ANALYTICAL AND COMPUTATIONAL MICROMECHANICS ANALYSIS OF THE EFFECTS OF INTERPHASE REGIONS ON THE EFFECTIVE COEFFICIENT OF THERMAL EXPANSION OF CARBON NANOTUBE-POLYMER NANOCOMPOSITES

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Abstract

Analytic and computational micromechanics techniques based on the finite element method and composite cylinders method, respectively, have been used to determine the effective CTE of carbon nanotube-epoxy nanocomposites containing aligned nanotubes. Both techniques have been used in a parametric study of the influence of interphase stiffness and interphase CTE on the effective CTE of the nanocomposites. For both the axial and transverse CTE of aligned nanotube nanocomposites with and without interphase regions, the computational and analytic micromechanics techniques were shown to give similar results. The good agreement between computational and analytic results gives confidence that the computational micromechanics approach can be used to study the effects of clustering of nanotubes and clustering of nanotubes with interphase regions currently under study.

1 Introduction

The interest in developing multifunctional materials for use in advanced structures in the aerospace industry has been one of the contributing factors encouraging the development of nanocomposites. In particular, nanocomposites consisting of single-wall carbon nanotubes (SWCNTs) dispersed in a polymer matrix have been proposed by many as a material capable of providing enhanced elastic, thermal and electrical properties relative to the neat polymer matrix materials typically used in traditional structural carbon fiber composites [1, 2, 3, 4]. The intent is to allow for the development of carbon fiber composites which can serve not only as a key structural element, but which are capable of providing improved thermal management, electrostatic static discharge, and structural health monitoring abilities with negligible increases in weight [4, 5, 6]. As a result of the orders of magnitude difference in properties between SWCNTs and most polymers, it is believed that only a small amount of SWCNTs would be needed to impart large increases in the elastic, thermal and electrical properties. Recent characterization efforts have shown this to certainly be the case for the electrical properties of nanocomposites where fractions of a weight percent of SWCNTs have been shown to lead to percolation and a corresponding six to eight orders of magnitude increases in electrical conductivity relative to that of the neat polymer [10, 11, 12, 13, 14, 15]. Relatively large increases of 20 - 30% and 30-100% have also been observed in elastic properties [16, 17, 18] and thermal conductivities [19, 20, 21], respectively, of nanocomposites containing on the order of 1% SWCNTs, thereby confirming the potential of nanocomposites as multifunctional matrix materials for use in structural carbon fiber composites.

In an effort to explore the design space for multifunctional nanocomposite materials, there has been a significant amount of research devoted to develop-

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2Young's modulus, thermal conductivity and electrical conductivity of SWCNTs can be as much as 3, 4, and 14 orders of magnitude, respectively, larger than typical values reported for neat epoxy [7, 8, 9]
ing multiscale models for carbon nanotube-polymer nanocomposites[22, 23]. Some of our recent work in this area has focused on the development of both analytic and computational micromechanics models[24, 25, 26, 27, 28, 29, 30] for assessing the effects of interphase regions, clustering, orientation, distribution, and nanoscale effects such as interfacial thermal resistance[26] and electron hopping[27] on the effective elastic properties and thermal and electrical conductivities of carbon nanotube-polymer nanocomposites; making use of input from lower length scale molecular dynamics simulations when possible. In particular, our efforts to model the thermal conductivity of nanocomposites have made use of molecular dynamics simulations for the measurement of the nanoscale effect associated with an interfacial thermal resistance between the nanotube and the surrounding polymer. This effect has been incorporated into both analytic and computational micromechanics approaches as a zero-thickness interface layer in the calculation of the effective thermal conductivity of nanocomposites containing randomly oriented carbon nanotubes, the results of which have compared favorably with nanocomposite characterization efforts. While these models provide a design tool for the primary variable regarding the use of nanocomposites in thermal management applications in structural composites, also of significant interest, particularly in terms of thermal cycling and its effects on service life estimates, is controlling the mismatch in coefficient of thermal expansion between the structural fibers and the surrounding matrix. As such, the present work is focused on developing a multiscale model for determining the effective coefficient of thermal expansion in carbon nanotube-polymer nanocomposites for incorporation with the thermal conductivity model developed, and thereby allowing for improved design of nanocomposites for thermal management applications.

In the present work, analytic and computational micromechanics techniques are applied towards predicting the effective coefficients of thermal expansion of polymer nanocomposites containing aligned bundles of SWCNTs. For well-dispersed SWCNTs, plane strain composite cylinders analytic micromechanics approaches are applied for determining the coefficients of thermal expansion for aligned nanotube cases. In computational micromechanics approaches, periodic arrangements of well-dispersed SWCNTs are studied using the commercially available finite element software COMSOL Multiphysics 3.4. Periodic boundary conditions corresponding to axial and transverse constrained uniform temperature increase are applied to determine the corresponding local stress distribution within a given representative volume element (RVE), and subsequently, the components of the concentration tensors. RVEs are constructed with either hollow CNTs (in what would be termed a single step method), or using effective solid nanotubes having transversely isotropic effective properties determined from a composite cylinder approach (i.e., a two-step method), and are observed to yield nearly identical results for effective bundle coefficient of thermal expansion. The influence of the presence of an interphase region on the effective coefficient of thermal expansion is considered in a parametric study in terms of both interphase thickness, elastic properties, and coefficient of thermal expansion. Special emphasis is placed on assessing the impact of interphase percolation on the effective coefficient of thermal expansion. The resulting changes in effective coefficient of thermal expansion due to the presence of interphase regions are then put into context by comparison with an analogous parametric study on the effects of interphase regions on the effective elastic properties and thermal and electrical conductivities of nanocomposites.

2 Description of Micromechanics Models

The multiscale modeling idealization for nanocomposites comprised of randomly oriented bundles of SWCNTs dispersed in a polymer matrix.
in turn, depends on the nanoscale details in terms of SWCNT arrangement within the bundle and whether the SWCNTs are surrounded by an interphase layer intended to capture the nanoscale effects of polymer structure perturbation. For a given set of boundary conditions at the macroscale, the macroscale stress, $\sigma$, can be determined from the static equilibrium equations which can be expressed in vector-tensor notation as:

$$\nabla \cdot \sigma + f = 0$$  \hspace{1cm} (1)

where $f$ is the macroscale body force and the del operator ($\nabla$) is applied with respect to the macroscale coordinate system ($x_i$). The macroscale infinitesimal total strain, $\varepsilon^\text{Tot}$, is expressed in terms of the macroscale displacement, $u$, by

$$\varepsilon^\text{Tot} = \frac{1}{2} \left( \nabla u + (\nabla u)^T \right)$$  \hspace{1cm} (2)

where the superscript $T$ denotes the transpose of the displacement gradient. The macroscale infinitesimal total strain can be decomposed into two parts, the macroscale infinitesimal elastic strain, $\varepsilon^\text{El}$, and the thermal strain, $\varepsilon^\text{Th}$, i.e.,

$$\varepsilon^\text{Tot} = \varepsilon^\text{El} + \varepsilon^\text{Th}$$  \hspace{1cm} (3)

where the thermal strain can be expressed in terms of the temperature change between the current and reference configurations as

$$\varepsilon^\text{Th} = \alpha \varepsilon^\text{El} \Delta T = \alpha \varepsilon^\text{El} (T - T_0)$$  \hspace{1cm} (4)

with $T$ and $T_0$ denoting the temperature in the current and reference configurations, respectively. The macroscale stress is related to the macroscale infinitesimal strain through the linear elastic constitutive relation expressed as:

$$\sigma = L^\text{eff} \varepsilon$$  \hspace{1cm} (5)

The tensors $\alpha^\text{eff}$ and $L^\text{eff}$ in Eqs 4 and 5 are the effective coefficient of thermal expansion and effective elastic stiffness for the nanocomposite, respectively, both of which are determined from the macroscale representative volume element (RVE) with input obtained from the nanoscale RVE. Thus, the macroscale thermoelastic constitutive relationship can be expressed in terms of both the effective coefficient of thermal expansion and effective stiffness as

$$\sigma = L^\text{eff} (\varepsilon^\text{Tot} - \alpha^\text{eff} \Delta T)$$  \hspace{1cm} (6)

so that the focus is therefore on determining effective properties by studying the micro- and nanoscale RVEs.

### 2.1 Composite Cylinders Method for Effective Coefficient of Thermal Expansion

In the composite cylinder method, the nanoscale RVE is identified as a concentric set of cylinders, the composite cylinder assemblage, which in the present work consists of a hollow CNT, an interphase region, and the polymer matrix. The CNT is taken to have an outer radius of 0.85 nm and a thickness of 0.34 nm, while the interphase and matrix thicknesses are variable depending on the parametric study and volume fraction, respectively.

Anticipating that the effective properties of the nanoscale RVE will have transversely isotropic material symmetry, the effective axial ($\hat{\alpha}^{\text{eff}}_{11}$) and transverse ($\hat{\alpha}^{\text{eff}}_{22}$) coefficient of thermal expansion components are obtained by solving the equations

$$\langle \hat{\sigma}_{11} \rangle = (2\hat{\kappa}^{\text{eff}}_{23}\hat{\rho}^{\text{eff}}_{12}) \left( \langle \varepsilon^\text{Tot}_{22} \rangle - \hat{\alpha}^{\text{eff}}_{11} \Delta T \right)$$

$$+ (2\hat{\kappa}^{\text{eff}}_{23}\hat{\rho}^{\text{eff}}_{12}) \left( \langle \varepsilon^\text{Tot}_{33} \rangle - \hat{\alpha}^{\text{eff}}_{11} \Delta T \right)$$

$$+ \left( \hat{E}_{11}^{\text{eff}} + 4 (\hat{\rho}^{\text{eff}}_{12})^2\hat{\kappa}^{\text{eff}}_{23} \right) \left( \langle \varepsilon^\text{Tot}_{11} \rangle - \hat{\alpha}^{\text{eff}}_{11} \Delta T \right)$$

$$\langle \hat{\sigma}_{22} \rangle = (\hat{\kappa}^{\text{eff}}_{23} + \hat{\rho}^{\text{eff}}_{23}) \left( \langle \varepsilon^\text{Tot}_{22} \rangle - \hat{\alpha}^{\text{eff}}_{22} \Delta T \right)$$

$$+ (\hat{\kappa}^{\text{eff}}_{23} + \hat{\rho}^{\text{eff}}_{23}) \left( \langle \varepsilon^\text{Tot}_{33} \rangle - \hat{\alpha}^{\text{eff}}_{22} \Delta T \right)$$

$$+ (2\hat{\kappa}^{\text{eff}}_{23}\hat{\rho}^{\text{eff}}_{12}) \left( \langle \varepsilon^\text{Tot}_{11} \rangle - \hat{\alpha}^{\text{eff}}_{11} \Delta T \right)$$

(7)

where the $\langle \bullet \rangle$ denote volume averages of the stress and total strain over the composite cylinder assemblage expressed in cartesian coordinates, and where $\hat{\kappa}^{\text{eff}}_{23}$, $\hat{\rho}^{\text{eff}}_{23}$, $\hat{E}^{\text{eff}}_{11}$ and $\hat{\rho}^{\text{eff}}_{12}$ are the in-plane bulk modulus, in-plane shear modulus, axial Young’s modulus, and axial Poisson’s ratio, respectively, all of which are determined from isothermal composite cylinders solutions as summarized in Ref. [24]. The solution of Eqs. 7 yields:

$$\hat{\alpha}^{\text{eff}}_{11} = \frac{1}{\hat{E}^{\text{eff}}_{11} \hat{\Delta T}} \left( \hat{E}^{\text{eff}}_{11} \langle \varepsilon^\text{Tot}_{11} \rangle - \langle \hat{\sigma}_{11} \rangle + 2\hat{\rho}^{\text{eff}}_{12} \langle \hat{\sigma}_{22} \rangle \right)$$

$$+ 2\hat{\rho}^{\text{eff}}_{12} \hat{\mu}^{\text{eff}}_{23} \left( \langle \varepsilon^\text{Tot}_{33} \rangle - \langle \hat{\sigma}_{22} \rangle \right)$$

$$\hat{\alpha}^{\text{eff}}_{22} = \frac{1}{2\hat{E}^{\text{eff}}_{11} \hat{\kappa}^{\text{eff}}_{23} \hat{\Delta T}} \left[ 2\hat{\kappa}^{\text{eff}}_{23} \langle \hat{\sigma}_{11} \rangle \right]$$

$$- \left( \hat{E}^{\text{eff}}_{11} + 4 (\hat{\rho}^{\text{eff}}_{12})^2\hat{\kappa}^{\text{eff}}_{23} \right) \langle \hat{\sigma}_{22} \rangle$$

$$+ \left( \hat{E}^{\text{eff}}_{11} (\hat{\kappa}^{\text{eff}}_{23} + \hat{\rho}^{\text{eff}}_{23}) + 4 (\hat{\rho}^{\text{eff}}_{12})^2\hat{\kappa}^{\text{eff}}_{23}\hat{\mu}^{\text{eff}}_{23} \right) \langle \hat{\sigma}_{22} \rangle$$

$$+ \left( \hat{E}^{\text{eff}}_{11} (\hat{\kappa}^{\text{eff}}_{23} + \hat{\rho}^{\text{eff}}_{23}) - 4 (\hat{\rho}^{\text{eff}}_{12})^2\hat{\kappa}^{\text{eff}}_{23}\hat{\mu}^{\text{eff}}_{23} \right) \langle \hat{\sigma}_{33} \rangle$$

(8)
2.2 Computational Micromechanics Model for Effective Coefficient of Thermal Expansion

The computational micromechanics nanoscale RVE consists of a periodic hexagonal array of CNTs as shown in Figure 2. The three-dimensional computational domain consists of on the order of 50 thousand tetrahedral elements, with on the order of 10 elements through the thickness (i.e. in the CNT axis direction). The boundary and interface matching conditions consist of stress free internal CNT surfaces, constrained outer boundary displacements, and continuity of displacements and tractions along interface boundaries between phases. The Structural Mechanics Module of Comsol 3.4 is used to compute the displacement field in the RVE resulting from the application of a nominal $\Delta T$. The volume averaged stress and total strain are then obtained from the post-processed data and are used to solve for the axial and transverse coefficients of thermal expansion using Eqn. 8 in cartesian coordinates form, with effective elastic properties for the nanocomposite provided by the composite cylinder method.

3 Results and Discussion

Effective axial ($\tilde{\alpha}_{11}^{\text{eff}}$) and transverse ($\tilde{\alpha}_{22}^{\text{eff}}$) coefficients of thermal expansion obtained for the nanoscale RVE from the analytic and computational micromechanics solutions are provided in Figure 4. Two types of CNT representations are considered in the computational micromechanics approaches, one in which the CNTs are treated as a hollow tube with isotropic properties in the annulus and the second where the CNT has been replaced by an effective nanofiber having transversely isotropic material properties obtained from a composite cylinders model. The material properties in all phases for each case are provided in Table 1. For cases of nanocomposites consisting of aligned CNTs, these nanoscale RVE effective coefficients of thermal expansion would correspond to the effective properties of the nanocomposite. As such, a large range of volume fractions up to 0.9 is provided in order to demonstrate the comparison between the three nanoscale RVE results (Figure 4) and will be used in ongoing studies to assess the effects of clustering. In Figure 4, the effective axial CTE of the nanocomposite is observed to rapidly decrease from the matrix value of $6.08E - 05/°K$ to a value on the order of $2E - 06/°K$, reaching a value of $3.8E - 06/°K$ at a volume fraction of 0.1. This rapid decrease is due to the dominance of the CNT properties on the axial response of the nanocomposite, as has been observed for other axial properties such as the axial Young’s modulus, thermal conductivity and electrical conductivity. However, in the latter, the predicted properties followed a linear rule of mixtures results while in the present case, the effective axial CTE appears more like exponential decay towards the nanotube axial CTE value. In contrast, the effective transverse CTE demonstrates an initial increase in value above that of the matrix out to a volume fraction of 0.04 before beginning to decrease towards the nanotube transverse CTE value. From the present analysis it is difficult to say exactly what is driving this response, however, it is believed this is due to the interplay of matrix CTE and nanotube transverse elastic properties. These trends in effective CTE are observed for all three methods, i.e. FEA hollow and solid and composite cylinders methods, with relatively good agreement in values observed between all three methods for both the axial and transverse CTEs throughout the range of volume fractions. The percent difference between the FEA hollow and solid axial CTEs at a volume fraction of 0.8 is 28% and for the transverse CTEs is 24%, while the percent differences between the FEA hollow and composite cylinders method at a volume fraction of 0.8 are 27% and 9%, respectively. At a volume fraction of 0.1, the maximum of the range of epoxy-CNT nanocomposite volume frac-

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3In Ref. [25] it was observed that the composite cylinders and finite element based computational micromechanics approaches gave similar results for the elastic properties of nanocomposites.
Figure 3: Contour plot of transverse stress ($\bar{\sigma}_{22} = \bar{\sigma}_{xx}$ with $z$ out of the page in the nanotube axis direction and $x$ positive to the right) for nanoscale RVEs of a hollow CNT representation with a one CNT radius thick interphase at a CNT volume fraction of 0.4.

Figure 4: Nanoscale RVE effective coefficient of thermal expansion components as a function of CNT volume fraction as obtained by the composite cylinder method and the computational micromechanics method using the hollow CNT and solid effective nanofiber representations.

Figure 5: Comparison of the displacement along a radial line of 30° for the hollow finite element and composite cylinders method results at a volume fraction of 0.3 and at $\Delta T$ of 10°C.

Table 1: Table of material properties for the polymer matrix, CNT, and effective nanofiber.

<table>
<thead>
<tr>
<th></th>
<th>Matrix</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>2.97 GPa</td>
<td>1100 GPa</td>
</tr>
<tr>
<td>$\nu$</td>
<td>0.36</td>
<td>0.14</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>6.08E-05 $/{}^\circ K$</td>
<td>1.50E-06 $/{}^\circ K$</td>
</tr>
<tr>
<td>$\alpha_{22}$</td>
<td>6.08E-05 $/{}^\circ K$</td>
<td>7.50E-06 $/{}^\circ K$</td>
</tr>
<tr>
<td>Effective Nanofiber</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{11}$</td>
<td>704 GPa</td>
<td>$\tilde{E}_{21}$</td>
</tr>
<tr>
<td>$\nu_{12}$</td>
<td>0.14</td>
<td>$\tilde{\nu}_{12}$</td>
</tr>
<tr>
<td>$\alpha_{11}$</td>
<td>1.50E-06 $/{}^\circ K$</td>
<td>$\tilde{\alpha}_{21}$</td>
</tr>
<tr>
<td>$\alpha_{22}$</td>
<td>1.13E-05 $/{}^\circ K$</td>
<td>-</td>
</tr>
</tbody>
</table>

Agreement within the nanotube, but begin to diverge slightly in the matrix as the midpoint distance between two neighboring nanotubes is approached. It was observed based on substitution of material properties into Eqn. 8 that effective CTE results were more sensitive to the transverse components of stress than they were to any of the total strain components. Another small source of error can be identified by looking at the geometry of the contour plots in Figures 2 and 3. While the perfect hexagonal array of nanotubes shown is taken to represent a transversely isotropic material, this arrangement best matches such a case at 60° intervals around the central nanotube along lines which connect nearest neighbor nanotube centers (e.g., 30° above the x-axis as in the line plots in Figure 5). Between these orientations, for
example at 0° relative to the x-axis, the distance be-
tween nearest neighbor nanotube centers (i.e. second
nearest neighbors) can be more than double, mak-
ing the stress and strain plots along such lines differ
slightly more than their composite cylinder counter-
parts than was observed along the 60° intervals, and
thus contributing to the small differences in volume
averaged total strain and stress calculations needed
to obtain the effective CTE components.

3.1 Interphase Effects on Effective
Coefficient of Thermal Expansion
Calculations

The influence of an interphase region on the effec-
tive CTE components was explored in a parametric
study on interphase properties using a 0.34nm thick
interphase region4. The interphase elastic and ther-
moelastic properties were varied in three cases: i) an
increase in elastic stiffness by a factor of 10 relative
to the matrix stiffness (labeled 10E), ii) an increase
in CTE of a factor of 10 relative to the matrix CTE
(labeled 10a), and iii) an increase of both a factor of
10 in stiffness and in CTE relative to the matrix
(labeled 10Ea). It is noted that the inclusion of an
interphase region leads to what is termed an inter-
phase percolation as the volume fraction is increased
to the interphase percolation volume fraction. This
is the volume fraction at which the interphase regions
of neighboring nanotubes comes into contact and be-
gins to overlap. This overlap precludes the use of the
composite cylinder method as the interphase layer is
no longer circular. As the volume fraction is further
increased, the 3-phase (nanotube, interphase, matrix)
RVE transitions to a 2-phase (nanotube, interphase)
RVE where the composite cylinders method can again
be used.

The results for axial CTE and transverse CTE
obtained from both the FEA hollow computational
micromechanics and composite cylinder method ap-
proaches for all three interphase cases along with the
no-interphase composite cylinder method results are
provided in Figures 6 and 7, with the 3-phase to
2-phase transition region associated with interphase
percolation clearly identified. There it is again ob-
served for all three interphase cases and for both effec-
tive axial and transverse CTEs that the FEA hollow
and composite cylinder method yield nearly identi-
cal results. For the effective axial CTE (Figure 6, all
three interphase cases demonstrate a similar trend: a
sharp decay prior to the interphase percolation, fol-
lowed by a nearly linear decrease post interphase per-
colation. However, their behavior relative to the no-
interphase case differ. For the 10E and 10a cases an
increase of 100% relative to the no-interphase case is
observed for the axial CTE at a volume fraction of
0.4, while at the same volume fraction, a much larger
increase of 1300% is observed. These results indicate
the strong interactions between elastic and thermoe-
lastic properties which can lead to large increases in
stress, and hence, in effective axial CTE, particularly
when both properties are increased5. Based on ob-
servations from the no-interphase case, it is expected
that the effective axial CTE of the nanocomposite
should be dominated by the nanotube axial CTE.
This is in fact the case for the 10E and 10a inter-
phase cases as the effective axial CTE is much closer
to the nanotube value than to either the matrix or
interphase values. However, for the 10Ea case, the
effective axial CTE is an order of magnitude larger
than the axial CTE of the nanotube (i.e., it is on the
order of the matrix value), indicating that the inter-
phase region has become a significant influence on the
effective axial CTE which is more than just a sum-
mation of the individual effects of identical increases
in elastic and thermoelastic properties.

The transverse CTE results for the three inter-
phase cases in Figure 6 demonstrate a sharply differ-
ent behavior than was observed in the axial CTE case.
There, the 10E case is observed to behave very sim-

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4 The value for interphase thickness was selected to be con-
sistent with previous studies [24] which has selected the value
based on TEM images of nanotube pull-out from a polymer
matrix.

5 A stiffer material may be more likely to have a lower CTE
than a higher one, and vice versa.
Figure 7: Comparison of the effects of interphase elastic properties and CTE on the effective transverse CTE of the nanocomposite for an interphase thickness of 0.34nm.

Similar to the no-interphase case, beginning with an initial increasing region, before following a decreasing trend with increasing volume fraction, maintaining relatively good agreement even in the post interphase percolation region. At a volume fraction of 0.4, the percent difference of the 10E case transverse CTE relative to that of the no-interphase case is 1%. In contrast, the 10a and 10Ea cases demonstrate a sharp, nearly linear increase in transverse CTE with increasing volume fraction up until the interphase percolation volume fraction, and subsequently demonstrate a linearly decreasing behavior in the post interphase percolation region. In fact, prior to interphase percolation, both the 10a and 10Ea cases increase by a factor of 50, while in the matrix, the 10a case increases by a factor of 50 and the 10Ea by a factor of 100. In terms of the transverse normal stress, the 10E case demonstrates at most a factor of 2 increase in the interphase region, while the 10a case demonstrates on average a factor of 4 increase. In contrast, the 10Ea case not only shows larger increases (factors of 10 and 6 in the interphase and matrix, respectively), but also demonstrates a change in sign of the transverse stress in the nanotube from compression to tension. The axial normal stress in the nanotube and matrix for all three interphase cases is increased by less than a factor of two. The same is true for the axial normal stress in the interphase region for cases 10E and 10a, however, for case 10Ea, axial normal stress increases by a factor of 14.

These regional variances in the total strain and stress will significantly effect the volume averages, and therefore the effective CTE components of the nanocomposite. In particular, the factor of 14 increase in the axial stress of the 10Ea case is the direct cause of the large increase in effective axial CTE observed in Figures 6 and 7. While the transverse normal stress and transverse total normal strain exhibit increases of similar scale and larger, both of these volume averaged components are marginalized in calculating the effective axial CTE due to multiplication with the Poisson’s ratio as seen in Eqn. 8 which effectively reduces their contributions by a factor of 10. For the effective transverse CTE, it is the increases observed in the transverse normal stress which lead to the behaviors observed for the three interphase cases. In looking at effective transverse CTE in Eqn. 8, it is observed that the axial normal stress is multiplied by $\kappa_{23}^\text{eff}$ while the transverse normal stress is multiplied by the much larger $E_{11}^\text{eff}$. Though the transverse total...
normal strains are multiplied by both quantities, the strain values are so small that they remain overshadowed by the stress contributions, and more specifically the transverse normal stress. That the 10a and 10Ea effective transverse CTEs demonstrate similar behavior in Figures 6 and 7 despite the 10Ea case having a much larger increase in the interphase transverse normal stress can be understood in terms of the contribution of the nanotube transverse normal stress for the 10Ea case having changed sign from compression to tension, and therefore reducing the overall volume averaged stress. Thus, it is the interphase and impact of the interphase on neighboring layers which can have substantial impact on the effective CTE of the nanocomposite both before and after interphase percolation. This is in contrast to previous observations regarding the elastic, thermal, and electrical properties where it was observed that the interphase had limited impact on the effective properties until after interphase percolation[24, 26, 27].

4 Conclusions

Analytic and computational micromechanics techniques based on the finite element method and composite cylinders method, respectively, have been used to determine the effective CTE of carbon nanotube-epoxy nanocomposites containing aligned nanotubes. Both techniques have been used in a parametric study of the influence of interphase stiffness and interphase CTE on the effective CTE of the nanocomposites. For both the axial and transverse CTE of aligned nanotube nanocomposites with and without interphase regions, the computational and analytic micromechanics techniques were shown to give similar results. The good agreement between computational and analytic results gives confidence that the computational micromechanics approach can be used to study the effects of clustering of nanotubes and clustering of nanotubes with interphase regions currently under study. In terms of specific contributions of the interphase regions to the effective CTE components, it was observed that increases in interphase CTE, and even more so, increases in interphase CTE accompanied with increases in interphase stiffness, could yield significant impact on the effective axial and transverse CTEs, even prior to interphase percolation volume fractions.

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