A MODELING TOOL FOR CONTACT PROBE TESTS ON

NANO-PARTICLE FILLED MATERIALS

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ABSTRACT

With the recent advances in nano-scale science and engineering, materials containing reinforcement with superior mechanical properties can be found in many advanced products. The accurate prediction of the mechanical properties of this class of composite materials is important to ensure the reliability of the products. Characterization methods based contact probe such as nano-indentation and scratch tests have been developed in recent years to measure the mechanical properties of the new class of nano materials. This paper presents a constitutive modeling framework for predicting the mechanical properties of nano-particle reinforced composite materials. The formulation directly considers the effects of inter-nano-particle interaction and performs a statistical averaging to the solution of the problem of two-nano-particle interaction. Final constitutive equations are obtained in analytical closed form with no additional material parameters. The predictions from the proposed constitutive model are compared with experimental measurement from nanoindentation tests. This constitutive model for nano-paticle reinforced composites can be used to determine the volume concentration of the reinforcing nano-particles in nano-indentation test.

Keywords: nanocomposite, constitutive modeling, contact probe test, nanoindentation, nanoparticle

1 INTRODUCTION

Composite materials containing reinforcement with superior strength manufactured with nanotechnology have emerged in many applications. For example, carbon nanotubes have been utilized in field emission display as indicated in Qian et al [1]. Thin coatings with nano-particle-filled sol-gel have also become popular in many advanced products including the protective topcoat of recording films in optical storage disks (Malzbender et al. [2]). For the reliability of these advanced products, accurate predictions of the mechanical properties of this class of composite materials are important.

In many existing constitutive models for composite materials, the effects of interaction among reinforcing elements have been neglected mostly due to the following two reasons. First, the difference of the mechanical strength between the reinforcement and the original matrix material may not be too large. Secondly, the volume concentration of the reinforcement may not be high. With the advance in modern nanotechnology, these two assumptions are no longer valid because some materials produced with nano-scale material engineering can have superior mechanical strength than traditional materials. In addition, the size of the reinforcement material can be made very small with nano-scale material engineering and thus greatly increase the homogeneity of the final composite material. This allows the volume concentration of the reinforcement to be increased to achieve much better overall mechanical properties.

This paper presents a material modeling framework for composites with nano-particles. The major advantage of the proposed model is that the effects of inter-nano-paticle interaction are captured into the constitutive model through statistical averaging on the solution of a two-particle interaction problem. Analytical closed-form formulations can be derived to predict the mechanical properties of nano-particle reinforced composites. The constitutive equations are expressed in terms of the volume concentration of the nano-particles and the material properties of the original matrix material and the reinforcing material. No additional material parameter needs to be introduced.

2 AVERAGE FIELDS THEORY

The determination of the exact internal local stress or strain field in a composite system is in general formidable due to the high degree of complexity of the arbitrary geometry and concentration of the reinforcing material. In many applications, it is sufficient to have the average of the field concerned. A method based on the averages of stress and strain fields was introduced by Hill [3] to describe the effective properties of composite materials.

In the average field theory, a concentration factor is introduced to represent the relationship between the local field and the average of the global field. For example, the stress at any local point for a specific material phase is related to the average stress for the global composite system

via the stress concentration factor. If only the average of the local stress field is required, upon averaging over the local material phase, we have the following relationship

$$\bar{\sigma}_a = \mathbf{P}_\alpha : \bar{\sigma} \tag{1}$$

where σ represents the stress tensor, the fourth rank tensor $\mathbf{P}_\alpha$ is the volume averaged stress concentration factor tensor for phase α, an over-bar represents the volume average of the corresponding quantity, and the subscript α denotes the material phase. Similar definition is made for the strain field

$$\bar{\varepsilon}_a = \mathbf{Q}_\alpha : \bar{\varepsilon} \tag{2}$$

in which ε represents the strain tensor and $\mathbf{Q}_\alpha$ is the volume averaged strain concentration factor tensor for phase α.

From elasticity theory, the elastic stiffness and compliance tensors, $\mathbf{C}_\alpha$ and $\mathbf{D}_\alpha$, respectively, for material phase α relate the local average stress and strain fields according to the following two equations

$$\bar{\sigma}_a = \mathbf{C}_\alpha : \bar{\varepsilon}_a \tag{3}$$

$$\bar{\varepsilon}_a = \mathbf{D}_\alpha : \bar{\sigma}_a \tag{4}$$

Similarly, the macroscopic elastic properties can be expressed by the following equations through the global elastic moduli

$$\bar{\sigma} = \mathbf{C}_* : \bar{\varepsilon} \tag{5}$$

$$\bar{\varepsilon} = \mathbf{D}_* : \bar{\sigma} \tag{6}$$

Subscripts 0, 1, and * denotes the matrix, nano-particle, and overall composite material, respectively. Based on the definitions in Equations (1)-(6), the global effective elastic moduli are expressed in terms of the volume fractions, elastic moduli of the constituent phases, and the concentration factor tensors as shown in the following two equations

$$\mathbf{C}_* = \mathbf{C}_\alpha + \phi_\beta (\mathbf{C}_\beta - \mathbf{C}_\alpha) \cdot \mathbf{Q}_\beta \tag{7}$$

$$\mathbf{D}_* = \mathbf{D}_\alpha + \phi_\beta (\mathbf{D}_\beta - \mathbf{D}_\alpha) \cdot \mathbf{P}_\beta \tag{8}$$

From Equations (7) and (8), the global effective elastic moduli for a two-phase composite system can be calculated provided that any one of stress or strain concentration factor tensors is available.

3 INTERACTION OF TWO NANO-PARTICLES

For the simplicity of presentation and mathematical operation, we assume that the material properties for both the matrix phase and the particle phase are isotropic and the loading at any local material point remains within the elastic limit. However, the framework that is presented in this paper is valid for the general composite system with any arbitrary material property for the constituent phase. It is further assumed that the particles do not intersect each other and the material properties of both phases remain unchanged for the loading considered.

Extending from Mura [4], when applying the Eshelby's Equivalence Principle to the inclusion problem without considering the effects of inter-particle interaction, the equation for determining the unknown eigenstrain, which has been proved to be constant throughout the entire spherical region, can be written as

$$-\mathbf{A} : \varepsilon^{*0} = \varepsilon^0 + \mathbf{S} : \varepsilon^{*0} \tag{9}$$

where

$$\mathbf{A} = (\mathbf{C}_1 - \mathbf{C}_0)^{-1} \cdot \mathbf{C}_0 \tag{10}$$

in which $\mathbf{C}_0$ and $\mathbf{C}_1$ are the stiffness tensor for the matrix and inclusion phase, respectively. Tensor product is denoted by $\mathbf{A} \cdot \mathbf{B}$. In Equation (9), $\mathbf{S}$ is the Eshelby's tensor for a spherical inclusion and is defined as

$$\mathbf{S} = \int_\Omega \mathbf{G}(\mathbf{x} - \mathbf{x'}) d\mathbf{x'}, \qquad \mathbf{x} \in \Omega \tag{11}$$

where the elasticity Green's function tensor $\mathbf{G}(\mathbf{x} - \mathbf{x'})$ is defined by the following equation

$$\varepsilon(\mathbf{x}) = \int \mathbf{G}(\mathbf{x} - \mathbf{x'}) : \varepsilon^*(\mathbf{x'}) d\mathbf{x'} \tag{12}$$

in which $\varepsilon(\mathbf{x})$ denotes the strain tensor at location $\mathbf{x}$, $\varepsilon^*(\mathbf{x})$ is the tensor of eigenstrain, and $\varepsilon^{*0}(\mathbf{x})$ represents the eigenstrain tensor for the non-interacting particles. The explicit form for the tensor components of $\mathbf{S}$ can be found in Mura [4] for the spherical inclusion considered in the present study. Taking into account the effects of inter-particle interaction, the integral equation governing the distributed eigenstrain can be expressed as

$$-\mathbf{A} : \varepsilon^*(\mathbf{x}) = \varepsilon^0 + \int_{\Omega_i} \mathbf{G}(\mathbf{x} - \mathbf{x'}) : \varepsilon(\mathbf{x'}) d\mathbf{x'} + \int_{\Omega_j} \mathbf{G}(\mathbf{x} - \mathbf{x'}) : \varepsilon(\mathbf{x'}) d\mathbf{x'} \tag{13}$$

In the case that we are considering, many equal-sized spherical particles are assumed to distribute randomly among an elastic solid. Based on the solution for Equation (13), which represents the effect of pair-wise interaction, and assuming that the distribution of the particles is uniform and no particle overlaps with each other, ensemble-volume averaged eigenstrain perturbation in a particle can be written as

$$\left\langle \overline{\varepsilon}^* \right\rangle = \Gamma : \varepsilon^{*0} \tag{14}$$

where the components for the isotropic *interaction tensor* Γ are defined as

$$\Gamma_{ijkl} = \gamma_1 \delta_{ij} \delta_{kl} + \gamma_2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \tag{15}$$

in which δ_{ij} is the Kronecker delta,

$$\gamma_1 = \frac{5\phi}{4\beta^2} \left\{ -2(1-\nu_0) - 5\nu_0^2 - \frac{4\alpha}{3\alpha+2\beta}(1+\nu_0)(1-2\nu_0) \right\} \tag{16}$$

and

$$\gamma_2 = \frac{1}{2} + \frac{5\phi}{8\beta^2} \left\{ 11(1-\nu_0) + 5\nu_0^2 - \frac{3\alpha}{3\alpha+2\beta}(1+\nu_0)(1-2\nu_0) \right\} \tag{17}$$

where

$$\alpha = 2(5\nu_0 - 1) + 10(1-\nu_0)\left(\frac{\kappa_0}{\kappa_1 - \kappa_0}\right)\left(\frac{\mu_0}{\mu_1 - \mu_0}\right) \tag{18}$$

and

$$\beta = 2(4 - 5\nu_0) + 15(1-\nu_0)\frac{\mu_0}{\mu_1 - \mu_0} \tag{19}$$

In Equations (16) and (17), ν, κ, and μ represent the Poisson ratio, bulk modulus, and shear modulus, respectively, for the corresponding material phase which is denoted via the corresponding subscript and ϕ denotes the volume fraction of the particles in the composite material under consideration.

4 CONCENTRATION FACTORS

With an additional averaging over the volume of the representative volume element, the equation relating the average strain $\overline{\varepsilon}$, the uniform remote strain ε^0, and the average eigenstrain $\overline{\varepsilon}^*$ can be expressed as:

$$\overline{\varepsilon} = \varepsilon^0 + \phi S : \overline{\varepsilon}^* \tag{21}$$

With Equations (8), (9) and (14), we get

$$\overline{\varepsilon}^* = B : \overline{\varepsilon} \tag{22}$$

where

$$B = \Gamma \cdot \left[-A - S + \phi S \cdot \Gamma \right]^{-1} \tag{23}$$

Averaging the fundamental equation for the Eshelby's equivalence principle:

$$C_1 : \varepsilon(x) = C_0 : \left[\varepsilon(x) - \varepsilon^*(x) \right] \tag{24}$$

the relationship between the local strain average and the eigenstrain average can be written as

$$C_1 : \overline{\varepsilon}_1 = C_0 : \left[\overline{\varepsilon}_1 - \overline{\varepsilon}^* \right] \tag{25}$$

Further utilizing Equation (10), we arrive at

$$\overline{\varepsilon}_1 = A : \overline{\varepsilon}^* \tag{26}$$

then, with Equation (8),

$$\overline{\varepsilon}_1 = -(A \cdot B) : \overline{\varepsilon} \tag{27}$$

Hence, upon comparing Equation (27) with Equation (2), the strain concentration factor tensor considering the effect of inter-particle interaction can be written as

$$Q_1 = -A \cdot B \tag{28}$$

and the corresponding stress concentration factor tensor can be derived in a similar fashion. The explicit expression for the stress concentration factor tensor takes the following form:

$$P_1 = -C_1 \cdot A \cdot B \cdot \left[I - \phi B \right]^{-1} \cdot C_0^{-1} \tag{29}$$

The tensor components for P_1 can be obtained by carrying out the lengthy tensor operation in Equation (29). The fourth rank tensor P_1 is found to be isotropic and its components are

$$(P_1)_{ijkl} = p_1 \delta_{ij} \delta_{kl} + p_2 (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \tag{30}$$

where

$$3p_1 + 2p_2 = \frac{30\kappa_1(1-\nu_0)(3\gamma_1 + 2\gamma_2)}{(\kappa_0 - \kappa_1)[(3\alpha+2\beta) + 20(1-2\nu_0)(3\gamma_1 + 2\gamma_2)]} \tag{31}$$

and

$$p_2 = \frac{15\mu_1(1-\nu_0)\gamma_2}{(\mu_1 - \mu_0)[\beta + 2(7-5\nu_0)\phi\gamma_2]} \tag{32}$$

5 EFFECTIVE ELASTIC PROPERTIES

As an example, the stress and strain concentration factor tensors derived in the previous section are employed to construct the effective elastic properties for particle-

reinforced composites. Through Equations (7) and (29), the effective elastic stiffness tensor incorporating the effect of inter-particle interaction reads

$$\mathbf{C}_* = \mathbf{C}_0 \cdot \left\{ \mathbf{I} - \phi \mathbf{\Gamma} \cdot \left(-\mathbf{A} - \mathbf{S} + \phi \mathbf{S} \cdot \mathbf{\Gamma} \right)^{-1} \right\} \quad (43)$$

Since the particles are assumed to distribute uniformly among the matrix material, the composite is isotropic. The effective elastic property can be represented by the effective bulk modulus κ_* and the effective shear modulus μ_* can be explicitly written as

$$\kappa_* = \kappa_0 \left\{ 1 + \frac{30(1-\nu_0)\phi(3\gamma_1 + 2\gamma_2)}{3\alpha + 2\beta - 10(1+\nu_0)\phi(3\gamma_1 + 2\gamma_2)} \right\} \quad (44)$$

and

$$\mu_* = \mu_0 \left\{ 1 + \frac{30(1-\nu_0)\phi\gamma_2}{\beta - 4(4-5\nu_0)\phi\gamma_2} \right\} \quad (45)$$

6 COMPARSON WITH EXPERIMENTAL RESULTS

In Malzbender et al. [2], nanoindentation tests were conducted to measure the mechanical properties of nano-particle-filled sol-gel coatings on glass. The material surface is indented with a small indentor loaded with a force. Based on the depth of the indentation, mechanical properties of the thin coating can be calculated.
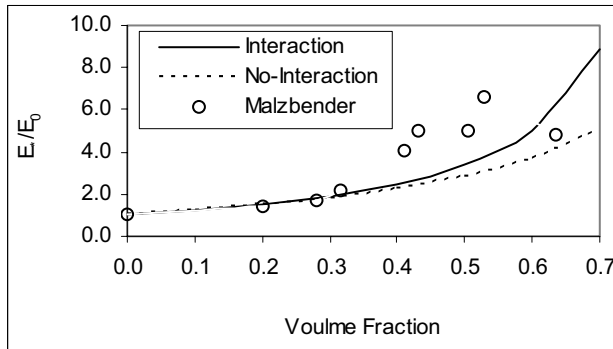

Figure 1: Effects of inter-nano-particle interaction.

Figure 1 compares the experimental results from indentation tests reported in Malzbender et al. [2] with the prediction from the constitutive equations presented in this paper. Nanoindentation has been conducted to measure the mechanical properties of alumina filled coating on glass. The solid curve in Figure 1 represents the mechanical properties predicted by Equations (44) and (45) including the effects of inter-nano-particle interaction. The dashed curve in Figure 1 corresponds to the mechanical properties

predicted by Equations (44) and (45) with neglected effects of inter-nano-particle interaction. The difference in these two curves indicates that as the volume concentration of nano-particles increases, the effects of inter-nano-particle interaction become more important and cannot be neglected. Figure 1 also suggests that the predictions with inter-nano-particle interaction effects are closer to the experimental measurements.

7 CONCLUSIONS

A constitutive modeling framework to predict the mechanical properties of nano-particle reinforced composite materials has been presented. The predictions on mechanical properties from the current model have been compared with experimental data measured by nanoindentation tests. The effects of inter-nano-particle interaction are significant and cannot be neglected especially when the volume concentration of the nano-particles is high.

The constitutive model presented in this paper has the potential of being used for numerical simulation based on finite element analysis to solve practical engineering problems involving composites reinforced with nano-particles up to moderately-high volume concentration. During the constitutive modeling process presented in this paper, no additional material parameter has been introduced. The mechanical properties are related to the volume concentration of the nano-particles. This constitutive model provides a possible tool for the prediction of the volume concentration of nano-particles based on the measurements from nano-indentation tests.

REFERENCES

[1] D. Qian, G.J. Wagner, W.K. Liu, M.F. Yu, and R.S. Ruoff, Applied Mechanics Review, 55(6), 495, 2002.
[2] J. Malzbender, J.M.J. den Toonder, A.R. Balkenende, and G. de With, Materials Science and Engineering R 36, 47, 2002.
[3] R. Hill, Journal of Mechanics and Physics of Solids, 48, 367, 1963.
[4] T. Mura, Micromechanics of Defects in Solids, Second Revised Edition, Kluwer Academic Publishers, 1987.