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CARBON NANOTUBE BASED COMPOSITES FILM HEATER FOR DE-ICING APPLICATION

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Abstract

Light weight, highly conductive (both electrically and thermally) multiwalled carbon nanotube (MWNTs) sheets can be used as an effective electric heating element. In this paper, silver nanoparticles were anchored onto carboxyl functionalized multiwalled carbon nanotubes (MWNTs) by photochemical reaction to enhance the transport properties of the resultant nanohybrid sheet. The nanohybrid sheet was then integrated into the Kevlar/epoxy sandwich structure by resin infusion method. When conducting a current through an area of 24.6×20.7mm, the sample temperature reached the steady-state value (e.g. 110^{o}C) within 13s by consuming a power density of 0.58W/in^2. In addition, the laminate structure showed a stable reversibility after a number of heating cycles, which indicated it's potential for thermal interface materials, sensors and de-icing applications.

1 Introduction

To fully explore the excellent properties of carbon nanotubes (CNTs), work in the past has been focused on generating CNTs networks, films and sheets (buckypaper) using spraying or vacuum infiltrating method [1, 2] onto solid substrates or integrating with polymers. Compared with single walled carbon nanotubes (SWNTs), multiwalled carbon nanotubes (MWNTs) are much cheaper and better suited to large scale industrial applications exception of their much lower conductivity than SWNTs. Dai [3] reported that chemical doping led to orders of magnitude reduction in the resistance of bulk SWNT materials due to the increase in the average of hole or electron carrier in the nanotubes. For both SWNT and MWNT sheets, there are two predominant nanotube junctions that govern the electrical properties of a nanotube network, namely: (1) Y junction – ambipolar behavior and (2) crossed junction--rectification characteristics [4]. Therefore, two approaches can be used to improve the electrical conductivity of MWNT sheets: (1) minimize the contact resistance between nanotubes by improving the alignment of nanotubes and by increasing the lengths of individual tubes; (2) improve the conductivity of individual nanotubes by post-synthesis treatments [5]. To achieve low-resistance ohmic contacts in these structures, metals can be deposited onto the nanotube surface by using techniques such as, impregnation [6], electroless plating [7], self-assembly [8], electro-deposition [9], and physical vapour deposition [10], etc..

From an engineering perspective, the highly conductive CNTs can be explored for many applications, among which one specific application to be addressed in the present work is to use CNT sheets as a heating element for potential de-icing in aeronautical industry. The conventional de-icing heater uses metal foil as the heating element. One disadvantage for the metal foil as heating element is that it does not have a good, durable bond to the protecting layer. Another disadvantage is that heating may not be uniform, resulting in cold spots which hold ice on the airplane, and hot spots which cause the ice to melt and refreeze at different sites [11]. A composite-composite bonding in a composite material heater is more uniform and stronger than the composite-metal bonding found in conventional de-icers. Good bonding of CNT sheet/fabric matrix would result in a much more uniform heating. Due to the high electrical conductivity of CNT sheet, heating can be achieved in a relative thin layer (37 μm thick in the model heater) without need of high voltages. Therefore the amount of heat accumulated by the composite heater is minimized. In addition, electricity can penetrate through the heating element in the transverse direction despite the low transverse electrical conductivity.

In the present work, Ag/MWNT hybrid sheets were prepared using silver nanoparticles decorated MWNTs and were then integrated into aerospace composites. The resulting composites showed a quick temperature response to input power and very stable thermal cycles, which could be ideal for de-icing applications.

2 Experimental Details

2.1 Silver decorated MWNTs and the MWNT sheets

The pristine MWNTs (Sigma Aldrich, UK) were produced by chemical vapour deposition (CVD), with a purity of > 99 %, up to 20 μm in length and their diameters around 12 nm. Pristine MWNTs (4.32 g) were added into hot acid mixture H_2SO_4/HNO_3 (3:1 by volume, 120 ml) and the mixture was then sonicated in an ultrasonic bath (40 kHz) for 30 minutes before stirring for 4 h at a temperature of 100°C. The suspension was diluted with distilled water and no sediment was found after a whole night. The resulting solution was then filtered through a 0.22 μm Millipore alumina membrane and subsequently washed with distilled water until the pH value of the filtrate was ca. 7. The filtered solid was dried under vacuum for 24 h at 40°C, yielding MWNT-COOH (2.588 g). 100 mg of acid-treated MWNTs were dispersed in distilled water in the presence of TX-100 surfactant, and a 250 ml silver nitrate solution (0.2 wt%) was then added into the MWNTs suspension and stirred under UV light with a wave length of 365nm at 60°C. The densely packed MWNT sheets were fabricated by filtering the above suspension through Millipore alumina filters and subsequently washed with distilled water and ethanol.

2.2 MWNT sheets integrated laminate composites

In this study, commercially available Kevlar 129™ fabric and HexPly 914 resin film were used in this study and the vacuum assisted resin transfer molding (VARTM) process was used to fabricate the laminates embedded with carbon nanotube sheets via the following three steps. In the first step, Kevlar fabric, HexPly 914 resin film and carbon nanotube sheets were placed on the bottom of an aluminum mold coated with release agent. After the lay-up operation was completed, a peel ply, release film, breather, and vacuum bag film were placed on the top of Kevlar fabric, see in Figure 1. The vacuum film bag was then sealed around the perimeter of the mold and a vacuum pump was used to draw a vacuum within the mold cavity. The next step was to put the bagging stuff into oven at 175°C for 75 minutes, during which the resin film was melted and sucked into the mold under atmospheric pressure. In the final step, the composite part was post cured at 190°C for 4 hours (Figure 1). During the curing process, the carbon nanotubes sheet experienced the same temperature cycle as the baseline laminates.

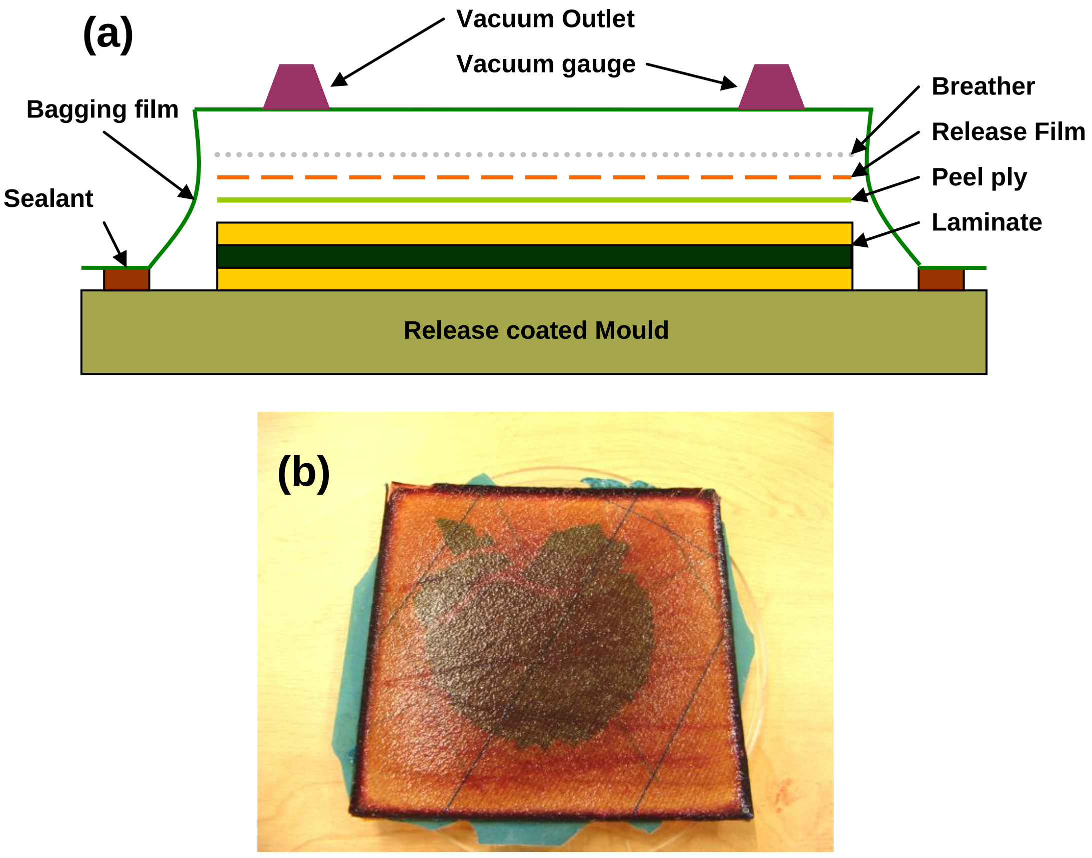

Figure 1 **(a)** Vacuum assisted resin transfer molding *(VARTM) setup* and **(b)** Kevlar/MWNT sheet laminate.

Scanning electron microscopy (SEM) was used to characterize the interfacial morphologies of the MWNT sheets/Kevlar laminate. The morphologies of nanoparticles decorated MWNTs were observed by using transmission electron microscopy (TEM, JEOL 1200). To prepare the TEM samples, a tiny drop of well dispersed samples was placed onto the carbon coated TEM copper grid. Copper electrode wires were attached to the MWNT sheet/Kevlar laminate by silver paste and the power source was directly connected to the electrode wire. An infrared thermal imager (NEC TH9100) was used to record the temperature distribution and evolution of the sample with inputting powers.

3 Results and discussions

3.1 Morphology of silver decorated MWNTs and their hybrid sheet

While acid treated MWNTs can supply nucleating sites for Ag nanoparticles, the particle size could not be controlled effectively. TX-100 can not only act as surfactant but also help control the particle size, as well as acting as reducing agent at the same time. In this experiment, silver nanoparticles were synthesized by using the same amount of acid-treated MWNTs in the presence of 1vol% of TX-100, and the silver nanoparticles were stabilized onto the nanotubes and well dispersed with a narrow size distribution between 20 and 30 nm. This indicated that the TX-100 is necessary in controlling the nanoparticle size, size distribution and preventing agglomeration. Although the TEM samples were prepared by dispersing the resulting nanohybrids in water using strong sonication, the nanotubes were still tightly connected by the nanoparticles to form a conductive path, which is expected to enhance the transport properties of the future nanotube sheets, as shown in Figure 2a The silver nanoparticles decorated nanotube sheets were prepared using a vacuum infiltration procedure. For relatively short carbon nanotube, there is a minimum thickness to keep a free standing nanotube sheet, which is 20 µm for MWNTs in this experiment. As shown in Figure 2b, the thickness of the MWNT sheet is 37 µm, and it can be tailored depending on the specific requirements.

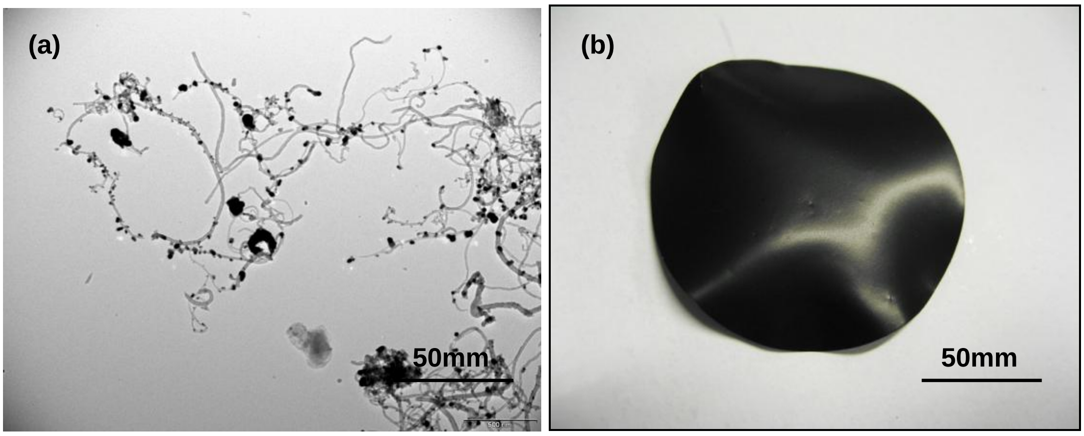

Figure 2 (a) TEM images of Ag/CNT-COOH in the presence of TX100, and (b) silver decorated MWNTs sheets 37µm.

3.2 Interfacial microstructure investigations

The nanotube sheets made by silver nanoparticle decorated MWNTs had good strength and flexibility to allow for handling like traditional aerospace fabric. The sheet is free standing due to the inter-nanotube van der Waals forces and mechanical interlocking within the nanotube sheet. Figure 3a showed the SEM image of MWNT sheet embedded in Kevlar matrices, indicating a sound interface between Kevlar and MWNT sheets by quite rough surface. Also it can be clearly seen that resin had completely penetrated the carbon nanotube sheet through the entire thickness direction during the VARTM process and wet well with nanotubes (Figure 3b).

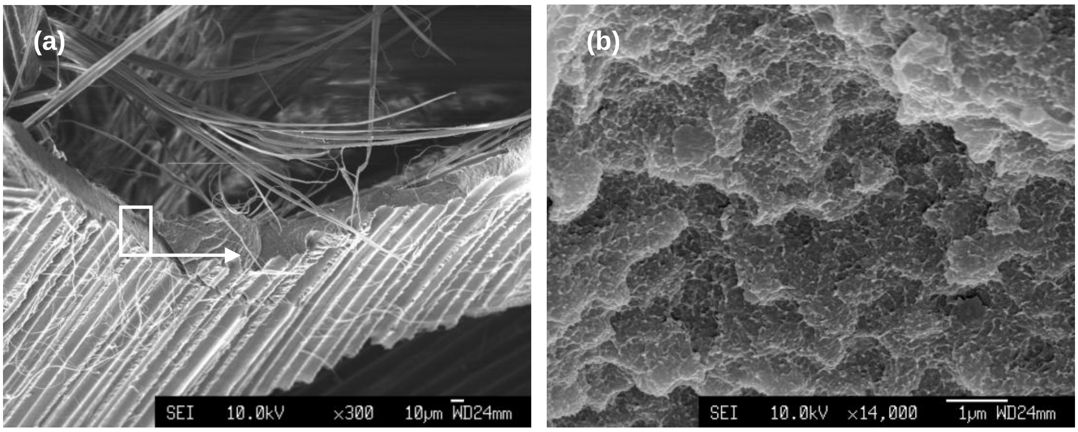

Figure 3 SEM images of (a) Kevlar laminate with infused MWNT sheet and (b) fracture surface the infused sheet area, as indicated by white frame and arrow.

3.3 Electrical conductive properties

Knowing that the MWNT heat element in Kevlar was 37 μm thick and 2.10 cm wide, the distance between the foil in the middle section of the heater was 2.05 cm, and the voltmeter reading was 5v when the resistance was 62.7 Ω, the conductivity of this particular composite was calculated to be 430 S/m. The $I-V$ characteristics of the MWNT sheet and its composites showed linear characteristics, which means they are good conductors even when the nanotubes were infused with insulating matrix materials (Figure 4). It is worth mentioning that carbon nanotubes are robust under most weather conditions, and show very little change in conductivity either at temperature ranging from -20 to 80^{o}C [12], or repetitive bending of the composite, indicating that it is fairly durable under mechanical distortions.

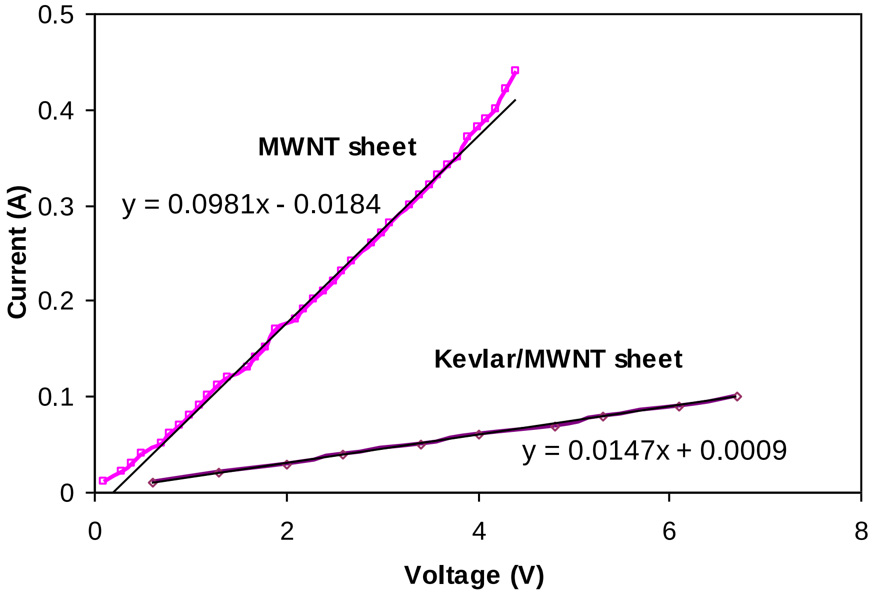

Figure 4 I-V data and fitting curves of MWNT sheets and its composites.

3.4 Joule-heating behavior of MWNT laminates for de-icing application

The heater was heated at room environment with varying input voltages. The temperature history was monitored by a noncontact IR thermocamera. Temperature as a function of heating time was recorded, including ramping up, steady-state and cooling down. As seen in Figure 5, the highest temperatures increased consistently with the heating current. Consequently, the ramp-up time decreases with increasing highest temperature while the cooling down time increases with the highest temperature. Similar phenomenon was also found in Ref. [13]. The fast ramp-up and cool-down rate is very promising for de-icing application.

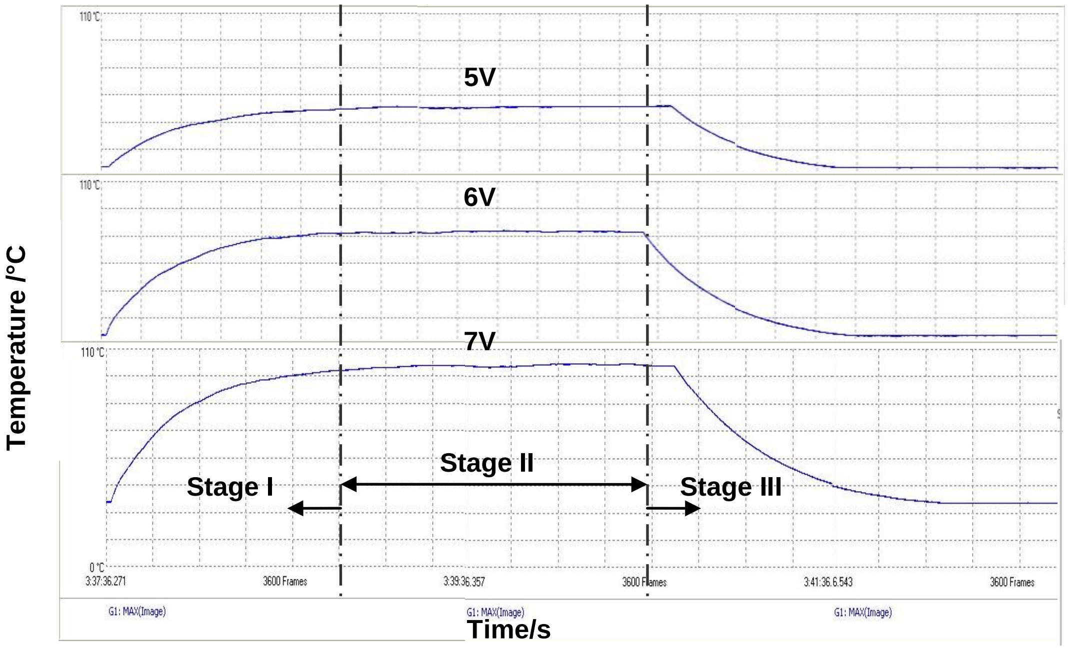

Figure 5 Thermal cycles with 5, 6, 7V of input voltages: stage I, ramping up, stage II: stable-state and stage III: cooling down.

The equation relating the input power and the heater's resistivity and dimensions is:

$$P_{LW} = IE = -I^2 \rho L / Wt \tag{1}$$

where, I is the current conducted through the heater, E is the voltage drop across the heater, P is the power per unit area of the heater, ρ, L, W and t are the resistivity, length, width, and thickness of the heater, respectively. It is found that the steady-state temperatures increased with more power inputting. It only needed an input power of 0.58W to improve the temperature from starting heating to 110°C (Figure 6). According to the thermal radiation images shown from bottom to up, the temperatures are 65 °C, 95°C and 110°C, respectively.

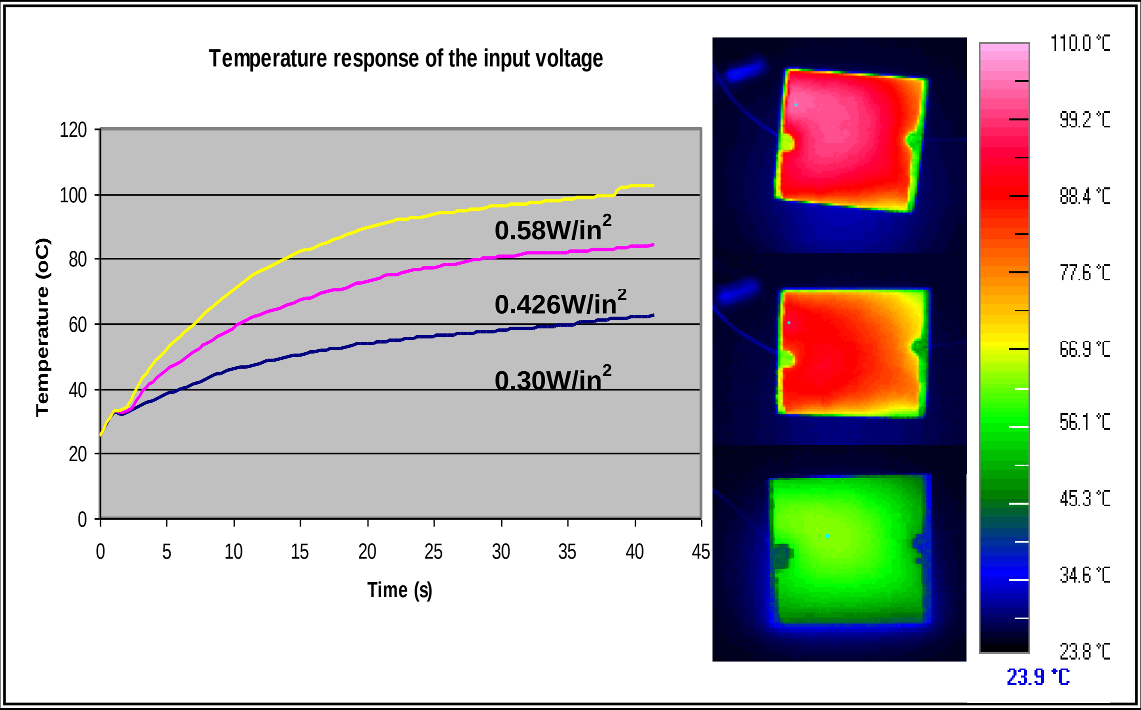

Figure 6 Ultimate temperatures of MWNT sheet/Kevlar laminate with different input powers.

3.5 Thermal conductivity

For the CNT sheets/Kevlar composites, the values of thermal conductivity are much lower than that of the pristine CNT sheets, because the matrix has a much lower thermal conductivity (0.2 W/mK) [14]. The thermal conductivities of the composites can be obtained from theoretical models, including the rule of mixture and Nan's model [15]:

$$k_c = k_m(1-V_f) + k_f V_f \qquad \textbf{(2)}$$

$$k_c = (3k_m + k_f V_f)/(3-2V_f) \qquad \textbf{(3)}$$

where k_c, k_m and k_f are the thermal conductivities of composite, epoxy matrix and CNTs, respectively. The measured values of k_m and k_{sheet} are 0.2 W/mK and 200 W/mK, respectively [16]. The volume fraction of MWNTs in the composites is $V_f = 0.33$ (33 vol.%), and the thermal conductivity of the Kevlar/MWNT composite should be between 66.13 and 28.46 W/mK, according to equation (2) and (3). Aliev reported that the thermal conductivity along the aligned CVD-grown MWNT sheet is 50W/mK while the value is 2.1W/mK along the transverse alignment direction [17, 18]. Considering the random distribution of nanotubes in this study, Nan's model (28.46 W/mK) gave a better approximation to the true value of the conductivity.

4 Conclusions

A hybrid laminate consisting of Ag decorated MWNT sheets was prepared by vacuum assistant resin transfer method. The presence of Ag nanoparticles has been confirmed by TEM and EDX by showing that the narrow particle size distribution silver nanoparticles have anchored onto nanotubes to bridge individual nanotube. The SEM characterization shows a perfect interface of the laminate and a dense resin infused microstructure. A consistent electrical conductivity of 430S/m is obtained and the relatively higher resistance promises a fast temperature response to low input powers. The analytical analyses showed that Nan's mode (e.g. 28.46 W/mK) gave a better approximation to the experimental value of the thermal conductivity of the hybrid sheets. All these indicate that the MWNT sheets can be used as heating elements in de-icing application in aerospace industry.

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References

[1] Xu, H., et al., Frequency-and electric-field-dependent conductivity of single-walled carbon nanotube networks of varying density. Physical Review B, 2008. 77(7): p. 75418.
[2] Wu, Z., et al., Transparent, conductive carbon nanotube films. Science. 2004. 305(5688): p. 1273-1276.
[3] Dai, H., Carbon nanotubes: opportunities and challenges. Frontiers in surface and interface science, 2002. 500: p. 218-241.
[4] Lee, H.C., et al., Selective metal pattern formation and its EMI shielding efficiency. Applied Surface Science, 2006. 252(8): p. 2665-2672.
[5] Dangelewicz, A.M., et al., Structure-Dependent Electrical Properties of Carbon Nanotube Fibers. Adv. Mater, 2007. 19: p. 3358-3363.
[6] Planeix, J.M., et al., Application of carbon nanotubes as supports in heterogeneous catalysis. Journal of the American Chemical Society, 1994. 116(17): p. 7935-7936.
[7] Wang, F., S. Arai, and M. Endo, Metallization of multi-walled carbon nanotubes with copper by an electroless deposition process. Electrochemistry communications, 2004. 6(10): p. 1042-1044.
[8] Ellis, A.V., et al., Hydrophobic anchoring of monolayer-protected gold nanoclusters to carbon nanotubes. Nano Letters, 2003. 3(3): p. 279-282.
[9] Quinn, B.M., C. Dekker, and S.G. Lemay, Electrodeposition of noble metal nanoparticles on carbon nanotubes. J. Am. Chem. Soc, 2005. 127(17): p. 6146-6147.
[10] Zhang, Y., et al., Metal coating on suspended carbon nanotubes and its implication to metal–tube interaction. Chemical Physics Letters, 2000. 331(1): p. 35-41.
[11] Hung, C.C., M.E. Dillehay, and M. Stahl, A heater made from graphite composite material for potential deicing application. J. Aircr., 1987. 24(10): p. 725-730.
[12] Hecht, D.S., L. Hu, and G. Grüner, Electronic properties of carbon nanotube/fabric composites. Current Applied Physics, 2007. 7(1): p. 60-63.
[13] Liu, P., et al., Fast High-Temperature Response of Carbon Nanotube Film and Its Application as an Incandescent Display. Advanced Materials, 2009. 21(35): p. 3563-3566.
[14] Biercuk, M.J., et al., Carbon nanotube composites for thermal management. Applied Physics Letters, 2002. 80(15): p. 2767-2769.
[15] Nan, C.W., Z. Shi, and Y. Lin, A simple model for thermal conductivity of carbon nanotube-based composites. Chemical Physics Letters, 2003. 375(5-6): p. 666-669.
[16] Yang, D.J., et al., Thermal conductivity of multiwalled carbon nanotubes. Physical Review B, 2002. 66(16): p. 165440.
[17] Aliev, A.E., et al., Thermal conductivity of multi-walled carbon nanotube sheets: radiation losses and quenching of phonon modes. Nanotechnology. 2010. 21: p. 035709.
[18] Aliev, A.E., et al., Thermal transport in MWCNT sheets and yarns. Carbon, 2007. 45(15): p. 2880-2888.