Flexible carbon nanotube/polyurethane electrothermal films

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Abstract

Carbon nanotube (CNT)-based composites are ideal materials for electrothermal applications because of their lightweight, excellent conductivity, heat sensitivity, and easy processability. In this study, high-performance electrothermal films were synthesized by a novel layer-by-layer method. Electrothermal films were prepared by pouring CNT solution into the designed mold and subsequent curing of thermoplastic polyurethane (TPU) applied on the CNT layer. The flexible films showed sensitive electrothermal performance, and a steady-state temperature of $\sim 140\text{ }^{\circ}\text{C}$ could be reached at 10 V. In addition, temperature versus voltage and time-dependent temperature results show that the heating performance was strongly dependent on the CNT content and input power. Moreover, they can bear large deformations, which could be widely used in defogging and defrosting applications.

1. Introduction

Electrothermal materials have been widely used in special conditions as they can convert electric power into heat energy by the so-called electrothermal effect^[1]. Traditional electrothermal materials such as Cu and Fe–Cr–Al-based alloy show high thermomechanical stability. However, they have some disadvantages such as heavyweight, complicated fabrication process, high power consumption, and intolerance to acids and bases^[2, 3]. Because of its high electrical conductivity and easy processing, indium tin oxide (ITO) has attracted significant research interests,^[4] but the limited supply of indium, fragility under mechanical deformation, and slow thermal response impede its applications^[4–7]. Hence, since the discoveries of carbon nanotube (CNT) in 1991^[8] and monocrystalline graphitic films by Manchester's group,^[9] carbon materials have been serving as excellent candidates for electrothermal materials because they are lightweight, have high thermal conductivity and excellent electrical properties, and show high efficiency in electrothermal conversion^[10–12].

As one-dimensional nanostructures of covalently bonded carbon atoms, CNTs exhibit high electrical conductivity, extraordinary mechanical properties, and high thermal conductivity^[13–15]. Single-walled carbon nanotube (SWCNT)-based electrothermal materials exhibit excellent electrothermal properties^[16]; however, there still exist many issues such as removing semiconducting tubes, requiring acid treatments, and high preparation cost. Transparent electrothermal films produced with graphene by spin-coating,^[3] transferring the CVD graphene,^[17] and layer-by-layer doping methods require complicated fabrication process,^[18] The films cannot be stabilized without a surfactant and are difficult to be produced in a large scale. From

the economic point of view, compared to graphene and SWCNT-based electrothermal films, multi-walled carbon nanotube (MWCNT)-based electrothermal materials can be easily processed with low cost, which is promising for commercial applications. Fan and his coworkers spun-aligned MWCNT bundles to prepare freestanding electrothermal films, which can be heated to high temperature and show fast high-temperature response, but this film could be easily destroyed and is not suited for large-scale practical application^[19–23]. MWCNT films fabricated by spin-coating of MWCNT aqueous solution also showed good electrothermal performance, but have a large sheet resistance^[24]. Thermosetting resin-like epoxy-based electrothermal materials were commonly investigated, but they cannot be bent or twisted^[25]. Therefore, it is very necessary to develop new methods for large-scale production of CNT films with high-efficient electrothermal conversion and flexibility.

The proposed layer-by-layer process in this study is not strictly dependent on the viscosity of the solution. It is easy to process and is suitable for large-scale practical application, flexibility, and different sample sizes^[26–29]. We found that thin-layer CNTs play an important role in forming effective conductive pathways for the transport of electric current^[30]. The electrical resistance of this special CNT thermoplastic polyurethane (TPU) films (CTFs) was as low as ~30 Ohm/sq. because of the high distribution of CNTs in the composites. The as-prepared CTFs exhibit excellent electrothermal performance, which can reach steady-state temperature rapidly after adjusting the voltage. Accordingly, the as-prepared electrothermal films can be applied in various areas such as controllable electrothermal, wearable cotton

fabrics,^[31] floor heating,^[32] mirror/window defrosting, and deicing units^[32, 33].

2. Experimental Section

2.1 Fabrication of electrothermal film

Three commercially available MWCNTs were used for the study: Cnano FT9000 CNT (FT9000, Chengdu Organic Chemical Co. Ltd.), Nanocyl NC7000 (Nanocyl S.A., Sambreville, Belgium), and KJ-2 (Zhongshan CNM Plastic Co. Ltd.). We also attempted to grow CNTs by the floating catalyst chemical vapor deposition (FCCVD) method and named the products as floating CNTs^[38, 39, 52]. The properties of four different CNTs are summarized in **Supporting Information S1, Table S1**.

The detailed process of the preparation of electrothermal films is illustrated in **Figure 1a–c**. First, TPU (Suzhou Plastics Co., Ltd.) particles were melted in N,N-dimethylformamide (DMF) solution with mechanical stirring for 3 h and then kept overnight to remove air bubbles. Controlled content of CNT (0.1, 0.3, 0.5, 0.7, 1.0 wt%) was dispersed with 0.5 wt% hydroxypropyl methyl cellulose (HPMC) DMF solution and then sonicated at 200 W for 60 min. Controlled volume CNT dispersion solution was added into the polytetrafluoroethylene (PTFE) mold by a pipette, and then heated in an oven at 60 °C for 2 h. Subsequently, 500 µl of TPU hybrid solution was added into the module, and the mixture was heated at 60 °C for 3 h in the oven. After the module was removed, several different-sized flexible spiral CTFs were obtained, as shown in **Figure 1d**. The longest electrothermal film fabricated by us measured approximately 24.0 cm. Films of other different lengths can be achieved by cutting the film fixed on the smooth substrates such as glasses or other hard substrates

with a scalpel knife.

2.2 Characterizations

To identify the morphological features and the dispersion state of different CNTs, the samples were cryogenically fractured in a liquid nitrogen bath and their fractured surfaces were characterized by field emission scanning electron microscopy (SEM, JSM-6390). Raman spectra were obtained using a LabRAM ARAMIS Raman confocal microscope (HORIBA Jobin Yvon) equipped with a 532-nm diode-pumped solid-state (DPSS) laser. Glass slide was used as a substrate for Raman spectroscopy measurements.

The sheet resistance of CTF strips was measured by a semiconductor characterization system (Keithley, 4200-SCS) and multifunction digital four-probe tester (ST-2258A). The widths and lengths of the specimens were kept constant at 10 and 30 mm, respectively. To evaluate the electric heating behavior of CTF, direct electric current (DC, MS-605D) was applied to the sample through two copper wires pasted at the film edges. A thermocouple was used to test the maximum temperature change on each electrothermal film surface in real time. Thermal infrared (IR) images were then obtained by an imaging IR thermometer (FLIR TG165), which can measure temperatures from -25 to 380 °C. Thermal stability of the composite films was measured by thermal gravimetric analysis (TGA, 209 F1) from 50 °C to 900 °C at a heating rate of 10 °C/min under the air flow of 20 ml/min. The plots of weight loss versus temperature were recorded.

3 Results and discussions

3.1 Flexible CTF preparation and characterization

Flexible CTFs were prepared through a simple layer-by-layer method, and the detailed fabrication process is illustrated in Experimental Section and **Figure 1**. Briefly, controlled volume CNT dispersion solution was added into the PTFE mold and then heated in an oven at 60 °C for 2 h. Subsequently, 500 μ l of TPU solution was added into the module and thermally cured at 60 °C for 3 h to hold the CNT layer. After removal of the mold, several different-sized spiral CTFs were produced, as shown in **Figure 1d and e**. In addition, we can also weave the electrothermal blanket through as-prepared CTFs as shown in **Figure 1f**. The IR thermal image in the inset of **Figure 1f** shows the electrothermal behavior of CNT-functioned cotton fabrics, which will be discussed later.

Figure 1. Schematic diagram of CTF fabrication procedure.

CNTs play an important role in the bilayer structure that constructed a rich conductive network. Therefore, four CNTs were used in this study to achieve low electrical resistance. Three of them (FT9000, NC7000, and KJ-2) are commercially available and one is grown in our FCCVD system (see **Supplementary Information**).

CNT solution with concentration up to 1.0 wt% was obtained by simple ultrasonication^[34]. The as-prepared four types of CTFs (rectangle sample: $3 \times 1 \text{ cm}^2$) exhibit different electrical properties. As shown in **Figure 2a**, the NC7000 CTFs had a relatively low sheet resistance, which is attributed to the low I_D/I_G value and small diameter (see **Figure S1** and **Table S1**). The sheet resistance of NC7000 CTFs was as low as 30 Ohm/sq, which is in accordance with Jiang's^[35] work and even lower than the reported results^[2, 16, 18, 24, 31]. In addition, as shown in the inset of **Figure 2a**, the samples prepared by the proposed layer-by-layer method exhibited better electrical properties than those fabricated by direct mixing. The surface morphologies of the four types of CNT were characterized by SEM, as shown in **Figure S2**. NC7000 sample has the smallest diameter and very large surface area, and hence it can form more rich conductive pathways for electron transport^[36]. Although floating CNT has large aspect ratio and excellent crystallization property^[37], residual catalyst particles and amorphous carbon on the surface of CNTs may significantly affect its conductivity (see **Figure S2 a and e**)^[38–40].

Figure 2. (a) The sheet resistance of four types of CTFs with different CNT content. The inset shows the square resistance of NC7000 CTFs fabricated by direct mixing with different CNT content. (b) TGA and (c) DTG curves of NC7000, neat

TPU, and their CTF composites under air.

In addition to the electrical properties, thermal stability of CTFs is very important. From the TG and TGA curves of NC7000 in **Figure 2b** and **c**, we found that the amount of amorphous carbon is very little and can be ignored in our samples^[41]. Furthermore, the thermal degradation behavior of CTFs was improved by CNTs compared to that of the neat TPU film^[33, 42-44]. It has been reported that the thermal degradation of TPU begins with the breakage of the hydrogen bonds generated by the N-H and C=O groups, followed by hard block decomposition at relatively low temperatures and soft block disruption at high temperatures^[32, 44-46].

3.2 Electrothermal performances of CTFs

The electrothermal behaviors of the bilayer films (valid heating area: $3 \times 1 \text{ cm}^2$) were investigated under ambient condition by applying direct current voltages from 1 to 60 V. The voltage-dependent temperature curves of CTFs with different CNT content in **Figure 3a** show that the T_{max} of CTFs with high CNT content monotonically increases linearly with increasing voltage, and can reach to $\sim 140 \text{ }^\circ\text{C}$ for 1 wt% CNT samples with the application of a voltage of 10 V, which was attributed to the good dispersion of NC7000 CNTs and rich conductive networks formed on the thin-layer surface. It should be noted that the steady-state T_{max} of our samples was lower than the reported results, because of the partial block of the heat transfer by the insulating TPU layer in CTFs^[18]. However, the flexible TPU layer can hold the CNT layer and enable the composites to have different shapes and sizes. In addition, the TPU polymer we used has relatively high decomposition temperature of

about 360.1 °C as shown in **Figure 2b** and **c**, which is higher than the maximum steady-state electrothermal temperature of our films. Regular rectangular films were prepared very easily. As mentioned above, this shape exhibited excellent electrothermal performances as shown in **Figure 3a**. In addition, we prepared different lengths of CTFs with constant width to investigate their electrothermal behaviors. As shown in **Figure 3b**, the shorter is the length, the higher is the $T_{\max}$ of the specimen. This may be attributed to the low resistance and the high transduction of electrical energy into Joule heating^[24, 31]. A plot of the electrical resistance of the CTFs versus the length is shown in **Figure 3c**. The relationship curve was nearly proportional to their length. According to the theoretical results, the electrical resistance should be below $\sim 1.0 \text{ K}\Omega$ as indicated by the pink ellipse in **Figure 3c** for our CTFs to be safely used under appropriate voltage range^[16, 33].

Figure 3. Electrothermal performances of rectangular films. Temperature versus voltage profiles of CTFs with different CNT content (a) and with different lengths (b). (c) The resistance curves for five different CTFs lengths. The thickness, length, and width of the as-prepared sample were $\sim 100 \mu\text{m}$, 3 cm, and 1 cm, respectively.

Furthermore, we successfully fabricated spiral and serpentine shapes of CTFs, whose electrothermal performances are shown in **Figure 4**. As shown in **Figure 4a–c**,

the application of external voltage on spiral CTF with low CNT content resulted in an excellent electrothermal behavior. IR images of spiral CTF changed from bright yellow to red with time, and they exhibited uniform temperature distribution, which was attributed to the well-distributed CNTs in CTF^[24, 31]. As shown in **Figure 4 d and e**, after external voltage was applied on serpentine CTF with silver paste electrodes, similar results were observed. IR image of serpentine CTF also changed from bright yellow to red with time (**Figure 4e**), which confirmed the excellent thermal and electrical conductivities of NC7000 CNTs as well as the highly uniform surface of the CNT thin layer. According to above results, the electrothermal behavior of the as-prepared CTFs can be controlled effectively by adjusting power and the content of CNTs. Meanwhile, this type of uniform and flexible CTFs could be used in defogging and defrosting according to the requirements.

Figure 4. Different shapes of CTFs: (a–c) spiral and (d, e) serpentine CTFs. (a) Spiral CTF with electrodes. (b) and (c) IR images of spiral CTF after applying 20 V

for 50 s (b) and 115 s (c), respectively. (d) Serpentine CTFs with silver paste electrodes. (e) IR thermal image of serpentine CTF after applying 50 V for 118 s.

3.3 Electrothermal response and stability of CTFs

The temperature response of the CTFs was also investigated. The response time, which is the time taken for the CTFs to reach a steady-state temperature from room temperature, did not depend on the type of heater^[18]. **Figure 5a–c** shows the time-dependent temperature of three lengths of CNT-based heaters treated with various input voltages. The size of the heaters was 3×1 , 6×1 , and 12×1 cm², respectively. For high voltage, the temperature increased rapidly, reached a saturation temperature within 100–150 s, but cooled slowly to room temperature when the voltage was turned off for 615 s. Furthermore, the $T_{\max}$ increased sharply with the increase in the applied voltage, as presented in **Figure 5a–c**. This type of CTFs can be used for floor heating and defrosting. Using the as-prepared CTFs, we showed that they can heat a color-changing mug easily as shown in **Figure S3 a–e**. When applying certain voltage for different time, the mug changed its color from black to bright yellow. We also found that the electrothermal behavior was highly related to the resistance. In the cases of CTFs with low CNT content, no significant temperature changes were observed below the applied voltages of 10 V, which indicated that there was no obvious electric heating behavior (**Fig. 5b and c**)^[32].

Figure 5. Time-dependent temperature profiles of different-length CTF heaters at applied voltage of 5–50 V: (a) 3×1 , (b) 6×1 , (c) 12×1 cm². (d) Resistance change and temperature response of 3 cm CTF at 8 V. The left inset in (d) shows the measured sample with electrodes for the electric heating experiment and the right inset depicts the Raman spectrum of CTF before and after electrothermal test.

To analyze the temperature response rapidity, the time-dependent temperature curves in **Figure 5a–c** were distributed into three regions: the heating region (0–200 s), the stable region (200–615 s), and the cooling region (615–1200 s) ^[47–50]. The reasons for this heating time growth phenomenon were (1) the thermocouple has a slow heat response and it could be easily affected by surroundings and (2) there was a slight difference between the thermocouple measurement and the IR-based measurement, which was proved by previous studies^[18].

To characterize the long-term stable state during the electrothermal process, thermal aging test with constant temperature was conducted. The tested sample with electrodes for the electric heating experiment is shown on the left inset of **Figure 5d**. As shown in the figure, the temperature and electrical resistance slightly changed during thermal aging test at 8 V for 10 h. During the thermal aging test, temperature initially increased and then gradually decreased after 7 h, but the difference was very small, which indicates that CTFs have good electrothermal stability. From the Raman spectrum of the CTF before and after the electrothermal process in the right inset of **Figure 5d**, it is inferred that the CNT layer could sustain high temperature and its good quality without obvious variations before and after electrothermal measurements.

Because of the excellent electrical properties of NC7000 CNTs, the input electric power was converted to heat through resistance heating or Joule heating on the CNT layer surface. However, the local temperature close to CNT surface was much higher than the interface temperature between the CNT layer and TPU substrate during the electrothermal process, which indicated that the TPU matrix impedes the heat transfer during the electrothermal process^[33]. When the temperature is too high, TPU substrates would be destroyed due to severe thermal damage of TPU^[24]. As shown in **Figure 6**, the thermal degradation deformation phenomenon of TPU matrix was characterized by the microstructural images before and after electrical heating (E-heating) over 300°C. Several voids appeared that would result in the disconnection of local electrical networks on the surface and a significant increase in the electrical

resistance^[33, 51]. As presented in **Figure 6d**, some voids were also observed in the interface between the CNT thin layer and TPU substrate. Thus, apart from the CNT content factors, we should also pay close attention to the application of external voltage^[24]. According to the thermal degradation curves of the composites in **Figure 2b** and **c**, the electrothermal temperature should be lower than the thermal decomposition temperature of the TPU matrix. To increase the electrothermal temperature, other polymers with high heat resistance will be needed.

Figure 6. SEM images of the CTFs before (a, c) and after (b, d) electrothermal measurements. (a, b) Plane images. (c, d) Cross-sectional images.

4. Conclusions

In summary, we prepared flexible CTFs by a simple layer-by-layer method. The electrothermal performance of these CTFs was systematically investigated. The excellent electrical and thermal stability properties and electrothermal performance of

the CTFs were attributed to the good dispersion of NC7000 and its high conductivity. The $T_{\max}$ of CTFs could be finely controlled by adjusting the applied voltage. We found that the electrothermal behavior of the as-prepared CTFs was strongly dependent on the conductivity of CNTs and applied voltage. Furthermore, the CTFs exhibited excellent electrothermal performance even under large spiral and serpentine deformation, which was due to the improved flexibility of the TPU layer. Even though these CTFs are ideal heater materials because of their easy processability, lightweight, and rapid heating, careful consideration is necessary for their application. Accordingly, from the economic point of view, it is highly expected that flexible and conductive CTFs could be widely applied in defogging and defrosting applications.

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