Annular Coated Inclusion model and applications for polymer nanocomposites – Part I: Spherical inclusions

Z. Wang, R. J. Oelkers, K. C. Lee, and F. T. Fisher

Department of Mechanical Engineering

Stevens Institute of Technology

1 Castle Point on Hudson, Hoboken, NJ 07030

Phone: 1-201-216-8913, email: Frank.Fisher@stevens.edu

Abstract

There is considerable interest in using various nanoparticles to create multifunctional polymer nanocomposite materials with enhanced properties. Due to the large amount of surface area available within the nanocomposite, the effects of non-bulk polymer in the vicinity of the nanoinclusion, with different properties than the bulk polymer, can complicate micromechanical predictions of effective properties. Several micromechanical approaches require one to calculate the dilute strain concentration tensor, for which elegant solutions are available for separate, physically distinct ellipsoidal inclusion geometries using the well-known Eshelby tensor. Here the general coated inclusion problem is formulated for the case of a spherical inclusion, such that the components of the dilute strain concentration tensors for both the inclusion and the interphase/coating region are analytically determined, from which they can then be directly implemented within standard micromechanical models. Model predictions indicate that the proposed coated inclusion is able to accurately capture the effects of the interphase coating. Moreover, several published experimental data sets for soft interphase systems have been examined to illustrate the utility of the proposed model. **An advantage of the proposed method is that the solution of**

the auxiliary problems allows determination of the stress and strain fields which can be extended in a straightforward manner to enable a wide range of composite studies. It is anticipated that the proposed model will be particularly useful in evaluating the impact of chemical functionalization techniques and other strategies that seek to tailor the properties of the interphase region in these materials.

Keywords: Nano composites, Polymer-matrix composites (PMCs), Interphase, Modelling, Micromechanics

1. Introduction

Nanoparticle reinforcement is a key emerging technology to simultaneously impart enhanced mechanical properties while adding multifunctional characteristics to polymer materials and systems. One schema to classify nanocomposites is based on the geometry of the nanoparticles, with nanoplatelet, nanotubular, and nanoparticulate (equiaxed, or quasi-spherical) reinforcement referring to inclusions with effective aspect ratios of $L/d \ll 1$, $L/d \gg 1$, and $L/d \approx 1$, respectively, where L and d are the characteristic length scale and cross-sectional dimension of the nanoparticle. By convention, one the characteristic length scales is less than 100 nm to be classified as nanoscale reinforcement. Throughout this paper the term *nanoparticle* refers to a nanoinclusion phase of any arbitrary geometry, whereas the term *nanoparticulate* is reserved for those nanoinclusions with $L/d \approx 1$.

Due to the overwhelming interest in carbon nanotube (CNT)-reinforced polymers, a significant portion of polymer nanocomposites research has focused on the nanotubular

form of reinforcement as discussed in detail in several recent review articles [1, 2]. Their extraordinary mechanical properties make CNTs excellent candidates for reinforcement of polymer nanocomposites, while their exceedingly large aspect ratios help to enhance load transfer within the nanocomposite due to the surface area available over which the interfacial shear stress can be transferred to the inclusion.

On the other hand, nanoplatelet reinforcement refers to a general class of 2D plate-like filler material with lateral dimensions on the order of microns and thicknesses of the individual platelets on the order of nanometers. The interest in using nanoplatelet reinforcement in a polymer nanocomposite dates back to the pioneering work with nanoclays by researchers at Toyota at the end of the last century; see [3] for a recent review in the area. More recently, various forms of nanoplatelet-based graphene and its derivatives (graphene [4], expanded graphite [5], graphene oxide [6], etc.) have received considerable attention in the polymer nanocomposites community. Although stand-alone graphene layers have a wide variety of potential applications [7], a challenge when used for nanocomposite reinforcement lies in incomplete exfoliation (or subsequent restacking during processing) that significantly reduces the effective modulus values obtained for the nanocomposite [8]. Moreover, crumpled and wrinkled structures are often reported in composites when these thin platelets were dispersed in a polymer matrix, which also diminish their reinforcing effectiveness [9]. Aside from these structural issues, difficulties in both dispersing the graphene and controlling the interaction/adhesion between the graphene reinforcement and the polymer matrix are major challenges in the area [10, 11].

Lastly, a variety of equiaxed nanoparticulate fillers have been used to enhance the physical properties of the unfilled polymer, dating back to the earliest work with carbon

black. Examples of equiaxed nanoparticulates that have been widely used and studied in nanocomposites include titania (TiO_2) [12], silica (SiO_2) [13], and alumina (Al_2O_3) [14]. For example, epoxy composite resins filled with 12-nm spherical silica particles show significant enhancement in thermal and mechanical properties [15]. Commercially, spherical nanoparticles have been used to alter the optical and refractive properties of commodity plastics and paints. They are also widely used in surface modification of different materials such as abrasive paste and lubricants due to excellent tribological properties [16].

Irrespective of the dimensionality of the nanoparticle, common issues such as achieving (and quantifying) adequate dispersion of the nanoparticles within the transfer between the nanoinclusion and the host polymer, and the development of multiscale models based on atomic-scale interactions between the nanoinclusions and matrix remain challenges in the general field of polymer nanocomposites. In key feature in the field of polymer nanocomposites, independent of the aspect ratio of particle, is the influence that the embedded nanoparticles can have on the behavior of polymer matrix in close proximity to the embedded inclusions, which directly impacts effective properties of the nanocomposite [17]. For example, the formation of an region with altered polymer chain mobility in the nanocomposite is illustrated in

Figure 1a. Here a spherical nanoparticle of radius a is surrounded by a non-bulk polymer interphase of radius b , such that the thickness of the interphase is $t = b - a$. This non-bulk polymer is then surrounded by the bulk polymer, which is sufficiently physically separated from the embedded nanoinclusions such that the behavior of the polymer in this region is unaffected by the presence of the nanoinclusions. It has been shown that extent of this interphase region may be on the order of magnitude of the radius of gyration of the polymer, and hence several to tens of nanometers in thickness [18, 19]. As the radius of the nanoparticle decreases, the impact of the interphase region increases dramatically, which can be illustrated by plotting the ratio

of the interphase to bulk polymer as a function of nanoparticle radius for different values of the interphase thickness as shown in

Figure 1b.

Generally the interphase is not considered to contribute significantly to the overall composites properties in conventional polymer reinforcements system due to the fact its relative size is considerably smaller than matrix and the fillers. However, as shown in

Figure 1b, when the length scale of the inclusion is at the nanoscale, the surface area of the nanoparticles, which is several orders of magnitude larger than that of micron-sized fillers, can lead to an extensive amount of interphase even at small filler volume fractions. The presence of this interphase region, which often has mechanical properties different than that of the bulk polymer due to restricted polymer chain mobility, can have a remarkable impact on the overall composites properties [20].

In many cases, the influence of this non-bulk interphase region is most apparent through observation of changes in the glass transition temperature (T_g) of the nanocomposite, where experimental increases in T_g have been observed for poly(methyl methacrylate) nanocomposites reinforced with silica [21] and amide-functionalized single-walled carbon nanotubes [22], as well as poly(acrylonitrile) with functionalized graphene [23]. While efforts to directly characterize the properties of the interphase experimentally are extraordinarily difficult due to the size and nature of the interphase region in nanocomposites, earlier SEM imaging illustrating a significant adsorbed polymer layer on nanotubes protruding from fracture surfaces in a MWNT/polycarbonate system [24] is consistent with the formation of an interphase region in these materials. In addition, experimental work in the thin-film polymer community has shown large differences in

polymer-chain mobility and properties resulting from interactions with surfaces (including free surfaces) [25].

Figure 1. (a) Schematic representation of the interphase region in polymer nanocomposites, (b) Ratio of the fraction of interphase-to-matrix polymer as a function of spherical particulate inclusion radius for different values of the interphase thickness t .

Due to the importance and extent of this interphase region, various models have been proposed to estimate the interphase properties of nanocomposites. For example, molecular dynamics (MD) has been applied to quantify the interphase thickness in both clay-based polymer nanocomposites [26] and spherical inclusion reinforced polymer nanocomposites [27]. Rahimi et al., using a coarse-grained molecular dynamics technique, predicted the interphase stiffness of silica-polystyrene system through analysis of local segmental orientational and structural parameters [20]. Combining this local interphase/inclusion behavior with subsequent continuum modeling, a multiscale approach which has been implemented to estimate the overall bulk properties of carbon nanotube reinforced polymer

composites [28]. In spite of these efforts, a quantitative understanding of the structure and morphology of polymer interacting with nanoscale surfaces is still lacking.

It is for these reasons that there is a need for modeling approaches that can readily include the properties and geometry of this non-bulk interphase into predictions of effective composite properties. Here micromechanics approaches such as the Mori-Tanaka method are particularly appealing due to their ease of use and widespread popularity. However, a micromechanical approach that accurately captures the physicality of an annular interphase region surrounding the nanoparticle is clearly necessary for nanoparticulate-polymer nanocomposites. In the current work, an annular coated inclusion model is described where one can determine analytically the dilute strain concentration tensor for a coated spherical inclusion, which can then be used within traditional micromechanical techniques to account for the presence of a three-phase (spherical) inclusion-interphase-matrix composite geometry. In Part 2 of this work, an analogous approach to calculate the dilute strain concentration tensor for coated cylindrical inclusions [29] is developed.

2. Mori-Tanaka Micromechanical Approach

The field of micromechanics involves the determination of the effective properties of composites and other heterogeneous materials based on the composition of the materials and the properties of the constituent phases. Such micromechanics approaches can range from the simplistic rule-of-mixture type of approximations, where the geometry of the inclusion phases are not considered, to more sophisticated approaches where factors such as inclusion geometry and orientation are explicitly considered in the analysis. Several of the more rigorous micromechanical approaches are based on the calculation of the dilute strain concentration tensor, A_{dil}^r , a fourth-order tensor which relates the average strain of the r th inclusion $\bar{\varepsilon}^r$ to the average strain in the matrix $\bar{\varepsilon}^m$ such that

$$\bar{\varepsilon}^r = A_{dil}^r \bar{\varepsilon}^m \quad (1)$$

For the general case where the inclusions are ellipsoidal in shape, Eshelby's classical solution [30] allows the dilute strain concentration tensor A_{dil}^r to be written in terms of the Eshelby tensor S^r such that

$$A_{dil}^r = \left[I + S^r (C^m)^{-1} (C^r - C^m) \right]^{-1} \quad (2)$$

where C^m and C^r are the stiffness tensor of the matrix and the r th inclusion phase and I is the identity tensor. General forms for the Eshelby tensor for ellipsoidal inclusions, including the limit case of spherical inclusions, are readily available in the literature [31].

One common micromechanical approach that utilizes the dilute strain concentration tensor in the determination of effective composite properties is the Mori-Tanaka method. The reader is referred to the literature for an in-depth derivation and discussion of the method [32-34]. A key feature of the Mori-Tanaka formulation is that particle-particle

interactions are accounted for within the derivation, which results in more accurate micromechanical predictions for non-dilute concentrations of the inclusion phases. Given the dilute strain concentration tensor in (1), the Mori-Tanaka solution for the effective stiffness C of a composite with randomly oriented inclusions can be written as [34]

$$C = \left(f^m C^m + \sum_{n=1}^r f^n \{C^n A_{dil}^n\} \right) \left(f^m I + \sum_{n=1}^r f^n \{A_{dil}^n\} \right)^{-1} \quad (3)$$

where f^n and f^m are the volume fraction of the n th inclusion phase and the matrix, respectively, and brackets $\{\}$ denote the appropriate orientational average based on the orientation of the particles within the composite (see [35]). While for spherical inclusions the resulting composite properties are isotropic and orientational effects are not present, as discussed in the companion paper the form of (3) is particularly well suited for the determination of effective properties for composites with non-spherical geometries and a given orientational distribution of the inclusions [29].

The standard multiphase Mori-Tanaka method requires separate, physically distinct ellipsoidal inclusion phases for the calculation of the Eshelby tensor of each phase for substitution into (3) as shown in Figure 2a. However, the actual physical geometry of the interphase region in nanoparticulate-reinforced polymer systems is such that the interphase region is surrounding the nanoparticulate in the form of a coated inclusion (Figure 2b). While previous work in the literature has modeled a three phase composite using the standard multiphase Mori-Tanaka approach where the interphase region is a separate ellipsoidal inclusion in the composite [24, 36], the development of the dilute strain concentration tensor for coated spherical inclusions is necessary to more accurately account for the physicality of the system.

Figure 2. Schematic of micromechanics approaches. (a) Standard multiphase Mori-Tanaka approach. (b) Annular coated inclusion approach.

The novelty of the proposed model is that the general coated inclusion problem is formulated in such a manner that the components of the dilute strain concentration tensor as defined in (1) for both the inclusion and the interphase/coating region can be directly determined analytically, and then used within the standard Mori-Tanaka approach. Alternatively, in earlier work the authors and co-workers have used a hybrid finite element – micromechanics approach to determine the components of the strain concentration tensor numerically for problems where A_{dil}^r cannot be determined via the Eshelby tensor; for example, to account fiber waviness [37, 38] and coated inclusions of complex shapes [39]. The analytical solution for the dilute strain concentration tensor approach, initially presented here for coated spherical inclusions, is adapted for infinitely long coated cylindrical inclusions (i.e. $L/d \rightarrow \infty$) in the companion paper [29].

Below we first present the derivation of the determination of the dilute strain concentration tensors for the nanoparticulate and the interphase region, respectively, via the definition in (1). Subsequently, these tensors can be substituted directly into (3) to

determine the effective stiffness of the nanoparticulate-reinforced polymer. Numerical calculations are then presented to highlight the differences between the standard multiphase Mori-Tanaka approach (with the inherent assumption of physically separated inclusion and interphase regions) and the results obtained using the dilute strain concentration tensor for the case of coated spherical inclusions proposed in this work. Lastly, note that while the approach presented here can be applied for coated particle inclusions at any length scale, as discussed in Section 3 the motivation behind the model development is nanoparticulate-reinforced polymers, where non-bulk interphase effects are prevalent, significant, and require a model such as that proposed to account for this region in bulk nanocomposite predictions.

3. Annular Coated Inclusion (ACT) Model for Spherical Coated Inclusions

Various micromechanics approaches have been conducted to analyze the effective moduli of composites reinforced by coated inclusions. For example, Christensen and co-workers proposed three-phase composite models to estimate effective shear properties of the coated spherical inclusion problem and the coated cylindrical inclusion problem, respectively [40, 41]. Later, Luo et al presented a three-phase concentric solid model to obtain the complete elastic fields using a modified Mori-Tanaka method and Eshelby tensor [42, 43]. Benveniste et al and Chen used the Christensen approach in the solution of appropriately defined auxiliary loadings to predict the stress field and thermoelastic properties of coated orthotropic fiber composites [44, 45], while Fisher and co-workers investigated the effective moduli predictions of a three phase viscoelastic composite using the Benveniste solution [36]. In addition, Yang developed core-shell nanostructure consist

of three concentric spheres (a nanosphere, a shell structure, and a unit cell), then derived the dependence of stress distribution on interface energy through which they could determine the effective bulk modulus of the nanocomposite [46]. Lastly, the Double-Inclusion model proposed by Hori and Nemat-Nasser used an equivalent inclusion method [47]; this approach was later applied by Dunn and others to estimate the effective properties of multiphase composite systems [48-50]. However, as shown in the Appendix, one can prove that the Double-Inclusion model simplifies to the multiphase Mori-Tanaka solution given in (3) for the special case where the aspect ratios of the inclusion and the coating/interphase are identical.

3.1 The three-phase problem of composites reinforced by spherical inclusions

Analogous to the approach presented by Benveniste, who developed suitable auxiliary problems to analyze a composite with coated cylindrical inclusions [45], here the proposed model for spherical inclusions is developed by defining two suitable auxiliary problems: hydrostatic and shear. The solution to the latter auxiliary problem was given by Christensen [41], where the stress and strain fields of a single-coated spherical inclusion subjected to a series of appropriate far-field applied loading conditions are determined. In many respects this approach is similar to earlier work where the finite element method, rather than an analytical solution as used here, was used to determine the average stress and strain fields in ‘wavy’ fiber composites [37]. Here we will illustrate the model for the case of a spherical coated inclusion; a similar model for coated cylindrical inclusions will be reported in the sequel [29].

Figure 3a shows the schematic diagram of a coated spherical inclusion consisting of three phases: a spherical inclusion, an annular interphase of uniform thickness surrounding the core inclusion, and the polymer matrix material. For simplicity, here we assume all the materials are elastic, homogeneous, and isotropic. We use f , g , and m to denote the properties of inclusion, interphase, and matrix material, respectively. The radii of the inclusion and the interphase are denoted as a and b , respectively, such that the volume fraction of inclusion and interphase can be written as

$$f^f = \frac{4}{3} \pi a^3, \quad f^g = \frac{4}{3} \pi (b^3 - a^3) \quad (4)$$

where $f^f + f^g + f^m = 1$. Assuming that the volume fraction of the inclusion and interphase are known, one can solve for the radii a and b such that

$$a = \sqrt[3]{\frac{3f^f}{4\pi}}, \quad b = \sqrt[3]{\frac{3(f^f + f^g)}{4\pi}} \quad (5)$$

The goal of the current work is to determine the elements of the dilute strain concentration tensor A_{dil}^r of a coated spherical inclusion analytically. Using standard contracted notation, the forth order dilute strain concentration tensors can be written explicitly for the particulate and interphase regions, respectively, as

$$A_{dil}^f = \begin{bmatrix} A_{11}^f & A_{12}^f & A_{13}^f & 0 & 0 & 0 \\ A_{21}^f & A_{22}^f & A_{23}^f & 0 & 0 & 0 \\ A_{31}^f & A_{32}^f & A_{33}^f & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44}^f & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{55}^f & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66}^f \end{bmatrix}, \quad A_{dil}^g = \begin{bmatrix} A_{11}^g & A_{12}^g & A_{13}^g & 0 & 0 & 0 \\ A_{21}^g & A_{22}^g & A_{23}^g & 0 & 0 & 0 \\ A_{31}^g & A_{32}^g & A_{33}^g & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{44}^g & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{55}^g & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66}^g \end{bmatrix} \quad (6)$$

By inspection, for the case of an isotropic spherical particulate embedded in an isotropic matrix, one can take advantage of symmetry to simplify the dilute strain concentration tensor given in (6) in the following isotropic form, i.e.

$$A_{dil}^f = \begin{bmatrix} A_{11}^f & A_{12}^f & A_{12}^f & 0 & 0 & 0 \\ A_{12}^f & A_{11}^f & A_{12}^f & 0 & 0 & 0 \\ A_{12}^f & A_{12}^f & A_{11}^f & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{66}^f & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{66}^f & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66}^f \end{bmatrix}, \quad A_{dil}^g = \begin{bmatrix} A_{11}^g & A_{12}^g & A_{12}^g & 0 & 0 & 0 \\ A_{12}^g & A_{11}^g & A_{12}^g & 0 & 0 & 0 \\ A_{12}^g & A_{12}^g & A_{11}^g & 0 & 0 & 0 \\ 0 & 0 & 0 & A_{66}^g & 0 & 0 \\ 0 & 0 & 0 & 0 & A_{66}^g & 0 \\ 0 & 0 & 0 & 0 & 0 & A_{66}^g \end{bmatrix} \quad (7)$$

such that there are now three independent unknown components of the dilute strain concentration tensor A_{11}^r , A_{12}^r , and A_{66}^r for each phase (nanoparticle inclusion and interphase region). To find these unknown components of the dilute strain concentration tensor for these phases, we adopt the approach of Benveniste to solve the two auxiliary loading cases shown in Figure 3: the hydrostatic loading case for A_{11}^r and the shear loading case for A_{66}^r , while the requirement that the remaining component A_{12}^r satisfies isotropy requires that

$$A_{12}^r = A_{11}^r - A_{66}^r \quad (8)$$

An overview of the procedure is as follows. First, for given nanocomposite parameters, the Christensen solution is adopted to determine the stress and strain fields for the appropriate auxiliary problems. Once the analytical expressions for the stress and strain fields are determined, one can determine the volume-averaged strains and stresses in each phase as described below. From here, the individual components of the dilute strain concentration tensor in (7) for each phase can be determined using the definition in (1). Once this process has been completed for each auxiliary problem, the complete dilute strain

concentration tensor A_{dil}^r for each phase is known, which can then be used within the standard Mori-Tanaka approach to determine the effective composite properties using (3).

Figure 3. Schematic diagram of the three-phase model and (b, c) Hydrostatic and shear loading auxiliary problems that are used to determine the components of the dilute strain concentration tensor.

3.2 Hydrostatic loading auxiliary problem

For the case of a coated spherical inclusion subjected to hydrostatic loading as shown in Figure 3b, the non-zero radial displacements u_r^i ($i=f, g, m$) of the inclusion, interphase and the matrix in spherical coordinates can be written as [41]

$$\begin{aligned} u_r^f &= A_1^f r & r &\leq a \\ u_r^g &= A_1^g r + \frac{B_1^g}{r^2} & a &\leq r \leq b \\ u_r^m &= A_1^m r + \frac{B_1^m}{r^2} & r &\geq b \end{aligned} \quad (9)$$

where A_1^f , A_1^g , A_1^m , B_1^g and B_1^m are unknown constants to be determined from the solution of the auxiliary problem, and r is the radius from center of the inclusion. Subscript “1” is added to denote the hydrostatic loading case, while subscript “2” will be used later to denote the shear loading case.

Given that $u_\theta=0$ and $u_\phi=0$, from the strain-displacement equations in spherical coordinates the non-zero strain components can be written as

$$\begin{aligned} \varepsilon_{rr} &= \frac{\partial u_r}{\partial r} & \varepsilon_{\theta\theta} &= \frac{u_r}{r} & \varepsilon_{\phi\phi} &= \frac{u_r}{r} \\ \varepsilon_{r\theta} &= \frac{1}{2} \left(\frac{1}{r} \frac{\partial u_r}{\partial \theta} \right) & \varepsilon_{\theta\phi} &= 0 & \varepsilon_{\phi r} &= \frac{1}{2} \frac{1}{r \sin \theta} \frac{\partial u_r}{\partial \phi} \end{aligned} \quad (10)$$

Substitution of (9) into (10) yields

$$\begin{aligned} \varepsilon_{rr}^f &= A_1^f & \varepsilon_{\theta\theta}^f &= A_1^f & \varepsilon_{\phi\phi}^f &= A_1^f \\ \varepsilon_{rr}^g &= A_1^g - \frac{2B_1^g}{r^3} & \varepsilon_{\theta\theta}^g &= A_1^g + \frac{B_1^g}{r^3} & \varepsilon_{\phi\phi}^g &= A_1^g + \frac{B_1^g}{r^3} \\ \varepsilon_{rr}^m &= A_1^m - \frac{2B_1^m}{r^3} & \varepsilon_{\theta\theta}^m &= A_1^m + \frac{B_1^m}{r^3} & \varepsilon_{\phi\phi}^m &= A_1^m + \frac{B_1^m}{r^3} \end{aligned} \quad (11)$$

From Hooke's Law, the non-zero stress in each phase can now be calculated as

$$\begin{aligned}
\sigma_{rr}^f &= \sigma_{\theta\theta}^f = \sigma_{\phi\phi}^f = (2\mu^f + 3\lambda^f)A_1^f \\
\sigma_{rr}^g &= (2\mu^g + 3\lambda^g)A_1^g - \frac{4\mu^g}{r^3}B_1^g, \sigma_{\theta\theta}^g = (2\mu^g + 3\lambda^g)A_1^g + \frac{2\mu^g}{r^3}B_1^g, \\
\sigma_{\phi\phi}^g &= (2\mu^g + 3\lambda^g)A_1^g + \frac{2\mu^g}{r^3}B_1^g \\
\sigma_{rr}^m &= (2\mu^m + 3\lambda^m)A_1^m - \frac{4\mu^m}{r^3}B_1^m, \sigma_{\theta\theta}^m = (2\mu^m + 3\lambda^m)A_1^m + \frac{2\mu^m}{r^3}B_1^m, \\
\sigma_{\phi\phi}^m &= (2\mu^m + 3\lambda^m)A_1^m + \frac{2\mu^m}{r^3}B_1^m
\end{aligned} \tag{12}$$

As $r \rightarrow \infty$, the far field stresses in the matrix can be written as

$$\sigma_{rr}^m \Big|_{r \rightarrow \infty} = \sigma_{\theta\theta}^m \Big|_{r \rightarrow \infty} = \sigma_{\phi\phi}^m \Big|_{r \rightarrow \infty} = (2\mu^m + 3\lambda^m)A_1^m \tag{13}$$

Assuming perfect bonding between the phases and compatible radial displacements and stresses at $r=a$ and $r=b$, the boundary conditions for the hydrostatic loading case are

$$\begin{aligned}
u_r^f &= u_r^g, & \sigma_{rr}^f &= \sigma_{rr}^g & \text{at } r &= a \\
u_r^g &= u_r^m, & \sigma_{rr}^g &= \sigma_{rr}^m & \text{at } r &= b \\
\sigma_{rr}^m &= \sigma^\infty & & & \text{as } r &\rightarrow \infty
\end{aligned} \tag{14}$$

Substituting (9) and (12) into (14) yields the following system of equations, from which the five unknown displacement constants in (9) can be determined by

$$\begin{pmatrix}
a & -a & 0 & -\frac{1}{a^2} & 0 \\
0 & b & -b & \frac{1}{b^2} & -\frac{1}{b^2} \\
(2\mu^f + 3\lambda^f) & -(2\mu^g + 3\lambda^g) & 0 & \frac{4\mu^g}{a^3} & 0 \\
0 & (2\mu^g + 3\lambda^g) & -(2\mu^m + 3\lambda^m) & -\frac{4\mu^g}{b^3} & \frac{4\mu^m}{b^3} \\
0 & 0 & (2\mu^m + 3\lambda^m) & 0 & 0
\end{pmatrix} \cdot \begin{pmatrix} A_1^f \\ A_1^g \\ A_1^m \\ B_1^g \\ B_1^m \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ \sigma^0 \end{pmatrix} \tag{15}$$

where σ^0 is the arbitrary far-field applied stress shown in Figure 3.

Once the five unknown displacement constants $A_1^f, A_1^g, A_1^m, B_1^g$ and B_1^m are determined from (15), the analytical solution of the strains in each inclusion phase can be determined by substitution of these constants using (11). The phase average strains of each inclusion phase are defined as the integration of strains over the entire volume of each phase such that

$$\bar{\varepsilon}_{ij}^r = \frac{\int_0^\pi \int_0^{2\pi} \int_{r_i}^{r_o} \varepsilon_{ij}^r r^2 \sin \theta dr d\phi d\theta}{\frac{4}{3}\pi[r_o^3 - r_i^3]} \quad (16)$$

where r_i and r_o are the inner and outer radius of the phase.

For ease of manipulation it is best to convert the strain components into Cartesian coordinates prior to integration. Using (16), the average phase strain components of the inclusion and interphase can be shown to be

$$\begin{aligned} \bar{\varepsilon}_{xx}^f &= \bar{\varepsilon}_{yy}^f = \bar{\varepsilon}_{zz}^f = A_1^f \\ \bar{\varepsilon}_{xx}^g &= \bar{\varepsilon}_{yy}^g = \bar{\varepsilon}_{zz}^g = A_1^g \end{aligned} \quad (17)$$

while all other strain components vanish. The far-field strains in the matrix can be obtained for the case where $r \rightarrow \infty$, such that

$$\bar{\varepsilon}_{xx}^0 = \bar{\varepsilon}_{yy}^0 = \bar{\varepsilon}_{zz}^0 = A_1^m \quad (18)$$

where again all other strain components in the matrix vanish.

From the definition of the dilute strain concentration tensor (1), one can show that

$$A_{11}^r + 2A_{12}^r = \frac{A_1^r}{A_1^m} \quad (19)$$

Combined with (8), the requirement that the dilute strain concentration tensor is isotropic,

A_{11}^r and A_{12}^r can be written as

$$\begin{aligned} A_{11}^r &= \frac{1}{3} \left(\frac{A_1^r}{A_1^m} + 2A_{66}^r \right) \\ A_{12}^r &= \frac{1}{3} \left(\frac{A_1^r}{A_1^m} - A_{66}^r \right) \end{aligned} \quad (20)$$

where A_{66}^r will be obtained by solving the second auxiliary problem for the shear loading case as shown below.

3.3 Shear loading auxiliary problem

The A_{66}^r components of the dilute strain concentration tensors can be determined by considering the shear load auxiliary problem shown in Figure 3c. The general solution procedure follows that of the hydrostatic loading auxiliary problem; for brevity, only the critical steps and results of the procedure are presented here. From Figure 3c, one can show that the non-zero displacements of each phase can be written as [41]

$$\begin{aligned} u_r^f &= \left[A_1 r - \frac{6\nu^f}{1-2\nu^f} A_2 r^3 \right] \sin^2 \theta \cos 2\phi \\ u_\theta^f &= \left[A_1 r - \frac{7-4\nu^f}{1-2\nu^f} A_2 r^3 \right] \sin \theta \cos \theta \cos 2\phi \\ u_\phi^f &= \left[-A_1 r + \frac{7-4\nu^f}{1-2\nu^f} A_2 r^3 \right] \sin \theta \sin 2\phi \end{aligned}$$

$$\begin{aligned}
u_r^g &= \left[B_1 r - \frac{6\nu^g}{1-2\nu^g} B_2 r^3 + \frac{3B_3}{r^4} + \frac{(5-4\nu^g)}{(1-2\nu^g)} \frac{B_4}{r^2} \right] \sin^2 \theta \cos 2\phi \\
u_\theta^g &= \left[B_1 r - \frac{7-4\nu^g}{1-2\nu^g} B_2 r^3 - \frac{2B_3}{r^4} + \frac{2B_4}{r^2} \right] \sin \theta \cos \theta \cos 2\phi \\
u_\phi^g &= \left[-B_1 r + \frac{7-4\nu^g}{1-2\nu^g} B_2 r^3 + \frac{2B_3}{r^4} - \frac{2B_4}{r^2} \right] \sin \theta \sin 2\phi \\
\\
u_r^m &= \left[D_1 r + \frac{3D_3}{r^4} + \frac{(5-4\nu^m)}{(1-2\nu^m)} \frac{D_4}{r^2} \right] \sin^2 \theta \cos 2\phi \\
u_\theta^m &= \left[D_1 r^3 - \frac{2D_3}{r^4} + \frac{2D_4}{r^2} \right] \sin \theta \cos \theta \cos 2\phi \\
u_\phi^m &= \left[-D_1 r^3 + \frac{2D_3}{r^4} - \frac{2D_4}{r^2} \right] \sin \theta \sin 2\phi
\end{aligned} \tag{21}$$

where the nine unknown displacement constants are $A_1, A_2, B_1, B_2, B_3, B_4, D_1, D_3$ (with A, B , and D used to represent terms related to the inclusion, the interphase, and the matrix, respectively). Assuming perfect bonding between the phases, the following boundary conditions at $r=a$ and $r=b$ must be hold such that the radial displacements and stresses are continuous at each interface

$$\left. \begin{aligned} u_r^f &= u_r^g, & u_\theta^f &= u_\theta^g \\ \sigma_{rr}^f &= \sigma_{rr}^g, & \sigma_{r\theta}^f &= \sigma_{r\theta}^g \end{aligned} \right\} \quad \text{at } r = a$$

$$\left. \begin{aligned} u_r^g &= u_r^m, & u_\theta^g &= u_\theta^m \\ \sigma_{rr}^g &= \sigma_{rr}^m, & \sigma_{r\theta}^g &= \sigma_{r\theta}^m \end{aligned} \right\} \quad \text{at } r = b$$
(22)

The final boundary condition is that the far-field stresses components σ_{xx}^0 and σ_{yy}^0 in the matrix must equal the applied far-field stresses σ^0 and $-\sigma^0$, respectively, such for as

$r \rightarrow \infty$

$$\sigma_{xx}^0 = -\sigma_{yy}^0 = \sigma^0 \quad (23)$$

Given (21), we can again use standard strain-displacement equations such that the strain components in the inclusion phase can then be written as

$$\begin{aligned} \varepsilon_{rr}^f &= \left(A_1 - \frac{18\nu^f}{1-2\nu^f} A_2 r^2 \right) \sin^2 \theta \cos 2\phi \\ \varepsilon_{\theta\theta}^f &= \left[\left(A_1 - \frac{7-4\nu^f}{1-2\nu^f} A_2 r^2 \right) (2\cos^2 \theta - 1) + \left(A_1 - \frac{6\nu^f}{1-2\nu^f} A_2 r^2 \right) \sin^2 \theta \right] \cos 2\phi \\ \varepsilon_{\phi\phi}^f &= \left[\left(A_1 - \frac{7-4\nu^f}{1-2\nu^f} A_2 r^2 \right) (\cos^2 \theta - 2) + \left(A_1 - \frac{6\nu^f}{1-2\nu^f} A_2 r^2 \right) \sin^2 \theta \right] \cos 2\phi \\ \varepsilon_{r\theta}^f &= \left(A_1 - \frac{7+2\nu_f}{1-2\nu_f} A_2 r^2 \right) \sin \theta \cos \theta \cos 2\phi \\ \varepsilon_{\phi\theta}^f &= \left(-A_1 + \frac{7-4\nu_f}{1-2\nu_f} A_2 r^2 \right) \cos \theta \sin 2\phi \\ \varepsilon_{\phi r}^f &= \left(-A_1 + \frac{7+2\nu_f}{1-2\nu_f} A_2 r^2 \right) \sin \theta \sin 2\phi \end{aligned} \quad (24)$$

while the strain components in the interphase can be written as

$$\begin{aligned}
\varepsilon_{rr}^g &= \left[B_1 - \frac{18\nu^g}{1-2\nu^g} B_2 r^2 - \frac{12B_3}{r^5} - \frac{(5-4\nu^g)}{(1-2\nu^g)} \frac{2B_4}{r^3} \right] \sin^2 \theta \cos 2\phi \\
\varepsilon_{\theta\theta}^g &= \left[\left(B_1 - \frac{7-4\nu^g}{1-2\nu^g} B_2 r^2 - \frac{2B_3}{r^5} + \frac{2B_4}{r^3} \right) (2\cos^2 \theta - 1) \right. \\
&\quad \left. + \left[B_1 - \frac{6\nu^g}{1-2\nu^g} B_2 r^2 + \frac{3B_3}{r^2} + \frac{(5-4\nu^g)}{(1-2\nu^g)} \frac{B_4}{r^3} \right] \sin^2 \theta \right] \cos 2\phi \\
\varepsilon_{\phi\phi}^g &= \left[\left(B_1 - \frac{7-4\nu^g}{1-2\nu^g} B_2 r^2 - \frac{2B_3}{r^5} + \frac{2B_4}{r^3} \right) (\cos^2 \theta - 2) \right. \\
&\quad \left. + \left[B_1 - \frac{6\nu^g}{1-2\nu^g} B_2 r^2 + \frac{3B_3}{r^2} + \frac{(5-4\nu^g)}{(1-2\nu^g)} \frac{B_4}{r^3} \right] \sin^2 \theta \right] \cos 2\phi \\
\varepsilon_{r\theta}^g &= \left[B_1 - \frac{7+2\nu^g}{1-2\nu^g} B_2 r^2 + \frac{8B_3}{r^5} + \frac{(1+\nu^g)}{(1-2\nu^g)} \frac{2B_4}{r^3} \right] \sin \theta \cos \theta \cos 2\phi \\
\varepsilon_{\theta\phi}^g &= \left[-B_1 + \frac{7-4\nu^g}{1-2\nu^g} B_2 r^2 + \frac{2B_3}{r^5} - \frac{2B_4}{r^3} \right] \cos \theta \sin 2\phi \\
\varepsilon_{\phi r}^g &= \left[-B_1 + \frac{7+2\nu^g}{1-2\nu^g} B_2 r^2 - \frac{8B_3}{r^5} - \frac{(1+\nu^g)}{(1-2\nu^g)} \frac{2B_4}{r^3} \right] \sin \theta \sin 2\phi
\end{aligned} \tag{25}$$

and the strain components in the matrix can be written as

$$\begin{aligned}
\varepsilon_{rr}^m &= \left[D_1 - \frac{12D_3}{r^5} - \frac{(5-4\nu^m)}{(1-2\nu^m)} \frac{2D_4}{r^3} \right] \sin^2 \theta \cos 2\phi \\
\varepsilon_{\theta\theta}^m &= \left[\left(D_1 - \frac{2D_3}{r^5} + \frac{2D_4}{r^3} \right) (2\cos^2 \theta - 1) + \left(D_1 + \frac{3D_3}{r^2} + \frac{(5-4\nu^m)}{(1-2\nu^m)} \frac{D_4}{r^3} \right) \sin^2 \theta \right] \cos 2\phi \\
\varepsilon_{\phi\phi}^m &= \left[\left(D_1 - \frac{2D_3}{r^5} + \frac{2D_4}{r^3} \right) (\cos^2 \theta - 2) + \left(D_1 + \frac{3D_3}{r^2} + \frac{(5-4\nu^m)}{(1-2\nu^m)} \frac{D_4}{r^3} \right) \sin^2 \theta \right] \cos 2\phi \\
\varepsilon_{r\theta}^m &= \left[D_1 + \frac{8D_3}{r^5} + \frac{(1+\nu^m)}{(1-2\nu^m)} \frac{2D_4}{r^3} \right] \sin \theta \cos \theta \cos 2\phi \\
\varepsilon_{\theta\phi}^m &= \left[-D_1 + \frac{2D_3}{r^5} - \frac{2D_4}{r^3} \right] \cos \theta \sin 2\phi \\
\varepsilon_{\phi r}^m &= \left[-D_1 - \frac{8D_3}{r^5} - \frac{(1+\nu^m)}{(1-2\nu^m)} \frac{2D_4}{r^3} \right] \sin \theta \sin 2\phi
\end{aligned} \tag{26}$$

The far-field radial strain components can then be obtained by substituting $r \rightarrow \infty$ into (26)

$$\begin{aligned}
\mathcal{E}_{rr}^m \Big|^{r \rightarrow \infty} &= D_1 \sin^2 \theta \cos 2\phi \\
\mathcal{E}_{\theta\theta}^m \Big|^{r \rightarrow \infty} &= D_1 \cos^2 \theta \cos 2\phi \\
\mathcal{E}_{\phi\phi}^m \Big|^{r \rightarrow \infty} &= -D_1 \cos 2\phi \\
\mathcal{E}_{r\theta}^m \Big|^{r \rightarrow \infty} &= D_1 \sin \theta \cos \theta \cos 2\phi \\
\mathcal{E}_{\theta\phi}^m \Big|^{r \rightarrow \infty} &= -D_1 \cos \theta \sin 2\phi \\
\mathcal{E}_{\phi r}^m \Big|^{r \rightarrow \infty} &= -D_1 \sin \theta \sin 2\phi
\end{aligned} \tag{27}$$

Once all the radial strain components are known, the radial stress components of each phase can be readily found using Hooke's Law.

With the expressions for the stresses in each phase determined, one can apply the boundary conditions given in (22) and (23) to determine the unknown displacement constants (21); converting from polar to Cartesian coordinates simplifies the analysis. From analysis of the far-field stress conditions in (23), one can show

$$D_1 = \frac{\sigma^0}{2\mu^m} \tag{28}$$

To determine the remaining constants, the boundary conditions (22) can be written as system of equations in matrix form such that

$$[A] \cdot [x] = [y] \tag{29}$$

where $[x] = [A_1, A_2, B_1, B_2, B_3, B_4, D_1, D_3, D_4]^T$, $[y] = [0, 0, 0, 0, 0, 0, 0, 0, \sigma^0]$, and the matrix $[A]$ is provided in the Appendix.

Once the unknown displacement constants have been determined for the shear loading auxiliary case, the phase-average strains in each inclusion phase can be determined as before such that

$$\begin{aligned}
A_{66}^f &= \frac{A_1 - \frac{21a^2}{5(1-2\nu^f)}A_2}{D_1} \\
A_{66}^g &= \frac{B_1 - \frac{21}{5} \frac{(a^4 + a^3b + a^2b^2 + ab^3 + b^4)}{(a^2 + ab + b^2)(1-2\nu^g)}B_2}{D_1}
\end{aligned} \tag{30}$$

3.4 The new dilute strain concentration tensor

Having determined A_{66}^r , from (20) we have

$$\begin{aligned}
A_{12}^f &= \frac{1}{3} \left(\frac{A_1^f}{A_1^m} - A_{66}^f \right) = \frac{1}{3} \left[\frac{A_1^f}{A_1^m} - \frac{1}{D_1} \left[A_1 - \frac{21a^2}{5(1-2\nu^f)}A_2 \right] \right] \\
A_{12}^g &= \frac{1}{3} \left(\frac{A_1^g}{A_1^m} - A_{66}^g \right) = \frac{1}{3} \left[\frac{A_1^g}{A_1^m} - \frac{1}{D_1} \left[B_1 - \frac{21}{5} \frac{(a^4 + a^3b + a^2b^2 + ab^3 + b^4)}{(a^2 + ab + b^2)(1-2\nu^g)}B_2 \right] \right]
\end{aligned} \tag{31}$$

With all unknown components of dilute strain concentration tensor for each phase (see (20), (30) and (31)) determined, the dilute strain concentration tensors for the inclusion and interphase regions given in (7) can be used in the standard Mori-Tanaka formulation given in (3).

For the sake of comparison, in the next section the results from the proposed model (which we refer to as the **Annular Coated Inclusion model**) are compared to those obtained from a standard multiphase Mori-Tanaka approach, referred to here as the original Mori-Tanaka (MT) method. For the multiphase MT method, the Eshelby tensor for each inclusion phase is determined based on a spherical geometry such that

$$\begin{aligned}
S_{1111} &= S_{2222} = S_{3333} = \frac{7 - 5\nu_0}{15(1 - \nu_0)} \\
S_{1122} &= S_{2233} = S_{3311} = \frac{5\nu_0 - 1}{15(1 - \nu_0)} \\
S_{1212} &= S_{2323} = S_{3131} = \frac{4 - 5\nu_0}{15(1 - \nu_0)}
\end{aligned} \tag{32}$$

More general forms of the Eshelby tensor valid for ellipsoidal inclusions can be found in the literature [51]. Note that when the Eshelby tensor is expressed in contracted notation, $S_{44} = 2S_{2323}$, $S_{55} = 2S_{1313}$, and $S_{66} = 2S_{1212}$ [52]. Recall that as described previously, when the shapes of the inclusion and the coating/interphase region are identical, the multiphase Mori-Tanaka method is equivalent to the Double-Inclusion model of Hori and Nemat-Nasser.

4. Results and Discussion

As discussed above, it is desirable to have suitable micromechanics models available that can account for non-bulk interphase regions surrounding the embedded nanoparticle. The proposed approach analytically determines the dilute strain concentration tensor of each phase via an extension of the approach of Benveniste [45], and more accurately represents the physical location of the interphase region directly surrounding the embedded inclusion. As shown below, this method can be directly incorporated within the standard Mori-Tanaka formulation for the determination of effective composite properties.

In this section we first compare the predictions of the proposed **Annular Coated Inclusion (ACI) model** to the effective property predictions obtained by the original Mori-Tanaka (MT) method as shown in Figure 2. Here we will limit the discussion to coated spherical inclusions, while in a companion paper this approach will be extended to

infinitely-long coated cylindrical inclusions [29], where the proposed methodology can be more directly applied to account for composites with randomly oriented or orientational distributions of coated inclusions. In Section 4.2, we illustrate the use of the ACI model to examine several experimental data sets presented in the literature examining composites with coated spherical inclusions.

4.1 Comparison with original multiphase Mori-Tanaka (MT) method

In the discussion below, we refer to two distinct cases: a stiff interphase case where the interphase has a larger modulus than the matrix, and a soft interphase case where the interphase has a smaller modulus than the matrix. (In all cases unless otherwise specified the modulus of the inclusion is the largest of the three phases.) Here the subscripts *inc*, *int*, and *m* to refer to the inclusion, interphase, and matrix regions, respectively. For simplicity, unless otherwise specified we assume unitless moduli values are 100, 10, and 1, respectively, while each phase is assumed to have a Poisson's ratio of 0.4. Where appropriate all results in this section are normalized with respect to the modulus of the matrix. Lastly, an important requirement for the proposed model is of course that its results simplify to those of the standard two-phase Mori-Tanaka method when appropriate; for example, when the interphase material has properties equal to those of the matrix or the inclusion, respectively. This can be easily verified for all appropriate two-phase composite geometries.

Figure 4 shows a comparison between the results of the standard MT method and the proposed ACI method as a function of inclusion volume fraction for two different ratios of inclusion volume fraction to interphase volume fraction. As shown in Figure 4a, when the

interphase is stiffer than the matrix material, the results of both two methods are quite close with the elastic modulus of the composite enhanced with the addition of the inclusions. As expected, for the case with the larger ratio of interphase volume fraction (i.e. $f_{int} = 0.9f_{inc}$), the increase in effective modulus is significantly higher at a particular inclusion content as the interphase has a larger modulus than the matrix in this case. Noteworthy here is that the results from the original MT method and ACI methods are practically identical.

On the other hand, for the soft interphase case shown in Figure 4b, there is clearly a significant difference between the predictions of the two models. For both ratios of interphase to inclusion volume fraction shown, the ACI predictions are much lower than that of the standard MT model. This is attributed to the phenomenon of “stress shielding”, where stress transfer between inclusion and polymer matrix is hindered by the soft surrounding annular interphase. While the soft interphase in the MT method is treated as a separate phase, the MT method is not able to accurately capture the nature of the physical annular geometry of the soft interphase, which results in overestimation of the effective modulus of the composite. Moreover, the discrepancy between the two models increases as the volume fraction of the inclusion increases. Similar but even more drastic results are observed for the case of high interphase content ($f_{int} = 0.9f_{inc}$). Similar results for the impact of a soft interphase have been demonstrated analytically by Boutaleb et al [53]. These results clearly indicate the significant differences between the original MT method and proposed ACI method for those cases where the interphase is the softest phase.

Figure 4. Normalized composite modulus as a function of inclusion volume fraction: (a) stiff interphase and (b) soft interphase. The inclusion modulus $E_{inc} = 100$ while the interphase and matrix moduli are 10 or 1, respectively.

The differences between the two methods are further illustrated in Figure 5, which shows the normalized composite effective modulus as a function of interphase volume fraction for both the stiff and soft interphase case. Again we see that when the interphase is stiffer than the matrix, the predictions of standard MT method and the proposed ACI methods are very close. As shown in Figure 5b, the difference between the two methods is much more pronounced for the soft interphase case; a difference that becomes larger as the content of interphase increases. Interestingly, for the soft interphase case the normalized composite modulus from the ACI method (solid symbols in the figure) with low inclusion content ($f_{int} = 0.1f_{inc}$) are very similar to the case for the high inclusion content ($f_{int} = 0.9f_{inc}$), while the MT methods shows significant difference between these two cases. This suggests that in the ACI model the mere presence of a softer interphase region may dominate the effective properties of the composite due to the stress-shielding effect.

Figure 5. Normalized composite modulus as a function of interphase volume fraction: (a) stiff interphase and (b) soft interphase. The inclusion modulus $E_{inc} = 100$ while the interphase and matrix moduli are 10 or 1, respectively.

This finding is further examined in more detail in Figure 6, which shows the differences between the original MT model and the proposed ACI method regarding the normalized modulus predictions for the case of the soft interphase composite. As shown in Figure 6a, for a given interphase volume fraction of 40%, the ACI method is relatively insensitive to the increasing volume fraction of inclusion. On the other hand, the MT method again fails to capture the stress-shielding effect of the annual soft interphase, and thus predicts a composite modulus that increases with increasing volume fraction of inclusion. However, when the inclusion volume fraction is held constant (Figure 6b), the predictions of both methods decrease with increasing interphase volume fraction, with the predictions of the proposed ACI model decreasing more drastically (again, due to the more drastic effects of a softer interphase better captured in the proposed ACI method). In other words, while for the case of a stiff interphase the MT and ACI methods are quite close (see Figure 4 and Figure 5), for the case of a soft interphase the ACI method provides a much

more accurate prediction of the normalized composite modulus as it is better able to capture the impact of the interphase on the reinforcement provided by the inclusion.

Figure 6. Normalized elastic modulus of a soft interphase composite (a) as a function of f_{inc}/f_{int} for a constant interphase volume fraction of 0.4, and (b) as a function of f_{int}/f_{inc} for a constant inclusion volume fraction of 0.4.

The impact of inclusion radius and thickness of the interphase on the normalized composite modulus assuming a constant inclusion volume fraction of 5% is shown in Figure 7. Also shown in Figure 7 are the predictions for a two-phase composite (i.e. $t = 0$). As before, there is very little difference between the predictions of the standard MT method and that of ACI method for the stiff interphase case, where the matrix is the softest phase (Figure 7a). For a given interphase thickness, the overall composite stiffness experiences an asymptotical decrease as the influence of the interphase is reduced a decrease of its relative volume fraction with increasing inclusion radius. Similarly, for the case of a soft interphase composite, the effective modulus of the composite initially increases at smaller inclusion radii before gradually plateauing as the radius of inclusion further increases (Figure 7b). In

addition, for a given interphase thickness, the predictions of the ACI model are lower than that of MT model, again reflecting the ability of the ACI model to better capture the impact of the soft interphase geometry.

Figure 7. Variation of normalized composite modulus as a function of non-dimensional inclusion radius for different interphase thicknesses ($t = 0, 5, 15, 25$) for (a) stiff interphase and (b) soft interphase composite.

The impact of the interphase and inclusion moduli on the overall modulus of the composite is presented in Figure 8, where the variable modulus value (E_{inc} or E_{int}) ranges from 10^{-3} to 10^5 while the corresponding moduli of the other two phases are 10 and 1, respectively. This allows one to analyze the differences in the two models for all possible combinations of arrangements that are possible with respect to the phase properties.

In Figure 8a, the cases of a soft and stiff interphase are analyzed as a function of modulus of the inclusion. For the soft interphase case, where $E_{mat} = 10$ and $E_{int} = 1$, we see that for small inclusion moduli the difference between the two models is initially small, although the difference increases drastically for inclusion modulus values greater than 10

(the modulus of the matrix). In addition, as discussed previously, for the soft interphase case the predictions from the ACI method are smaller than those of the standard MT method (even when the two curves are almost indistinguishable in the plots in Figure 8). On the other hand, the opposite is true for the stiff interphase case ($E_{\text{mat}} = 1$ and $E_{\text{int}} = 10$), where the difference between the two models is quite large for very small values of the inclusion modulus, but becomes almost negligible once the inclusion modulus is greater than the modulus of the matrix. For the stiff interphase case, in all scenarios the ACI method provides a larger prediction than the MT method.

A related behavior is observed in Figure 8b, which examines the cases of a soft and stiff inclusion as a function of modulus of the interphase. For the soft inclusion case (i.e. when $E_{\text{inc}} = 1$ and $E_{\text{mat}} = 10$), the predictions from the two methods are very close for small interphase modulus values, but there is a significant difference between the two methods when the interphase is larger than the matrix modulus. Conversely, for the stiff inclusion case where $E_{\text{inc}} = 10$ and $E_{\text{mat}} = 1$, the two predictions display their largest discrepancy for very small values of interphase modulus, while the predictions are very close for larger values of interphase modulus (when the interphase modulus is larger than the matrix modulus).

The behavior shown in Figure 8 is consistent with the findings described above, where the ACI method is better able to capture the impact of an annular interphase region surrounding the inclusion (recall Figure 2). Both the ACI and the standard MT methods provide similar results when the inclusion and the interphase are both stiffer (or both softer) than the matrix, as in this case the nature of the annular coating does not significantly affect the stress transfer from the matrix to the inclusion (through the interphase). On the other

hand, when the interphase is softer than the matrix (for a stiff inclusion) or the interphase is stiffer than the matrix (for a soft inclusion), the results from the two methods show clear differences as the annular coating directly affects the stress transfer between the matrix and inclusion phases.

In addition, as shown in Figure 8b, the ACI model predicts that the composite moduli for both the stiff and the soft inclusion cases converge to the same value at maximum and minimum values of interphase modulus, respectively, while the MT results approach asymptotical values for the composite moduli values that are based on the inclusion modulus. This is due to the fact that the ACI model predictions can be greatly influenced by the interphase properties due to the “stress shielding” phenomena described above. Lastly, note that the MT predictions in Figure 8a and Figure 8b are identical, as the MT method does not distinguish between the inclusion and interphase regions.

Figure 8. Normalized composite modulus as a function of (a) inclusion modulus and (b) interphase modulus. In each plot, the two other composite phases have constant moduli values of 10 for the stiffer phase and 1 for the softer phase.

4.2 Use of ACI model to examine results from the literature

To further illustrate the utility of the proposed coated inclusion approach, below the ACI method will be used to analyze two sets of data available in the literature. First, Figure 9 shows the comparison with experimental results from Abbate et al. [54] in which silica/polyimide composites were prepared using a sol-gel process and the mechanical properties were examined via tensile testing. Here the inclusion and matrix properties (R_{inc} , E_{inc} , E_{mat}) match those used in their experiment [54], while various interphase moduli are assumed to illustrate the proposed model (the interphase modulus is not known from their experiments). A density of 2.65g/cm^3 was used to calculate the appropriate volume fraction for the 35nm radius silica particles. Based on the discussion below, the behavior of this composite observed experimentally is consistent with that of a stiff interphase composite.

As shown in Figure 9, the predictions from a two-phase composite in which the interphase is not considered (indicated by dashed lines in Figure 9), clearly underestimate the experimental results. However, by assuming various values for the thickness of modulus of an interphase region that may be hypothesized to exist within the material, one can show that the presence of such an interphase may be responsible for the effective composite behavior that is observed experimentally. For example, for a given interphase modulus 10x that of the matrix (Figure 9a), predictions with different interphase thicknesses generate diverse composite moduli curves as a function of inclusion volume fraction, with only a small window of interphase thickness values appearing to at least approximate the behavior observed experimentally. On the other hand, predictions assuming a constant interphase thickness (15 nm) with different interphase modulus (Figure 9b) are quite close, particularly when the modulus of the interphase is large. These results

imply that the interphase thickness (volume fraction) might play a more important part than its elastic modulus on influencing effective composite properties.

Figure 9. Comparison of normalized composite modulus values found experimentally and based on ACI predictions with varying (a) interphase thickness and (b) interphase elastic modulus. Experimental data from [54].

The second example from the literature involves the experimentally determined mechanical properties of cycloolefin copolymer (COC)-polyhedral oligomeric silsesquioxanes (POSS) nanocomposites prepared by melt compounding as studied by Dorigato et al [55]. They found that the measured elastic modulus of the composite decreased with increasing filler content using both quasi-static tensile tests in the solid state and rheological measurements on melts, which they attributed to the presence of isobutylic groups on the POSS nanoparticles that resulted in a layer of soft interphase which affected the stress transfer processes within the composite.

Using the proposed ACI model, the elastic modulus predictions of a composite with varying interphase properties (based on their experimental parameters [55]) are compared

with their experimental results as shown in Figure 10. As before, different combinations of interphase properties (elastic modulus and thickness) were examined with the ACI model to obtain a scenario which matches well with their experimental results. Note that the particular values of assumed interphase modulus and thickness shown below were obtained through a process of trial and error. Figure 10a shows that, for an assumed interphase modulus of 1.3 GPa, the composite modulus predictions from the ACI model decrease with increasing inclusion content for an interphase region above a certain thickness. Similarly, as shown in Figure 10b, an assumption of a relatively soft interphase modulus is necessary to obtain an overall composite modulus which decreases with increasing filler content. In addition, the two-phase model predictions (without an interphase) shown in Figure 10 clearly indicate that such a model would be insufficient to capture the behavior of the composite captured experimentally.

Figure 10. Comparison of composite modulus found experimentally and based on ACI predictions with varying (a) interphase thickness and (b) interphase elastic modulus. Experimental data from [55].

5. Conclusions

The work describes a micromechanical approach, referred to as the ACI (Annular Coated Inclusion) model, where the components of the dilute strain concentration tensor are directly calculated analytically using solutions provided by Christensen [40] following an approach first described by Benveniste [45]. While such a micromechanical model is applicable to any composite with uniformly coated spherical inclusions, such a model is specifically developed for the case of polymer nanocomposites, where non-bulk interphase effects are prevalent, significant, and require a model to account for this region in bulk nanocomposite predictions.

The effective elastic modulus of polymer nanocomposites calculated by the proposed ACI model was been compared with the original multiphase Mori-Tanaka (MT) model, which was shown to be equivalent to the Double-Inclusion model of Hori and Nemat-Nasser [47] for the special case where the aspect ratios of the inclusion and the coating/interphase region are the same (in this case, spherical). The results indicate that there is minimal difference between the ACI and original MT methods for the case of a "stiff interphase", while the ACI results differ from (and are more accurate than) than the MT method when the interphase is softer than the polymer matrix. A parametric study using the proposed model suggests that the effectiveness of nanocomposite reinforcement is strongly influenced by the interphase stiffness. Lastly, the ACI model has also been used to interpret two sets of experimental data presented in the literature as case studies of how the approach may be used to interpret trends observed in experimental data which may not be captured using more traditional micromechanical approaches which do not explicitly account for the physicality of an annular interphase region.

The Annular Coated Inclusion model is extended for coated cylindrical fibers in the companion paper [29]. An additional advantage of the proposed method is that the solution of the auxiliary problems allows determination of the stress and strain fields which can be extended in a straightforward manner to enable a wide range of composite studies; for example, the incorporation of spring-layer interfacial conditions proposed by Hashin [56] to study the impact of imperfect interface bonding is the subject of ongoing work. It is anticipated that the Annular Coated Inclusion model will be particularly useful in evaluating the impact of chemical functionalization techniques and other strategies that seek to tailor the properties of the interphase region in these materials.

Acknowledgements

Financial support for this work from the National Science Foundation (Grant No. 0846937) is gratefully acknowledged.

References

- [1] Sahoo NG, Rana S, Cho JW, Li L, Chan SH. Polymer nanocomposites based on functionalized carbon nanotubes. *Progress in Polymer Science*. 2010;35(7):837-867.
- [2] Zeng QH, Yu AB, Lu GQ. Multiscale modeling and simulation of polymer nanocomposites. *Progress in Polymer Science*. 2008;33(2):191-269.
- [3] Panwar A, Choudhary V, Sharma D. Review: A review: Polystyrene/clay nanocomposites. *Journal of Reinforced Plastics and Composites*. 2011;30(5):446-459.
- [4] Gómez H, Ram MK, Alvi F, Villalba P, Stefanakos E, Kumar A. Graphene-conducting polymer nanocomposite as novel electrode for supercapacitors. *Journal of Power Sources*. 2011;196(8):4102-4108.

- [5] Konwer S, Maiti J, Dolui SK. Preparation and optical/electrical/electrochemical properties of expanded graphite-filled polypyrrole nanocomposite. *Materials Chemistry and Physics*. 2011;128(1–2):283-290.
- [6] Zhu M, Chen P, Liu M. Graphene oxide enwrapped Ag/AgX (X= Br, Cl) nanocomposite as a highly efficient visible-light plasmonic photocatalyst. *Acs Nano*. 2011;5(6):4529-4536.
- [7] Zhu Y, Murali S, Cai W, Li X, Suk JW, Potts JR, et al. Graphene and graphene oxide: synthesis, properties, and applications. *Advanced Materials*. 2010;22(35):3906-3924.
- [8] Fornes TD, Paul DR. Modeling properties of nylon 6/clay nanocomposites using composite theories. *Polymer*. 2003;44(17):4993-5013.
- [9] Wakabayashi K, Pierre C, Dikin DA, Ruoff RS, Ramanathan T, Brinson LC, et al. Polymer-graphite nanocomposites: Effective dispersion and major property enhancement via solid-state shear pulverization. *Macromolecules*. 2008;41(6):1905-1908.
- [10] Schaefer DW, Justice RS. How nano are nanocomposites? *Macromolecules*. 2007;40(24):8501-8517.
- [11] Paul DR, Robeson LM. Polymer nanotechnology: Nanocomposites. *Polymer*. 2008;49(15):3187-3204.
- [12] Colombo A, Tassone F, Mauri M, Salerno D, Delaney JK, Palmer MR, et al. Highly transparent nanocomposite films from water-based poly (2-ethyl-2-oxazoline)/TiO₂ dispersions. *Rsc Advances*. 2012;2(16):6628-6636.
- [13] Yang C-C, Li YJ, Liou T-H. Preparation of novel poly (vinyl alcohol)/SiO₂ nanocomposite membranes by a sol–gel process and their application on alkaline DMFCs. *Desalination*. 2011;276(1):366-372.

- [14] Emamgholizadeh A, Omrani A, Rostami AA. Chemical synthesis, characterization and electro-oxidation of hydrazine via a carbon paste electrode modified with poly (P-phenylendiamine/ Al_2O_3) nanocomposite. *Electrochimica Acta*. 2012;81:166-171.
- [15] Chen C, Justice RS, Schaefer DW, Baur JW. Highly dispersed nanosilica-epoxy resins with enhanced mechanical properties. *Polymer*. 2008;49(17):3805-3815.
- [16] Artemov AS. Polishing nanodiamonds. *Physics of the Solid State*. 2004;46(4):687-695.
- [17] Ciprari D, Jacob K, Tannenbaum R. Characterization of polymer nanocomposite interphase and its impact on mechanical properties. *Macromolecules*. 2006;39(19):6565-6573.
- [18] Jesson DA, Watts JF. The interface and interphase in polymer matrix composites: Effect on mechanical properties and methods for identification. *Polymer Reviews*. 2012;52(3):321-354.
- [19] Pakzad A, Simonsen J, Yassar RS. Gradient of nanomechanical properties in the interphase of cellulose nanocrystal composites. *Composites Science and Technology*. 2012;72(2):314-319.
- [20] Rahimi M, Iriarte-Carretero I, Ghanbari A, Bohm MC, Muller-Plathe F. Mechanical behavior and interphase structure in a silica-polystyrene nanocomposite under uniaxial deformation. *Nanotechnology*. 2012;23(30).
- [21] Rittigstein P, Priestley RD, Broadbelt LJ, Torkelson JM. Model polymer nanocomposites provide an understanding of confinement effects in real nanocomposites. *Nature Materials*. 2007;6(4):278-282.

- [22] Ramanathan T, Liu H, Brinson LC. Functionalized SWNT/polymer nanocomposites for dramatic property improvement. *Journal of Polymer Science Part B: Polymer Physics*. 2005;43(17):2269-2279.
- [23] Ramanathan T, Abdala AA, Stankovich S, Dikin DA, Herrera-Alonso M, Piner RD, et al. Functionalized graphene sheets for polymer nanocomposites. *Nature Nanotechnology*. 2008;3(6):327-331.
- [24] Eitan A, Fisher FT, Andrews R, Brinson LC, Schadler LS. Reinforcement mechanisms in MWCNT-filled polycarbonate. *Composites Science and Technology*. 2006;66(9):1162-1173.
- [25] Killgore JP, Overney RM. Interfacial mobility and bonding strength in nanocomposite thin film membranes. *Langmuir*. 2008;24(7):3446-3451.
- [26] Xu W, Zeng QH, Yu AB, Paul DR. Determination of interphase thickness and mechanical properties of effective nanofillers in polymer nanocomposites by molecular dynamic simulation. *Materials Science Forum*, vol. 654: Trans Tech Publ; 2010. p. 1654-1657.
- [27] Brown D, Marcadon V, Mele P, Alberola N. Effect of filler particle size on the properties of model nanocomposites. *Macromolecules*. 2008;41(4):1499-1511.
- [28] Unnikrishnan V, Reddy JN. Multiscale analysis of the core nanotube in a nanocomposite system. *Finite Elements in Analysis and Design*. 2012;49(1):13-18.
- [29] Wang Z, Fisher FT. Annular Coated Inclusion model and applications for polymer nanocomposites - Part II: Cylindrical inclusions. *Mechanics of Materials*. Under review.

- [30] Eshelby JD. The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, vol. 241: The Royal Society; 1957. p. 376-396.
- [31] Tandon GP, Weng GJ. Average stress in the matrix and effective moduli of randomly oriented composites. *Composites Science and Technology*. 1986;27(2):111-132.
- [32] Benveniste Y. A new approach to the application of Mori-Tanaka's theory in composite materials. *Mechanics of Materials*. 1987;6:147-157.
- [33] Mori T, Tanaka K. Average stress in matrix and average elastic energy of materials with misfitting inclusions. *Acta Metallurgica*. 1973;21:571-574.
- [34] Weng GJ. The theoretical connection between Mori-Tanaka's theory and the Hashin-Shtrikman-Wadpole bounds. *International Journal of Engineering Science*. 1990;28(11):1111-1120.
- [35] Chen T, Dvorak GJ, Benveniste Y. Mori-Tanaka estimates of the overall elastic moduli of certain composite materials. *Journal of Applied Mechanics*. 1992;59:539-546.
- [36] Fisher FT, Brinson LC. Viscoelastic interphases in polymer matrix composites: Theoretical models and finite element analysis. *Composites Science and Technology*. 2001;61(5):731-748.
- [37] Fisher FT, Bradshaw RD, Brinson LC. Fiber waviness in nanotube-reinforced polymer composites-I: Modulus predictions using effective nanotube properties. *Composites Science and Technology*. 2003;63(11):1689-1703.
- [38] Bradshaw RD, Fisher FT, Brinson LC. Fiber waviness in nanotube-reinforced polymer composites: II. Modelling via numerical approximation of the dilute strain concentration tensor. *Composites Science and Technology*. 2003;63(11):1705-1722.

- [39] Liu H, Brinson LC. A hybrid numerical-analytical method for modeling the viscoelastic properties of polymer nanocomposites. *Journal of Applied Mechanics*. 2006(73):758-768.
- [40] Christensen RM, Lo KH. Solutions for effective shear properties in three phase sphere and cylinder models. *Journal of the Mechanics and Physics of Solids*. 1979;27(4):315-330.
- [41] Christensen R. *Mechanics of Composite Materials*: Wiley; 1979.
- [42] Luo HA, Weng GJ. On Eshelby's inclusion problem in a three-phase spherically concentric solid, and a modification of Mori-Tanaka's method. *Mechanics of Materials*. 1987;6(4):347-361.
- [43] Luo HA, Weng GJ. On Eshelby's S-tensor in a three-phase cylindrically concentric solid, and the elastic moduli of fiber-reinforced composites. *Mechanics of Materials*. 1989;8(2-3):77-88.
- [44] Chen T, Dvorak GJ, Benveniste Y. Stress fields in composites reinforced by coated cylindrically orthotropic fibers. *Mechanics of Materials*. 1990;9(1):17-32.
- [45] Benveniste Y, Dvorak GJ, Chen T. Stress fields in composites with coated inclusions. *Mechanics of Materials*. 1989;7(4):305-317.
- [46] Yang F. Size effect on the effective bulk modulus of nanocomposites with core-shell nanospherical inclusions. *Materials Science and Engineering: A*. 2010;527(16-17):3913-3917.
- [47] Hori M, Nemat-Nasser S. Double-inclusion model and overall moduli of multi-phase composites. *Mechanics of Materials*. 1993;14(3):189-206.
- [48] Dunn M, Ledbetter H. Elastic moduli of composites reinforced by multiphase particles. *Journal of Applied Mechanics*. 1995;62(4):1023-1028.

- [49] Shodja HM, Sarvestani AS. Elastic fields in double inhomogeneity by the equivalent inclusion method. *Journal of Applied Mechanics*. 2001;68(1):3-10.
- [50] Odegard G, Clancy T, Gates T. Modeling of the mechanical properties of nanoparticle/polymer composites. *Polymer*. 2005;46(2):553-562.
- [51] Mura T. *Micromechanics of Defects in Solids*. Second ed. Dordrecht: Kluwer Academic Publishers; 1987.
- [52] Fisher FT. *Nanomechanics and the viscoelastic behavior of carbon nanotube-reinforced polymers*. Northwestern University, 2002.
- [53] Boutaleb S, Zaïri F, Mesbah A, Naït-Abdelaziz M, Gloaguen JM, Boukharouba T, et al. Micromechanics-based modelling of stiffness and yield stress for silica/polymer nanocomposites. *International Journal of Solids and Structures*. 2009;46(7–8):1716-1726.
- [54] Abbate M, Musto P, Ragosta G, Scarinzi G, Mascia L. Polyimide-silica hybrids: Spectroscopy, morphology and mechanical properties. *Macromolecular Symposia*, vol. 218: Wiley Online Library; 2004. p. 211-220.
- [55] Dorigato A, Pegoretti A, Migliaresi C. Physical properties of polyhedral oligomeric silsesquioxanes-cycloolefin copolymer nanocomposites. *Journal of Applied Polymer Science*. 2009;114(4):2270-2279.
- [56] Hashin Z. Thermoelastic properties of particulate composites with imperfect interface. *Journal of the Mechanics and Physics of Solids*. 1991;39(6):745-762.

Appendix A. Equivalence of Double-Inclusion and Mori-Tanaka models for identical aspect ratios

Hori and Nemat-Nasser proposed the Double-inclusion model to predict the moduli of composites with a double inhomogeneity [47], where an ellipsoidal inclusion Ω^{gf} , which contains an ellipsoidal heterogeneity Ω^f with elasticity C^f , is embedded in an infinite homogeneous solid B with elasticity C^m , with the region Ω^g defined as $\Omega^g = \Omega^{gf} - \Omega^f$ with elasticity C^g (see Figure A1). The equivalent homogeneous inclusion method was applied by considering an infinite homogenous solid B^* of elasticity C^m within which eigenstrains ε^* are distributed in the region Ω^{gf*} , where $\Omega^{gf*} = \Omega^{g*} + \Omega^{f*}$ as shown in Figure A1.

Figure A1. Schematic of Double-inclusion model. (a) A double inclusion $\Omega^{gf} = \Omega^g + \Omega^f$ is embedded in a uniform infinite domain B . (b) Equivalent solid domain B^* with eigenstrains ε^* .

The Double-inclusion model was applied by Dunn *et al.* to estimate the elastic moduli of a three-phase composite consisting of a matrix reinforced by two-phase particles [48].

There the dilute concentration factors A_{dil}^r for each phase were derived as

$$\begin{aligned}
A_{dil}^f &= I + \Delta S \Phi^g + S^f \Phi^f \\
A_{dil}^g &= I + \left[S^{gf} - \frac{f^f}{f^g} \Delta S \right] \Phi^g + \frac{f^f}{f^g} \Delta S \Phi^f \\
A_{dil}^{gf} &= I + S^{gf} \Phi^{gf} = \frac{f^g}{f^g + f^f} A_{dil}^g + \frac{f^f}{f^g + f^f} A_{dil}^f
\end{aligned} \tag{A1}$$

where $\Delta S = S^f - S^{gf}$ and S^f and S^{gf} are the Eshelby tensors calculated using domains Ω^f and $\Omega^{gf} = \Omega^g + \Omega^f$, respectively. The definition of the fourth-order tensors Φ^f , Φ^g and Φ^{gf} can be found in [48]. Based on this derivation, the effective stiffness tensor from the Double-inclusion model was written in terms of the (non-dilute) concentration tensors A^f and A^{gf} as [48]

$$C = C^m + (f^g + f^f)(C^g - C^m)A^{gf} + f^f(C^f - C^g)A^f \tag{A2}$$

Through tedious algebraic manipulation, one can show that when the aspect ratios of the coating and inclusion are identical (as is the case being considered here), the substitution of the dilute strain concentration tensors in (A1) into the expression for the effective stiffness of the Double Inclusion model (A2) yields a solution that is identical to that of the multiple phase Mori-Tanaka model (3). We stress that this equivalence is only for the case where the aspect ratios of the inclusion and coating regions are identical.

First, one can show that the (non-dilute) strain concentration tensor A^{gf} of domain Ω^{gf} can be expressed as

$$A^{gf} = A_{dil}^{gf} \left[f^m I + (f^g + f^f) A_{dil}^{gf} \right]^{-1} \tag{A3}$$

while the (non-dilute) strain concentration tensor A^f can be written as

$$A^f = A_{dil}^f \left[f^m I + (f^g + f^f) A_{dil}^{gf} \right]^{-1} \tag{A4}$$

Upon substitution of (A3) and (A4) into (A2), the overall stiffness of the Double-inclusion model can be expressed as

$$C = \left[f^m C^m + \sum_{n=1}^r f^n C^n A_{dil}^n \right] \left[f^m I + \sum_{n=1}^r f^n A_{dil}^n \right]^{-1} \quad r = f, g \quad (A5)$$

Thus the effective stiffness prediction of the Double-inclusion model (A5) has the same structure as that of the Mori-Tanaka method (3), except that the definition of the dilute strain concentration tensors of each phase A_{dil}^r for the Double-inclusion model (A1) are different than the form for the dilute strain concentration tensors given in (2). However, if one can show that these definitions of A_{dil}^r are equivalent for the case of uniformly coated spherical inclusions, then the micromechanical predictions from the Double-inclusion model and the multiphase Mori-Tanaka model will be identical for the special case where inclusion and coating/interphase have the same aspect ratio. We now show this below.

Based on the general forms from [31], the Eshelby tensor S^r are functions of the aspect ratio of inclusion and the Poisson's ratio of the matrix. Thus the Eshelby tensor S^f of the ellipsoidal heterogeneities and S^{gf} of the Double-inclusion model should be identical if they have the same aspect ratio, such that

$$\Delta S = S^f - S^{gf} = 0 \quad (A6)$$

Substituting (A6) into (A1), and again skipping the intermediate steps, the dilute strain concentration tensor of the inclusion and interphase becomes

$$\begin{aligned}
A_{dil}^f &= I + S^f \Phi^f \\
&= \left[I + S^f (C^m)^{-1} (C^f - C^m) \right]^{-1}
\end{aligned} \tag{A7}$$

$$\begin{aligned}
A_{dil}^g &= I + S^{gf} \Phi^g \\
&= \left[I + S^f (C^m)^{-1} (C^g - C^m) \right]^{-1}
\end{aligned}$$

When the inclusion and interphase region are both spherical, the Eshelby tensor of the inclusion and interphase are identical such that $S^f=S^g$. Thus the dilute strain concentration tensors of both phases (A7) are the same as that given in (2). With this equivalency and (A5), this proves that for the special case considered when the inclusion and the interphase/coating region are the same shape, the effective stiffness tensor found from the Double-Inclusion method is identical to the solution provided by the multiphase Mori-Tanaka method. This point is consistent with the related discussions provided in [47].