Preparation and performance evaluation of electrothermal actuators using aligned carbon nanotube reinforced epoxy composites

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Abstract
By using an aligned multi-walled carbon nanotube (MWCNT) reinforced epoxy composite, an electrothermal bimorph actuator was fabricated and its load and deformation capacities were investigated. The composite has a negative coefficient of thermal expansion (CTE) as well as large Young’s modulus. To evaluate the actuator property, a composite/aluminum laminate was prepared and a U-shaped actuator was formed by cutting off the middle part of the composite/aluminum laminate. The Young’s modulus of the composites increased linearly with increasing MWCNT volume fraction, and that of the composite containing 27 vol.% MWCNTs reached 56.8 ± 3.9 GPa. We also demonstrated that the actuator showed a large bending displacement and force output under low voltage stimulation. The bending displacement and force output of the actuator with the free length of 16 mm reached 7.6 mm and 9.0 mN under a DC voltage of 5.2 V, respectively. Furthermore, the actuator fabricated in this study showed higher values of work output per unit volume compared to the actuators reported in previous studies within the frequency between 0.05 Hz and 0.5 Hz. The enhanced performance was attributable mainly to the high Young’s modulus of both composite and aluminum layers and the huge mismatch of the coefficient of thermal expansion in the composite/aluminum laminate.

Key words: Carbon nanotube, Composite, Young’s modulus, Coefficient of thermal expansion, Actuator

1. Introduction

Electrothermal actuators, which have a displacement/force output at low voltage operation conditions and a simple fabrication process, are good for precise-tracking positioning devices, artificial muscles, manipulators and so on (Yang, et al., 2005, Zhu, et al., 2005, Lima, et al., 2012). One of the electrothermal actuation schemes is the so-called bimorph effect (Timoshenko, 1925), where two materials with different thermal expansions are combined in a bimorph cantilever. The thermal expansion mismatch between two layers of the cantilever can produce bending displacement when current is passed through the component. Traditionally used bimorph materials include metals, metal oxides, and silicon (Yang, et al., 2005, LeMieux, et al., 2006, Liu, et al., 2012). Currently, the synthesis and characterization of carbon nanotube (CNT)/polymer composite actuators are topics of intense research activity (Chen, et al., 2011, Seo, et al., 2012, Zeng, et al., 2015). CNTs have been attracting much interest because of potential applications as a next generation electronic materials. In particular, their superior electrical, thermal and mechanical properties, including
high electrical and thermal conductivity (Ruoff and Lorents, 1995, Ebbesen, et al., 1996) and extremely high mechanical strength that exceeds 100 GPa (Peng, et al., 2008), make them a candidate material for nano and microscale actuators, composites and electronic devices. Seo, et al. (2012) fabricated a 33 mm long electrothermal actuator which is based on a polydimethylsiloxane (PDMS) slab sandwiched by upper and lower active layers of single-walled CNT (SWCNT)/PDMS composites (the thickness of the composite layer and PDMS layer is about 0.5 µm and 500 µm, respectively). They reported to achieve a large bending displacement of 3.5 mm at a DC voltage of 60 V. Zeng, et al. (2015) reported a large displacement up to 28 mm in 48 mm long bimorph actuator consisting of multi-walled CNT (MWCNT)/silicone rubber composite (240 µm thick) and CNT/waterborne polyurethane composite (130 µm thick) under the low DC voltage of 7 V. Recently, Zhang, et al. (2005) have developed to form continuous MWCNT sheets by directly drawing MWCNTs from super-aligned MWCNT arrays. Utilizing this technology, Chen, et al. (2011) fabricated the 30 mm-length of aligned MWCNT-based PDMS composite electrothermal bimorph actuator (the thickness of the composite layer and PDMS layer is 20 µm and 750 µm, respectively) and achieved bending displacement of 9.5 mm at the DC voltage of 40 V. Even though the as mentioned actuators have the large bending displacements, no information of the force output has been given in the literatures. Their force output is expected to be limited because of the randomly oriented CNTs in the matrix, low CNT volume fraction and the thinner non-CNT material layer compared to the composite layer.

In this study, we demonstrate an electrothermal bimorph actuator having a large bending displacement and high force output by using an aligned MWCNT reinforced epoxy composite and thin aluminum foil. The MWCNT sheet fabrication technology as mentioned above allowed aligned MWCNT reinforced polymer composites to be prepared and resultant composites had high MWCNT volume fraction and achieved high Young’s modulus (Cheng, et al., 2008, Bradford, et al., 2010, Liu, et al., 2011, Ogasawara, et al., 2011, Wang, et al., 2013). In addition, we have found that the MWCNTs in the axial direction have the negative CTE, and the CTE of the composites in the MWCNT alignment direction became negative by addition of more than 10.4 vol.% MWCNTs (Shirasu, et al., 2015). Thus, by using the high volume fraction aligned MWCNT composite and thin aluminum foil, the same temperature rise leads to an exceptional bending actuation of the structure since the thermal expansion mismatch between the composite layer in the direction parallel to MWCNT alignment and the aluminum layer is enormous. Furthermore, as the Young’s modulus of the composites is expected to be enhanced by including aligned MWCNTs to the polymer matrix as mentioned above, it is expected to increase the force output of actuators.

2. Experimental procedure

MWCNTs were vertically grown on an oxidized silicon wafer substrate with chemical vapor deposition using C2H2 and FeCl2 as the base material and the catalyst, respectively. Hereafter, the vertically aligned MWCNTs grown on a substrate are referred to as MWCNT arrays. The detailed procedure for the fabrication of MWCNT arrays has been reported elsewhere (Inoue, et al., 2008). The average diameter and length of the MWCNTs were 39 nm (15–57 nm) and > 600 µm, respectively. MWCNT monolithic sheets were drawn out of the MWCNT arrays and wound onto a rotating plate. In this study, four kinds of stacked MWCNT monolithic sheets (50, 90, 200 and 250 layers) were prepared.

Aligned MWCNT/epoxy composites were prepared by a hot-melt prepreg method (Ogasawara, et al., 2011). A partially cured epoxy resin (B-stage epoxy) with a release paper was used as the starting materials. The epoxy resin consists of bisphenol-A type epoxy, novolac type epoxy, and an aromatic diamine curing agent. 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 release paper from the MWCNT sheet impregnated the epoxy resin (prepreg sheet), the prepreg sheet was cured at 130°C for 1.5 h at the pressure of 1 MPa using the hot press, forming a film specimen. In order to evaluate the actuator properties, an aligned MWCNT reinforced epoxy composite/aluminum laminate was prepared. The prepreg sheet was prepared under the same processing condition as mentioned above. After peeling off the release paper from the prepreg sheet, the aluminum foil was stacked on the prepreg sheet and cured at 130°C for 1.5 h at the pressure of 1 MPa using the hot press. 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).

Results

The MWCNT distribution in the composite as observed by SEM is shown in Fig. 2a. The majority of the MWCNTs are aligned, although some MWCNTs are inclined with respect to the drawing direction. TEM image shown in Fig. 2b

thin sample for TEM observations was prepared using a focus ion beam milling machine (FIB, Hitachi FB2200, Japan). The machined area was approximately 20 μm wide, 4 μm deep and 0.3 μm thick.

Tensile tests of the aligned MWCNT/epoxy composites were performed using an Instron 5965 testing machine with a 50 N load cell. Strain was measured by a laser displacement meter (KEYENCE LS-7600, Japan) with resolution of 0.1 μm. Young’s modulus was calculated from the slope of the stress-strain curve. The thickness and width dimension of the tensile testing samples was measured by SEM. Gage length was about 18 mm and testing speed was 0.2 mm/min. At least three samples were tested from each batch of composites.

The experimental setup used to characterize the actuator performance is shown in Fig. 1. To evaluate the actuator property, an electrothermal actuator was prepared using the composite/aluminum laminate. As shown in Fig. 1a, a U-shaped actuator was formed by cutting off the middle part of the composite/aluminum laminate. The CNT-aligned direction is parallel to the length direction of the U-shaped actuator. The dimensions of the entire U-shaped actuator was 20 × 5 × 0.038 mm (length × width × thickness), while the width of each beam was around 2 mm. A gold coating was sputtered onto the surface of the composite layer in order to decrease the contact resistance between the composite layer and copper electrodes, and enhance the conductivity in the composite layer. The edge of the sample was masked during deposition by a polyimide tape to prevent electrical shorting on the sidewalls of the sample by the gold layer. The top of the sample was sandwiched between glass plates, and the composite layer was attached to two copper electrodes. The free length of the actuator was 16 mm. The sample was suspended vertically in a glove box chamber. A DC voltage was applied using a KEITHLEY 2400 source meter. We controlled square waveform input voltage on the composite layer using a Labview program. The bending of the sample is captured by the laser displacement meter. Sample surface temperature during actuation was measured using an infrared thermography (Apiste FSV-1200, Japan). The temperature data were obtained from the bare surface of the composite layer. Calibration of the thermography was performed by heating the sample on a hot plate using a thermocouple placed on the composite layer to measure sample temperature. The emissivity of the composite was determined based on temperature measurements by the thermocouple. The temperature, displacement and applied voltage values were automatically recorded every 200 ms to a text file using data logger (GRAPHTEC GL220, Japan).

3. Results

The MWCNT distribution in the composite as observed by SEM is shown in Fig. 2a. The majority of the MWCNTs are aligned, although some MWCNTs are inclined with respect to the drawing direction. TEM image shown in Fig. 2b
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 were successfully fabricated using the present processing method. The dependence of the Young’s modulus of the composites on the MWCNT volume fraction is shown in Fig. 3. The Young’s modulus of the composites increases linearly with the increasing MWCNT volume fraction. The Young’s modulus of the composite containing 27 vol.% MWCNTs reaches 56.8 ± 3.9 GPa, which is one order of magnitude higher than that of randomly oriented CNT/polymer composites (Spitalsky et al., 2010). In these MWCNT/epoxy composites, the MWCNTs had the high aspect ratio (length/diameter > 15000) and were aligned along the same direction. It suggests that the composites prepared in this study can be modeled as continuous fibers aligned in parallel within the epoxy matrix (Hull and Cryne, 1996). Therefore, the Young’s modulus of the composites in the direction of the MWCNT alignment $E_c$ may be expressed using the rule of mixtures as follows (Hull and Cryne, 1996):

$$E_c = (1-V_f)E_m + V_f E_f$$

(1)

where, $E_m$ and $E_f$ are Young’s modulus of the epoxy and MWCNTs and $V_f$ is the MWCNT volume fraction. According to Eq. (1), the Young’s modulus of the MWCNTs was calculated to be 210 GPa, which is close to the Young’s modulus of the individual MWCNTs measured by uniaxial tensile tests (180 GPa) (Shirasu, et al., 2015). The solid line in Fig. 3 is a regression line provided by the least-squares regression analysis (the regression coefficient $R^2$ is calculated to be 0.97). These results suggest that the Young’s modulus of the composites in the direction of the MWCNT alignment can be evaluated by the rule of mixtures.

Fig. 2 Aligned MWCNT/epoxy composites showing in-plane MWCNT distribution acquired by (a) SEM and (b) TEM (MWCNT volume fraction is (a) 27 vol.% and (b) 22 vol.%).

Fig. 3 Young’s modulus of the aligned MWCNT reinforced epoxy composites as a function of MWCNT volume fraction.

Fig. 4 SEM image showing the cross-section of the composite/aluminum laminate.
The cross-sectional view of the composite/aluminum laminate is shown in Fig. 4. The MWCNT volume fraction in the composite layer was 27 vol.%. The SEM image indicates that two layers are tightly bonded to each other using the present processing method without delamination in the laminate. The composite layer and aluminum layer have thicknesses of about 30 μm and 8 μm, respectively. We now evaluate the bending actuation of the U-shaped actuator composed of the MWCNT reinforced epoxy composite/aluminum laminate. Figure 5 shows the bending actuation performance and temperature variation of the laminate consisting of the aluminum and composite containing 27 vol.% MWCNTs. When a DC voltage of 3.0 V was applied, the actuator began to bend immediately and the free-end displacement of the actuator reached up to 3.0 mm. The free-end returned to its initial position after the power source was cut off. The bending displacement was almost consistent with the temperature variation during the actuation process. The dependences of the displacement on the applied voltage and temperature are shown in Fig. 6a and 6b. The glass transition temperature of the epoxy used in this study is 130°C. Thus, we have evaluated the bending displacement of the actuator at the temperature range below the glass transition temperature and the temperature range was 30°C to 120°C. The bending displacement is proportional to the temperature difference and square of the applied voltage, and reaches 7.6 mm under a DC voltage of 5.2 V. This result suggests that the actuation mechanism is due to the Joule heating. The CTE of the composite in the MWCNT alignment direction has been measured to be -0.7 × 10^{-6} K^{-1} (Shirasu, et al., 2015). Thus, upon applying an electric voltage on the actuator, the composite layer is directly heated which shrinks along its length. On the other hand, the aluminum layer is heated up by the heat diffused from the composite layer and results in a thermal expansion. The vast thermal expansion mismatch between the composite layer and aluminum layer is expected to cause large bending displacement for the actuator under electric stimulation. The
The force output $F$ is calculated by the following equation assuming that the bending displacement is equal to that of a cantilever model subject to a tip concentrated load:

\[ F = \frac{3\delta(E_1I_1 + E_2I_2)}{L^2} \] (2)

where $\delta$ is the bending displacement, $E$ the Young’s modulus, $I$ the second moment of inertia, and $L$ the length of the actuator, respectively. The subscripts 1 and 2 refer to the composite layer and aluminum layer, respectively. Figure 6c shows that the force output is nearly in line with the temperature difference, and reaches 9.0 mN at 5.2 V. Figure 7 shows the vibration amplitude and calculated force output of the actuator at the square wave voltage with different frequencies. With the increasing frequency higher than 0.25 Hz, both vibration amplitude and force output gradually decrease. According to the thermal actuation mechanism, the maximal vibration frequency of the actuator is determined by its heat generation and dissipation rate. For the electrical induced thermal actuator, the heating and cooling rate will lag the rate of the current charge at a frequency higher than 0.25 Hz, which leads to the decrease of the vibration amplitude and force output.

Where an actuator must operate cyclically, considerations of frequency and power become relevant. The maximum power output per unit volume $P_{\text{max}}$ is defined by Eq. (3).

\[ P_{\text{max}} = \frac{W_{\text{max}}}{\frac{t}{2}} = 2fW_{\text{max}} \] (3)
where \( t \) is the period of time, \( f \) the frequency and \( W_{\text{max}} \) the maximum work output per unit volume, respectively. \( W_{\text{max}} \) is calculated by Eq. (4).

\[
W_{\text{max}} = \frac{F_{\text{max}} \delta_{\text{max}}}{8WL(h_1 + h_2)}
\]

(4)

where \( w \) and \( h \) are the width and thickness of the actuator, respectively. Because the actuator prepared in this study was stimulated with a square wave voltage, the maximum work output per unit volume was divided by one-half of the period of time in order to calculate the maximum power output per unit volume. Figure 8 allows for a comparison of the frequency and power output per unit volume. Dashed lines in Fig. 8 link actuators which can produce equal \( W_{\text{max}} \) in each cycle. In addition to the experimental results of this study, Fig. 8 gives some literature data for the previously reported CNT composite electrothermal actuators (Chen, et al., 2011, Seo, et al., 2012), conventional electrothermal microactuators consisting of metals, ceramics and silicon (Yang, et al., 2005, Boutchich, et al., 2007) and other kinds of bending actuators (Wang, et al., 1999, Wang, et al., 2010, Cottinet, et al., 2011). Wang, et al. (1999) prepared and evaluated a RAINBOW (reduced and internally biased oxide wafer) actuator consisting of a reduced electromechanically passive layer and an unreduced piezoelectric lead zirconate titanate (PZT) layer. Wang, et al. (2010) investigated sulfonated poly(styrene-ran-ethylene) (SPSE) as a new ion-change membrane for use in ionomic polymer–metal composite (IPMC) actuators. Cottinet, et al. (2011) studied an IPMC actuator using Nafion membrane and MWCNT buckypapers. Young’s moduli of the silicon, silicon oxide, silicon nitride, titanium tungsten, SPSE membrane, Nafion membrane, MWCNT buckypaper and PZT used in the above previous studies were estimated on the basis of the literature values. On the other hand, no information of the Young’s moduli of the composites and matrices has been given in the literatures. Thus, we estimated the Young’s modulus of the composites using the rule of mixtures. We substituted \( E_m = 0.85 \) MPa and \( E_t = 480 \) GPa in the Eq. (1) to estimate the Young’s modulus of the aligned MWCNT/PDMS composite prepared by Chen et al. These values have been reported in the literatures (Chen, et al., 2008, Yamamoto, et al., 2014). In the case of the actuators prepared by Seo, et al., CNTs were randomly oriented in the composite layers. Therefore, we estimated the upper and lower limits of the composite Young’s modulus using Eq. (1) and following Eq. (5), respectively (Hull and Cryne, 1996).

\[
E_s = \left[ \frac{V_f}{E_f} + \frac{(1-V_f)}{E_m} \right]^{-1}
\]

(5)

The Young’s moduli of the PDMS (\( \approx 0.85 \) MPa) and SWCNTs (\( \approx 1200 \) GPa) have been reported in the literatures (Tombler, et al., 2000, Chen, et al., 2008). As shown in Fig. 8, the actuator prepared in this study has higher values of power and work per unit volume compared to the CNT composite actuators (Chen, et al., 2011, Seo, et al., 2012) and IPMC actuators (Wang, et al., 2010, Cottinet, et al., 2011). This is mainly due to the high Young’s modulus of the actuator’s constituents and the large bending displacement of the actuator. Although the actuators prepared by Chen, et al. and Seo, et al. can produce a large bending displacement, the thick pure PDMS layer of the bimorph may limit its force output. On the other hand, the actuator prepared in this study showed the large bending displacement and high force output by using the aligned MWCNT reinforced epoxy composite and thin aluminum foil. The RAINBOW actuator (\( 7.0 \times 1.02 \times 40.0 \) mm (length × width × thickness)) has large power output per unit volume under the frequency of 250 Hz even though the bending displacement is in the range of 600 \( \mu \)m. This is mainly because the piezoelectric actuator provides the high force output at high operating frequency. On the other hand, it may provide the power output per unit volume comparable to that of the IPMC actuators with the frequency between 0.05 Hz and 2.5 Hz. In addition, the work output per unit volume is \( \leq 10^{-4} \) mJ/mm\(^3\), which is one order of magnitude lower than that of the actuator prepared in this study. The dimension of the electrothermal microactuators prepared by Boutchich, et al. and Yang, et al. had a size of 500-550 × 40-400 × 3.5 \( \mu \)m\(^3\) (length × width × thickness). Even though the dimension of the actuators prepared in this study is much larger compared to the actuators prepared by Boutchich, et al. and Yang, et al., it shows comparable or higher power and work output per unit volume under the frequency of 1.0 Hz. Furthermore, the applied voltage is 1-2 orders of magnitude smaller than that of the CNT composite electrothermal actuators (Chen, et al., 2011, Seo, et al., 2012) and the RAINBOW actuator (Wang, et al., 1999), which is almost identical to that of the IPMC actuators and electrothermal microactuator (Yang, et al., 2005, Wang, et al., 2010, Cottinet, et al., 2011). By
employing the microfabrication technology including photolithography, the dimension of the electrothermal actuator can be decreased to the microscale with a length of hundreds of micrometers. Thus the rate of heat dissipation as well as the frequency of the generated actuation can be greatly enhanced due to the enhancement of the large surface to volume ratio. In addition, it is expected that the applied voltage may be potentially reduced because of the decrease in the electrical resistance of the actuator. Further studies should be carried out to miniaturize the CNT composite actuator. In this study, we indicate contributions from three sources towards the increased bending displacement and force output in the actuator: (i) preparing the MWCNT/polymer composite having high Young’s modulus and negative CTE with the aid of aligned MWCNT monolithic sheet, (ii) choosing materials with high Young’s modulus and large CTE as the second layer of the laminate, and (iii) designing the dimensional parameters of the actuator.

4. Conclusions

Combining the aligned MWCNT reinforced polymer composite which has negative CTE in the MWCNT alignment direction with the aluminum foil, composite/aluminum bimorph affords unique opportunities for the development of novel electrothermal actuators. The bending displacement and force output of the actuator consisting of the composite containing 27 vol.% MWCNTs and thin aluminum foil with the free length of 16 mm reached 7.6 mm and 9.0 mN under a DC voltage of 5.2 V, respectively. Furthermore, the actuator fabricated in this study showed higher values of power and work output per unit volume compared to the actuators reported in previous studies with the frequency between 0.05 Hz and 0.5 Hz. This was mainly due to the high Young’s modulus of both composite and aluminum layers as well as the huge mismatch of the CTEs in the composite/aluminum bimorph. The Young’s modulus of the composites increased linearly with the increasing MWCNT volume fraction. The composite containing 27 vol.% MWCNTs gave the highest Young’s modulus and its value was 56.8 ± 3.9 GPa. In view of the significance of the Young’s modulus and thermal expansion mismatch in the actuators, further studies should be carried out to miniaturize the actuators, which results in reducing driving voltage and increasing the operating frequency. By developing CNT composite microactuators, a wide range of micro- and nanoscale applications can be envisioned where mechanical motion is needed at high displacement, high force, and high speed, such as micromanipulation, optomechanical and electromechanical switch and mirror, microfluidic valving and pumping, heat regulation, and artificial muscles.

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