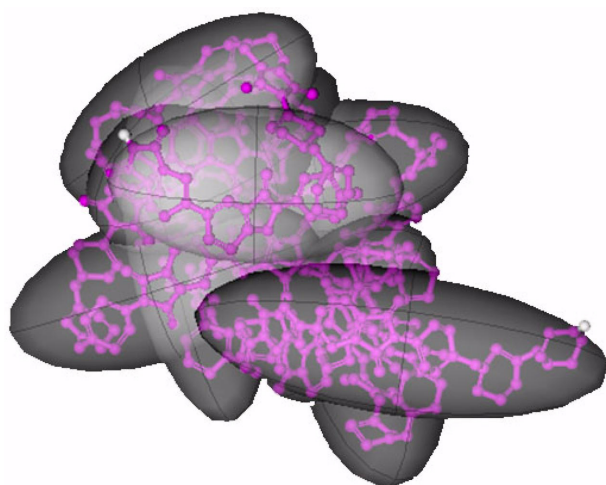


Fig. 4 Polyimid matrix after MD at 300 K

nanoparticle. Note that similar MD simulations were done by Odegard *et al.* (2005).

The polymer is based on a polyimid from 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA) and 1, 3-bis (4-aminophenoxy) benzene (APB) monomers shown in Fig. 3 (cf. Srinivas *et al.* 1997, Hergenrother *et al.* 2002, Odegard *et al.* 2005). As shown in Fig. 3, the copolymer of BPDA combined with APB in a random equivalent molecular repartition is used to form a new base monomer. In order to construct atomistic models of polymer chains, 7 polymer chains of 10 repeating units are computationally generated using the “Polymer Builder” tool of the Materials Studio program. Using the “Amorphous Cell” module, smart optimization of the geometry is then carried out to construct three-dimensional periodic structures of polymeric systems. In accordance with Odegard *et al.* (2005), the MD simulation at 650K until relaxation, with a final MD of 200 ps at 300K, is subsequently conducted. In each case, the constant-valence forcefield (cvff) potential (Dauber-Osquthorpe *et al.* 1988) in the Materials Studio program is used for the description of the inter-atomic interactions. Fig. 4 shows the polyimid matrix after MD simulation at 300K. After the MD simulation, the mechanical properties of the polyimid matrix are obtained using the “Synthia” module, which estimates polymer properties using empirical and semiempirical methods. The estimated elastic properties of the polyimid matrix from the MD simulation are shown in Table 1.

MD simulation of the SiO_2 nanoparticle is also carried out. For the SiO_2 nanoparticle, the crystal structure of α -quartz symmetry, corresponding to P3221 group symmetry, is modeled using the

Table 1 The elastic properties of the polymer matrix and SiO_2 nanoparticle obtained from the present MD simulations and the simulations by Odegard *et al.* (2005).

	Polymer matrix		SiO_2 nanoparticle	
	Young's modulus (GPa)	Bulk modulus (GPa)	Young's modulus (GPa)	Bulk modulus (GPa)
Present MD simulations	4.1	7.0	87.3	39.3
Odegard <i>et al.</i> (2005)'s simulations	4.2	7.0	88.7	35.3

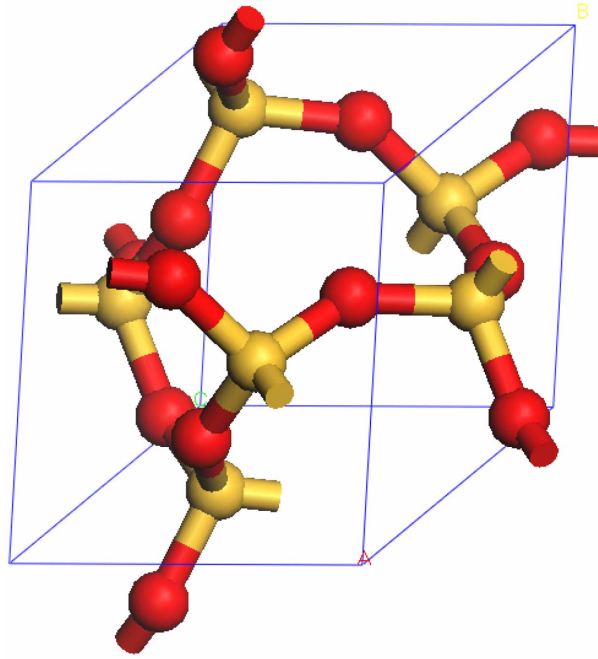


Fig. 5 Crystal α -quartz structure for the MD simulation of SiO_2 nanoparticles

“Crystal Builder” tool of the Materials Studio program. In “Crystal Builder”, only a single repeat unit (unit cell) of the SiO_2 nanoparticle is considered in the MD simulation. The lattice and atomic parameters of the crystal α -quartz structure are selected from Ikuta *et al.* (2007). Fig. 5 shows the crystal α -quartz structure obtained using “Crystal Builder” of the Materials Studio program. Geometry optimization and MD simulation of the crystal α -quartz structure are carried out using the “CASTEP” module, which is a state-of-the-art quantum mechanics-based program designed specifically for solid-state materials science. For geometry optimization of the crystal α -quartz structure, the generalized gradient approximation (GGA) of PBE (Perdew *et al.* 1996) is used as an exchange-correlation potential type of density function theory (DFT). The crystal α -quartz structure is subjected to DFT/GGA (PBE)-based molecular dynamics at 650 K and 300 K using the ensemble of the constant volume and temperature (NVT). The elastic constants of the crystal α -quartz structure are finally analyzed, as listed in Table 1.

For the validation of the present MD simulations, the elastic properties of the polymer matrix and the SiO_2 nanoparticle obtained from the MD simulations are compared with those previously

obtained by Odegard *et al.* (2005). The elastic properties of the polymer matrix and the SiO_2 nanoparticle obtained by Odegard *et al.* (2005) can also be found in Table 1. The Young's modulus and bulk modulus of the polymer matrix and the Young's modulus of the SiO_2 nanoparticle obtained from the present MD simulations are shown to be similar to those obtained from the simulations by Odegard *et al.* (2005), whereas the bulk modulus of the SiO_2 nanoparticle obtained from the present MD simulations is slightly higher than that of Odegard *et al.* (2005) due to the nature of two different MD approaches.

4.2 Numerical simulations of nanoparticle-reinforced polymer composites

Using the elastic properties obtained in the present MD simulations, a series of numerical studies are carried out to obtain the effective elastic moduli of nanoparticle-reinforced polymer composites. The influence of the nanoparticle radius on the effective elastic moduli of nanoparticle-reinforced polymer composites is investigated. The material properties of the polymer matrix and SiO_2 nanoparticles used here are listed in Table 1. The volume fraction of the nanoparticles is assumed to be $\phi_1 = 0.05$. In addition, the interface moduli are obtained using the data from Odegard *et al.* (2005) as: $\lambda_s = 1.8$ N/m and $\mu_s = 0.9$ N/m. The effective elastic moduli of the nanoparticle-reinforced polymer composites are calculated by the proposed micromechanics-based constitutive model described in Section 2.

Figs. 6 and 7 illustrate the predicted effective Young's modulus and bulk modulus, respectively, of the nanoparticle-reinforced polymer composites versus the radius of nanoparticle. It is apparent that the effective Young's modulus and bulk modulus decrease as the radius of the nanoparticle continues to increase, finally showing a similarity to the case in which no interface effect can be observed. The size effects are shown to be definitive when the size of the nanoparticle is less than approximately 3 nm. It can be said that the modulus of $R > 3$ nm is nearly equal to the classical case (without interface effect), due to the small ratios (κ_s^r and μ_s^r) between the intrinsic length scales (l_k and l_μ) and the size of the nanoparticle (R). Here, intrinsic length scales related to the property of

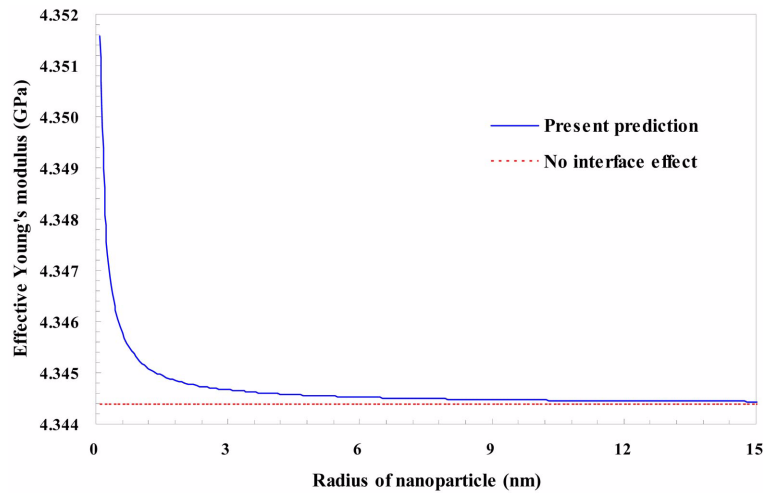


Fig. 6 The predicted effective Young's modulus of nanoparticle-reinforced polymer composites according to the radius of nanoparticles

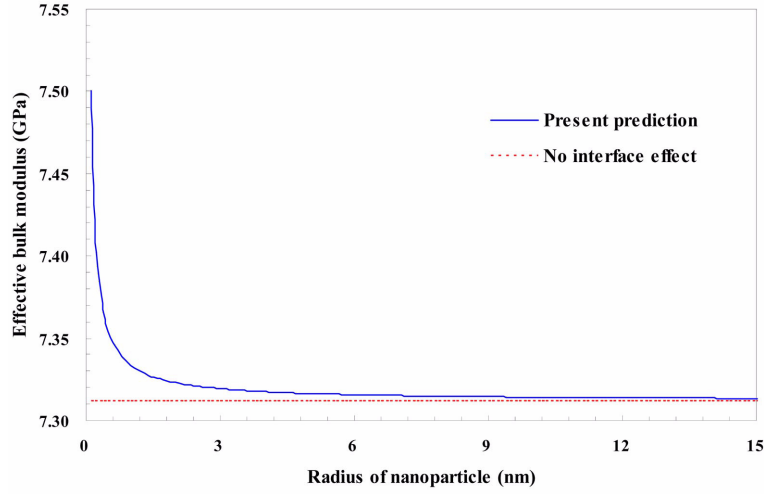


Fig. 7 The predicted effective bulk modulus of nanoparticle-reinforced polymer composites according to the radius of nanoparticles

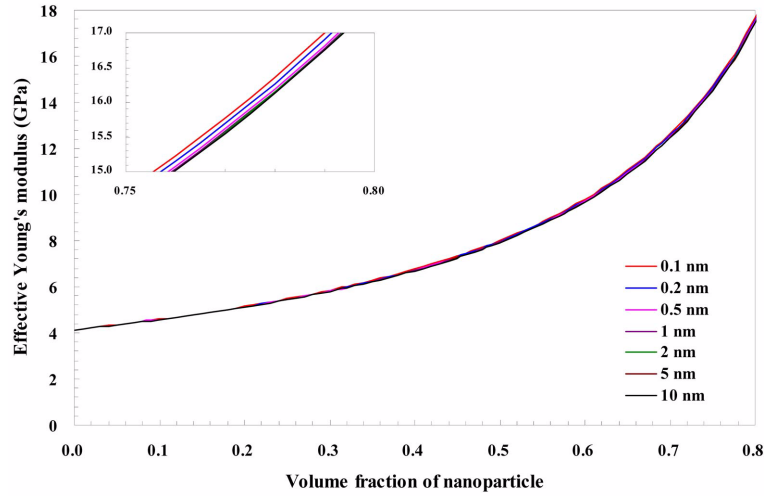


Fig. 8 The predicted effective Young's modulus of nanoparticle-reinforced polymer composites according to the volume fraction of nanoparticles

the interface are below 0.1 nm (Duan *et al.* 2005a, Chen *et al.* 2007). In addition, the size effect on the bulk modulus is much more pronounced than that on the Young's modulus.

An additional investigation on the volume fraction of nanoparticle is conducted. Figs. 8 and 9 highlight the predicted effective Young's modulus and bulk modulus, respectively, of nanoparticle-reinforced polymer composites according to the volume fraction of the nanoparticle. These results show that the increase in effective Young's modulus and bulk modulus coincide with the increase in volume fraction of the nanoparticle.

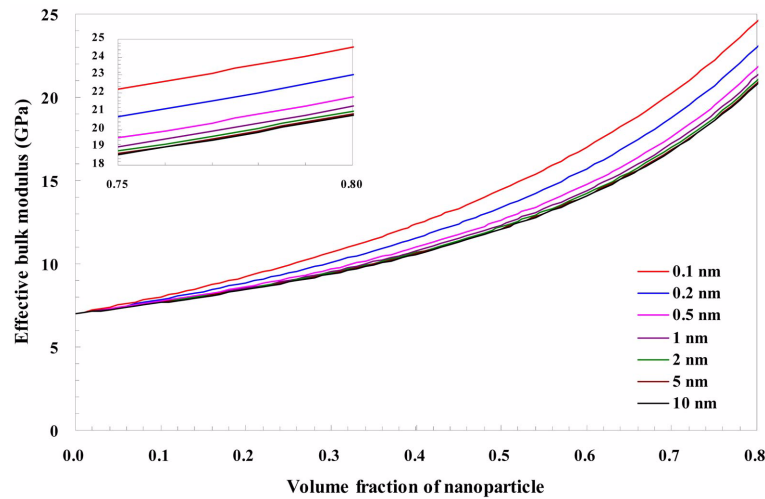


Fig. 9 The predicted effective bulk modulus of nanoparticle-reinforced polymer composites according to the volume fraction of nanoparticles

5. Conclusions

In this study, a multiscale approach has been presented to predict the overall elastic behavior of nanoparticle-reinforced composites. Based on the ensemble-volume average method and on MD simulations, the effective elastic moduli of the composites are explicitly obtained. A numerical investigation is carried out to validate the proposed micromechanics-based constitutive model, and a parametric study on the interface moduli is conducted to investigate the effect of interface moduli on the overall behavior of the composites. In addition, MD simulations are performed to determine the mechanical properties of the nanoparticles and polymer. Finally, the overall elastic moduli of the nanoparticle-reinforced polymer composites are estimated using the proposed multiscale approach combining the ensemble-volume average method and the MD simulation.

The prediction on effective elastic moduli of nanoparticle-reinforced polymer composites obtained from the proposed micromechanics-based constitutive model is shown to have a good correlation with the experimental data (Kuo *et al.* 2005) as a whole. The numerical investigation shows that the increase in effective Young's modulus and bulk modulus coincide with the increase in volume fraction of the nanoparticle. The present study has demonstrated the suitability of the proposed multiscale modeling approach for predicting the mechanical properties of nanoparticle-reinforced polymer composites.

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References

- Adnan, A., Sun, C.T. and Mahfuz, H. (2007), "A molecular dynamics simulation study to investigate the effect of filler size on elastic properties of polymer nanocomposites", *Compos. Sci. Technol.*, **67**, 348-356.
- Boutaleb, S., Zaïri, F., Mesbah, A., Naït-Abdelaziz, M., Gloaguen, J.M., Boukharouba, T. and Lefebvre, J.M. (2009), "Micromechanics-based modelling of stiffness and yield stress for silica/polymer nanocomposites", *Int. J. Solids Struct.*, **46**, 1716-1726.
- Chen, T., Dvorak, G.J. and Yu, C.C. (2007), "Size-dependent elastic properties of unidirectional nano-composites with interface stresses", *Acta Mechanica*, **188**, 39-54.
- Chen, H., Hu, G. and Huang, Z.P. (2007), "Effective moduli for micropolar composite with interface effect", *Int. J. Solids Struct.*, **44**, 8106-8118.
- Cho, J., Joshi, M.S. and Sun, C.T. (2006), "Effect of inclusion size on mechanical properties of polymeric composites with micro and nano particles", *Compos. Sci. Technol.*, **66**, 1941-1952.
- Dauber-Osguthorpe, P., Roberts, V.A., Osguthorpe, D.J., Wolff, J., Genest, M. and Hagler, A.T. (1988), "Structure and energetics of ligand binding to proteins: Escherichia coli dihydrofolate reductase-trimethoprim, a drug-receptor system", *Proteins: Struct. function Bioinformatics*, **4**, 31-47.
- Dingreville, R., Qu, J. and Cherkaoui, M. (2005), "Surface free energy and its effect on the elastic behavior of nano-sized particles, wires and films", *J. Mech. Phys. Solids*, **53**, 1827-1854.
- Duan, H.L., Wang, J., Huang, Z.P. and Karihaloo, B.L. (2005a), "Eshelby formalism for nano-inhomogeneities", *Proceedings of the Royal Society of London, Series A, Mathematical and Physical Sciences*, **461**, 3335-3353.
- Duan, H.L., Wang, J., Huang, Z.P. and Luo, Z.Y. (2005b), "Stress concentration tensors of inhomogeneities with interface effects", *Mech. Mater.*, **37**, 723-736.
- Fermeglia, M. and Priol, S. (2007), "Multiscale modeling for polymer systems of industrial interest", *Prog. Org. Coat.*, **58**, 187-199.
- Glotzer, S.C. and Paul, W. (2002), "Molecular and mesoscale simulation polymers", *Ann. Rev. Mater. Res.*, **32**, 401-436.
- Gurtin, M.E. and Murdoch, A.I. (1975a), "A continuum theory of elastic material surfaces", *Arch. Rat. Mech. Anal.*, **57**, 291-323.
- Gurtin, M.E. and Murdoch, A.I. (1975b), "Addenda to our paper: a continuum theory of elastic material surfaces", *Arch. Rat. Mech. Anal.*, **59**, 389-390.
- Guz, A.N. and Guz, I.A. (2006), "On models in the theory of stability of multiwalled carbon nanotubes in matrix", *Int. Appl. Mech.*, **42**, 617-628.
- Hergenrother, P.M., Watson, K.A., Smith Jr, J.G., Connell, J.W. and Yokota, R. (2002), "Polyimides from 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride and aromatic diamines", *Polymer*, **43**, 5077-5093.
- Ikuta, D., Kawame, N., Banno, S., Hirajima, T., Ito, K., Rakovan, J.F., Downs, R.T. and Tamada, O. (2007), "First in situ X-ray identification of coesite and retrograde quartz on a glass thin section of an ultrahigh-pressure metamorphic rock and their crystal structure details", *Am. Mineral.*, **92**, 57-63.
- Ju, J.W. and Chen, T.M. (1994), "Effective elastic moduli of two-phase composites containing randomly dispersed spherical inhomogeneities", *Acta Mechanica*, **103**, 123-144.
- Kuo, M.C., Tsai, C.M., Huang, J.C. and Chen, M. (2005), "PEEK composites reinforced by nano-sized SiO_2 and Al_2O_3 particulates", *Mater. Chem. Phys.*, **90**, 185-195.
- Lee, H.K. and Pyo, S.H. (2007), "Micromechanics-based elastic damage modeling of particulate composites with weakened interfaces", *Int. J. Solids Struct.*, **44**, 8390-8406.
- Li, Z.R., Lim, C.W. and He, L.H. (2006), "Stress concentration around a nano-scale spherical cavity in elastic media: effect of surface stress", *Eur. J. Mech. A - Solid*, **25**, 260-270.
- Liang, Z., Lee, H.K. and Suaris, W. (2006), "Micromechanics-based constitutive modeling for unidirectional laminated composites", *Int. J. Solids Struct.*, **43**, 5674-5689.
- Lim, C.W. and He, L.H. (2004), "Size-dependent nonlinear response of thin elastic films with nano-scale thickness", *Int. J. Mech. Sci.*, **46**, 1715-1726.
- Miller, R.E. and Shenoy, V.B. (2000), "Size-dependent elastic properties of nanosized structural elements", *Nanotechnology*, **11**, 139-147.
- Odegard, G.M., Clancy, T.C. and Gates, T.S. (2005), "Modeling of the mechanical properties of nanoparticle/

- polymer composites”, *Polymer*, **46**, 553-562.
- Perdew, J.P., Burke, K. and Ernzerhof, M. (1996), “Generalized gradient approximation made simple”, *Phys. Rev. Lett.*, **77**, 3865-3868.
- Rojek, J. and Oñate, E. (2008), “Multiscale analysis using a coupled discrete/finite element model”, *Interact. Multiscale Mech.*, **1**(1), 1-31.
- Scocchi, G., Posocco, P., Fermeglia, M. and Pricl, S. (2007), “Polymerclay nanocomposites: a multiscale molecular modeling approach”, *J. Phys. Chem. B*, **111**, 2143-2151.
- Sharma, P., Ganti, S. and Bhate, N. (2003), “Effect of surfaces on the size-dependent elastic state of nano-inhomogeneities”, *Appl. Phys. Lett.*, **82**, 535-537.
- Srinivas, S., Caputo, F.E., Graham, M., Gardner, S., Davis, R.M., Mc-Grath, J.E. and Wilkes, G.L. (1997), “Semicrystalline polyimides based on controlled molecular weight phthalimide end-capped 1, 3-bis (4-aminophenoxy) benzene and 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride: synthesis, crystallization, melting and thermal stability”, *Macromolecules*, **30**, 1012-1022.
- Walpole, L.J. (1981), “Elastic behaviour of composite materials: theoretical foundations”, *Adv. Appl. Mech.* (ed. Chia-Shun Yih), **21**, 169-242, New York, Academic Press.
- Wang, G.F., Feng, X.Q., Wang, T.J. and Gao, W. (2008), “Surface effects on the near-tip stresses for mode-I and mode-III cracks”, *J. Appl. Mech.*, **75**, 011001 1-5.
- Yang, F.Q. (2004), “Size-dependent effective modulus of elastic composite materials: spherical nanocavities at dilute concentrations”, *J. Appl. Phys.*, **95**, 3516-3520.
- Zhao, H. and Aluru, N.R. (2008), “Molecular dynamics simulation of bulk silicon under strain”, *Interact. Multiscale Mech.*, **1**(2), 303-315.
- Zeng, Q.H., Yu, A.B., and Lu, G.Q. (2008), “Multiscale modeling and simulation of polymer nanocomposites”, *Prog. Polym. Sci.*, **33**, 191-269.
- Zhang, W.X., Wang, T.J. and Chen, X. (2008), “Effect of surface stress on the asymmetric yield strength of nanowires”, *J. Appl. Phys.*, **103**, 1235271-5.