



Article

# Coefficient of Thermal Expansion of Single-Wall Carbon Nanotube Reinforced Nanocomposites

Chensong Dong

School of Civil and Mechanical Engineering, Curtin University, GPO Box 1987, Perth, WA 6845, Australia; c.dong@curtin.edu.au

**Abstract:** A study on the coefficient of thermal expansion (CTE) of single-wall carbon nanotube (SWCNT)-reinforced nanocomposites is presented in this paper. An interfacial adhesion factor (IAF) is introduced for the purpose of modelling the adhesion between SWCNTs and the matrix. The effective CTE and modulus of SWCNTs are derived using the IAF, and the effective CTE of the nanocomposite is derived by the Mori–Tanaka method. The developed model is validated against experimental data and good agreement is found.

**Keywords:** single-wall carbon nanotube (SWCNT); coefficient of thermal expansion (CTE); interfacial adhesion factor (ICF)

## 1. Introduction

Since the discovery of multi-wall carbon nanotubes (MWCNTs) in 1991 by Iijima [1], and subsequent synthesis of single-wall carbon nanotubes (SWCNTs) [2,3], numerous experimental and theoretical studies have been carried out to investigate the electronic, chemical, and mechanical properties of CNTs. SWNT-polymer composites are theoretically predicted to have both exceptional mechanical and special functional properties that carbon fibre-polymer composites cannot offer [4].

The magnitude of the coefficient of thermal expansion (CTE) depends on the structure of the materials. For single-phase materials, CTE is determined from atomic bonding, molecular structure, and molecular assembly. An elevated temperature would increase thermal energy and lead to increasing atomic movement. Weak atomic bonding with a low bonding energy would show a large CTE owing to an increasing interatomic distance. For multiphase materials, such as composites, the CTE are dependent on each component phase and also the interactions between each phase. Weak interface bonding between phases could not effectively incorporate the contributions of each component, while strong interface bonding could compromise each ingredient for thermal-expansion properties [5].

Molecular dynamics (MD) predictions [6] have shown that the axial CTEs of SWCNTs are negative in a wide low temperature range, and vary nonlinearly with the temperature. These axial CTEs may become positive as the temperature increases. This indicates that the CTE could be significantly reduced by adding SWCNTs into a polymer matrix, provided good interfacial bonding is achieved.

Wei et al. [7] investigated the CTE of SWNT-polyethylene composites through MD simulation, showing that the CTE increases with nanotube loading, which is attributed to phonon modes and Brownian motions. Guo et al. [8] studied the properties of polyacrylonitrile (PAN)/SWNT composite films and the CTE of the composite was  $1.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  at a weight loading of 40%. Xu et al. [9] found that the CTE of SWNT/poly(vinylidene fluoride) (PVDF) composites decreased with increased SWNT content. Wang et al. [10] studied the CTEs of nanocomposites reinforced by functionalized SWCNTs, and found that a reduction of 52% is observed below the glass transition temperature  $T_g$ . However, the CTE above  $T_g$  increases significantly due to the contribution of phonon modes and Brownian motions. These studies show inconsistent results, which can be attributed to



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two competing mechanisms: (1) the high stiffness and low CTE will restrain the expansion of the matrix, causing the decrease in the CTE; (2) the phonon modes and Brownian motions increase the CTE. The resulting CTE is a combined effect of these two mechanisms, and highly dependent on the interfacial bonding.

Extensive investigations into the preparation and characterization of SWNT-polymer composites have been reported [11,12]. However, the properties of the composites are not as expected, because of poor dispersion and weak interfacial bonding. One possible solution to acquire high-performance nanocomposites is functionalization. Some recent experimental results indicate that the mechanical properties of SWNT-polymer composites are significantly enhanced through functionalization, [10,13,14], which demonstrates potential applications in structural and multifunctional materials.

Since dispersion and interfacial bonding play an important role in the properties of SWCNT-polymer composites, their effects have to be taken into account when predicting the properties. The Halpin–Tsai equation [11,15], Mori–Tanaka method [16–18], and finite element analysis [19] have been used for predicting the properties of composites. In this paper, a micromechanical model based on the Mori–Tanaka method, which takes into account the interfacial bonding, is presented. An interfacial adhesion factor (ICF) was introduced. This model was validated against the experimental data. It is shown that functionalization increases the IAF and thus improves the interfacial bonding.

## 2. Approach

### 2.1. Interfacial Adhesion Factor

The effective longitudinal and transverse moduli of SWCNTs were estimated to be 704 and 346 GPa, respectively [18]. The longitudinal and transverse CTE of SWCNTs were estimated to be  $-12 \times 10^{-6}$  and  $-1.5 \pm 2 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ , respectively [20–22], and these were further validated by X-ray measurements [23]. Ruoff and Lorents [24] argued that the CTE of SWCNTs are isotropic. Both the longitudinal and transverse CTE of SWCNTs were estimated to be  $-1.5 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ . Because of the high stiffness and negative CTE of SWCNTs, it is expected that the modulus of SWCNT-reinforced composites will be significantly improved and the CTE will be significantly reduced compared to the matrix. However, it is shown from the experiments that the modulus is significantly lower than expected, while the CTE is significantly higher. These differences are commonly attributed to the poor interfacial adhesion between SWCNTs and the matrix. Fibre-matrix interfacial shear stress is a critical parameter controlling the efficiency of stress transfer and hence, some of the important mechanical properties of the composite such as elastic modulus, tensile strength, and fracture toughness [25]. When no interfacial adhesion exists, the volume being excluded by the embedded SWCNTs increases with temperature due to the phonon modes and Brownian motions of the SWCNTs [7,10]. The high-frequency optical-phonon modes lead to strong expansion in the axial direction [26]. As a result, the CTE increases. When perfect interfacial adhesion exists, the CTE decreases because of the high stiffness and low CTE of SWCNTs. Between these two extremes, when an imperfect interfacial adhesion exists, the behaviours of stiffness and CTE are quite complex.

In order to provide a practical prediction for the CTE of SWCNT-reinforced composites, an IAF,  $\lambda$ , is introduced. When  $\lambda = 0$ , there is no interfacial adhesion, i.e., no reinforcing effect, and the effective modulus of the SWCNTs is assumed to be the modulus of the matrix. When  $\lambda = 1$ , perfect interfacial adhesion exists. The effective modulus of the SWCNTs,  $E_{NTe}$ , is given by

$$E_{NTe} = \lambda E_{NT} + (1 - \lambda) E_m \quad (1)$$

where  $E_{NT}$  and  $E_m$  are the moduli of SWCNTs and the matrix, respectively.

The effective CTE,  $\alpha_{NTe}$ , is given by

$$\alpha_{NTe} = \lambda \alpha_{NT} + (1 - \lambda) \alpha_{NTp} \quad (2)$$

where  $\alpha_{NT}$  and  $\alpha_{NTp}$  are the CTE of SWCNTs and the equivalent CTE of SWCNTs in phonon modes, respectively.

When the IAF is known, the effective modulus and CTE of SWCNTs from Equations (1) and (2) can be used to derive the effective stiffness and CTE of the SWCNT-reinforced composites. It should be noted that Equations (1) and (2) do not include the effect of SWCNT volume fraction and agglomeration. These will be taken into account by the SWCNT volume fraction and effective aspect ratio in the Mori–Tanaka method.

### 2.2. Mori–Tanaka Method

The elastic and thermoelastic properties of SWCNT-reinforced composites are modelled using the method proposed by Taya et al. [27,28] based on Eshelby’s inclusion theory [29] and Mori–Tanaka’s mean field theory [17]. It is proved by Seidel and Lagoudas [18] that the Mori–Tanaka method provides accurate results.

For a general ellipsoidal inclusion, the components of Eshelby’s tensor,  $S_{ijkl}$ , are dependent on the aspect ratio. For a fibre-like inclusion, e.g., SWCNT ( $x_1 = x_2 < x_3$ ), the aspect ratio is given by  $a = x_3/x_1 = l/d$ , as shown in Figure 1.

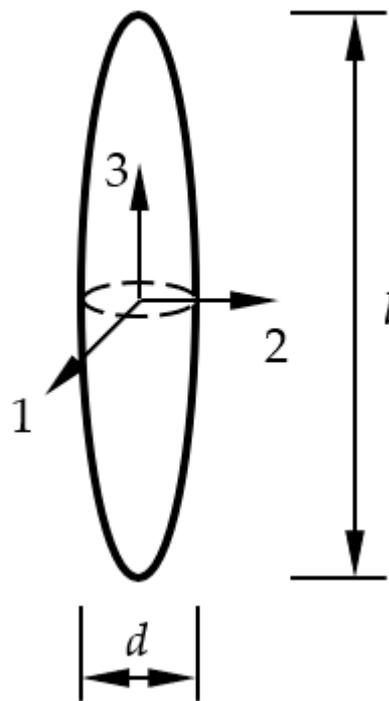


Figure 1. A fibre-like inclusion.

The effective stiffness and CTE of the composite are given by

$$C = \left[ (1 - V_f) C_m + V_f C_f A \right] \left[ (1 - V_f) I + V_f A \right]^{-1} \tag{3}$$

$$\alpha = \alpha_m + V_f \left\{ C_m + (C_f - C_m) \left[ (1 - V_f) S + V_f I \right] \right\}^{-1} C_f (\alpha_f - \alpha_m) \tag{4}$$

$$A = \left[ I + S C_m^{-1} (C_f - C_m) \right]^{-1} \tag{5}$$

where  $\alpha_f$  and  $\alpha_m$  are the CTE of the fibres and the matrix, respectively;  $C_f$  and  $C_m$  are the stiffness tensors for the matrix and fibres, respectively;  $A$  is the concentration factor relating the average strain in the effective reinforcement to that of the unknown effective material in which it is embedded;  $S$  is Eshelby’s tensor; and  $V_f$  is the fibre volume fraction.

The longitudinal and transverse CTE are  $\alpha_{33}$  and  $\alpha_{11}$ , respectively, and the longitudinal and transverse moduli,  $E_{33}$  and  $E_{11}$ , can be found from the stiffness tensor.

### 2.3. Orientation Average

A SWCNT-reinforced composite can be idealized to be a 2D random composite. Thus, the orientation average is needed. At a given aspect ratio, the effective modulus of a 2D random composite is given by taking the orientation average, i.e.,

$$E_{2D} = \frac{2}{\pi} \int_0^{\frac{\pi}{2}} E_{xx}(\theta) d\theta \tag{6}$$

where the relationship between the stiffness  $E_{xx}(\theta)$  and the fibre angle  $\theta$  can be approximately given by

$$E_{xx}(\theta) = E_T + (E_L - E_T) \cos^4 \theta \tag{7}$$

where  $E_L$  and  $E_T$  are the longitudinal and transverse moduli of the SWCNT-reinforced nanocomposite, respectively.

The effective modulus of a 2D random composite is then

$$E_{2D} = \frac{3}{8} E_L + \frac{5}{8} E_T \tag{8}$$

The effective CTE of a 2D random composite is given by

$$\alpha_{2D} = \frac{\int_0^{\frac{\pi}{2}} E_{xx}(\theta) \alpha_{xx}(\theta) d\theta}{\int_0^{\frac{\pi}{2}} E_{xx}(\theta) d\theta} \tag{9}$$

where the relationship between the CTE  $\alpha_{xx}(\theta)$  and the fibre angle  $\theta$  can be approximately given by

$$\alpha_{xx}(\theta) = \alpha_L + (\alpha_T - \alpha_L) \sin^2 \theta \tag{10}$$

where  $\alpha_L$  and  $\alpha_T$  are the longitudinal and transverse CTE of the SWCNT-reinforced nanocomposite, respectively.

The effective CTE of a 2D random composite is then

$$\alpha_{2D} = \frac{(5E_L + 3E_T)\alpha_L + (E_L + 7E_T)\alpha_T}{2(3E_L + 5E_T)} \tag{11}$$

It is shown from Equations (8) and (11) that the effective modulus and CTE of the SWCNT-reinforced nanocomposite can be calculated from the longitudinal and transverse moduli and CTE.

### 3. Results

Based on the data from the literature, a SWNT loading of 1% by weight corresponds to approximately 0.743% by volume. In this study, the CTE of SWCNT-reinforced composites from the experiments in the literature [9,10] were predicted using this method.

First, the effective CTE of the SWNT-poly(vinylidene fluoride) (PVDF) composites [9] are calculated. The modulus and CTE of PVDF are 2.22 GPa and  $2.2 \times 10^{-4} \text{ }^\circ\text{C}^{-1}$ , respectively. The SWCNT volume fraction is varied from 5% to 49%. As shown in Figure 2, good agreement between the experimental results and model predictions is found when the equivalent aspect ratio is 8 and the IAF  $\lambda = 0.4$ . The very low aspect ratio suggests the SWCNTs are not properly dispersed, and the IAF suggests poor interfacial adhesion. It is shown the CTE of the composite decreases with increasing SWCNT volume fraction, which is due to the lower CTE and higher stiffness of SWCNT.

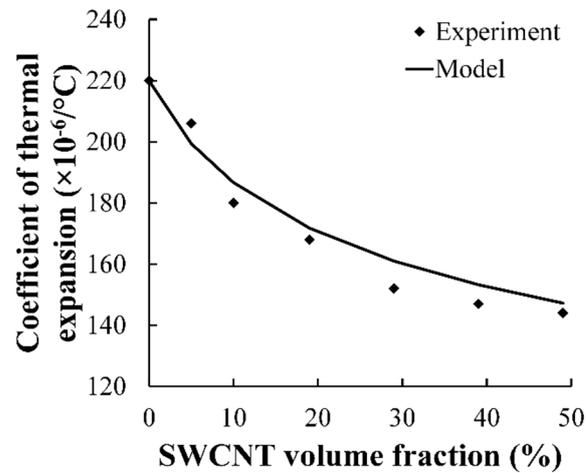


Figure 2. Effective coefficient of thermal expansion (CTE) of SWNT-PVDF composites.

Secondly, the CTE of epoxy nanocomposites reinforced by functionalized SWCNTs [10] are calculated. The modulus and CTE of the epoxy are 3 GPa and  $6.4 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ , respectively. Using these material properties, the interfacial factors are calculated from the CTE of nanocomposites. The CTE below and above the glass transition temperature  $T_g$  are shown in Figure 3. It is shown that a reduction of 52% is observed below  $T_g$ . However, the CTE above  $T_g$  increases significantly due to the contribution of phonon modes and Brownian motions.

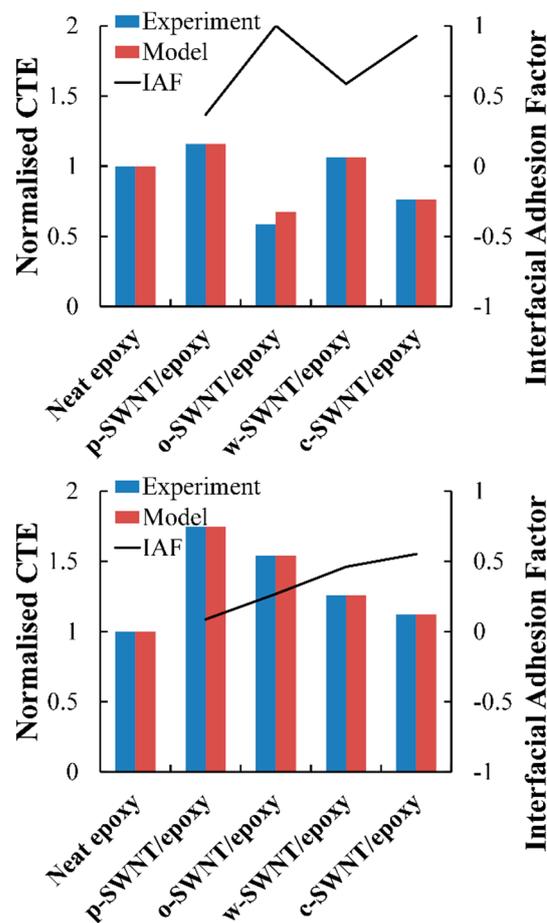


Figure 3. Above: CTE of SWNT/epoxy composites below  $T_g$ ; below: CTE of SWNT/epoxy composites above  $T_g$ .

It is shown that the interfacial factors below and above  $T_g$  are 0.4–0.8 and 0.2–0.4, respectively, which indicate that the interfacial bond factors below  $T_g$  are significantly higher than those above  $T_g$ . It is also shown that functionalization can promote the bond between SWCNTs and the matrix.

#### 4. Conclusions

An IAF is introduced to model the interfacial adhesion between SWCNTs and the matrix. Using the IAF, the effective modulus and CTE of SWCNTs are derived. The effective CTE of SWCNT-reinforced nanocomposites is derived by the Mori–Tanaka method. This simple model is validated against the experimental data and good agreement is found. It is shown that interfacial adhesion plays an important role in the effective CTE of nanocomposites. An IAF of 1 means a perfect bond between SWCNTs and the matrix, while an IAF of 0 means no bond between SWCNTs and the matrix. It is shown from the experiments that the interfacial bond factors below  $T_g$  are significantly higher than those above  $T_g$ .

The SWCNT-reinforced nanocomposite in this paper is assumed to be 2D randomly oriented, which is close to thin films. Future work will be needed to address 3D bulk nanocomposites.

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