Multiwalled carbon nanotube/polydimethylsiloxane composite films as high performance flexible electric heating elements

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High performance elastomeric electric heating elements were prepared by incorporating various contents of pristine multiwalled carbon nanotube (MWCNT) in polydimethylsiloxane (PDMS) matrix by using an efficient solution-casting and curing technique. The pristine MWCNTs were identified to be uniformly dispersed in the PDMS matrix and the electrical percolation of MWCNTs was evaluated to be at ~0.27 wt. %, where the electrical resistivity of the MWCNT/PDMS composite films dropped remarkably. Accordingly, the composite films with higher MWCNT contents above 0.3 wt. % exhibit excellent electric heating performance in terms of temperature response rapidity and electric energy efficiency at constant applied voltages. In addition, the composite films, which were thermally stable up to 250 °C, showed excellent heating-cooling cyclic performance, which was associated with operational stability in actual electric heating applications. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4892545]

Carbon nanotubes (CNTs) have been investigated tremendously to have high carrier mobility of 1000–4000 cm² V⁻¹ s⁻¹, electrical conductivity of 10⁴–10⁵ S cm⁻¹, Young’s modulus of 0.27–1.25 TPa, thermal conductivity of 3000–6600 W m⁻¹ K⁻¹, and thermal stability up to ~700 °C in air.¹–³ These superlative mechanical, thermal, and electronic properties of CNTs make them ideal reinforcing nano-fillers for high performance and multifunctional polymer composites.⁴ Especially, the electrically conductive polymer composites with CNT fillers have potential applications in advanced areas such as electromagnetic shielding,⁵,⁶ super-capacitors,⁷,⁸ sensors,⁹,¹⁰ smart actuators,¹¹,¹² energy harvesting,¹³ and biomedical devices.¹⁴,¹⁵ Since CNT/polymer composites provide comprehensive characteristics such as light weight, mechanical resiliency, cost-effectiveness, facile processability, scalability, and compliance, they could be applied as electric heating elements.¹⁶–¹⁸ In general, electric heating materials or devices, which are a kind of electrical resistors that convert electrical energy into thermal energy as heat by the collision of moving electrons with the atoms that make up the body of the conductor, are used for advanced applications including floor heating, mirror/window defrosting, road deicing, medical instruments, functional textiles, industrial processes, etc. Accordingly, the electric heating composites based on thermally stable polymeric matrices such as aramid and epoxy have already been investigated.¹⁶–¹⁸ However, although aramid and epoxy-based polymeric matrices are thermally stable, which are good for the electric heating application, they are not flexible and biologically compatible.

Polydimethylsiloxane (PDMS), a kind of silicon-based elastomer, has several attractive properties including excellent optical transparency, chemical/biological inertness, non-toxicity, gas permeability, and flexibility,¹⁹,²⁰ which is thus considered as an ideal candidate for elastomeric composite matrices. Additionally, for CNT/polymer composites, the tunneling resistance depends not only on the inter-tube distance but also on the polymer type determining the tunneling energy barrier height λ. The PDMS possesses relative low tunneling barrier height of 0.73 eV,²¹ comparing to the epoxy with 1.5 eV, resulting in lower tunneling resistances.²²

In this study, a series of PDMS-based composite films with different multiwalled CNT (MWCNT) contents of 0.0–10.00 wt. % were manufactured by using an effective solution-casting and curing technique. The electric heating performance of the MWCNT/PDMS composite films was systematically investigated as functions of MWCNT content and applied voltages by considering the microstructure and electrical properties.

For obtaining the composite films, pristine MWCNT (CM-95, Hanwha Chemical) with 10–15 nm diameter and 10–20 μm length, produced by thermal chemical vapor deposition, was used as conductive reinforcing nanofiller. PDMS and curing agent (Sylgard 184 Silicone Elastomer Kit, Dow Corning) were used as elastomeric polymer matrix. n-Hexane (Samchun Pure Chemical) was used as solvent for preparing MWCNT/PDMS solutions.

MWCNT/PDMS composite films were manufactured by solution-casting and curing technique. First, the n-hexane solutions with different MWCNT contents (0.0–10.0 wt. % of PDMS) were prepared by ultrasonication for 1 h using a bath-type ultrasonicator (50–60 Hz). After adding predetermined amounts of PDMS into the MWCNT/n-hexane solutions, another ultrasonication was applied for 1 h. Subsequently, the curing agent (10:1 weight ratio) was added into the MWCNT/PDMS/n-hexane solutions, which were casted onto glass petri-dishes and cured at room temperature for 24 h and at 70 °C for 2 h. During the curing process, the n-hexane solvent could be evaporated. Finally, the MWCNT/PDMS composite films were dried in a vacuum oven at 40 °C for 24 h. The final samples were named as

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MWCNT/PDMS_x, where x denotes the MWCNT content in the composite films by wt. %.

The morphological features of the composite films were examined by cross-section observation using a cold type field emission scanning electron microscope (SEM) (S-4800, Hitachi). To obtain the SEM images, the fracture surface of the composite films was coated with osmium conductive metal. Electrical current and power of the composite films with different MWCNT contents were measured as a function of applied voltage by using multiple sourcemeter and nanovoltmeter (2400, 2182A, Keithley Instruments). Electric heating behavior of the composite films under a variety of voltages of 1–100 V was characterized with an infrared camera (SE/A325, FLIR Systems) and a sourcemeter (2400, Keithley Instruments). For the electrical experiments, the distance between electrical test probes on the composite films (5.0 mm × 20.0 mm) was fixed at 10.0 mm. The thermal stability and the thermal degradation behavior of the composite films were investigated under N₂ atmosphere using a thermogravimetric analyzer (TGA/DSC 1, Mettler-Toledo) from 25 to 800 °C at a heating rate of 10 °C/min.

Figure 1(a) exhibits a representative digital image of a MWCNT/PDMS composite film in bending deformation. It illustrates that the composite film is highly flexible and compliance due to the natural physical property of PDMS and the good dispersion of MWCNTs in the PDMS matrix. The SEM images of pristine MWCNT, neat PDMS, and MWCNT/PDMS composite films with different MWCNT contents are shown in Figures 1(b), 1(c), and 1(d)–1(f), respectively. For the pristine MWCNTs with high aspect ratio, none obvious damages can be observed for the pristine MWCNTs, confirming that the ultrasonication is an efficient way to disperse MWCNT in the polymer matrix within our experimental condition (Figure 1(b)). The fracture surface of the neat PDMS is very clean and smooth without any defects (Figure 1(c)), indicating that perfect PDMS and its composite films can be effectively processed via the solution casting and curing technique used in this study. For the MWCNT/PDMS composite films, MWCNTs are found to be uniformly and randomly dispersed in the PDMS matrix (Figures 1(d)–1(f)).

The electrical properties of MWCNT/PDMS composite films were investigated as functions of MWCNT content and applied voltage. The current-voltage (I-V) and electric power-voltage (P-V) curves of the composite films with different MWCNT contents are represented in Figures 2(a) and 2(b), respectively. For the neat PDMS and the composite films with 0.1 wt. % MWCNT, the electric current and power were quite low over the applied voltage range of 1–100 V. This result demonstrates that, for the composite films with low MWCNT content of 0.1 wt. %, the conductive network paths of MWCNTs cannot be formed due to the physical barrier among MWCNTs that hinders the flow of charge carrier through the PDMS matrix. In cases of the composite films with high MWCNT contents of 0.3–10.0 wt. %, the electric current and power increased considerably with the applied voltage and their increases were greater for the composite films with higher MWCNT contents. Therefore, it is speculated that the interpenetrating network structure of MWCNTs is formed in the PDMS matrix at a critical percolation threshold between 0.1 and 0.3 wt. % MWCNT, and that the conductive network is improved quantitatively with the MWCNT content within the PDMS matrix. It should be also noted that the electric current increased linearly at low applied voltage (Figure 2(a)), while the slopes of the I-V curves increased positively at high applied voltage. This result indicates that the electrical transport of MWCNT/PDMS composite films with 0.3–10.0 wt. % MWCNTs at low applied voltages obeys the Ohm’s law of $I = V/R$, where $R$ indicates the electrical resistance, whereas the electrical transport was enhanced at higher applied voltage owing to the temperature increment of composite films by electrical heating, as will be discussed below. On the other hand, in Figure 2(b), the electric power of the composite films increased quadratically with the applied voltage, according to the equation of $P = IV = V^2/R$.

The electrical resistance $R$ of the MWCNT/PDMS composite films was evaluated from the initial slopes of I-V curves in Figure 2(a) and the values were plotted as a function of the MWCNT content, as can be seen in Figure 2(c). In addition, the electrical resistivity $\rho$ of the composite films could be calculated by using the equation $R = \rho (L/A)$, where

![FIG. 1. (a) Digital image of a MWCNT/PDMS composite film in bending and (b)–(f) SEM images of pristine MWCNT, neat PDMS, and MWCNT/PDMS composite films.](image-url)
$L$ is the sample length between electrodes and $A$ is the cross-sectional area of a film sample, and the results were also presented in Figure 2(c). It was found that electrical resistivity decreased dramatically from $\sim 10^7 \ \Omega \ \text{cm}$ for the neat PDMS to $\sim 10^5 \ \Omega \ \text{cm}$ for the composite with 10.0 wt. % MWCNT by displaying a typical percolation behavior. The low electrical resistivity of MWCNT/PDMS composite films is strongly related with the morphological feature (SEM images in Figures 1(d)–1(f)). For the composite films with higher MWCNT contents, the MWCNTs are more densely dispersed in the PDMS matrix and the barrier thickness of PDMS among MWCNTs is also even thinner, which results in facilitating the electron tunneling among MWCNTs for the efficient electrical conduction. Especially, it appears that the electrical percolation threshold is formed at certain MWCNT content between 0.1 and 0.3 wt. %. It is generally accepted that, when the CNT content reaches the electrical percolation threshold, a conductive path is formed in the composite matrix due to the network of MWCNTs.\textsuperscript{24–26} To determine the electrical percolation threshold, the power law relation $\sigma \propto (p - p_c)^{\alpha}$ was adopted,\textsuperscript{27,28} where $\sigma$ is the electrical conductivity (the inverse of electrical resistivity), $p$ is the MWCNT volume fraction, $p_c$ is the critical volume fraction at electrical percolation, and $\alpha$ is the critical exponent. The straight line with $p_c = 0.001655$ ($\sim 0.27$ wt. %) and $\alpha = 2.3162$ gives a good fit to the experimental data of log $\sigma$ vs. log ($p - p_c$) plot (Figure 2(d)). Theoretically, the critical exponent as an index of the system dimensionality has been predicted to be 1.3 and 1.94 for ideal 2-D and 3-D systems, respectively.\textsuperscript{27} Since the percolation theory associated with the above power law relation cannot take into account either of particle shape, dispersion, orientation, and interaction, the value of $\alpha$ varies with particular composite systems. Computer model on a system of randomly placed rigid rods connected by free joints predicted a critical exponent value of 2.\textsuperscript{29} Other experimental studies of polymer composites with homogeneous isotropic dispersion of CNTs have frequently reported values of 1.6–3.2.\textsuperscript{30} Thus, the $\alpha$ value of 2.3162 for the MWCNT/PDMS composite films indicates that MWCNTs with high aspect ratio form a quasi-3-D network structure in the PDMS matrix above the percolation threshold of $\sim 0.27$ wt. % MWCNT. In addition, it is speculated that the low $p_c$ value arises from the uniform and random dispersion of MWCNTs in the PDMS matrix. As the result, for the composite films with high MWCNT of 3.0–10.0 wt. %, the quite low electrical resistivity of $\sim 10^5 \ \Omega \ \text{cm}$ can be attained.

Electric heating behaviors of the composite films with different MWCNT contents were investigated by applying different constant voltages from 1 to 100 V. There were no apparent temperature changes for the composite films with 0.0–0.1 wt. % MWCNT contents at applied voltages of 1–100 V. In the case of MWCNT/PDMS 0.3, the slight temperature change was observed at only high applied voltages. For the composite films with MWCNT contents of 0.5–10.0 wt. %, the temperature increased steeply once a voltage above response point as applied at 0 s, reached a maximum value within $\sim 20$ s, and decreased quickly to

![Figure 2. (a) Current voltage (I-V) and (b) electric power-voltage (P-V) curves for neat PDMS and its composite films with different MWCNT contents. (c) Electrical resistance and resistivity of MWCNT/PDMS composite films as a function of the MWCNT content. (d) log $\sigma$ vs. log ($p - p_c$) plot from the power relation $\sigma \propto (p - p_c)^{\alpha}$ with the experimental electrical conductivity data.](image)
room temperature when an applied voltage was off at 185 s. For instance, time-dependent temperature changes for MWCNT/PDMS_2.0, in addition to digital and infrared images for electric heating experiment, are shown in Figure 3(a). It was found that the electric heating behavior of the MWCNT/PDMS composite films was strongly dependent on the MWCNT contents as well as the applied voltages (Figure 3(b)). The maximum temperature increased with the increment of the applied voltage and MWCNT content.

To pursue more detailed analysis for the electric heating behavior, the time-dependent temperature curves in Figure 3(a) were divided into three regions: the temperature growth (heating) region (0–20 s), the equilibrium (maximum temperature) region (20–185 s), and the temperature decay (cooling) region (185–250 s). During the first region, the temperature growth with time can be empirically expressed as

\[
T_t = T_0 + (T_m - T_0) \exp \left( -\frac{t}{\tau_g} \right),
\]

where \(T_0\) and \(T_m\) are the initial ambient and the maximum temperatures, respectively, \(T_t\) is the arbitrary temperature at time \(t\), and \(\tau_g\) is the characteristic growth time constant. For the composite films showing electric heating behavior, the \(\tau_g\) values could be calculated by fitting the data in the first stage of temperature versus time plots, and the resulting values for all the composite films with 0.5–10.0 wt. % MWCNT are listed in Table I.

During the second region in equilibrium, heat gain by electric power is equal to heat loss by radiation and convection according to the conservation law of energy. The heat transferred by radiation and convection, \(h_{r+c}\), is expressed as

\[
h_{r+c} = \frac{I_c V_0}{T_m - T_0},
\]

where \(I_c\) is the steady-state current and \(T_0\) is the applied voltage. Accordingly, the \(h_{r+c}\) values could be calculated, as summarized in Table I.

During the third region, the composite films at maximum temperatures are left to cool down to the ambient temperature according to Newton’s law of cooling, which states that the rate of change of the temperature of an object is proportional to the difference between its own temperature and the surrounding temperature.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Voltage (V)</th>
<th>(\tau_g) (s)</th>
<th>(\tau_d) (s)</th>
<th>(h_{r+c}) (mW/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWCNT/PDMS_0.5</td>
<td>30–100</td>
<td>5.31 ± 1.10</td>
<td>5.50 ± 0.32</td>
<td>10.61 ± 1.06</td>
</tr>
<tr>
<td>MWCNT/PDMS_0.7</td>
<td>30–100</td>
<td>5.41 ± 0.64</td>
<td>5.59 ± 0.78</td>
<td>10.99 ± 1.09</td>
</tr>
<tr>
<td>MWCNT/PDMS_1.0</td>
<td>20–90</td>
<td>6.49 ± 0.76</td>
<td>6.72 ± 0.81</td>
<td>7.10 ± 2.26</td>
</tr>
<tr>
<td>MWCNT/PDMS_1.5</td>
<td>20–80</td>
<td>4.34 ± 0.77</td>
<td>4.75 ± 0.20</td>
<td>7.39 ± 1.14</td>
</tr>
<tr>
<td>MWCNT/PDMS_2.0</td>
<td>10–70</td>
<td>3.18 ± 0.57</td>
<td>3.63 ± 0.45</td>
<td>8.23 ± 1.80</td>
</tr>
<tr>
<td>MWCNT/PDMS_3.0</td>
<td>10–40</td>
<td>2.86 ± 0.48</td>
<td>3.13 ± 0.38</td>
<td>6.01 ± 1.22</td>
</tr>
<tr>
<td>MWCNT/PDMS_5.0</td>
<td>5–30</td>
<td>2.55 ± 0.48</td>
<td>2.34 ± 0.12</td>
<td>5.57 ± 0.91</td>
</tr>
<tr>
<td>MWCNT/PDMS_7.0</td>
<td>5–30</td>
<td>1.46 ± 0.28</td>
<td>1.74 ± 0.12</td>
<td>5.33 ± 1.49</td>
</tr>
<tr>
<td>MWCNT/PDMS_10.0</td>
<td>5–25</td>
<td>0.95 ± 0.59</td>
<td>0.81 ± 0.11</td>
<td>6.26 ± 1.81</td>
</tr>
</tbody>
</table>
the ambient temperature. Therefore, the temperature decreases with time, which can be described by the following empirical formula:

$$\frac{T_t - T_0}{T_m - T_0} = \exp(-t/\tau_d),$$

where $\tau_d$ is the characteristic decay time constant. The $\tau_d$ values can be calculated by fitting experimental time-dependent temperature decay data, as summarized in Table I. For all the composite films with 0.5–10.0 wt. % MWCNT, the values of $\tau_g$, $\tau_{r+c}$, and $\tau_d$ have a trend of decline with the increment of MWCNT content within the experimental error, demonstrating that the composite films with higher MWCNT content possess more sensitive temperature responsibility to applied voltages. Additionally, the average values of $\tau_g$, $\tau_{r+c}$, and $\tau_d$ are evaluated to be $3.62 \pm 1.89$ s, $7.99 \pm 2.46$ mW/$^\circ$C, and $3.80 \pm 1.98$ s, which are found to be far lower than the ones for inorganic filler-reinforced polymer composites reported in literatures. It indicates that the MWCNT/PDMS composite films exhibit unusually rapid temperature responses to applied voltages as well as high electric heating efficiency requiring relatively low electric energy to maintain the maximum temperatures.

It is noticeable that the maximum temperatures ($T_{\text{max}}$) of the composite films with 0.5–10.0 wt. % MWCNT increased quadratically with the increment of the applied voltages, as can be seen in Figure 3(b). This result is quite reasonable by considering the facts that the electric power is quadratically proportional to the applied voltage, based on the relationship of $P = IV = V^2/R$, and that the electric power is transferred to heat by the resistance heating or Joule heating process in the composite films. In addition, a relevance between the electric power and generated heat (i.e., maximum temperature) was found, as illustrated in Figure 3(c). The $T_{\text{max}}$ of all the MWCNT/PDMS composite films was found to respond linearly to the applied voltage with the coincident tendency. According to this consequence, a desired maximum temperature can be effectively controlled by adjusting applied electric power.

The operational stability of the MWCNT/PDMS composite films as electric heating elements was investigated by evaluating cyclic electric heating-cooling performance. Figure 3(d) shows the temperature response of MWCNT/PDMS_1.0 under a stepwise periodic change of 70 V. It was found that, over the periodic voltage change of 70 V, the electric heating and cooling behavior as well as the maximum temperature of ~218 $^\circ$C remain constant without any structural change of the composite film, which is due to the excellent thermomechanical stability of the PDMS matrix. From the thermogravimetric analysis, the MWCNT/PDMS composites films were thermally stable up to ~250$^\circ$C (not shown here).

In summary, MWCNT/PDMS composite films as flexible electric heating elements were prepared successfully using solution-casting and curing method. The MWCNTs were found to be uniformly and randomly dispersed in the PDMS matrix. The electrical resistivity of the composite films changed considerably with the MWCNT content from $\sim 10^8$ $\Omega$ cm for neat PDMS film to $\sim 10^6$ $\Omega$ cm for MWCNT/PDMS_10.0. The electrical percolation threshold was evaluated to be $\sim 0.27$ wt. % MWCNT. The electric heating performance of the composite films with 0.5–10.0 wt. % MWCNT was strongly dependent on the MWCNT content as well as the applied voltage. The maximum temperature of the composite films increased with the increment of the applied voltage and MWCNT content. In addition, the composite films exhibited outstandingly rapid temperature response and high electric power efficiency at a given applied voltage. The MWCNT/PDMS composite films with good thermomechanical stability up to ~250$^\circ$C were found to have excellent operational stability in stepwise periodic electric heating-cooling conditions. Overall, it is valid to contend that MWCNT/PDMS composite films could be utilized as high performance flexible electric heating elements or devices for floor heating, window defrosting, road deicing, medical instruments, and functional textiles.