

Fabrication and properties of aligned multiwalled carbon nanotube-reinforced epoxy composites

Qunfeng Cheng, Jiaping Wang,^{a)} Kaili Jiang, Qunqing Li, and Shoushan Fan
*Department of Physics and Tsinghua-Foxconn Nanotechnology Research Center,
Tsinghua University, Beijing 100084, People's Republic of China*

(Received 16 April 2008; accepted 25 July 2008)

A method to fabricate continuous and aligned multiwalled carbon nanotube (CNT)/epoxy composites is presented in this paper. CNT/epoxy composites were made by infiltrating an epoxy resin into a stack of continuous and aligned multiwalled CNT sheets that were drawn from super-aligned CNT arrays. By controlling the amount and alignment of the continuous multiwalled CNT sheets, a CNT/epoxy composite with high content of well-dispersed CNTs can be obtained. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) results show that the thermal stability of these CNT/epoxy composites was not affected by the addition of CNTs. The mechanical properties and electrical properties of the CNT/epoxy composites were dramatically improved compared to pure epoxy, suggesting that the CNT/epoxy composites can serve as multifunctional materials with combined mechanical and physical properties.

I. INTRODUCTION

Carbon nanotube (CNT)/epoxy composites have been widely investigated in the last decade since CNT/thermosetting resin composites were first fabricated by Ajayan et al. in 1994.¹ CNTs are considered to be the ideal reinforcing materials for making polymer composites due to their large specific surface area and aspect ratio, high tensile strength and Young's modulus,^{2,3} and superior thermal⁴ and electrical properties.⁵ However, the mechanical and physical properties of CNT polymer composites are much lower than the predicted values. For example, the tensile modulus of CNT/epoxy composites was only improved from 3.1 to 3.71 GPa with 5 wt% multiwalled nanotubes (MWNTs), corresponding to 20% improvement.⁶ The critical issues for achieving desirable properties of the CNT/polymer composites are to introduce a high content of CNTs with uniform dispersion and controlled alignment throughout the polymer matrix and improve CNT/epoxy interface properties.⁷

High-strength epoxy resins are commonly used polymers in the formation of CNT/polymer composites that can serve as multifunctional materials with light weight, high strength, and high electrical conductivity for many industrial applications, such as aircrafts and electronics products. Depending on the chemical compositions and

curing kinetics of the epoxy resins, it is possible to vary their mechanical properties such as Young's modulus, strength, and hardness, and physical properties such as thermal conductivity and electrical conductivity. Epoxy resins start in a liquid form to facilitate dispersion of CNTs. Afterward, the mixture of CNTs and epoxy resins is cured when a hardener or agent is added to form a solid-state CNT/epoxy composite. There are many methods to disperse CNTs in epoxy resins for preparing CNT/epoxy composites, such as blending,^{6,8-10} solution mixing,^{11,12} and buckypaper-based processing.^{13,14} Blending is a direct method to mix CNTs with epoxy resins by high shear forces or ultrasonication. The disadvantages of blending are that CNTs cannot be effectively dispersed in epoxy resins and CNT content is limited due to the high viscosities of the epoxy resins at higher CNT contents. Solution mixing is the most common method as it can facilitate better dispersion of CNT in epoxy resins. This method generally involves dispersion and mixing of CNTs and epoxy in a suitable solvent by mechanical stirring, magnetic agitation, or high-energy sonication, followed by controlled evaporation of the solvent. The dispersion of CNTs can be improved by adding surfactants or modifying CNTs by chemical functionalization.^{11,15,16} However, the chemical modification process may destroy the structure of the CNTs and decrease both the Young's modulus and tensile strength,¹⁷ and the distribution of CNTs in epoxy resins may become inhomogeneous during slow solvent evaporation. Besides the dispersion issue, the rapidly increasing viscosity of the

^{a)}Address all correspondence to this author.
e-mail: jpwang@tsinghua.edu.cn
DOI: 10.1557/JMR.2008.0356

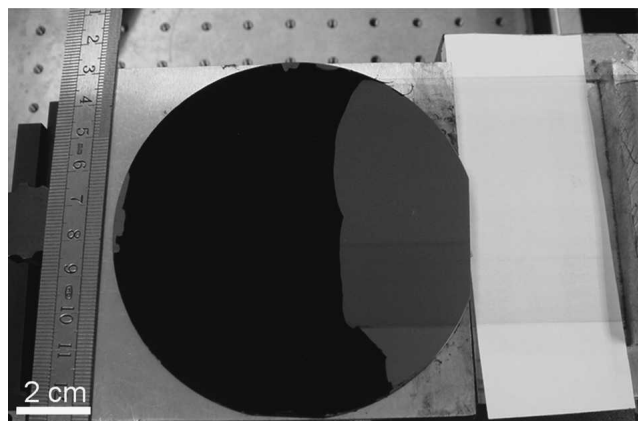
epoxy resin makes it difficult to achieve higher CNTs content in the composites. The buckypaper based processing is a new method to fabricate CNT/epoxy composites with a high content of single-walled CNTs,^{14,18} which involves the infiltration of an epoxy resin from solution into buckypaper membranes as a pre-existing CNT network. Buckypaper membranes were generally made through multistep dispersion and micro-filtration of a suspension of CNTs, which is time consuming. CNTs in the buckypaper membranes are randomly oriented, so the mechanical and physical properties of the CNT/epoxy composites might not be desirable.

CNT/epoxy composites fabricated by the methods mentioned above cannot yield significant improvements in composite performance because effective dispersion and controlled orientation of a high CNT content in the epoxy resin matrix cannot be achieved. In 2002, our group successfully fabricated super-aligned CNT arrays from which continuous CNT yarn or sheets can be directly drawn.^{19,20} These continuous and aligned CNT sheets can be stacked together to form a CNT preform for preparing CNT/polymer composites. Here we present a method for fabricating CNT/epoxy composites by infiltrating epoxy resins into a stack of continuous and aligned multiwalled CNT sheets to achieve homogeneous dispersion, controlled orientation, and high CNT content. The mechanical and electrical properties of the CNT/epoxy composites were investigated.

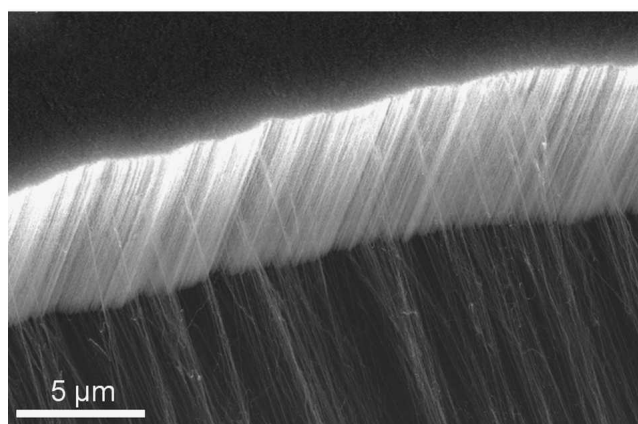
II. EXPERIMENTAL METHODS

Super-aligned multiwalled CNTs arrays were synthesized on a 4-in. silicon wafer in a low-pressure chemical vapor deposition (LPCVD) system by using Fe film as the catalyst and acetylene as the precursor.^{19,21} The height of the CNT arrays was around 300 μm . Continuous and aligned CNTs sheets were drawn from these super-aligned CNT arrays. Figure 1(a) shows the experimental setup for drawing a CNTs sheet from super-aligned CNT arrays on a silicon wafer. The super-aligned CNTs have very clean surfaces, and there are strong van der Waals forces among them. When pulling the CNTs from the super-aligned array, it is the van der Waals force that makes the CNTs join end to end, forming continuous and aligned CNTs sheets.²¹ Figure 1(b) is a scanning-electron-microscopy (SEM) image showing that continuous CNTs are drawn from super-aligned CNT arrays. Figures 1(c) is a SEM image of a continuous and aligned CNTs sheet. The width and thickness of the CNTs sheet were 10 cm and 0.2 μm , respectively.

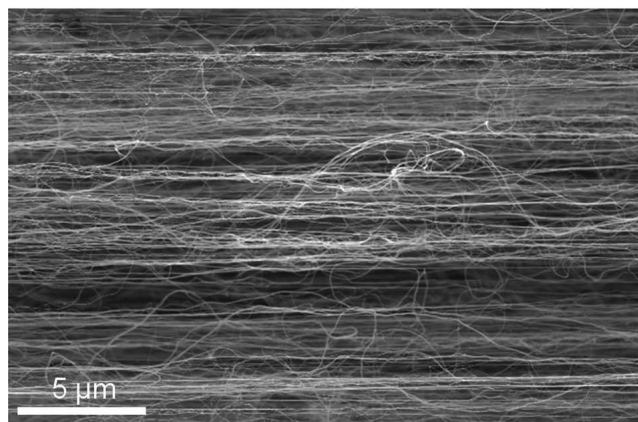
Three kinds of CNT preforms were made by loosely stacking 10, 100, and 1750 layers of such CNT sheets aligned in the same direction, and they are labeled as $[0^\circ]_{10}$, $[0^\circ]_{100}$, and $[0^\circ]_{1750}$ CNT preforms. For comparison, another CNT preform was made by stacking 1750



(a)



(b)



(c)

FIG. 1. Continuous and aligned multiwalled CNT sheet: (a) experimental setup for drawing a CNT sheet from super-aligned CNT arrays, (b) SEM image showing that CNTs are drawn from super-aligned CNT arrays, and (c) SEM image of a continuous and aligned CNT sheet.

CNT layers alternately in two perpendicular directions and was labeled as $[0^\circ/90^\circ]_{1750}$ CNT preform. CNT/epoxy composites were fabricated by infiltrating an epoxy resin into the CNT preforms using a vacuum-assisted resin infiltration (VARI) method, which requires low viscosity of the epoxy resin. In this study, an epoxy resin

(epoxy 3266, Beijing Institute of Aeronautical Materials, China²²) consisting of two standard epoxy resins, glycidyl ester (A), and resorcinol diglycidyl ethers (B), was used as the matrix. MHHPA (Hexahydrophthalic Anhydride) was used as the curing agent (C). The epoxy resins and the curing agent were mixed at a weight ratio of A:B:C = 50:50:100. At the infiltration temperature (60 °C), the viscosity of this epoxy system can be kept at as low as 50 cPa s for more than 12 h. Some of the mechanical and physical properties of the epoxy 3266 are listed in Table I.

The schematic of the VARI process is shown in Fig. 2. First, a glass mold was coated with a thin layer of releasing agent and the CNT preform was inserted and pressed in the glass mold [Fig. 2(a)]. The thickness of the glass mold can be controlled by inserting steel strips with various thicknesses between two glass panels. Then the epoxy resin was injected into the glass mold to overflow and fully infiltrate the CNTs preform at 60 °C in a vacuum oven [Fig. 2(b)]. The vacuum level was around 0.1 Pa to facilitate better infiltration of the epoxy resin into the CNT preform and to remove air bubbles in the CNT/epoxy sample [Fig. 2(c)]. The temperature of the oven was increased to 120 °C at a rate of 2 °C/min and held at 120 °C for 12 h to cure the CNT/epoxy, forming a solid state composite [Fig. 2(d)]. Afterward, the glass mold was cooled down to room temperature and the CNT/epoxy composite was released from the mold. In this study, five kinds of epoxy and CNT/epoxy composites were fabricated by the VARI process, and they are listed in Table II.

The CNT contents and the thermal stability of the CNT/epoxy composites were evaluated using a thermogravimetric analyzer (TGA, Netzsch STA 409C, Selb, Germany). Specimens were heated from 50 to 950 °C at a rate of 20 °C/min in flowing nitrogen. The glass transition temperatures (T_g) of the CNT/epoxy composites were measured using a differential scanning calorimeter (DSC, TA Instruments Q2000, New Castle, DE). Specimens were heated from 25 °C to 200 °C at a rate of 10 °C/min in flowing nitrogen.

Tensile test samples were cut from the CNT/epoxy composite sheets with dimensions of 40 mm (length) × 5 mm (width) × 0.3 mm (thickness) and tested in tension at room temperature using a Zwick/Roell 2005 testing

machine (Ulm, Germany) at a crosshead speed of 2.0 mm/min. The gauge length was chosen at 20 mm. For the $[0^\circ]_{10}$ and $[0^\circ]_{100}$ CNT/epoxy composites, the samples were cut in a way that the CNT alignment was parallel to the length direction and the axis of the tensile loading. For the $[0^\circ]_{1750}$ CNT/epoxy composite, the samples were prepared in a way that the CNT alignment was either parallel or perpendicular to the length direction and the axis of the tensile loading. In the $[0^\circ/90^\circ]_{1750}$ CNT/epoxy composite sample, the alignment of half of the CNT sheets was parallel to the axis of the tensile loading, and the alignment of the other half of the CNT sheets was perpendicular to the axis of the tensile loading. CNT yarns that were pulled from super-aligned CNT arrays²¹ were also tested in tension for comparison.

After tensile tests, the specimens were cleaned in an ultrasonic bath and dried for 4 h at 60 °C in vacuum. Fracture surfaces of the tensile specimens were coated with a 20 nm thick gold layer and observed using a scanning electron microscope (SEM; Tecnai 20 G2 S-TWIN, FEI, Hillsboro, OR), to understand the failure mechanism.

The electrical properties of the CNT/epoxy composites were characterized by a two-point method using a source meter (Keithley 237, Cleveland, OH). Silver paste was applied on two ends of the CNT/epoxy samples to ensure good electrical contact between the sample and two electrodes. The electrical conductivities of the CNT/epoxy composites in directions parallel and perpendicular to the CNT alignment were measured.

III. RESULTS AND DISCUSSION

A. Thermal characterizations

TGA curves for pure epoxy, $[0^\circ]_{10}$ CNT/epoxy, $[0^\circ]_{100}$ CNT/epoxy, and $[0^\circ]_{1750}$ CNT/epoxy composites with different CNTs contents are shown in Fig. 3(a), and the initial and final decomposition temperatures of the CNT/epoxy composites can be obtained. All specimens started to decompose around 375 °C and completed decomposition around 430 °C. The residual mass of the pure epoxy sample is about 8.53 wt% at 950 °C. The residual masses of the CNT/epoxy composites with 10, 100, and 1750 CNT sheets are approximately 9.16, 9.49, and 15.97 wt%, respectively. CNTs are thermally stable in nitrogen gas environment below 1000 °C; thus the CNTs contents in composite specimens with 10, 100, and 1750 CNT sheets are calculated to be 0.69, 1.05, and 8.13 wt%, respectively. Alternatively the CNT contents can be calculated based on the dimensions and weights of the CNT preform and the CNT/epoxy composites, and the results were similar to those obtained by the TGA measurements. DSC curves of these specimens are shown in Fig. 3(b), and their glass transition temperatures are around 102–103 °C. Both the decomposition

TABLE I. Physical and mechanical properties of epoxy 3266.

Properties	Epoxy 3266
Density (g/cm ³)	1.2
Electrical conductivity (S/m)	10 ⁻¹²
Tensile strength (MPa)	89
Young's modulus (GPa)	2.5
Flexural strength (MPa)	151
Flexural modulus (GPa)	3.8

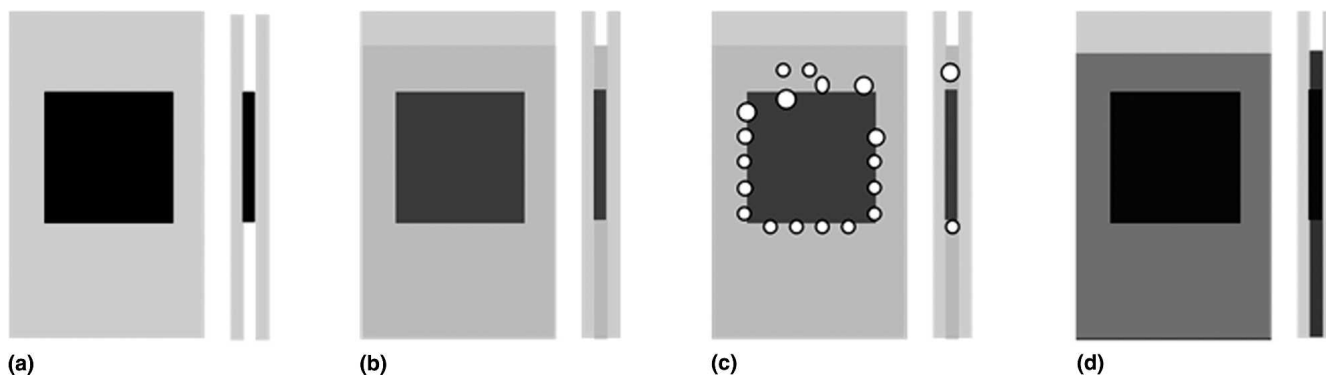


FIG. 2. Schematic illustration of the VARI process: (a) CNT preform was inserted and pressed in a glass mold; (b) epoxy resin was injected into the glass mold to infiltrate the CNTs preform; (c) air bubbles in the CNT/epoxy sample were removed in vacuum; and (d) CNT/epoxy composite was cured at 120 °C to form a solid state composite.

TABLE II. Epoxy and CNT/epoxy composite specimens fabricated in this study.

Specimen Number	Description
1	Pure epoxy 3266
2	[0°] ₁₀ CNT sheets/epoxy composite
3	[0°] ₁₀₀ CNT sheets/epoxy composite
4	[0°] ₁₇₅₀ CNT sheets/epoxy composite
5	[0°/90°] ₁₇₅₀ CNT sheets/epoxy composite

temperatures and the glass transition temperatures remain almost constant for these specimens with various CNT contents showing that the incorporation of CNTs into epoxy 3266 does not dramatically affect the cross-linked density and thermal stability of the epoxy.

B. Microstructure and mechanical characterizations

Tensile stress–strain curves for pure epoxy, CNT yarn, and CNT/epoxy composites are shown in Fig. 4(a), and the Young's modulus and tensile strength of these specimens are shown in Figs. 4(b) and 4(c). It can be seen in Fig. 4(a) that the CNT yarn showed a much higher Young's modulus and tensile strength and limited plasticity compared to the epoxy matrix. As the CNT content increased, both the Young's modulus and tensile strength increased, but the plasticity decreased. The Young's modulus of pure epoxy and CNT are 2.50 and 40 GPa, respectively. Comparatively, the Young's modulus of the [0°]₁₀CNT/epoxy, [0°]₁₀₀CNT/epoxy, and [0°]₁₇₅₀CNT/epoxy composites with 0.69, 1.05, and 8.13 wt% CNT contents that were tensile tested in the direction parallel to the CNT alignment increased to 2.51, 3.10, and 11.2 GPa, respectively, corresponding to 0.4%, 24%, and 347% improvement. The effect of CNT content on tensile strength follows the same trend with Young's modulus. The tensile strength increased from 89 MPa for the pure epoxy to 130 MPa for the [0°]₁₇₅₀CNT/epoxy composite with 8.13 wt% CNTs content, corresponding to

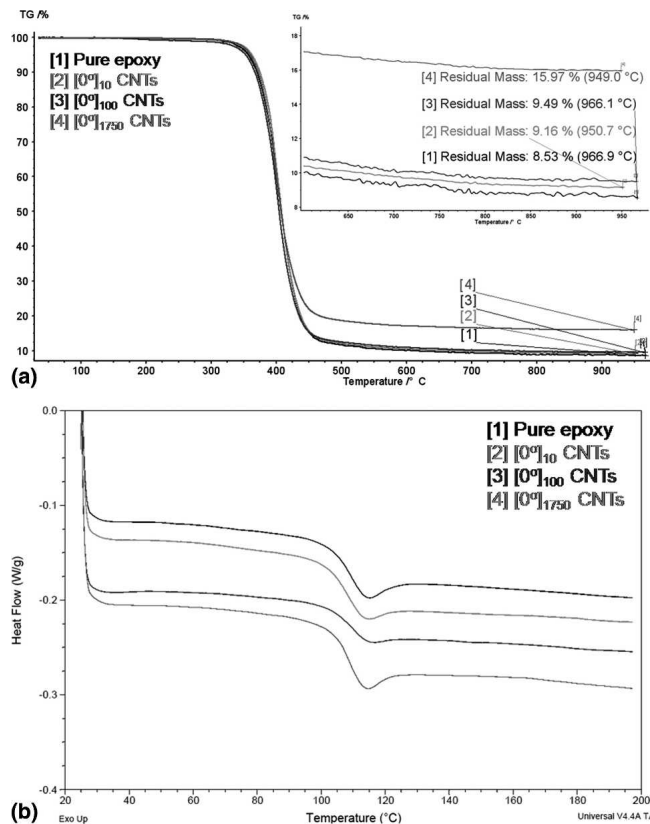


FIG. 3. (a) TGA curves of the CNT/epoxy composites with various CNTs contents measured at a heating rate of 20 °C min⁻¹ in nitrogen. (b) DSC curves of the CNT/epoxy composites with various CNTs contents measured at a heating rate of 10 °C min⁻¹ in nitrogen.

45% improvement. The improvement of tensile strength was not as significant as that of Young's modulus, which might be due to any large defects presented in the sample to decrease the strength values.

In these CNT/epoxy composites, the CNTs were continuous and aligned along the same direction. When the composites were loaded in the direction of the CNT alignment direction, the elastic modulus and strength of

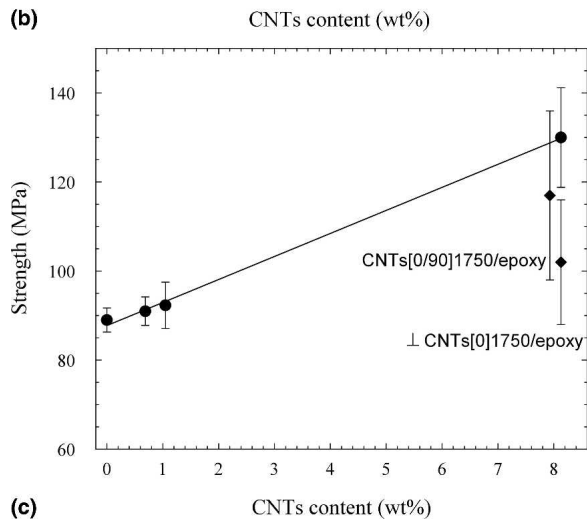
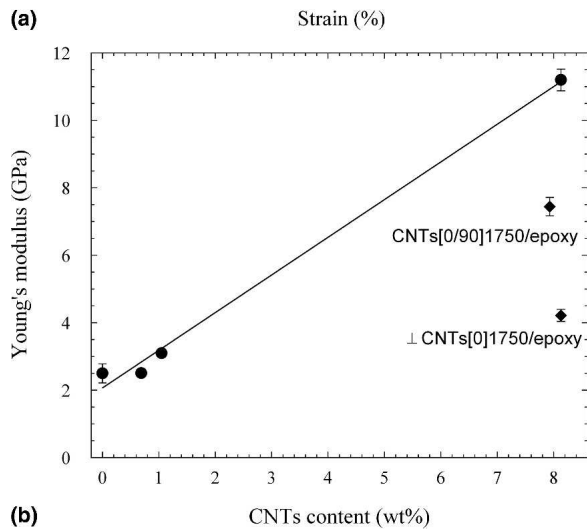
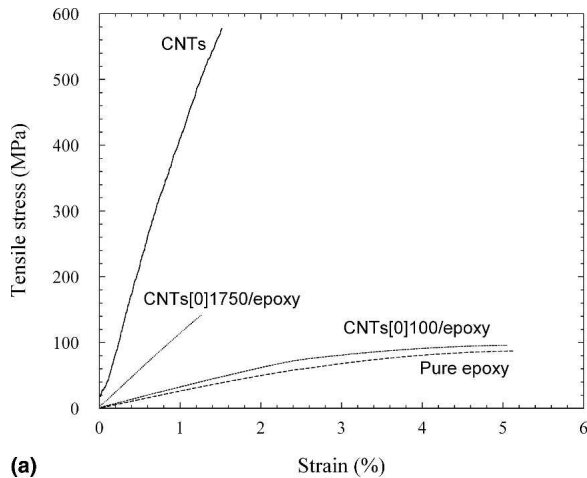


FIG. 4. Mechanical properties of the CNT/epoxy composites: (a) stress–strain curves of CNTs, pure epoxy, and CNT/epoxy composites with different CNT contents, (b) Young’s modulus as a function of the CNTs content, and (c) tensile strength as a function of the CNT content.

the composites, E_c and σ_c , can be expressed using the rule of mixture²³:

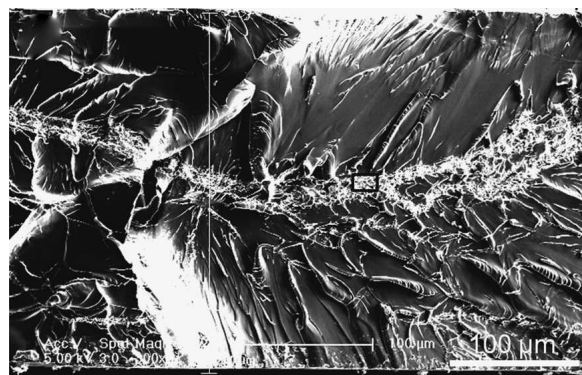
$$E_c = V_{\text{CNTs}}E_{\text{CNTs}} + E_{\text{epoxy}}(1 - V_{\text{CNTs}}) \quad , \quad (1)$$

$$\sigma_c = V_{\text{CNTs}}\sigma_{\text{CNTs}} + \sigma_{\text{epoxy}}(1 - V_{\text{CNTs}}) \quad , \quad (2)$$

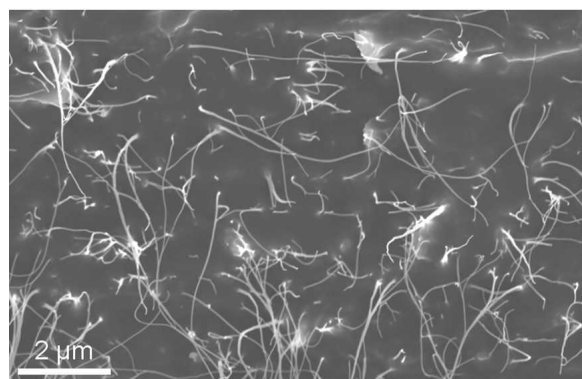
where E_{CNTs} and E_{epoxy} are Young’s modulus of CNTs and epoxy, σ_{CNTs} and σ_{epoxy} are strength of CNTs and epoxy, and V_{CNTs} is the volume content of CNTs. Given the densities of CNTs and epoxy as 2.01 and 1.2 g/cm³, volume percents of CNTs in the composites can be calculated from the weight percent data. By performing linear fits for data shown in Figs. 4(b) and 4(c), we can calculate that E_{CNTs} and σ_{CNTs} are 176 GPa and 746 MPa, respectively, which were higher than the measurement data for the CNT fibers at 40 GPa and 643 MPa. In particular there was a relatively large deviation on the Young’s modulus of the CNT fibers, and this will be further investigated.

In Figs. 4(b) and 4(c), we also plotted the Young’s modulus and tensile strength of the [0°/90°]₁₇₅₀CNT/epoxy composite with 7.93 wt% CNT, where only half of the CNT sheets were aligned along the axis of the tensile loading. The Young’s modulus and tensile strength of this sample were 7.45 GPa and 117 MPa, which were smaller than those of the [0°]₁₇₅₀CNT/epoxy composite, due to their different alignments. The Young’s modulus and strength of the [0°]₁₇₅₀CNT/epoxy composite that was tested in the direction perpendicular to the CNT alignment showed even lower values at 4.22 GPa and 102 MPa. In this sample, CNT sheets were aligned perpendicular to the tensile loading, and only a limited number of entangled CNTs might align parallel to the tensile loading, resulting in very low values of Young’s modulus and tensile strength.

Fracture surfaces of the [0°]₁₀₀CNT/epoxy composite with 0.69 wt% CNT content are shown in Fig. 5. The CNT preform was locally distributed in the composite. The thickness of the CNT/epoxy composite region was around 15 μm, which was much smaller compared to the thickness of the specimen at 300 μm [Fig. 5(a)]. In the CNT/epoxy composite region, CNTs were homogeneously dispersed in the epoxy matrix [Fig. 5(b)]. Most parts of the sample were pure epoxy and showed features of brittle fracture. CNTs were either broken or pulled out from the epoxy matrix during tensile testing. Even though the CNTs were not chemically functionalized, the liquid epoxy wetted the CNT preform very well during epoxy infiltration, and there was good adhesion between the CNTs and the epoxy matrix. As a result, the extruding CNTs were coated with epoxy resin with diameters larger than the original CNTs (not shown). Fracture surfaces of the [0°]₁₀₀CNT/epoxy composite with 1.05 wt% CNTs content are shown in Fig. 6. The CNT preform was also locally distributed in the composite [Fig. 6(a)]. About one third of the volume (100 μm thick) contained the CNT/epoxy composite, and the remaining parts were pure epoxy. In the CNT/epoxy composite region, there was good dispersion of CNTs in the epoxy matrix [Fig. 6(b)], and the amount of CNTs was clearly higher than the previous sample with lower overall CNT content [Fig. 5(b)].



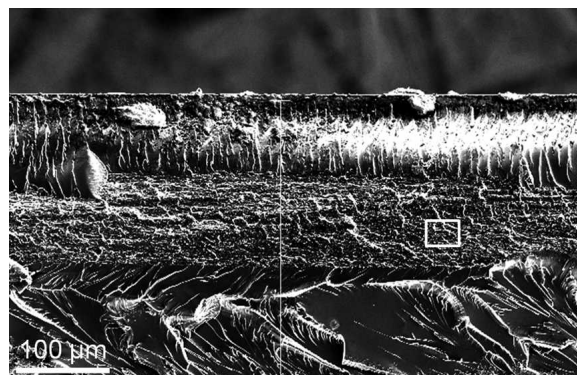
(a)



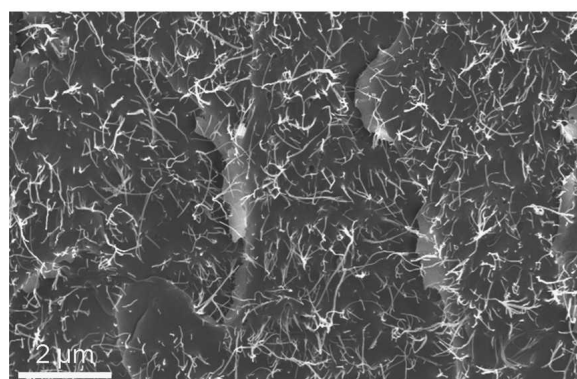
(b)

FIG. 5. SEM images of fracture surfaces of a CNT/epoxy composite with 0.69 wt% CNTs after tensile testing: (a) at low magnification and (b) at high magnification.

It can be seen from Figs. 5(a) and 6(a), due to the limited number of CNT sheets and thus the limited thickness of the CNT preforms, both samples showed an epoxy layer–CNT/epoxy composite layer–epoxy layer structure. To achieve homogenous dispersion of CNTs in the whole sample, a much thicker CNT preform with 1750 aligned CNT sheets was used to make a CNT/epoxy composite with higher CNT loading. SEM images of fracture surfaces of the $[0^\circ]_{1750}$ CNT/epoxy composite are shown in Fig. 7. Most parts of the sample are CNT/epoxy composite regions [Fig. 7(a)]. Some thin epoxy layers were still observed due to the structure of the CNT preform. For this sample, the thick CNT preform was made by stacking several thinner CNT preforms together so that there might be several relatively large gaps among separate CNT preforms, and pure epoxy layers were formed in these regions. This problem can be overcome by directly stacking many CNT sheets together to form a single thick CNT preform. In the CNT/epoxy composite regions, CNTs were homogeneously dispersed in the epoxy matrix [Fig. 7(b)], and the amount of CNTs in these regions was much larger than that in previous samples with lower overall CNT contents [Figs. 5(b) and 6(b)]. Fracture surfaces of this sample were much rougher than that of the pure epoxy sample. The increased surface



(a)

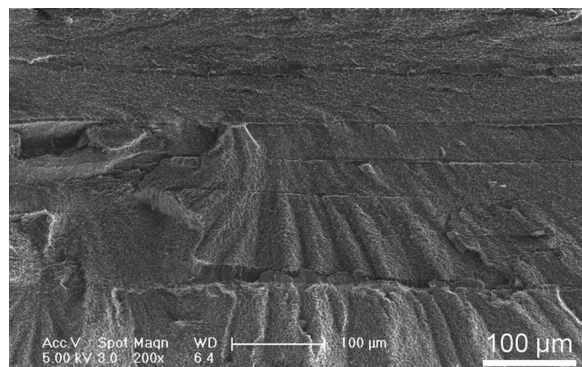


(b)

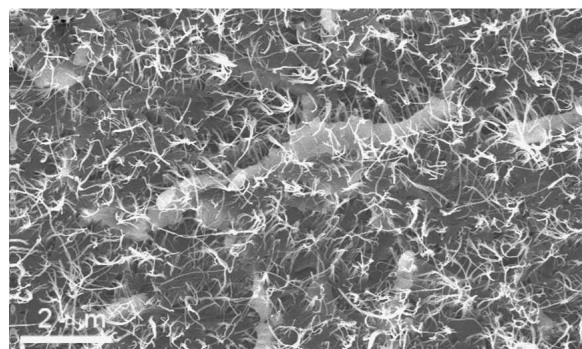
FIG. 6. SEM images of fracture surfaces of a CNT/epoxy composite with 1.05 wt% CNTs after tensile testing: (a) at low magnification and (b) at high magnification.

roughness implies that the path of the crack front deviated when it interacted with CNTs, thus absorbing more energy and making crack propagation more difficult. Figure 8 shows a fracture surface of the $[0^\circ]_{1750}$ CNT/epoxy composite that was fractured in the direction parallel to the CNT alignment, showing that fracture occurred at either the epoxy matrix or the interface between CNTs and the epoxy matrix. Fracture of CNTs was rarely observed. This was in agreement with the relatively low-strength data of this sample. Fracture surface of the $[0^\circ/90^\circ]_{1750}$ CNT/epoxy composite showed a combination of fracture of epoxy matrix, CNT/epoxy interface, and CNTs (not shown), resulting in a moderate strength value.

Some Young's modulus and storage modulus data of CNT-reinforced epoxy composites reported in literature and our experimental results are shown in Table III. In general, the Young's modulus of CNT/epoxy composites increased with increasing CNT content. Homogeneous dispersion and better alignment of CNTs in the epoxy matrix can result in further improvement on the Young's modulus.⁷ The Young's modulus data of the CNT/epoxy composites fabricated by direct blending and solution mixing methods showed only a moderate enhancement



(a)



(b)

FIG. 7. SEM images of fracture surfaces of a CNT/epoxy composite with 8.13 wt% CNTs after tensile testing: (a) at low magnification and (b) at high magnification.

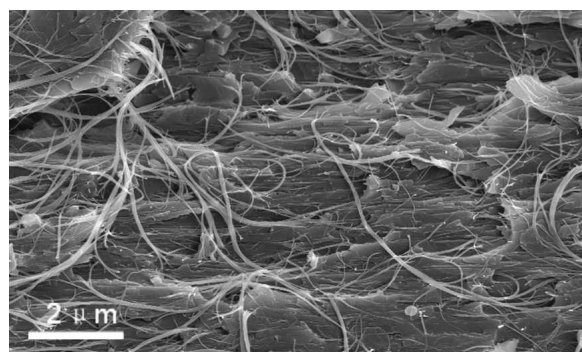


FIG. 8. SEM image of fracture surface of a CNT/epoxy composite with 8.13 wt% CNTs that was fractured in the direction parallel to the CNT alignment.

compared to pure epoxy. The CNT content can be dramatically improved in the CNT/epoxy composites prepared by the buckypaper method, and the storage modulus of the CNT/epoxy composites increased significantly compared to pure epoxy. However, the CNTs in the buckypaper membranes were randomly oriented and the effective reinforcement was still low compared to the continuous and aligned CNT/epoxy composites fabricated by the VARI method in this study. The storage modulus of the CNT/epoxy composite with 28.1 wt%

randomly oriented SWNTs made by the buckypaper-based method increased to 11.45 GPa, corresponding to 349% improvement. In this study the same level of reinforcement (347% improvement on Young's modulus) can be achieved with only 8.13 wt% continuous and aligned CNTs, which is three times more effective. The good alignment of the continuous CNTs together with homogeneous dispersion in the epoxy matrix played a key role in the mechanical reinforcement. In addition, the successful removal of air bubbles using the VARI process eliminated microvoids in the CNT/epoxy composites and contributed to the high modulus values.

C. Electrical characterizations

The electrical conductivities of pure epoxy, $[0^\circ]_{10}$ CNT/epoxy, $[0^\circ]_{100}$ CNT/epoxy, and $[0^\circ]_{1750}$ CNT/epoxy composites in the directions parallel to the CNT alignment are shown in Fig. 9. The electrical conductivity of pure epoxy was as low as 10^{-12} S/m. The continuous and aligned CNT sheets were used as the conductive medium with excellent electrical conductivity at 4.5×10^4 S/m. The electrical conductivity dramatically increased with increasing CNT content. As the CNT content increased to 8.13 wt%, the electrical conductivities increased to 4220 S/m. The electrical conductivities of the $[0^\circ/90^\circ]_{1750}$ CNT/epoxy composite with a similar CNT content was only 2205 S/m, since in this sample only half of the CNT sheets were aligned along the measurement direction. The electrical conductivity of the $[0^\circ]_{1750}$ CNT/epoxy composite in the direction perpendicular to the CNT alignment was as low as 833 S/m, with only some entangled CNTs contributing to the electrical conductivity. In previous reports,^{12,24–26} the electrical conductivities of CNT/epoxy composites were generally below 5 S/m, as shown in Table IV, due to the randomly oriented CNT network with limited CNT content in the composites. In our study, the CNT/epoxy composites made by the VARI process contained high CNT content, and the continuous and well-aligned CNTs were uniformly dispersed in most parts of the composites. Therefore, the improvement of the electrical conductivity is much more significant compared to that reported in previous studies.

The continuous and aligned CNT/epoxy composites with high CNT content fabricated by the VARI process remain thermally stable and show improved mechanical properties and electrical properties. This fabrication method can be further generalized so that CNT sheets can be aligned in different directions in the CNT preforms, thus providing more opportunities to design better composites. Therefore, they are suitable for a variety of applications, especially in the aerospace industry, that require a combination of improved mechanical and physical properties, such as electrostatic dissipation and electromagnetic interference shielding.

TABLE III. Modulus of CNT/epoxy resin composites.

Approaches	CNTs content (wt%)	Modulus <i>E</i> (GPa)	Refs.
Blending with ultrasonic	MWNTs	Young's modulus	6
	pure epoxy	3.1	
Blending with ultrasonic	5 wt%	3.71	8
	MWNTs	Young's modulus	
	pure epoxy	3.13	
Solution mixing	6 wt%	4.13	11
	Pure epoxy	2.03	
	SWNT: 1 wt%	2.12	
	Functionalized SWNT: 1 wt%	2.65	
Buckypaper impregnation	SWNT	Storage modulus (DMA)	14
	Pure epoxy	2.55	
	28.1 wt%	11.45	
	31.3 wt%	15.10	
	37.7 wt%	13.49	
	39.1 wt%	13.24	
VARI	Continuous and aligned CNT sheets	Young's modulus	This study
	Pure epoxy	2.50	
	0.69 wt%	2.51	
	1.05 wt%	3.09	
	8.13 wt%	11.17	

DMA, dynamic mechanical analysis.

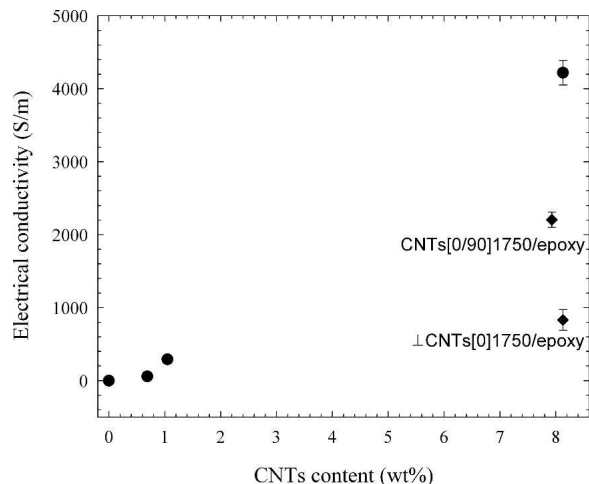


FIG. 9. Electrical conductivities of CNT/epoxy composites as a function of the CNT content.

IV. CONCLUSIONS

In this study, continuous and aligned CNT/epoxy composites with uniform dispersion and high content of CNTs were successfully fabricated by a vacuum-assisted resin infiltration (VARI) process, which involved infiltrating a preformed continuous and aligned CNT network with an epoxy resin, removing air bubbles in vacuum, and curing the epoxy at high temperatures. This method can also be extended to other suitable thermosetting resins, such as bismaleimide (BMI), cyanate ester (CE), and so on. DSC and TGA results indicated that the thermal

TABLE IV. Electrical conductivity of CNT/epoxy resin composites.

Type of CNTs	CNTs content (wt%)	Electrical conductivity σ (S/m)	Refs.
SWNT	0.1–0.5	<0.1	24
MWNT	0.1–0.5	<0.1	25
SWNT	0.1–0.5	<1	
MWNT	0.1–0.5	<1	26
MWNT	1	0.1	
Continuous and aligned CNTs	0.69	57	This study
	1.05	291	
	8.13	4220	

stability of the epoxy composites was not affected by the addition of the CNTs. Both the Young's modulus and tensile strength of the CNT/epoxy composites increased with increasing CNT content. The Young's modulus and the tensile strength of the CNT/epoxy composite with 8.13 wt% of CNTs were improved by 347% and 45%, respectively, compared to the pure epoxy. The electrical conductivity of the CNT/epoxy composites was dramatically improved by the incorporation of the continuous and aligned CNT preform as a conductive network. The electrical conductivities of the CNT/epoxy composite with 8.13 wt% CNTs reached 4220 S/m in the direction parallel to the CNT alignment, while the electrical property of pure epoxy is only 10^{-12} S/m. With combined mechanical and physical properties, continuous and aligned CNT/epoxy composites have broad applications that require multifunctional properties of materials.

ACKNOWLEDGMENT

This work was supported by the National Basic Research Program of China (2005CB623606 and 2007CB935301).

REFERENCES

1. P.M. Ajayan, O. Stephan, C. Colliex, and D. Trauth: Aligned carbon nanotube arrays formed by cutting a polymer resin-nanotube composite. *Science* **265**, 1212 (1994).
2. R. Bacon: Growth, structure, and properties of graphite whiskers. *J. Appl. Phys.* **31**, 283 (1960).
3. M.F. Yu, O. Lourie, M.J. Dyer, K. Moloni, T.F. Kelly, and R.S. Ruoff: Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. *Science* **287**, 637 (2000).
4. H. Huang, C.H. Liu, Y. Wu, and S.S. Fan: Aligned carbon nanotube composite films for thermal management. *Adv. Mater.* **17**, 1652 (2005).
5. E.T. Thostenson and T.W. Chou: On the elastic properties of carbon nanotube-based composites: Modelling and characterization. *J. Phys. D: Appl. Phys.* **36**, 573 (2003).
6. L.S. Schadler, S.C. Giannaris, and P.M. Ajayan: Load transfer in carbon nanotube epoxy composites. *Appl. Phys. Lett.* **73**, 3842 (1998).
7. M. Moniruzzaman and K.I. Winey: Polymer nanocomposites containing carbon nanotubes. *Macromolecules* **39**, 5194 (2006).
8. Y. Breton, G. Desarmot, J.P. Salvetat, S. Delpeux, C. Sinturel, F. Beguin, and S. Bonnamy: Mechanical properties of multiwall carbon nanotubes/epoxy composites: Influence of network morphology. *Carbon* **42**, 1027 (2004).
9. F.H. Gojny, M.H.G. Wichmann, U. Kopke, B. Fiedler, and K. Schulte: Carbon nanotube-reinforced epoxy-compo sites: Enhanced stiffness and fracture toughness at low nanotube content. *Compos. Sci. Technol.* **64**, 2363 (2004).
10. F.H. Gojny, M.H.G. Wichmann, B. Fiedler, and K. Schulte: Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites—A comparative study. *Compos. Sci. Technol.* **65**, 2300 (2005).
11. J. Zhu, H.Q. Peng, F. Rodriguez-Macias, J.L. Margrave, V.N. Khabashesku, A.M. Imam, K. Lozano, and E.V. Barrera: Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes. *Adv. Funct. Mater.* **14**, 643 (2004).
12. J. Sandler, M.S.P. Shaffer, T. Prasse, W. Bauhofer, K. Schulte, and A.H. Windle: Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. *Polym.* **40**, 5967 (1999).
13. M.F. Islam, E. Rojas, D.M. Bergey, A.T. Johnson, and A.G. Yodh: High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. *Nano Lett.* **3**, 269 (2003).
14. Z. Wang, Z.Y. Liang, B. Wang, C. Zhang, and L. Kramer: Processing and property investigation of single-walled carbon nanotube (SWNT) buckypaper/epoxy resin matrix nanocomposites. *Composites Part A* **35**, 1225 (2004).
15. J. Chen, M.A. Hamon, H. Hu, Y.S. Chen, A.M. Rao, P.C. Eklund, and R.C. Haddon: Solution properties of single-walled carbon nanotubes. *Science* **282**, 95 (1998).
16. E.T. Mickelson, C.B. Huffman, A.G. Rinzler, R.E. Smalley, R.H. Hauge, and J.L. Margrave: Fluorination of single-wall carbon nanotubes. *Chem. Phys. Lett.* **296**, 188 (1998).
17. A. Garg and S.B. Sinnott: Effect of chemical functionalization on the mechanical properties of carbon nanotubes. *Chem. Phys. Lett.* **295**, 273 (1998).
18. A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund, and R.E. Smalley: Large-scale purification of single-wall carbon nanotubes: Process, product, and characterization. *Appl. Phys. A* **67**, 29 (1998).
19. K.L. Jiang, Q.Q. Li, and S.S. Fan: Nanotechnology: Spinning continuous carbon nanotube yarns—Carbon nanotubes weave their way into a range of imaginative macroscopic applications. *Nature* **419**, 801 (2002).
20. K. Liu, Y.H. Sun, L. Chen, C. Feng, X.F. Feng, K.L. Jiang, Y.G. Zhao, and S.S. Fan: Controlled growth of super-aligned carbon nanotube arrays for spinning continuous unidirectional sheets with tunable physical properties. *Nano Lett.* **8**, 700 (2008).
21. X.B. Zhang, K.L. Jiang, C. Teng, P. Liu, L. Zhang, J. Kong, T.H. Zhang, Q.Q. Li, and S.S. Fan: Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays. *Adv. Mater.* **18**, 1505 (2006).
22. L. Wei, Y.H. Xu, X.S. Yi, and X.F. An: Preliminary study on resin-transfer molding of highly-toughened graphite laminates by ex-situ method. *J. Mater. Sci.* **39**, 2263 (2004).
23. D. Hull and T.W. Clyne: *An Introduction to Composite Materials* (Cambridge University Press, Cambridge, UK, 1981).
24. F.H. Gojny, M.H.G. Wichmann, B. Fiedler, I.A. Kinloch, W. Bauhofer, A.H. Windle, and K. Schulte: Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. *Polym.* **47**, 2036 (2006).
25. A. Moisala, Q. Li, I.A. Kinloch, and A.H. Windle: Thermal and electrical conductivity of single- and multiwalled carbon nanotube-epoxy composites. *Compos. Sci. Technol.* **66**, 1285 (2006).
26. A. Allaoui, S. Bai, H.M. Cheng, and J.B. Bai: Mechanical and electrical properties of a MWNT/epoxy composite. *Compos. Sci. Technol.* **62**, 1993 (2002).