Carbon nanotube/epoxy composites fabricated by resin transfer molding

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ABSTRACT

Carbon nanotube (CNT)/epoxy composites with controllable alignment of CNTs were fabricated by a resin transfer molding process. CNTs with loading up to 16.5 wt.% were homogenously dispersed and highly aligned in the epoxy matrix. Both mechanical and electrical properties of the CNT/epoxy composites were dramatically improved with the addition of the CNTs. The Young's modulus and tensile strength of the composites reach 20.4 GPa and 231.5 MPa, corresponding to 716% and 160% improvement compared to pure epoxy. The electrical conductivity of the composites along the direction of the CNT alignment reaches over 1×10^4 S/m.

1. Introduction

As one of the most promising composite materials, CNT/epoxy composites need to be fabricated on a large scale and have excellent properties such as mechanical and physical properties for practical applications. Until now the fabrication methods for CNT/polymer composites are mainly limited at the lab manufacturing level, such as solution mixture, mechanical mixture, and buckypaper, CNT yarn, and CNT array impregnation [1–8]. Limitations of these methods include poor dispersion, low loading, and uncontrolled orientation of CNTs in the epoxy matrix. Both mechanical and physical properties of CNT/epoxy composites are much lower than expected.

We developed a method to form continuous CNT yarns or sheets by directly drawing CNTs from super-aligned CNT arrays [9–11]. These continuous and aligned CNT sheets can be stacked together to make a CNT preform with thickness on a centimeter scale. Thus it is possible to macroscopically fabricate CNT/epoxy composites using methods that were suitable for making carbon fiber reinforced composites such as resin transfer molding (RTM) [12]. RTM involves placing a textile preform into a mold, injecting the mold with a liquid resin at low injection pressure, and curing the resin to form a solid composite. RTM is a simple process that can make composites with large sizes and complex shapes within short cycle time and at low cost and can be applied to many kinds of low-viscosity thermosetting polymers.

In this study, CNT preforms with macroscopic sizes were made by stacking aligned and continuous CNT sheets drawn from super-aligned CNT arrays. CNT/epoxy composites were fabricated using a RTM process and their microstructure, mechanical, and electrical properties were investigated.

2. Experimental

2.1. Fabrication of the CNT/epoxy composites

Super-aligned multi-walled carbon nanotube (MWCNT) arrays were synthesized on a 4 in. silicon wafer in a low pressure chemical vapor deposition (LPCVD) system with iron as the catalyst and acetylene as the precursor [9–11]. CNTs were drawn from super-aligned arrays and joined end to end by van der Waals force to form a continuous and aligned CNT

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sheet. CNT sheets were stacked together at different orientations to make a CNT preform. Fig. 1a shows the schematic and scanning electron microscopy (SEM) images of stacking CNT sheets in the same direction [0] and in two perpendicular directions alternatively [0/90]. Three kinds of CNT preforms were fabricated for comparison. The samples containing 2000 and 4000 CNT sheets that were stacked in the same direction were labeled as $[0]_{2000}$ and $[0]_{4000}$, respectively. The sample containing 2000 CNT sheets that were stacked alternatively in two perpendicular directions was labeled as $[0/90]_{2000}$.

Fig. 1b shows the schematic of the RTM process for fabricating aligned CNT/epoxy composites. A CNT preform was inserted into the RTM mold. The thickness of the CNT/epoxy composites can be controlled by inserting steel strips with various thicknesses between two parts of the RTM mold. Epoxy 3266 (Beijing Institute of Aeronautical Materials, China) consists of two standard epoxy resins, glycidyl ester (A), and resorcinol diglycidyl ethers (B). 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. Typical physical and mechanical properties of epoxy 3266 were listed in a previous paper [13]. 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. Liquid epoxy resin was injected into the sealed RTM mold at a pressure of 0.2 MPa to overflow and fully infiltrate the CNT preform at 60 °C in a vacuum oven. Afterwards 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 epoxy, forming a solid state aligned CNT/epoxy composite. The RTM mold was then cooled down to room temperature and the CNT/epoxy composite sample was released from the RTM mold.

CNT concentrations in composites $[0]_{2000}$, $[0/90]_{2000}$, and $[0]_{4000}$ were determined by measuring the weights of the CNT preforms and the CNT/epoxy composites. Quality of the CNT/epoxy composite panel was checked by ultrasonic nondestructive imaging. The size and shape of the CNT/epoxy composites can vary by using different CNT preforms and RTM molds.

2.2. Characterization of microstructure and mechanical properties

Tensile test samples were cut from the CNT/epoxy composite panels 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). The crosshead speed and the gauge length were 2.0 mm/min and 20 mm, respectively. For CNT/epoxy
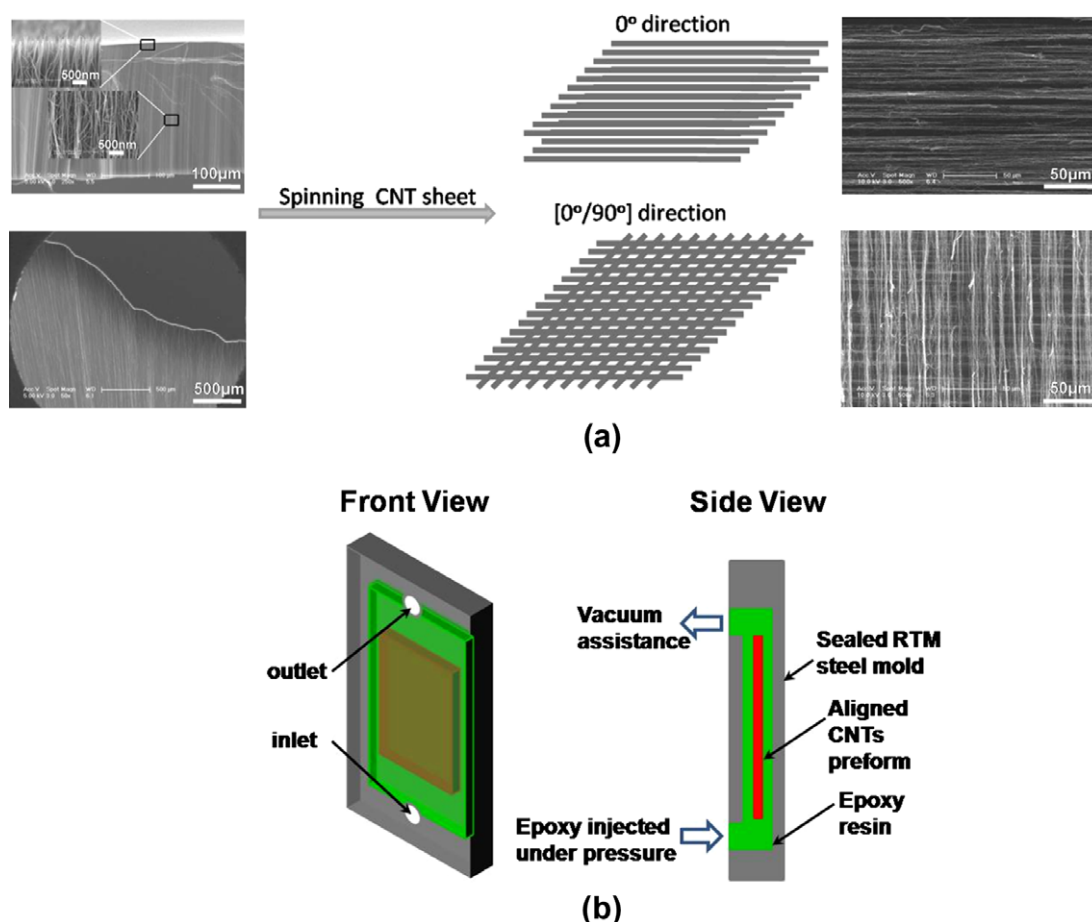

Fig. 1 – (a) Schematic and SEM images of CNT preforms with [0] and [0/90] alignment of CNT sheets and (b) schematic of the RTM process for fabricating CNT/epoxy composites.

composites $[0]_{2000}$ and $[0]_{4000}$, samples were cut in a way that the CNT alignment was parallel to the length direction and the axis of the tensile loading. For CNT/epoxy composite $[0/90]_{2000}$, the alignment of half of the CNT sheets was parallel to the axis of the tensile loading. Five specimens were tested for each CNT/epoxy composite. After tensile tests, fracture surfaces of the tensile specimens were coated with a 3 nm thick gold layer and observed using SEM (Tecnai 20 G2 STWIN, FEI, Hillsboro, OR). Transmission electron microscope (TEM) images were taken using a FEI Tecnai 20 with an acceleration voltage of 200 kV.

2.3. Measurement of electrical properties

Electrical conductivities of the CNT/epoxy composites were characterized by a standard two-probe method using a source meter (Keithley 237, Cleveland, OH). The dimensions of the samples are 40 mm (length) × 5 mm (width) × 0.3 mm (thickness). Silver paste was applied on two ends of the CNT/epoxy samples to ensure good electrical contact between the sample and the electrodes. Electrical conductivities of the CNT/epoxy composites $[0]_{2000}$ and $[0]_{4000}$ were measured in the direction parallel to the CNT alignment. Electrical conductivity of the CNT/epoxy composite $[0/90]_{2000}$ was measured in the direction parallel to the alignment of half of the CNT sheets.

3. Results and discussion

3.1. Analysis of the RTM process for fabricating CNT/epoxy composites

CNT concentrations in the CNT/epoxy composites $[0]_{2000}$, $[0/90]_{2000}$, and $[0]_{4000}$ are 9.94, 10.32, and 16.50 wt.%, respectively. Given the densities of epoxy and CNTs at 1.2 and 2.0 g/cm^3 [10], the volume fractions of CNTs in these composites were calculated as 6.21, 6.47, and 10.60 vol.%. Ultrasonic nondestructive testing of a CNT/epoxy composite $[0]_{4000}$ shows no big voids except that some damages occurred at or near the edge of the composite panel when releasing the composite panel from the RTM mold (Fig. 2).

The attempt to fabricate a CNT/epoxy composite with higher volume fraction of CNTs by using a preform of 6000 CNT sheets ($[0]_{6000}$) failed. It has been reported in literature that millimeter-scale CNTs/polymer composites with high volume fraction of CNTs (up to 22%) were fabricated by mechanical densification of CNT arrays and capillarity-induced polymer wetting [8]. In our study, the diameter of CNTs is around 20 nm, and the volume fraction of CNTs is approximately 20% with 20 nm of inter-CNT spacing, which is larger than the size of the epoxy resin molecule and allows the epoxy chains fill in the space between CNTs. However, for the material system used in this study, composites with 20 vol.% CNTs cannot be fabricated by the RTM process. In the RTM process, the key step is to impregnate the preform with liquid epoxy as quickly as possible before the epoxy cures to avoid undesirable flaws, such as incomplete filling, non-uniform wetting, and void in the composites. The unidirectional flow of the epoxy through the preform can be described as [14]:
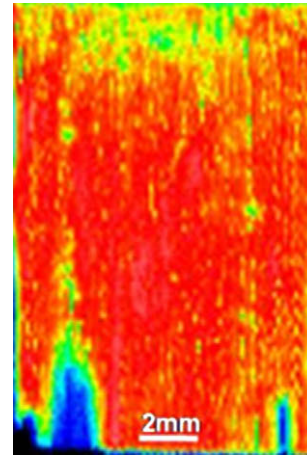

Fig. 2 – Ultrasonic nondestructive testing image of a CNT/epoxy $[0]_{4000}$ composite.

$$v = -\frac{k}{\eta}\nabla P \tag{1}$$

where v is the average flow velocity, k is the permeability of the preform, η is the fluid viscosity, and ∇P is the pressure gradient that drives the epoxy flow. The permeability of the preform is affected by the volume fraction and packing characteristics of the CNT sheets. Higher CNT volume fraction may result in lower permeability and flow rate of the epoxy and thus fail to make a CNT/epoxy composite by the RTM process. In our experiments, the viscosity of the epoxy resin is about 50 cPa s at 60 °C and the pressure gradient is about 0.2 MPa. As the number of CNT sheets increased to 6000, the permeability of the CNT preform became too low to allow the epoxy infuse into the space between CNTs. Methods of improving the permeability of the CNT preforms and decreasing the viscosity of the epoxy will be further investigated.

3.2. Mechanical properties and microstructure of the CNT/epoxy composites

Typical tensile stress–strain curves for the pure epoxy and the CNT/epoxy composites are shown in Fig. 3a, and the Young's modulus and tensile strength of these composites are shown in Fig. 3b. The Young's modulus of pure epoxy is 2.5 GPa. The Young's modulus of composites $[0]_{2000}$, $[0/90]_{2000}$, and $[0]_{4000}$ are significantly improved to 14.0, 8.1, and 20.4 GPa, respectively, corresponding to 461%, 223%, and 716% improvement. In composite $[0/90]_{2000}$, only half of the CNT sheets aligned with the tensile direction, so that the effective reinforcement is about half of composite $[0]_{2000}$. The tensile strength follows the same trend with Young's modulus and is enhanced from 89 MPa for pure epoxy to 231 MPa for composite $[0]_{4000}$, corresponding to 160% improvement. These experimental results show that the load transfer from the epoxy matrix to the CNTs was effective in the aligned CNT/epoxy composites. With increasing CNT loading, the reinforcement effect of CNTs became more significant. The gravimetric tensile strength of composite $[0]_{4000}$ is 180 MPa/(g/cm^3), which is higher than those of steel alloy 1040 at 75 MPa/(g/cm^3) and aluminum alloy 6061 at 115 MPa/(g/cm^3).
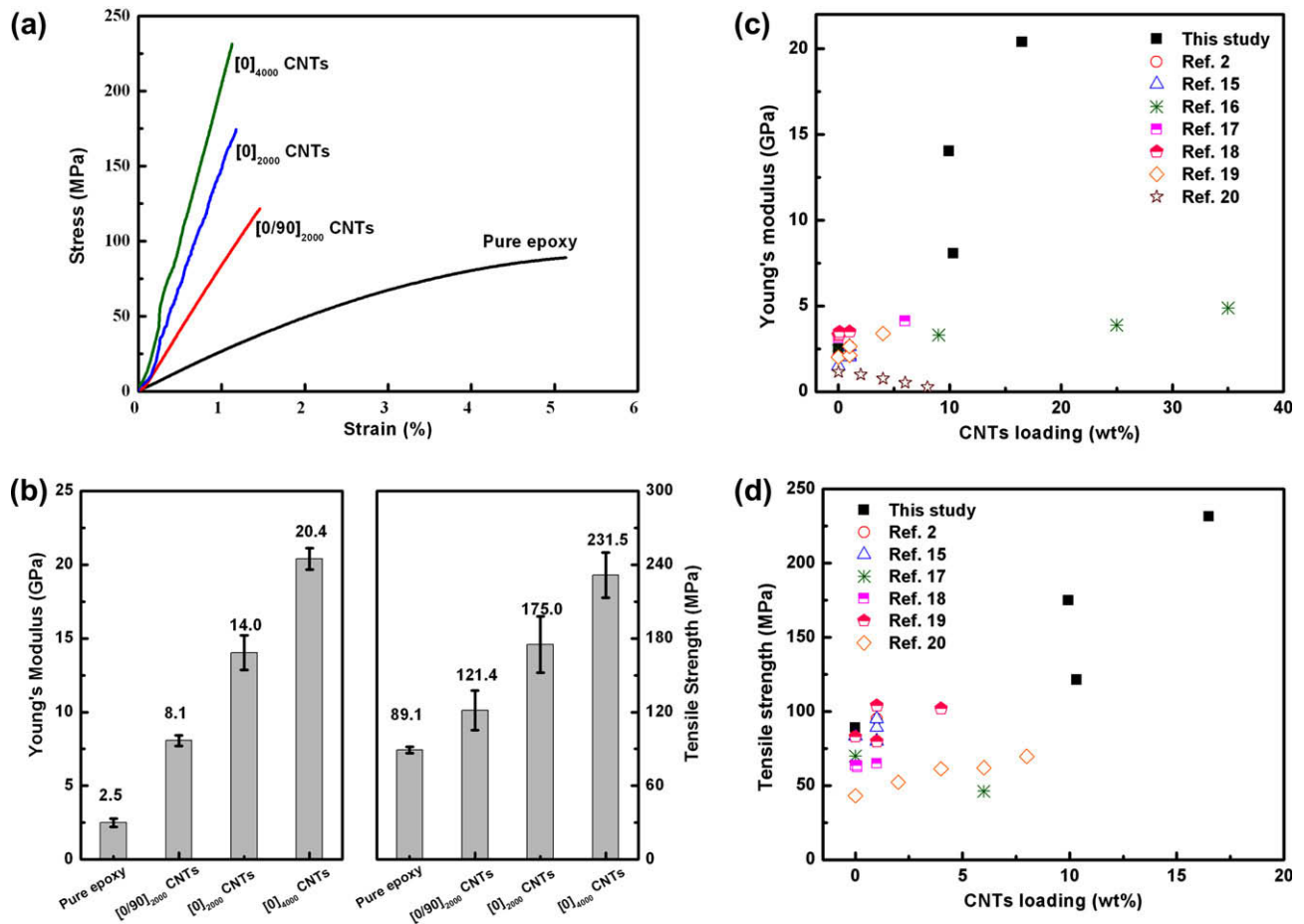
Fig. 3 – (a) Stress–strain curves of the CNT/epoxy composites, (b) Young's modulus and tensile strength of the CNT/epoxy composites, (c) comparison of Young's modulus of the CNT/epoxy composites, and (d) comparison of tensile strength of the CNT/epoxy composites.

Comparison of the tensile strength and Young's modulus of the CNT/epoxy composites reported in literature [2,15–20] with our experimental results are shown in Fig. 3c and d. In the single-walled carbon nanotube (SWCNT)/epoxy composites with 1 wt.% CNT loading, although SWCNTs were chemically functionalized to improve dispersion and interfacial bonding between CNTs and epoxy, the tensile strength and Young's modulus showed modest improvement from 83.2 to 95.0 MPa, and 2.03 to 2.63 GPa, respectively [2]. Other researchers reported that non-covalent and covalent methods were used to modify the surface of CNTs [15]. However, it was still difficult to fabricate CNT/epoxy composites with uniform dispersion and high loading of CNTs. In SWCNT/epoxy composites with 35 wt.% CNT loading made by solution method [16], CNT surfaces were functionalized with undesirable chemical groups or surface layer during the purification treatments which weakened the interaction between SWCNTs and epoxy, and the Young's modulus only increased from 2.4 to 4.6 GPa. Obviously, either chemical functionalization or high loading of CNTs does not directly lead to effective improvement in the mechanical properties of CNT/epoxy composites. Both alignment and length of CNTs are major factors as described in a previous paper [13]. Compared with the aforementioned literature, the alignment of CNTs was well

controlled in the CNT preforms in our study. CNTs with high volume fractions were homogeneously dispersed in the epoxy matrix during the RTM process. In addition, the successful removal of air bubbles using the RTM process eliminated voids in the CNT/epoxy composites. Therefore the resulting CNT/epoxy composites show superior mechanical properties.

Modified rule of mixtures (ROM) [21,22] equation was used to calculate the effective mechanical properties of the CNT preform.

$$E_c = \eta_0 \cdot \eta_L \cdot V_f \cdot E_f + (1 - V_f) \cdot E_m \qquad (2)$$
$$\sigma_c = \eta_0 \cdot \eta_L \cdot V_f \cdot \sigma_f + (1 - V_f) \cdot \sigma_m \qquad (3)$$

where E_c, E_m, and E_f are Young's modulus of the composite, matrix, and CNTs, σ_c, σ_m, and σ_f are tensile strength of the composite, matrix, and CNTs, respectively. V_f is the volume fraction of the CNTs. The length efficiency factor, η_L, was introduced to account for the efficiency of stress transfer from the matrix to the fibers due to the limited fiber length. η_L can vary between 0 and 1. In this study, the length of the aligned CNTs is approximately 300 μm, which is much larger than the diameter of the CNTs at 20 nm, therefore we set η_L as 1. The orientation factor, η_0, was introduced to account for the fiber orientation, which is equal to 1 for fully aligned fibers. CNTs in samples $[0]_{2000}$ and $[0]_{4000}$ are highly aligned

(Fig. 1a), so we set η_0 as 1. According to Eqs. (2) and (3), the effective Young's modulus and tensile strength of the CNT preform was calculated to be approximately 180 GPa and 1452 MPa, respectively.

Fracture surfaces of specimens after tensile testing were observed by SEM. Fig. 4a shows fracture surface of a pure epoxy sample, which exhibited a typical feature of brittle fracture behavior with many river-like patterns. Fig. 4b shows a much rougher fracture surface of a composite $[0]_{4000}$ sample. CNT bundles were coated with epoxy resin and breaking of CNT bundles were observed, showing strong adhesion between CNTs and the epoxy matrix and efficient load transfer from epoxy matrix to CNTs. Two typical fracture modes of CNT/epoxy composites have been reported in previous literature: CNT fracture and CNT pullout [17–20]. In our study, CNT fracture is the main fracture mode for the CNT/epoxy composites. CNT bundles and the epoxy resin that coated on the surface of the CNTs deformed together during tensile testing, until they broke together finally. CNT pullouts and the resulting microvoids in the epoxy matrix were rarely observed. Pure epoxy resin generally breaks in a brittle failure mode due to its molecular cross-linked network structure and thus high resistance to plastic deformation [23]. In particles or fibers filled epoxy composites, plastic shear yielding of the epoxy matrix may occur as reported in literature [24,25]. In our study, plastic deformation of the epoxy that coated on CNT bundles was observed from fracture surfaces of the CNT/epoxy composite samples. However, tensile stress–strain curves of the CNT/epoxy composites (Fig. 3a) mainly revealed the reinforcement effect of CNTs and brittle fracture of the CNT/epoxy composites with almost no plastic deformation. The disagreement between the stress–strain curves and fracture morphology will be further investigated. Fig. 5 is a TEM image of a composite $[0]_{4000}$ sample, indicating homogeneous dispersion of CNTs in the epoxy matrix. Most CNTs aligned along the same direction and some CNTs curled up forming an angle with the major alignment direction. The volume fraction of CNTs observed from the TEM image is similar to the value calculated by the measurement of the weights of
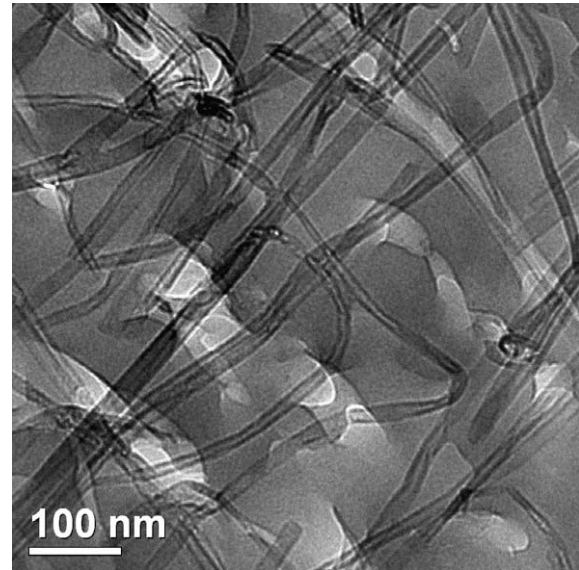

Fig. 5 – TEM image of a CNT/epoxy composite $[0]_{4000}$.

the CNT preform and the CNT/epoxy composite (about 10 vol.%).

3.3. Electrical properties of the CNT/epoxy composites

The current–voltage (I–V) curves for the CNT/epoxy composites $[0]_{2000}$ and $[0]_{4000}$ measured in the direction parallel to the CNT alignment and the composite $[0/90]_{2000}$ measured in the direction parallel to the alignment of half of the CNT sheets are shown in Fig. 6a. The linear curves indicate ohmic behavior of all the samples. The electrical conductivities of the composites are shown in Fig. 6b. The continuous and aligned CNT sheets were used as the conductive medium that has excellent electrical conductivity [26]. The electrical conductivity of the CNT/epoxy composite $[0]_{2000}$ was 7715 S/m, while the electrical conductivity of pure epoxy was as low as 10^{-12} S/m. As the CNT layers increase to 4000, the electrical
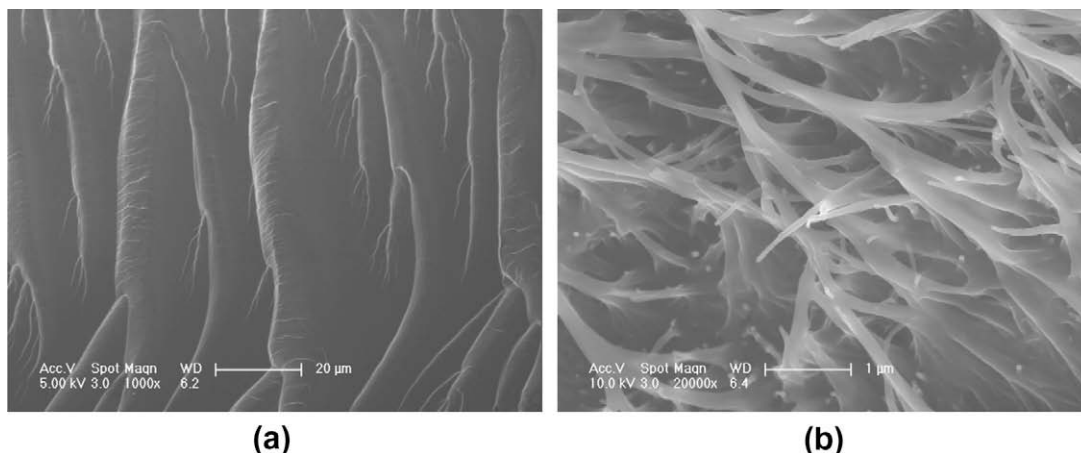

Fig. 4 – SEM images of fracture surfaces of tensile specimens. (a) Pure epoxy resin with "river-like" patterns and (b) CNT/epoxy composite $[0]_{4000}$.
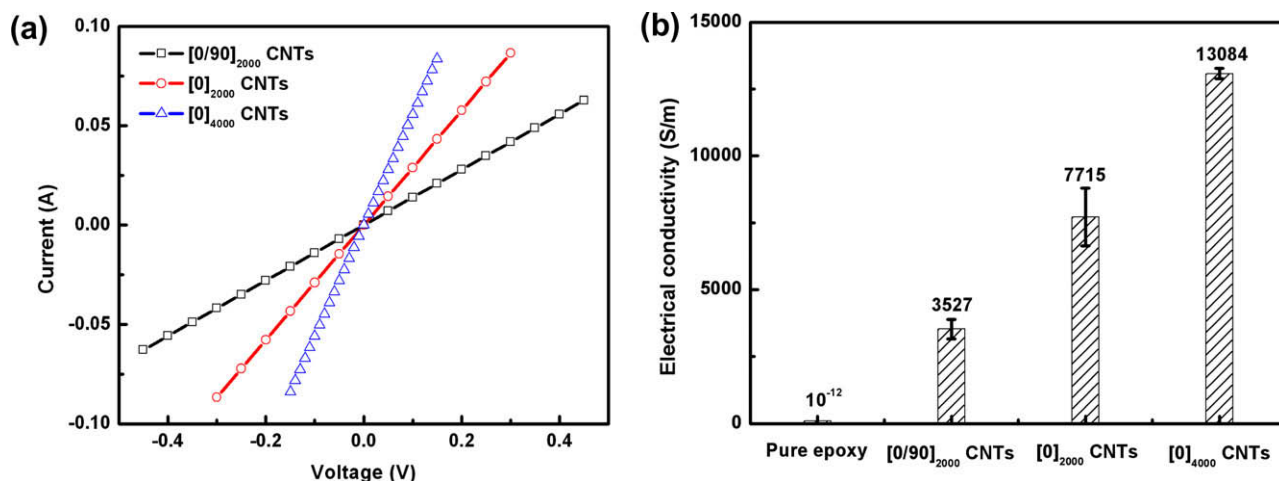
Fig. 6 – (a) Current–voltage (I–V) curves of the CNT/epoxy composites and (b) electrical conductivities of pure epoxy and CNT/epoxy composites containing different CNT contents.

conductivity was dramatically enhanced to 13,084 S/m. For the CNT/epoxy composite [0/90]$_{2000}$, only half of the CNT sheets aligned along the measurement direction, so that the electrical conductivity was 3527 S/cm, which is about half of the electrical conductivity of the composite [0]$_{2000}$. Previous literature [3,27–29] reported that the electrical conductivities of CNT/epoxy composites were generally below 5 S/m, due to the random orientation and limited volume fraction of CNTs in the composites. While in our study, the CNT/epoxy composites made by the RTM process contained high CNT contents and the continuous and aligned CNTs were uniformly dispersed in the epoxy matrix. Therefore, the improvement of the electrical conductivity is much more significant compared to previous studies. Meanwhile controlled orientation of CNTs can result in anisotropic CNT/polymer composites, and their physical properties in various directions will be further studied.

4. Conclusions

CNT/epoxy composites with homogenous dispersion, high loading, and controllable orientation of CNTs were successfully fabricated by a RTM process. These CNT/epoxy composites show significantly improved mechanical and electrical properties with Young's modulus up to 20.4 GPa, tensile strength up to 231.5 MPa, and electrical conductivity up to 13,084 S/m. CNT/epoxy composites with specific properties along various directions can be designed by controlling the volume fractions and orientation of the CNT sheets. Such composites can be made on a large scale and be used as multifunctional materials for practical applications such as electrostatic dissipation (ESD) and electromagnetic interference (EMI) shielding.

Acknowledgement

REFERENCES

[1] Ajayan PM, Stephan O, Colliex C, Trauth D. Aligned carbon nanotube arrays formed by cutting a polymer resin–nanotube composite. Science 1994;265(5176):1212–4.

[2] Zhu J, Kim J, Peng H, Margrave JL, Khabashesku VN, Barrera EV. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. Nano Lett 2003;3(8):1107–13.

[3] Sandler J, Shaffer MSP, Prasse T, Bauhofer W, Schulte K, Windle AH. Development of a dispersion process for carbon nanotubes in an epoxy matrix and the resulting electrical properties. Polymer 1999;40(21):5967–71.

[4] Schadler LS, Giannaris SC, Ajayan PM. Load transfer in carbon nanotube epoxy composites. Appl Phys Lett 1998;73(26):3842–4.

[5] Wang Z, Liang ZY, Wang B, Zhang C, Kramer L. Processing and property investigation of single-walled carbon nanotube (SWNT) buckypaper/epoxy resin matrix nanocomposites. Compos Part A Appl Sci 2004;35(10):1225–32.

[6] Wang SR, Liang ZY, Pham G, Park YB, Wang B, et al. Controlled nanostructure, high loading of single-walled carbon nanotubes reinforced polycarbonate composites. Nanotechnology 2007;18:095708-1–7.

[7] Zhang M, Atkinson KR, Baughman RH. Multifunctional carbon nanotube yarns by downsizing an ancient technology. Science 2004;306(5700):1358–61.

[8] Wardle BL, Saito DS, García EJ, Hart AJ, Villoria RGd, Verploegen EA. Fabrication and characterization of ultrahigh-volume-fraction aligned carbon nanotube–polymer composites. Adv Mater 2008;20(14):2707–14.

[9] Jiang KL, Li QQ, Fan SS. Nanotechnology: spinning continuous carbon nanotube yarns – carbon nanotubes weave their way into a range of imaginative macroscopic applications. Nature 2002;419:801.

[10] Zhang XB, Jiang KL, Teng C, Liu P, Zhang L, Kong J, et al. Spinning and processing continuous yarns from 4-inch wafer scale super-aligned carbon nanotube arrays. Adv Mater 2006;18(12):1505–10.

[11] Liu K, Sun YH, Chen L, Feng C, Feng XF, Jiang KL, et al. Controlled growth of super-aligned carbon nanotube arrays for spinning continuous unidirectional sheets with tunable physical properties. Nano Lett 2008;8(2):700–5.

[12] Potter K. Resin transfer moulding. 1st ed. London: Chapman and Hall; 1997. p. 1–26.

[13] Cheng QF, Wang JP, Jiang KL, Li QQ, Fan SS. Fabrication and properties of aligned multiwalled carbon nanotube-reinforced epoxy composites. J Mater Res 2008;23(11):2975–83.

[14] Chawla KK. Composite materials: science and engineering. 2nd ed. New York: Springer; 1998. p. 133–63.

[15] Khabashesku VN, Margrave JL, Barrera EV. Functionalized carbon nanotubes and nanodiamonds for engineering and biomedical applications. Diamond Relat Mater 2005;14(3–7):859–66.

[16] Vaccarini L, Desarmot G, Almairac R, Tahir S, Goze C, Bernier P. Reinforcement of an epoxy resin by single walled nanotubes. Electronic properties of novel materials-molecular nanostructrues: XIV International Winterschool/Euroconference. Kirchberg. Tirol (Austria): American Institute of Physics; 2000. p. 521–5.

[17] Breton Y, Désarmot G, Salvetat JP, Delpeux S, Sinturel C, Béguin F, et al. Mechanical properties of multiwall carbon nanotubes/epoxy composites: influence of network morphology. Carbon 2004;42(5–6):1027–30.

[18] Gojny FH, Wichmann MHG, Köpke U, Fiedler B, Schulte K. Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content. Compos Sci Technol 2004;64(15):2363–71.

[19] Zhu J, Peng H, Rodriguez-Macias F, Margrave JL, Khabashesku VN, Imam AM, et al. Reinforcing epoxy polymer composites through covalent integration of functionalized nanotubes. Adv Funct Mater 2004;14(7):643–8.

[20] Guo P, Chen X, Gao X, Song H, Shen H. Fabrication and mechanical properties of well-dispersed multiwalled carbon nanotubes/epoxy composites. Compos Sci Technol 2007;67(15–16):3331–7.

[21] Dunn ML, Ledbetter H, Heyliger PR, Choi CS. Elastic constants of textured short-fiber composites. J Mech Phys Solids 1996;44(9):1509–13.

[22] Cox HL. The elasticity and strength of paper and other fibrous materials. Br J Appl Phys 1952;3:72–9.

[23] Argon AS, Cohen RE. Toughenability of polymers. Polymer 2003;44(19):6013–32.

[24] Lee J, Yee AF. Inorganic particle toughening II: toughening mechanisms of glass bead filled epoxies. Polymer 2001;42(2):589–97.

[25] Kawaguchi T, Pearson RA. The moisture effect on the fatigue crack growth of glass particle and fiber reinforced epoxies with strong and weak bonding conditions: part 2. A microscopic study on toughening mechanism. Compos Sci Technol 2004;64(13–14):1991–2007.

[26] Wei Y, Jiang KL, Feng XF, Liu P, Liu L, Fan SS. Comparative studies of multiwalled carbon nanotube sheets before and after shrinking. Phys Rev B 2007;76(4):045423-1–7.

[27] Allaoui A, Bai S, Cheng HM, Bai JB. Mechanical and electrical properties of a MWNT/epoxy composite. Compos Sci Technol 2002;62(15):1993–8.

[28] Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, et al. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. Polymer 2006;47(6):2036–45.

[29] Moisala A, Li Q, Kinloch IA, Windle AH. Thermal and electrical conductivity of single- and multi-walled carbon nanotube–epoxy composites. Compos Sci Technol 2006;66:1285–8.