Coefficients of Thermal Expansion for Composites with Agglomerated Carbon Nanotubes

J Pan and L C Bian
Key Laboratory of Mechanical Reliability for Heavy Equipments and Large Structures of Hebei Province, Yanshan University, Qinhuangdao 06604, PR China

E-mail: panjing1234@qq.com

Abstract. In this paper, a micromechanics model is presented, which can predict the thermal expansion coefficients (CTE) of composites with agglomerated carbon nanotubes (CNTs). In the present model, two aggregation parameters are introduced. The Mori-Tanaka method and rule of mixture model are adopted to estimate the effect of CNT agglomeration on the thermal expansion coefficients of composites. The aim of the present paper is to investigate the CTEs of CNTs reinforced composites, with an emphasis on the influence of two agglomeration parameters on the CTEs. It is noted that the carbon nanotube agglomeration has a strong influence on the thermal expansion coefficients of composites.

1. Introduction
Carbon nanotubes are known to possess exceptional mechanical stiffness and strength. Since the discovery of carbon nanotubes, most of the research on CNTs composites focused on predicting the mechanical properties [1]. The CNT dispersion has been assumed to be uniform in the matrix and the analytical studies have neglected the agglomeration effects of CNTs. Inherent characteristics of CNTs, such as low bending stiffness (due to a small elastic modulus in the radial direction) and high aspect ratio, make CNTs easy to agglomerate in a polymer matrix [2-3]. Analyses of thermo elastic properties of composite materials have drawn considerable interest due to a very broad range of their current and projected applications [4-5]. Many micro mechanics models and bound relations have been suggested to predict effective coefficients of thermal expansion of various composites.

To date, many mechanics models have been developed to predict the effect of CNT aggregation and the thermal property on the effective elastic modulus. Barai and Weng [6] developed a two-scale micromechanical model to analyze the effect of CNT agglomeration and interface condition on the plastic strength of CNT/metal composites. It is shown that CNTs are indeed a very effective strengthening agent, but CNT agglomeration and imperfect interface condition can seriously reduce the effective stiffness and elastoplastic strength. Karevan et al. [7] researched the effect of filler content and the presence of interphase on the effective Young’s modulus of polypropylene based nanocomposites with exfoliated graphite nanoplatelets and carbon nanotubes. Jarali et al. [8] derived the effective elastic properties of multifunctional carbon nanotube composites with agglomeration of straight circular carbon nanotubes dispersed in soft polymer matrices. Hassanzadeh-Aghdam et al. [9] investigated the coefficients of thermal expansion (CTEs) of unidirectional glass fiber-reinforced polyimide composites containing silica nanoparticles. Lee and Song [10] investigated the
microstructure anisotropy of multiphase polymer composites with talcs and glass fibers and characterized the anisotropic thermomechanical properties of composites.

2. Basic theory

Based on the experimental results and micrograph images, the CNTs are easy to agglomerate in a polymer matrix. In order to study the influence of agglomeration of CNTs on the effective elastic property of composites, we adopt the morphology of Fig.1 in our model. The regions with concentrated CNTs are assumed to be spherical in shape and are considered as inclusions. The randomly oriented CNTs embedded in the original matrix to form a new matrix. The total volume $V$ of representative volume element (RVE) can be divided into the following two parts:

$$V = V_r + V_m$$  \hspace{1cm} (1)

where $V_r$ and $V_m$ denote the volume of CNTs and original matrix, respectively. The average volume fraction of CNTs in the composite is $c_r$

$$c_r = \frac{V_r}{V}$$  \hspace{1cm} (2)

The total volume $V_r$ of CNTs can be denoted as follows:

$$V_r = V_r^{in} + V_r^{m}$$  \hspace{1cm} (3)

where $V_r^{in}$ and $V_r^{m}$ denote the volumes of CNTs dispersed in the inclusions (concentrated regions) and in the original matrix, respectively.

To reflect such an agglomerated state, we introduce two aggregation parameters $\xi$ and $\lambda$ in the following analysis.

$$\xi = \frac{V_m}{V}, \lambda = \frac{V_r^{in}}{V_r}$$  \hspace{1cm} (4)

where $V_m$ is the volume of spherical inclusions in the representative volume element (RVE). The parameters $\xi$ and $\lambda$ denote the volume fraction of inclusions with respect to the total volume of the RVE and the volume ratio of CNTs that are dispersed in inclusions with respect to the total volume of nanotubes, respectively.

The effective elastic modulus of inclusions and new matrix can be calculated by Mori-Tanaka method provided by Qiu and Weng [11]. The bulk and shear modulus of the inclusions ($K_{in}$, $G_{in}$) and new matrix ($K_{out}$, $G_{out}$) can be written as follow

$$K_{in} = \frac{\left(\xi - \lambda c_r\right)K_m + \lambda c_r \xi^L A}{\xi - \lambda c_r + 3\lambda c_r \xi^A}$$  \hspace{1cm} (5)

$$G_{in} = \frac{\left(\xi - \lambda c_r\right)G_m + \lambda c_r \eta^L A}{\xi - \lambda c_r + 3\lambda c_r \eta^A}$$  \hspace{1cm} (6)

$$K_{out} = \left[1 - \xi - c_r (1 - \lambda)\right]K_m + c_r (1 - \lambda)\xi^L A + 3c_r (1 - \lambda)\xi^A$$  \hspace{1cm} (7)
\[ G_{\text{out}} = \frac{[1 - \xi - c_r(1 - \lambda)]G_m + c_r(1 - \lambda)\eta^{LA}}{[1 - \xi - c_r(1 - \lambda)] + 3c_r(1 - \lambda)\eta^A} \]  

where the detailed express of parameters \( \xi^A, \eta^A, \xi^{LA} \) and \( \eta^{LA} \) can be found in the study [11].

Based on the rule of mixture model, the thermal expansion coefficients of inclusions \( \alpha_{\text{in}} \) and new matrix \( \alpha_{\text{out}} \) can be obtained:

\[
\alpha_{\text{in}} = \frac{c_r(1 - \lambda)}{1 - \xi} \alpha_r + \frac{1 - \xi}{1 - \xi} \alpha_m
\]

\[
\alpha_{\text{out}} = \frac{c_r(1 - \lambda)}{1 - \xi} \alpha_r + \frac{1 - \xi}{1 - \xi} \alpha_m
\]

where \( \alpha_r \) and \( \alpha_m \) denote the thermal expansion coefficients of CNTs and original matrix, respectively.

The effective thermal expansion coefficients of composites can be obtained by Schneider model.

\[
\alpha_{11} = \frac{\xi\alpha_{\text{in}}E_{\text{in}} + (1 - \xi)\alpha_{\text{out}}E_{\text{out}}}{\xi E_{\text{in}} + (1 - \xi)E_{\text{out}}}
\]

\[
\alpha_{22} = \xi \alpha_{\text{in}} (1 + \nu_{\text{in}}) + (1 - \xi)\alpha_{\text{out}} (1 + \nu_{\text{out}}) - \alpha_{11} \left( \xi \nu_{\text{in}} + (1 - \xi)\nu_{\text{out}} \right)
\]

where \( \alpha_{11} \) and \( \alpha_{22} \) are longitudinal CTE and transverse CTE of composites. \( E_{\text{in}} \) and \( E_{\text{out}} \) denote the Young’s modulus of inclusions and new matrix. \( \nu_{\text{in}} \) and \( \nu_{\text{out}} \) denote the Poisson’s ratio of inclusions and new matrix. The detailed express can be found as follow:

\[
V_{\text{in}} = \frac{(3K_{\text{in}} - 2G_{\text{in}})}{2(3K_{\text{in}} + G_{\text{in}})} \quad V_{\text{out}} = \frac{(3K_{\text{out}} - 2G_{\text{out}})}{2(3K_{\text{out}} + G_{\text{out}})}
\]

\[
E_{\text{in}} = \frac{9K_{\text{in}}G_{\text{in}}}{3K_{\text{in}} + G_{\text{in}}} \quad E_{\text{out}} = \frac{9K_{\text{out}}G_{\text{out}}}{3K_{\text{out}} + G_{\text{out}}}
\]

**Fig 1.** Micromechanical model of agglomerated CNTs
3. Result and discussion
In the following, numerical calculations are depicted in Figs. 2-5. The elastic constants of CNTs and matrix are $E_m = 1.9\text{ GPa}$, $E_r = 450\text{ GPa}$, $\nu_m = \nu_r = 0.3$ The thermal expansion coefficients of materials are $\alpha_m = 52.5 \times 10^{-6}/\degree\text{C}$, $\alpha_r = 5 \times 10^{-6}/\degree\text{C}$.

Fig. 2 and Fig. 3 present the variation of longitudinal CTE and transverse CTE with CNTs volume fractions at different agglomeration parameters $\xi$. The value of $\lambda=0.5$ is used in Fig. 2 and Fig. 3. It can be found that the longitudinal CTE increases with the increase of agglomeration parameters $\xi$. However, the transverse CTE decreases with the increase of agglomeration parameters $\xi$. The reason could be that with the increase of parameter $\xi$, the agglomerated region, i.e., spherical inclusions applies to a reinforced effect on the longitudinal CTE.

Fig 2. The variation of longitudinal CTE with the agglomeration parameter $\xi$

![Graph showing the variation of longitudinal CTE with $\xi$](image)

Fig 3. The variation of transverse CTE with the agglomeration parameter $\xi$

The longitudinal CTE and transverse CTE changed with the agglomeration parameter $\lambda$ are given in Fig. 4 and Fig. 5. The value of $\xi=0.9$ is used in Fig. 4 and Fig. 5. As shown in Fig. 4 and Fig. 5, the longitudinal CTE decreases with increasing an agglomeration parameter $\lambda$, whereas the transverse CTE increases with it. With increasing parameter $\lambda$, the spherical inclusions region contains more
agglomerated CNTs and the new matrix encloses more of the original matrix. So, the parameter $\lambda$ is characterized by weakening effect in the longitudinal CTE with increasing it.

![Fig 4. Effect of agglomeration parameter $\lambda$ on the longitudinal CTE](image)

![Fig 5. Effect of agglomeration parameter $\xi$ on the transverse CTE](image)

4. Conclusions
In the present analysis, the mechanical and thermal properties of CNTs reinforced composites are studied. A new micromechanics method, which involves two agglomeration parameters, is presented and the thermal expansion coefficients of composites are derived. In the process of derivation, the Mori-Tanaka method and rule of mixture model are adopted to predict the mechanical and thermal properties of composites. The results show that the CNTs agglomeration has a critical effect on the longitudinal CTE and transverse CTE of composites. Besides, it is found that the two agglomeration parameters have a different effect on the longitudinal CTE and transverse CTE. The agglomeration parameter $\xi$ results a reinforced effect on the longitudinal CTE and the agglomeration parameter $\lambda$ has a weakening effect on the longitudinal CTE with its increase.

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