Title

Negative axial thermal expansion coefficient of carbon nanotubes: Experimental determination based on measurements of coefficient of thermal expansion for aligned carbon nanotube reinforced epoxy composites

Authors and affiliations

Keiichi Shirasu^{1*}, Go Yamamoto¹, Itaru Tamaki¹, Toshio Ogasawara², Yoshinobu Shimamura³, Yoku Inoue⁴ and Toshiyuki Hashida¹

¹Fracture and Reliability Research Institute, Tohoku University, 6-6-11, Aza-Aoba, Aramaki, Aobaku, Sendai, 980-8579, Japan

²Advanced Composite Center, Aerospace Research and Development Directorate, Japan Aerospace Exploration Agency (JAXA), 6-13-1, Osawa, Mitaka, Tokyo 181-0015, Japan

³Department of Mechanical Engineering, Shizuoka University, 3-5-1, Jyohoku, Naka-ku, Hamamatsu, Shizuoka 423-8561, Japan

⁴Department of Electronics and Materials Science, Shizuoka University, 3-5-1, Jyohoku, Naka-ku, Hamamatsu, Shizuoka 423-8561, Japan

***Corresponding author footnote**

Telephone number: +81-22-795-7524

Fax number: +81-22-795-4311

E-mail: keiichi.shirasu@rift.mech.tohoku.ac.jp

Abstract

Due to their superior material properties, carbon nanotubes (CNTs) have many potential applications such as actuators, composites and electronic components. These CNT-based devices may experience high temperature during manufacture and operation. This leads to thermal expansion and residual stress in devices, and affects the device reliability. Therefore, the coefficient of thermal expansion (CTE) of CNTs is an important property for CNT-based devices. Although the CTE in radial direction of CNTs have been investigated using X-ray diffraction, there is no experimental determination for the axial CTE of CNTs and only numerical and theoretical predictions exit. Here, we investigated the CTE of aligned multi-walled CNT (MWCNT) reinforced epoxy composites in the MWCNT alignment direction in the temperature range of 30–60°C. We demonstrated that the CTE of the composites in the MWCNT alignment direction became negative by addition of more than 10.4 vol.% MWCNTs, and the axial CTE of MWCNTs was deduced to be $-1.2 \times 10^{-5} \text{ K}^{-1}$ using the rule of mixtures. In addition, the thermal contraction phenomenon was observed in thin sheets of MWCNTs alone. The negative CTE may be explained by out-of-plane atomic vibrations predicted by theoretical and numerical studies.

1. Introduction

Carbon nanotubes (CNTs) have been attracting much interest because of potential applications as a next generation electronic materials because of their unique physical properties [1-10]. In particular, their superior electrical, thermal and mechanical properties, including high electrical and thermal conductivity [13] and extremely high mechanical strength that exceeds 100 GPa [8], make them a candidate material for nano and microscale actuators, composites and electronic devices. These CNT-based devices may experience high temperature during manufacture and operation processes. This leads to different thermal expansion and residual stress in devices, and affects the device reliability. Therefore, for such applications, knowledge of the coefficient of thermal expansion (CTE) of the CNTs is crucial.

For multi-walled CNTs (MWCNTs), several researchers have evaluated the CTE in radial direction using X-ray diffraction method [11-14]. Bandow [11] measured the MWCNT thermal expansion in the radial direction in the temperature range of 10–320 K and found that the radial CTE is almost the same as the CTE of graphite in the thickness direction. Maniwa et al. [12] found that the radial CTE of the MWCNTs is in the range of 1.6×10^{-5} – $2.6 \times 10^{-5} \text{ K}^{-1}$. On the other hand, even though some numerical and theoretical studies have been performed on the CTE in the axial direction of single-walled CNTs (SWCNTs) [15-19], there is no experimental study on the axial CTE of the SWCNTs and MWCNTs.

Recently, Zhang et al. [20, 21] have developed to form continuous MWCNT yarns or sheets by directly drawing MWCNTs from super-aligned MWCNT arrays. These technologies allowed aligned MWCNT reinforced polymer composites to be prepared, and resultant composites had high MWCNT volume fraction and achieved high

mechanical properties [22-31]. Because this kind of MWCNTs has high aspect ratio and is well aligned in the composites, it can be expected that the evaluation of the CTE of the composites in the MWCNT alignment direction makes it possible to evaluate the axial CTE of the MWCNTs.

In this study, in order to determine the axial CTE of MWCNTs, the CTE of aligned MWCNT reinforced epoxy composites in the MWCNT alignment direction is measured and the axial CTE of the MWCNTs is estimated using the rule of mixtures. As a supporting experiment, the CTE of MWCNT monolithic sheets in the MWCNT alignment direction is also evaluated.

2. Experimental

MWCNTs were vertically grown on an oxidized silicon wafer substrate with chemical vapor deposition using C_2H_2 and $FeCl_2$ as the base material and the catalyst, respectively [32, 33]. Vertically aligned MWCNTs on a substrate are called a MWCNT array. Detailed procedures for the fabrication of MWCNT arrays and sheets have been reported elsewhere [32, 33]. The average diameter and length of the MWCNTs were 39 nm (15–57 nm) and $> 600 \mu m$, respectively.

Aligned MWCNT/epoxy composites were prepared by a hot-melt prepreg method [25]. The details of composite preparation can be found in the reference [25]. A partially cured epoxy resin (B-stage epoxy) with release paper was obtained from a commercial prepreg company. The epoxy resin consisted of bisphenol-A type epoxy, novolac type epoxy, and an aromatic diamine curing agent. The recommended cure temperature and duration of the epoxy resin are $130^\circ C$ and 1.5 h, respectively. The areal weight of the epoxy resin film was controlled to be $30 g/m^2$. A stacked MWCNT monolithic sheet of

about 20 mm width and about 45 mm length was put on a polytetrafluoroethylene sheet, and covered with the epoxy resin film with the release paper. The epoxy resin was impregnated into the MWCNT monolithic sheet at 90°C for 3 min between steel plates of the hot press used in this study. After peeling off the MWCNT sheet impregnated the epoxy resin (prepreg sheet) from the release paper, it was cured at 130°C for 1.5 h at the pressure of 1 MPa using the hot press, yielding a film specimen. MWCNT volume fraction was controlled by changing the MWCNT areal weight. In this study, the composites containing 8.5, 10.4, 14.1, 21.2 and 27.0 vol.% MWCNTs were prepared and their thickness was in the range between 19 μm and 31 μm . The in-plane MWCNT alignment distribution for the composites was observed using a scanning electron microscope (SEM, JEOL JSM6510, Japan) and transmission electron microscope (TEM, JEOL JEM-2100F, Japan). Thin samples for TEM observations were prepared using a focus ion beam milling machine (FIB, Hitachi FB2200, Japan). The machined area is approximately 20 μm wide, 4 μm deep and 0.3 μm thick.

We measured the CTE of the aligned MWCNT/epoxy composite films. Schematic illustration of the experimental setup is shown in Fig. 1. The dimensions of the composite film sample were $19 \times 2 \times 0.019\text{--}0.030$ mm (length $\times$ width $\times$ thickness). The length is along the direction in parallel to MWCNT alignment. The sample was put on a hot plate. The temperature was measured by a thermocouple which was placed in contact with the composite sample. The length change was measured by a laser displacement meter (KEYENCE LS-7600, Japan) with resolution of 0.1 μm in the temperature range 30–60°C. The heating rate was in the range of 1.8–79.0 K/min. In this study, we evaluated the average CTE of the composites in the above-mentioned temperature range. The formula of CTE was given by the following equation:

$$\alpha_c = \frac{\Delta L/L}{\Delta T} \quad (1)$$

where L is the initial length of the composite sample, ΔL is the increased length, α_c is the CTE of the composites, and ΔT is the increased temperature (30 K). The slope of $\Delta L/L$ against ΔT curve over the temperature range was obtained using experimental data to determine α_c .

Fig. 1 Schematic illustration of experimental setup for determining CTE of MWCNT/epoxy composites.

Although the CTE of the MWCNT monolithic sheets was evaluated by the above-mentioned method, their original configuration could not be maintained during heating experiment. Fig. 2 shows a schematic of the experimental arrangement used for measuring the CTE of the MWCNT monolithic sheets. The dimensions of the MWCNT monolithic sheet were about $15 \times 3 \times 0.004$ mm (length $\times$ width $\times$ thickness). Initially, the MWCNT monolithic sheets were bent and fixed onto a glass plate at both edges using a silver conductive adhesive. Heating of the MWCNT monolithic sheets were

conducted employing a power supply (KEITHLEY 2400, US). Conductive wires were attached to the fixed MWCNT monolithic sheets and connected to the power supply. When a DC voltage was applied through the power supply, the MWCNT monolithic sheet was deflected by Joule heating. The temperature was raised up to about 90°C by controlling the applied voltage in the range 1–5 V. The amount of deflection of the MWCNT monolithic sheets was measured by the laser displacement meter. The temperature was measured using an infrared thermography (Apiste FSV-1200, Japan).

Uniaxial tensile tests of individual MWCNT were carried out with a manipulator inside the vacuum chamber of SEM [9, 10]. Further details of the experimental procedure are described elsewhere [10]. [In this study, the diameter of the individual MWCNTs was measured from TEM images. In the measurements, 18 MWCNTs were observed using TEM.](#)

Fig. 2 Schematic illustration of experimental setup for determining CTE of MWCNT monolithic sheets.

3. Results and discussion

A MWCNT array prepared in this study is shown in Fig. 3. Because of their high areal density and strong interaction between MWCNTs, well-aligned MWCNT monolithic sheets are produced easily from the MWCNT array by pulling it out [32]. In order to evaluate the Young's modulus of the individual MWCNTs, the uniaxial tensile tests of single MWCNTs were carried out using a nanomanipulator system in this study. The Young's modulus averaged for 18 MWCNTs was 180 GPa.

Fig. 4a shows the MWCNT distribution in the composite as observed by SEM. The majority of the MWCNTs are aligned, although some MWCNTs are inclined with respect to the alignment direction. A TEM image shown in Fig. 4b is the morphology of the internal structure of the composites. It is seen that the epoxy resin well penetrates between MWCNTs. The TEM image indicates that the dense aligned MWCNT composites are successfully fabricated using the present processing method with only a limited amount of pores as marked by black arrows.

Fig. 3 SEM image of a vertically aligned MWCNT array.

Fig. 4 (a) SEM and (b) TEM images of aligned MWCNT/epoxy composites showing in-plane MWCNT distribution (MWCNT volume fraction is (a) 27.0 vol.% and (b) 21.2 vol.%).

We now evaluate the CTE of the aligned MWCNT/epoxy composites. Fig. 5 shows the variation of the thermal strain of the composites in the axial direction of the MWCNT alignment and neat epoxy with temperature. The thermal strain of the epoxy increases with the increasing temperature. On the other hand, it dramatically decreases by the addition of 8.5 vol.% MWCNTs, and the thermal contraction can be observed in the composites containing more than 10.4 vol.% MWCNTs. The dependence of the CTE on the MWCNT volume fraction is shown in Fig. 6. It can be seen that even though

some variations are observed, the CTE tends to decrease with the increment of the MWCNT volume fraction. The CTE of the composites containing 0 (epoxy), 8.5, 10.4, 14.1, 21.2 and 27.0 vol.% MWCNTs are 7.0×10^{-5} , 0.4×10^{-5} , -0.6×10^{-5} , -1.4×10^{-5} , -0.5×10^{-5} and $-0.7 \times 10^{-5} \text{ K}^{-1}$, respectively. In these MWCNT/epoxy composites, the MWCNTs had the high aspect ratio and were aligned along the same direction. Therefore, the CTE of the composites in the direction of the MWCNT alignment α_c may be expressed using the rule of mixtures as follows [34]:

$$\alpha_c = \frac{\alpha_m(1 - V_f)E_m + \alpha_f V_f E_f}{(1 - V_f)E_m + V_f E_f} \quad (2)$$

where, E_m and E_f are Young's modulus of the epoxy and MWCNTs, α_m and α_f are the CTE of the epoxy and MWCNTs and V_f is the MWCNT volume fraction. As mentioned above, the epoxy resin well penetrates between individual MWCNTs (Fig. 4b). Thus, it may be reasonable to substitute the Young's modulus of the individual MWCNTs for E_f in the rule of mixtures. Substituting $E_m = 2.5 \text{ GPa}$ [25], $E_f = 180 \text{ GPa}$ and $\alpha_m = 7.0 \times 10^{-5} \text{ K}^{-1}$ in Eq. (2) and performing least square regression analyses for the data shown in Fig. 6, α_f is calculated to be $-1.2 \times 10^{-5} \text{ K}^{-1}$. The solid line in Fig. 6 is regression lines provided by the least-squares regression analysis (the regression coefficient R^2 is calculated to be 0.98).

Fig. 5 Thermal strain of composites as a function of temperature change.

Fig. 6 Coefficient of thermal expansion of composites as a function of MWCNT volume fraction.

The thermal contraction phenomenon was also observed in the thin sheets of MWCNTs only. The thermal strain of the MWCNT monolithic sheets was calculated using a both ends fixed beam model subjected to bending moments and axial loads. Details of the calculation can be found in the Supplementary material. The thermal strain calculated is shown in Fig. 7 as a function of the temperature change. In this study,

four kinds of stacked MWCNT monolithic sheets (20, 30, 50 and 100 layers) were prepared. It can be seen that the thermal strain of the MWCNT monolithic sheets decreases with the increasing temperature change. The experimental data may be approximated by a linear fitting line, and the CTEs of the MWCNT monolithic sheets were calculated by the slope of the fitting line. The solid lines in Fig. 7 are regression lines provided by the least-squares regression analysis. The regression coefficient R^2 of each data is calculated to be more than 0.96. The CTE of the stacked MWCNT monolithic sheets consisted of 20, 30, 50 and 100 layers of original MWCNT monolithic sheets are -1.2×10^{-6} , -1.2×10^{-6} , -0.7×10^{-6} and $-1.7 \times 10^{-6} \text{ K}^{-1}$, respectively. The average CTE of the MWCNT monolithic sheets is $-1.2 \times 10^{-6} \text{ K}^{-1}$ which is approximately one order of magnitude smaller than that deduced from the composite data. The MWCNT monolithic sheets are anticipated to contain a large amount of pore volume (relative density of the MWCNT monolithic sheets is estimated to be about 20%) and the MWCNTs are held each other by van der Waals forces alone. The compressive axial load induced in the MWCNT monolithic sheets due to the heating may cause relative movements of individual MWCNTs such as sliding, resulting in the smaller value of CTE. Therefore, the CTE value estimated from the experiment on the MWCNT monolithic sheets should be viewed as an only supporting data. These results suggest the MWCNTs in the axial direction have the negative CTE.

Fig. 7 Thermal strain of MWCNT monolithic sheets as a function of temperature change.

To date, the CTEs of CNT-reinforced composites have been measured experimentally in a few studies [35-37]. Even though the CTEs of the composites have been shown to decrease by adding the CNTs compared to the matrix alone, the determination of the CTEs of CNTs remains an open question. This is probably because the CNTs are randomly dispersed in the matrix in those studies. On the other hand, Chen *et al.* [38] reported that the CTE of an aligned MWCNT reinforced polydimethylsiloxane (PDMS) composite in the MWCNT alignment direction was measured to be $6 \times 10^{-6} \text{ K}^{-1}$, which was two orders of magnitude lower than that of pure PDMS. However, in their research, only low MWCNT loading (5 wt%) was carried out to fabricate the composites, and no evaluation of the CTE of the MWCNTs was made from the experimental data. In contrast, we demonstrated the negative CTE of the composites in the MWCNT alignment direction for the high volume fraction MWCNT composites prepared using the aligned MWCNT monolithic sheets. Furthermore, we

have also estimated the axial CTE of the MWCNTs alone from the CTE values measured on the composites on the basis of the rule of mixtures.

Some numerical and theoretical studies have been performed on the CTE in the axial direction of SWCNTs. The axial CTE values of the SWCNTs reported in the previous studies [15-19] are summarized in Table 1. The majority of the previous studies predict that the SWCNTs contract axially below the temperature of 400 K. The thermal expansion of solids is well understood in terms of Grüneisen theory [39]. Whether a solid expands or contracts upon heating depends on the balance between phonon modes with positive and negative Grüneisen parameters. At low temperatures, transverse acoustic modes which correspond to the out-of-plane atomic vibrations of the crystal lattice may exhibit negative Grüneisen parameters. Schelling *et al.* [16] reported that the CTE of the axial direction for the SWCNTs is $-0.9 \times 10^{-6} \text{ K}^{-1}$ at room temperature, and this fact is associated with the negative Grüneisen parameters. The axial CTE value of the MWCNTs measured in this study ($-1.2 \times 10^{-5} \text{ K}^{-1}$) is in a reasonable agreement with those of the SWCNTs reported previously [16-18]. Further studies should be carried out to examine the effect of the number of graphite layers and their interaction on the CTE of the MWCNTs in the axial direction. This finding of thermal contraction of the MWCNTs in the axial direction may enable CNT-based bulk structures to be used in electromechanical systems such as thermal actuators.

Table1 A full list of the axial CTE of SWCNTs. Shown are the SWCNT type, axial CTE of the SWCNTs, temperature range and method.

Material	CTE (K^{-1})	Temperature (K)	Method	Ref.
(5,5) SWCNT	0.39×10^{-5}	300 – 800	Simulation	15
(10,10) SWCNT	0.24×10^{-5}	300 – 800	Simulation	15
(10,10) SWCNT	-0.9×10^{-6}	Room temperature	Theory	16
(10,10) SWCNT	2.5×10^{-6}	High	Theory	16
(10,10) SWCNT	-1.2×10^{-5}	400	Simulation	17
(5,5) SWCNT	$-0.2 - 3.6 \times 10^{-6}$	250 – 1600	Theory	18
(9,0) SWCNT	$-0.4 - 3.3 \times 10^{-6}$	250 – 1600	Theory	18
(10,10) SWCNT	$0 - 2.1 \times 10^{-6}$	0 – 2000	Simulation	19

4. Conclusions

We investigated the CTE of the aligned MWCNT/epoxy composites in the MWCNT alignment direction experimentally. It was demonstrated that the thermal strain of the composite dramatically decreased by addition of 8.5 vol.% MWCNTs compared to the neat epoxy, and the thermal contraction was observed in the composites containing more than 10.4 vol.% MWCNTs in the temperature range 30–60°C. We have also shown that the axial CTE of the MWCNTs was deduced to be $-1.2 \times 10^{-5} \text{ K}^{-1}$ from the CTE values measured on the aligned MWCNT/epoxy composites using the rule of mixtures. Previous numerical studies reported that the SWCNTs had the negative CTE because of the out-of-plane atomic vibrations of the crystal lattice. It was shown that the axial CTE value of the MWCNTs measured in this study was close to those of the SWCNTs calculated in the numerical studies. As a supporting experiment, the thermal strain of MWCNT monolithic sheets in the MWCNT alignment direction was measured and the thermal contraction phenomenon was also observed. Based on these results, it may be reasonable to conclude that the MWCNTs in the axial direction have the negative CTE.

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