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Responses and thermal conductivity measurements of multi-wall carbon nanotube (MWNT)/epoxy composites

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Abstract In the present study, the MWNT/epoxy composites are prepared with three weight percentages (0.0, 0.3, and 0.5%) of multiwall carbon nanotube (MWNT). The temporal response of multi-wall carbon nanotube (MWNT)/epoxy composite with different wt% of multi-wall carbon nanotube (MWNT) is measured by experiment. Also, a cavity-type measuring system is designed to experimentally measure the surface temperatures and obtain the thermal conductivity of these composites at different heating rates. It is found that the responses of the 0.3 and 0.5% weight percentage of multi-wall carbon nanotube (MWNT)/epoxy composites are found to be about 25 and 47.8%, respectively, faster than that of the pure epoxy resin. Both the responding characteristics and the variation trends of the measured surface temperatures of these composites can be well predicted by the lumped-heat capacity model. Besides, the higher the weight percentage (wt%) of multi-wall carbon nanotube (MWNT) in the composite, the larger is the thermal conductivity. Relative to the pure epoxy, the thermal conductivities for the composites with 0.3 and 0.5% of multi-wall carbon nanotube (MWNT) increase by 15.9 and 44.9%, respectively. For the weight percentages studied, the thermal conductivity of these composites is found to increase mildly at low heating rates; however, it remains nearly constant at high heating rates.

Keywords Thermal conductivity · Responding time · Time constant · Temperature measurement · Lumped-heat-capacity model

Introduction

Following the discovery of the bucky ball (C_{60}) by Kroto et al. [1], Iijma [2] and Ijima and Ichihashi [3] reported two new needle-like carbon structures using an arc-discharge evaporation method. Namely, the multi-wall carbon nanotube (MWNT) and the single-wall carbon nanotube (SWNT). A SWNT is a graphene sheet rolled into a cylinder with typical diameter on the order of 1.4 nm. However, a MWNT consists of several concentric cylinders with diameters around 10–20 nm. From then on, the intriguing properties of carbon nanotubes (CNTs) became the most attractive research topic worldwide. Researches from different areas were devoted to understand the mechanical, the electrical, the optical, and the thermal properties of the CNTs. Their primary aims were to explore the key applications of this new material.

In terms of mechanical properties, CNTs were among the strongest and the most resilient material in nature. The tensile strength of a CNT is about a hundred times higher than the steel. A CNT has a Young's modulus of 1.2 TPa, and can tolerate large strain before mechanical failure [4–8]. What is more, in the results of Allaoui et al. [6], the Young's modulus and the yielding strength for the MWNT/epoxy composite with 1 and 4 wt% CNTs were about two and four times higher than that for pure epoxy resin. In the study of Gojny et al. [7], the dispersibility, the specific surface area, and the surface chemical functionalization are the key parameters in the development of CNT-based composites. Only small amount of CNT in epoxy can increase at least 10–15% of the strength and the stiffness; especially, the fracture toughness increases significantly about 43%. This unique mechanical property supports the potential of the CNTs as reinforcement fibers used in multi-functional structural material and other polymer composites [8].

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On the other hand, the thermal conductivities of CNTs are even superior to those of diamonds and graphite. The thermal conductivity of an individual MWNT was measured at least two orders of magnitude higher than that used in macroscopic sample. For examples, the measured longitudinal thermal conductivity of an individual MWNT can be as high as 3000 $\mathrm{Wm^{-1}\,K^{-1}}$; and the theoretical predicted value of a single SWNT approaches 6600 $\mathrm{Wm^{-1}\,K^{-1}}$ [9] at room temperature. Hone et al. [10] studied the thermal conductivity of the bulk sample of a SWNT bundle. The thermal conductivity is found to be large and dominated by phonons at all temperatures. Further, the thermal conductivity varied almost linearly at very low temperature range and increased monotonously up to the room temperature. Nan et al. [11] investigated the heat capacity of SWNT and MWNT at low temperature range (78–398 K). They demonstrated that the heat capacities of SWNT and MWNT are different; and both heat capacities increase with increasing temperature. Similar results of the heat capacity are also reported by Xu et al. [12]. Because of the excellent thermal conductivity, it is ideal to employ the CNT as the filler of the CNT-based composites for enhancing the heat transfer rate. For instance, the high power and high luminance of light emitting diode (LED) are now in market and in emergent needs to efficiently dissipate the generated heat energy. If the CNTs can be dispersed into epoxy material of LED, the poor thermal conductivity is expected to be largely improved. In such a case, the large amount of the heat generated by the high power LED can be effectively transferred to the environment, leading to long life time and efficient luminance of the LED [13].

The thermal analysis by Singh et al. [14] and by Song and Youn [15] reported that the equivalent or effective thermal conductivity of CNT-based composites increases as the length and the diameter (or the aspect ratio) of CNTs increase. Abdalla et al. [16] measured the thermal diffusivity and conductivity for the randomly dispersed MWNT in epoxy composite; and they showed a 70 and 107% increase, respectively, compared with the pure epoxy resin. In the studies of Gojny et al. [17], Wu et al. [9], and Cho et al. [18], the CNTs are employed as fillers to enhance the thermal conductivities for the epoxy-based, high-density polyethylene-based, and copper-based composites, respectively. All their results showed that the thermal conductivities increase almost linearly with increasing wt% of the CNTs in the composites. Further, Karippal et al. [19] employed the twin-screw extrusion process to disperse the MWNT into epoxy. They presented that the experimental measured thermal conductivities increased with the increase of the filler loading (or wt%) of MWNT. A maximum increase of 60% is found at 150 °C in case of 8 vol% of the MWNT.

The thermal conductivity of the composite material is usually measured through the laser flash analysis (LFA) [8, 9, 18]; but Gojny et al. [17] employed the Hot Disk thermal analyzer. In this study, a cavity-type system is designed so that the temperature difference measured on both the top and the bottom surfaces of the composite can be maintained nearly constant for a very long sampling period. Though the principle of measuring the thermal conductivity in the present study is similar to the above-mentioned methods, the constant temperature difference measured on both surfaces of the composite gives us a reliable indication that the heating process actually reaches a steady state. In such equilibrium conditions, the thermal conductivities calculated based on the Fourier’s law is reasonable at each specific heating rate studied herein. Therefore, the objective of the present study is to focus first on investigating the responding time of the MWNT/epoxy composites with different weight percentage (wt%) of MWNT subjected to a sudden change of temperature. Three different wt% (0.0, 0.3, and 0.5%) of MWNTs were prepared to form a bulk MWNT/epoxy composite specimen. Also, the effects of weight percentage (wt%) of MWNT and the heating rates on the thermal conductivity of the MWNT/epoxy composites are studied with an attempt to resolve the heat transfer problems in the high powered LED devices.

Experimental setup and measuring techniques

The epoxy resin used in this study is made by Sil-More Industrial Ltd. (Taiwan). It is a two-component transparent epoxy (H-190/E-190). The epoxy (H-190) and its hardener (E-190), with a weight ratio 100:40, were prepared to mix with the acylated MWNT. Agitate this mixture for 72 h to uniformly disperse the MWNT in the epoxy resin. The multi-walled carbon nanotube (MWNT) is produced by CVD method and is manufactured by Desunnano Ltd. Company (Taiwan). The averaged diameter is around 20 nm, the length is about 10–20 µm and the purity is higher than 92%.

Preparation of MWNT/epoxy composite specimen

In general, the CNTs are not soluble in the water and the organic solutions and they will aggregate into clusters due to the Van der Waals forces. To make it soluble, the functional group on the surfaces of the CNTs should be modified by the chemical means [1, 20]. The MWNT/epoxy composites were prepared in the following sequences: purification, carboxylation, acylation, and mixed with the epoxy. Finally, the liquid composite will be solidified into a thin disk-shaped bulk specimen. To purify the

MWNT, a solution containing DI water and 6 M HCl (1:1) is mixed with the MWNT. The mixture is stirred continuously by the electromagnetic agitator for 4 h, and then waits for complete sedimentation. Remove the transparent liquid phase, add DI water again and repeat the above procedure for four or five times. The purified (99.5%) MWNT is obtained when the moisture in the solid phase, maintained at 60 °C, is dried out. For the carboxylation, the solution of sulfuric (90%) and nitric (70%) acids (3:1) was first mixed with the purified MWNT. This solution is maintained at 50 °C and stirred continuously by the ultrasonic vibrator for 24 h. Use DI water to dilute the strong acid, and filter the solution with a pore diameter of 450 nm. The solid phase is maintained at 60 °C for 24 h until the moisture is removed. Finally, the carboxylic acid group is formed on the surfaces of the MWNT. For the process of acylation, the solvent $SOCl_2$ (thionyl chloride) was added into carboxylized MWNT and maintained at 70 °C. Meanwhile, it is agitated continuously for 24 h until the chemical reaction is completed. Cool down the solution to the room temperature, add the THF (tetrahydrofuran) to the solution and stir it for 24 h. Separate the solid/liquid phases by centrifugal. To complete the acylation of the MWNT, this process will be repeated for several times until the finalized solid phase was dried at room temperature within a vacuum chamber. After acylation, the acyl-chloride groups (R–COCl) formed on the surfaces of MWNT will make the MWNT soluble with the epoxy resin. Afterwards, the epoxy and its hardener with a weight ratio 100:40 were prepared to mix with the acylated MWNT. Agitate the mixture for 72 h until the MWNT is uniformly and randomly dispersed in the epoxy resin. Then, the liquid-state composite material was poured into the mould and was solidified into a disk-shape bulk specimen with 5.0 cm diameter and 3.4 mm thickness.

Designs and setups of experimental models

Temperature measuring technique

Surface temperature measurements are performed using a K-type thermocouple with a time constant of 1 ms. The measurable range of the temperature lies between −190 and 1400 °C, and the resolution is 0.5 °C. The analogous signals of the measured temperature were acquired via RS232 interfaced by a PC-based data acquisition system. A 12-bit analog-to-digital (A/D) converter had a maximum sampling rate of 330 kHz for single channel data acquisition. Since the time constant is 1 ms, a sampling frequency of 1 Hz is good enough to detect the temporal variations of the surface temperatures of the MWNT/epoxy composite. For each experimental condition, four temperature measurements were made. Each has a sampling length of 1200 s.

Evaluations on responding characteristic of composites

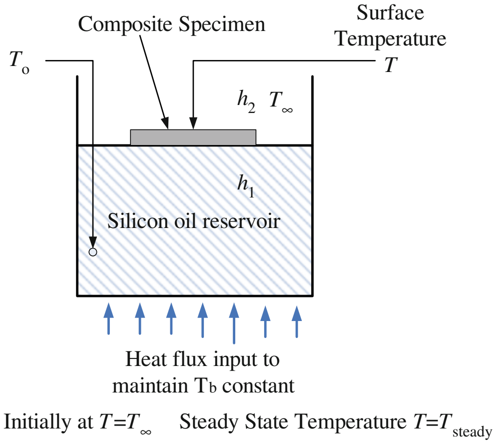
As shown in Fig. 1a, the silicon oil reservoir is preheated to a stable and constant temperature (T_o). Since the oil reservoir has a volume sufficiently large compared with that of the composite specimen studied, the oil temperature will be nearly constant ($T_o = 156$ °C) during the experiments. The ambient temperature is kept at room temperature (T_∞). After the specimen is carefully brought into contact with the free surface of the oil reservoir, the specimen is subjected to a sudden change of temperature. The instant at which the bottom surface of the specimen contacts with the oil surface is defined as $t = 0$. All the temporal responses of the top-surface temperature of the composite are recorded from $t = 0$ until the temperature reaches a steady state value (T_{steady}). These temporal variations of the top-surface temperature are used to evaluate the time constants or the responding characteristics of the composites with different wt% of MWNT.

Temperature measuring system and thermal conductivity calculation

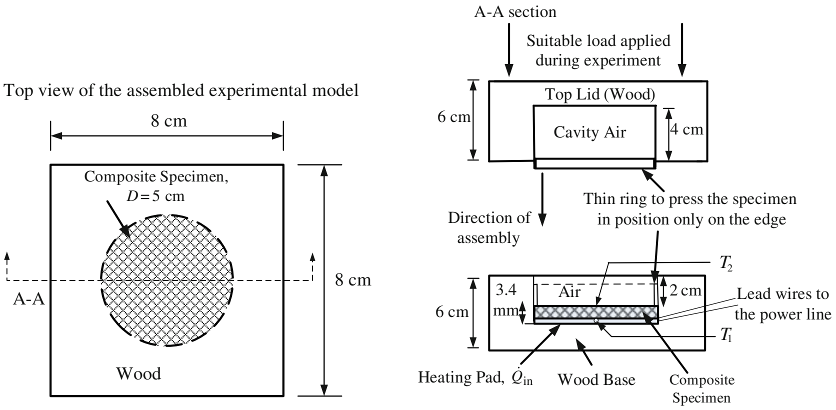
To calculate the thermal conductivity of the MWNT/epoxy composite, we design an enclosed cavity system shown in Fig. 1b to measure the surface temperatures and calculate the thermal conductivity of the MWNT/epoxy composite. Since the wood material has poor thermal conduction, the cavity walls, made of wood, provide ideal insulated conditions. A top lid of the same material is placed on the top to form an enclosed cavity. Within the cavity, the air is affected only by the natural convection over a heated horizontal surface. A heating pad, supplying a constant heating rate ($\dot{Q}_{in}$), is placed at the bottom of the cavity. The composite specimen is seated right on the top of the heating pad. To keep the heating pad to contact firmly with the specimen's bottom surface, a suitable compression load is applied to the top lid through a thin circular ring. This ring presses only on the outer rim of the circular specimen to keep the specimen in firm contact with the soft heating pad and minimize the thermal contact resistance between these two materials. Two thermocouples (T_1 and T_2) are located at the centers of the bottom and the top surfaces of the specimen to measure the temperature. The temperature differences ($T_1 - T_2$) will be employed to calculate the thermal conductivity of the bulk composite specimen.

Using this design, almost all the input energy is expected to be absorbed by the specimen and the air inside the cavity. Thus, the air temperature within the cavity and

Fig. 1 Experimental setups and arrangements of MWNT/Epoxy composite specimen for **a** the temperature response measurement, **b** the thermal conductivity measurement



(a) Lumped model for temperature response measurement



(b) Thermal conductivity measurement

the surface temperatures of the composite specimen are expected to increase during the experiments. Though the temperatures at the top and the bottom surfaces of the specimen do increase with time, shortly after the transient period, the temperature difference $(T_1 - T_2)$ is nearly constant during a long sampling period about 1000 s. Therefore, the thermal conductivity of each composite is calculated by the one-dimensional Fourier conduction law while the temperature difference $(T_1 - T_2)$ reaches a constant level. The averaged thermal conductivity was calculated from the four temperature measurements for each condition.

Additional temperature measurements are also performed at other radial locations of the specimen to ensure that the quasi one-dimensional heat conduction process is valid. For the specific heating rate $\dot{Q}_{in} = 2.99$ W, seven temperature measurements are performed and averaged. On the top surface, Fig. 2 shows the averaged temperature differences between the center $T_2(0)$ and those at other radial locations $T_2(r)$ at the highest heating rate $\dot{Q}_{in} = 2.99$ W. The maximum temperature difference averaged from seven sample measurements is 1.8 °C, leading to a maximum uncertainty of thermal conductivity around 7.2%. This implies that the one-dimensional thermal conduction process across the specimen is nearly valid for these thin composite specimen (thickness to diameter ratio, $t/D = 6.8\%$). Therefore, the temperature difference and the thermal conductivity obtained at the

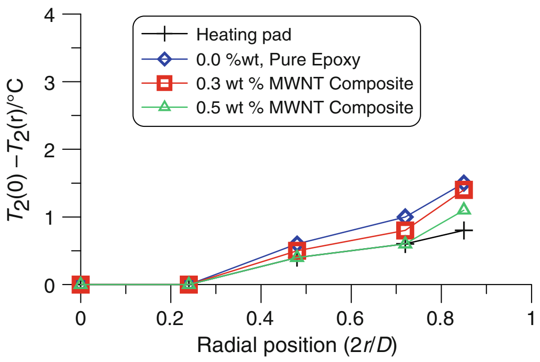


Fig. 2 Averaged temperature differences between the temperatures at the center and that at any radial locations of the specimen for $\dot{Q}_{in} = 2.99$ W

center position can be a representative value of the composite.

Mathematical models

Lump-heat-capacity model for temporal response

To illustrate the temporal response of the specimen's temperature, a lumped-heat-capacity system is modeled to interpret the variation trends of the experimental results. In the lumped-heat-capacity analysis, the temperature of the whole specimen is assumed constant but will change with time. The energy balance on the specimen for a one-dimensional, unsteady, lumped-heat-capacity system in Fig. 1a is given by

$$\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}\frac{\mathrm{d}T}{\mathrm{d}t} = \dot{Q}_{\mathrm{in}} - \dot{Q}_{\mathrm{out}} \tag{1}$$

where

$$\dot{Q}_{\mathrm{in}} = h_1 A_{\mathrm{s}}(T_{\mathrm{o}} - T), \text{ and } \dot{Q}_{\mathrm{out}} = h_2 A_{\mathrm{s}}(T - T_\infty). \tag{2}$$

Here, T denotes the lumped temperature of the specimen. T_∞, T_{o} and h_2, h_1 represent the temperatures and the convective heat transfer coefficients of the ambient air and the silicon oil reservoir, respectively. In Eqs. 1 and 2, the symbols, A_{S}, $\mathcal{V}_{\mathrm{S}}$, ρ_{S}, C_{pS}. represent, respectively, the contact surface area, the volume, the density, and the specific heat (or heat capacity) of the composite specimen. Define a steady state temperature and a time constant

$$T_{\mathrm{steady}} = (h_1 T_o + h_2 T_\infty)/(h_1 + h_2) \tag{3}$$

$$\tau = \rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}/(h_1 + h_2)A_{\mathrm{s}}. \tag{4}$$

Here, the heat capacity (or specific heat) and the density of the specimen can be expressed, respectively, as

$$C_{\mathrm{ps}} = f_{\mathrm{e}}C_{\mathrm{pe}} + f_{\mathrm{c}}C_{\mathrm{pc}}. \tag{5}$$

In Eq. 5, the symbols C_{pe}, C_{pc}, f_{e}, and f_{c} denote, respectively, the heat capacities and the wt% (or mass fraction) of the epoxy and MWNT. In case of a 0.5 wt% MWNT in the composite, the $f_{\mathrm{e}} = 0.995$ and $f_{\mathrm{c}} = 0.005$.

Assume the initial temperature is $T(0) = T_\infty$. The general solution of Eq. 1 will be given as

$$\ln\theta = -t/\tau. \tag{6}$$

Here, the non-dimensional temperature is defined as

$$\theta(t) = \left(T(t) - T_{\mathrm{steady}}\right)/\left(T_\infty - T_{\mathrm{steady}}\right). \tag{7}$$

In the present study, the time constant is employed to evaluate how fast the temperature will respond for the composite specimen with different wt% of MWNT.

Lump-heat-capacity model for conductivity measurement

During the initial stage, the temperature of the air inside the cavity nearly equals the ambient temperature, T_∞. The energy balance on the specimen is given by Eq. 8

$$\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}\frac{\mathrm{d}T_{\mathrm{s}}}{\mathrm{d}t} + h_{\mathrm{a}}A_{\mathrm{s}}(T_{\mathrm{s}} - T_\infty) = \dot{Q}_{\mathrm{in}}. \tag{8}$$

The temperature variations of the specimen can be expressed as

$$T_{\mathrm{s}}(t) = C_1 e^{\frac{-t}{\tau}} + T_\infty + \frac{\dot{Q}_{\mathrm{in}}t}{\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}}. \tag{9}$$

In Eq. 9, the transient temperature of the specimen does appear. After the transient period, the bulk temperature of the composite specimen will vary monotonously with time at a given heating rate $\dot{Q}_{\mathrm{in}}$.

(2) Within a later stage (or large time, t) and high heating rates, the supplied energy absorbed by both the specimen and the cavity air are comparable with each other. The energy balances on the specimen (subscripted by s) and the cavity air (subscripted by a) are given, respectively, by the following equations

$$\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}\frac{\mathrm{d}T_{\mathrm{s}}}{\mathrm{d}t} + h_2 A_{\mathrm{s}}(T_{\mathrm{s}} - T_{\mathrm{a}}) = \dot{Q}_{\mathrm{in}}, \tag{10}$$

$$\rho_{\mathrm{a}}\mathcal{V}_{\mathrm{a}}C_{\mathrm{pa}}\frac{\mathrm{d}T_{\mathrm{a}}}{\mathrm{d}t} = h_2 A_{\mathrm{s}}(T_{\mathrm{s}} - T_{\mathrm{a}}). \tag{11}$$

In this study, the designed dimensions of the cavity and the specimen gives $\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}} \approx 82\,\rho_{\mathrm{a}}\mathcal{V}_{\mathrm{a}}C_{\mathrm{pa}}$. Thus, the time constant ($\tau_{\mathrm{a}} = \rho_{\mathrm{a}}\mathcal{V}_{\mathrm{a}}C_{\mathrm{pa}}/h_{\mathrm{a}}A_{\mathrm{s}}$) of the air inside the cavity is much smaller than that of the specimen ($\tau_{\mathrm{s}} = \rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}/h_{\mathrm{a}}A_{\mathrm{s}}$). Shortly after a transient period, the temperature of the lumped air inside the cavity will approach that of the specimen ($T_{\mathrm{a}} = T_{\mathrm{s}}$). In such situation, Eqs. 10–11 can be rearranged by the following relation

$$\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}}\frac{\mathrm{d}T_{\mathrm{s}}}{\mathrm{d}t} + \rho_{\mathrm{a}}\mathcal{V}_{\mathrm{a}}C_{\mathrm{pa}}\frac{\mathrm{d}T_{\mathrm{s}}}{\mathrm{d}t} = \dot{Q}_{\mathrm{in}}. \tag{12}$$

Therefore, at large time, the surface temperature of the composite specimen, based on Eq. 12, approximately equals

$$T_{\mathrm{s}} = C + \dot{Q}_{\mathrm{in}}t/\left(\rho_{\mathrm{s}}\mathcal{V}_{\mathrm{s}}C_{\mathrm{ps}} + \rho_{\mathrm{a}}\mathcal{V}_{\mathrm{a}}C_{\mathrm{pa}}\right). \tag{13}$$

In Eq. 13, the constant C denotes the temperature that can be obtained by matching the two complete solutions (including the transient parts) of the initial and the later stages asymptotically within the intermediate region. Eqs. 9 and 13 showed that the surface temperature will vary linearly with time if the heat capacity and the heating rate are constants. In fact, the heat capacity of CNTs increases as the temperature increases [11, 12]. Therefore, during the heating process, the slopes (or the increasing rate) of the surface temperature of the composite reduce continuously and very mildly at a given heating rate.

Results and discussions

Temporal response of the MWNT/epoxy composite

Figure 3a depicts the temporal variations of the top-surface temperature of the specimen for three different weight percentages (wt%) of MWNT when the composite specimen is suddenly brought into contact with the silicon oil maintained at constant temperature ($T_o = 156$ C). In Fig. 3a, the silicon oil is maintained at a nearly constant temperature ($T_o = 156$ C, horizontal line) during the acquisition time elapse of 1200 s. On contacting with the reservoir oil, all the top-surface temperatures of the composite increase monotonously with time and approach asymptotically to a steady state temperature around $T_{\mathrm{steady}} = 120$ C for three different wt% of MWNT. To reveal the difference between the temperatures T_o and T_{steady}, Eq. 3 can be rearranged into Eq. 14

$$\frac{T_{\mathrm{steady}}}{T_o} = \frac{h_1 + h_2(T_\infty / T_o)}{(h_1 + h_2)}. \tag{14}$$

Equation 14 validates that the steady state temperatures (T_{steady}) is always smaller that of the oil reservoir (T_o) because the ratio T_∞ / T_o is much smaller than unity.

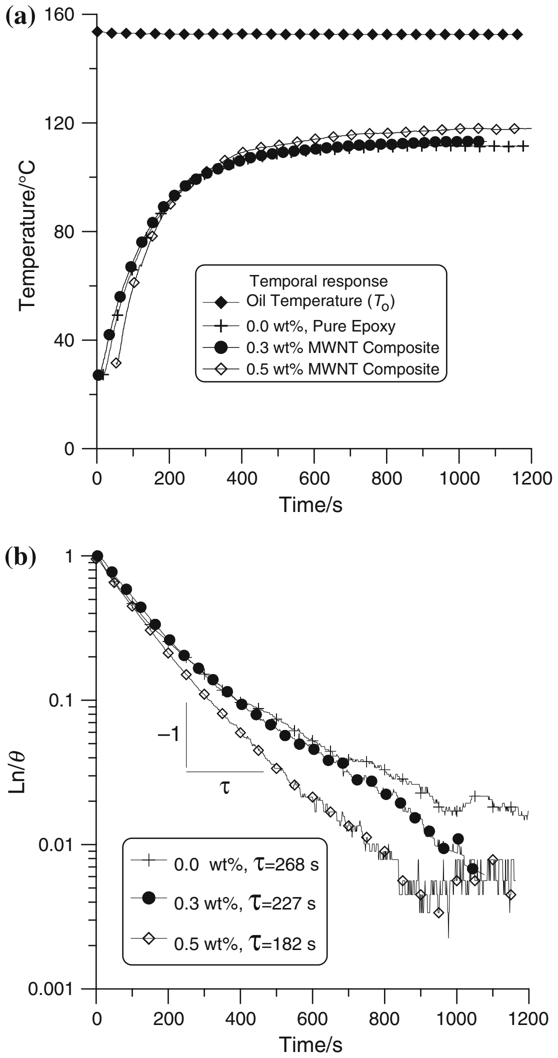


Fig. 3 **a** The temporal response of the composite temperature, **b** Non-dimensional temperature (in semi-logarithmic scale) of the composite specimen with three different wt% of MWNT. The symbol τ represents the time constant of the specimen

In Fig. 3b, the non-dimensional temperatures $\theta(t)$ are plotted in a logarithmic scale, and the abscissa is kept linear scale. In Fig. 3b, an approximately linear relationship of each curve with negative slope is shown for $t < 400$ s. In Fig. 3b, the slope is the steepest for the composite with 0.5 wt% of MWNT; and the slope decreases as the wt% of the MWNT decreases. From Eq. 6, a steep slope implies a small time constant. For the pure epoxy resin, inverse of the slope gives a time constant of 268 s and those for the MWNT/epoxy composite with 0.3 and 0.5 wt% are 227 and 182 s, respectively. Evidently, the higher the wt% of MWNT in the composite, the shorter time will it take to heat up the composite specimen. A small time constant implies a fast response of the composite to the sudden temperature change. The results in Fig. 3b clearly showed that, the higher the wt% of the MWNT in the composite, the faster is the temperature response to the sudden change of the temperature. It is found that the responses of the 0.3 and 0.5% wt% of MWNT/epoxy composites are found to be about 25 and 47.8%, respectively, faster than that of the pure epoxy resin. In Eq. 4, the A_s, V_s, and ρ_s are constants for each specimen. Also, the convective heat transfer coefficients (h_1, h_2.) do not alter significantly during the temperature range of each experiment. Based on the definition in Eq. 4, a small time constant (or the large slope) is very likely caused by the decreasing heat capacity (C_{ps}) of the composite with higher wt% of MWNT. Also, the reduction in heat capacity, based on the calculation in Eq. 5, corresponds to the trend of increasing thermal diffusivity of the epoxy/MWNT composite as the wt% of MWNT increases [9]. Further, within $t > 700$ s in Fig. 3b, the temperature variations gradually deviate from the linear relationship predicted by the lump-heat-capacity model with reducing slopes. During the heating process, the reduction in the slope is caused by the fact that the heat capacities of both epoxy and MWNT increase with increasing temperature [11, 12]. After the temperatures reach a steady level (or $t > 900$ s), the scattered data points are caused primarily by the combinations of possible variation of the environmental temperature (T_∞) during the measurement and the resolution of the thermocouples.

At room temperature, the typical heat capacities of the epoxy and the MWNT are 1.0 and 0.75 J g^{-1} K^{-1} [11, 12], respectively. The heat capacities of the composite specimen, calculated by Eq. 5, are 0.99925 and 0.99875 J g^{-1} K^{-1}, for the composite specimen with 0.3 and 0.5 wt%, respectively. The small reduction in heat capacity (0.075 and 0.125%) may not completely correspond to the large improvement of the response (25 and 47.8%) because the calculation of the heat capacity, based on Eq. 5, is too simplified. Namely, the types of CNTs, the wt%, the size, the concentration, and the CNTs/matrix bonding should be considered.

Temporal variations of surface temperature

In Fig. 4, the temperature variations (T_2) measured on the top surface of the specimen within the cavity-type measuring system are compared for various heating rates. All the temperatures first experience a transient period, and then show a monotonous increase with time. The larger the heating rate, the higher are the surface temperatures of the composite. According to Eqs. 9 and 13, the surface temperature should increase linearly with time for given properties ($\rho_s, C_{ps}, \forall_s, \rho_a, C_{pa}, \forall_a, \dot{Q}_{in}$) after the transient period. In fact, within $t \geq 400$ s·, the slope, denoted by the thick red line in Fig. 4, of the surface temperature (T_2) initially approximates the theoretical values ($\dot{Q}_{in}/\rho_s \forall_s C_{ps}$) predicted by Eq. 9; and reduce continuously and mildly as time goes by. Since the heat capacity of the CNTs increases with the increasing temperature [11, 12], the reduction in the slopes of the temperature (T_2) in Fig. 4 is primarily caused by the increasing heat capacity of the composite during the heating process. At a later stage ($t = 1200$ s, or large time), the slope, indicated by the thick blue line in Fig. 4, indeed follows the prediction by Eq. 13. For the heating rates within 0.45 W $\leq \dot{Q}_{in} \leq$ 1.862 W, the transient characteristic is clearly evident within $0 < t < 400$ s. However, at high heating rates ($\dot{Q}_{in} \geq$ 2.29W), the transient behaviors of the temperature curves are not so evident as those of the low heating rates ($\dot{Q}_{in} \leq$ 1.862 W).

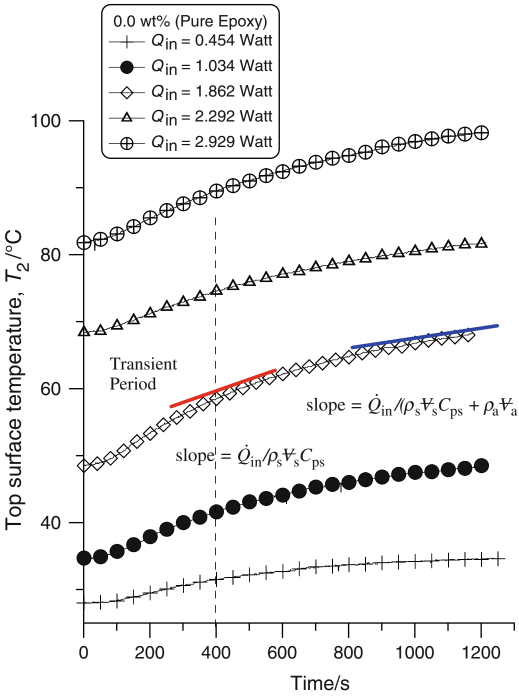


Fig. 4 The temporal variations of the temperature on the top surface (T_2) of the composite specimen at five different heating rates

Thermal conductivity measurement

Five different heating rates are employed for the thermal conductivity measurements of the MWNT/epoxy composites with three different wt% of MWNT. For each experimental condition, the sampling period is 1200 s.

Thermal conductivity for pure epoxy (0 wt%)

During the heating process, very little energy will be lost to the environment outside the cavity. Thus, the temperatures on the top and the bottom surfaces of the composite are expected to increase with time. Fig. 5a–e shows the temporal variations of the measured temperatures on the top (T_2) and the bottom surfaces (T_1) and their differences ($T_1 - T_2$) for the case of pure epoxy resin (0 wt%) at five different heating rates. Evidently, after the transient stage, all the temperature curves (T_1 and T_2) increase monotonously with time. As mentioned in the "Mathematical model" section, these variation trends coincide well with the theoretical prediction. Surprisingly, after a short transient period, all the temperature differences ($T_1 - T_2$) are kept nearly constant in Fig. 5a–e. Besides, in Fig. 5f, the temperature difference ($T_1 - T_2$) for four experimental runs depends almost linearly on the heating rate $\dot{Q}_{in}$.

Since the specimen is relatively thin compared with its diameter ($t/D = 6.8\%$), the results in Fig. 2 ensure the validity of the quasi one-dimensional heat conduction across the thickness of the composites. Therefore, the Fourier's law of the one-dimensional steady heat conduction is employed to calculate the thermal conductivities at any instant for the pure epoxy resin at various heating rates. In Fig. 6a, shortly after the transient period, the thermal conductivities reach steady levels with slightly different values at different heating rates. In Fig. 6b, the time-averaged thermal conductivity is obtained for four experiment runs at different heating rates while the thermal

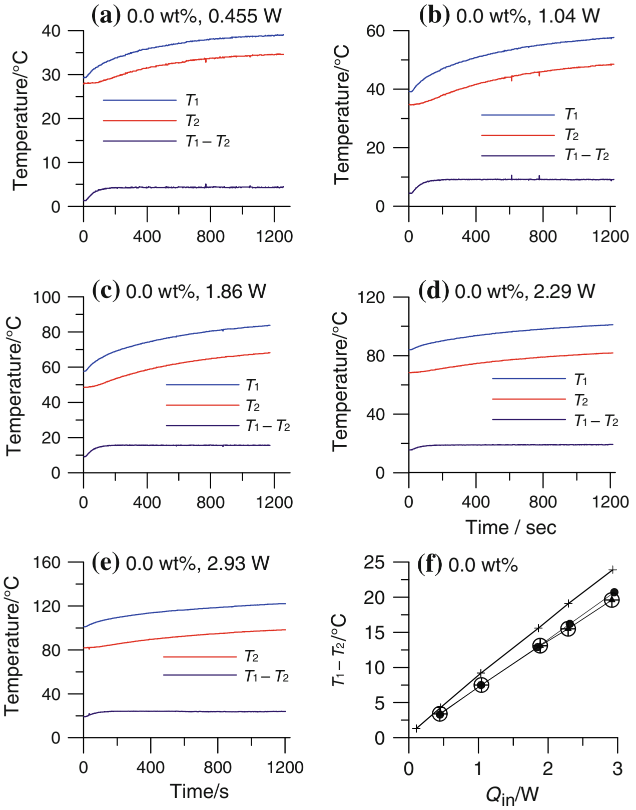


Fig. 5 **a–e** The temporal response of the top and the bottom surface temperatures (T_1 and T_2) of the pure epoxy resin specimen (0 wt%) at five different heating rates. **f** The temperature difference ($T_1 - T_2$) in relation to the heating rates

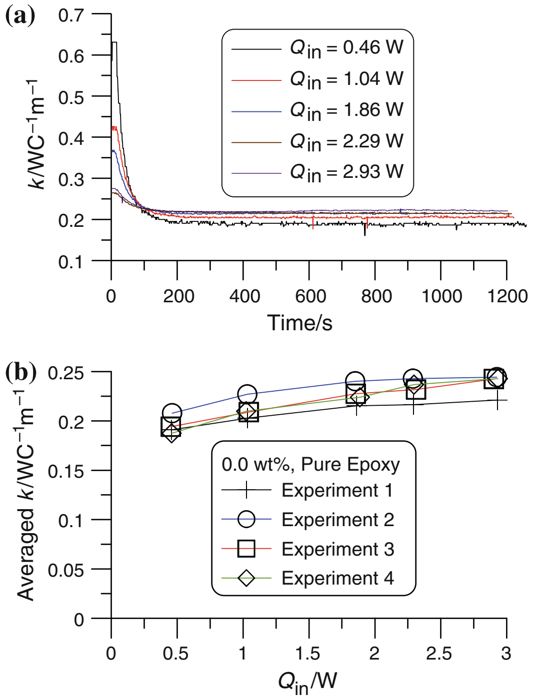


Fig. 6 **a** The time-dependent thermal conductivity (k) of the pure epoxy resin (0 wt%) at different heating rates; **b** The averaged thermal conductivity (k) as functions of heating rates for four experimental runs

conductivity in Fig. 6a reaches a constant level. The averaged thermal conductivity increases insignificantly within a range of 0.19–0.23 $\mathrm{WC^{-1}\ m^{-1}}$ for different heating rates. These averaged thermal conductivities are very close to that for pure epoxy resin (0.21 $\mathrm{WC^{-1}\ m^{-1}}$). The thermal conductivity for epoxy resin measured by Wróbel et al. [21] is around 0.22 $\mathrm{WC^{-1}\ m^{-1}}$. However, Thoetenson and Chou [7], and Gojny et al. [17] reported a thermal conductivity to be 0.225 and 0.242 $\mathrm{WC^{-1}\ m^{-1}}$, respectively. For the pure epoxy resin, the possible deviations of thermal conductivity among literature and the present study may be caused by different measuring techniques and different experimental conditions.

Thermal conductivity for composite of 0.3 and 0.5% MWNT/epoxy composite

Figure 7a–e shows the temporal variations of the temperatures measured on the top (T_2) and the bottom surfaces (T_1) of the composite specimen with 0.3 wt% of MWNT/epoxy at five different heating rates. Also shown are the temporal variations of the temperature difference ($T_1 - T_2$). Basic variation trends are similar to those in Fig. 5. Except for the short transient period, the temperature difference ($T_1 - T_2$) measured on the top and the bottom surfaces are nearly constant during the sampling period. Figure 7f also depicts that the temperature difference is almost linearly proportional to the heating rates. While the temperature difference reaches a constant value, the thermal conductivities are calculated for each experimental run and given in Fig. 8a. The time-averaged thermal conductivities, obtained by the time-averaged within $t > 200$ s, increase mildly with increasing heating rates and fall within a range of 0.24–0.27 $\mathrm{WC^{-1}\ m^{-1}}$. With the same technique, the surface temperatures and their differences are also measured for MWNT/epoxy composite with 0.5 wt%. The time-averaged thermal conductivities of MWNT/epoxy composite with 0.5 wt% are depicted in Fig. 8b. In this case, the calculated thermal conductivity is also smaller at low heating rates than those at high heating rates. At low heating rates, the thermal conductivities increase very mildly, but keep almost constant at high heating rates. The values of thermal conductivity for four experimental runs fall within a range of 0.29–0.34 $\mathrm{WC^{-1}\ m^{-1}}$. In case of 0.5wt% of MWNT, the thermal conductivities, obtained in this study is slightly larger than those of Thostenson and Chou [18]. By averaging the thermal conductivities from the four experimental runs in Figs. 6b, 8a, b, the averaged thermal conductivity of the MWNT/epoxy composites with different

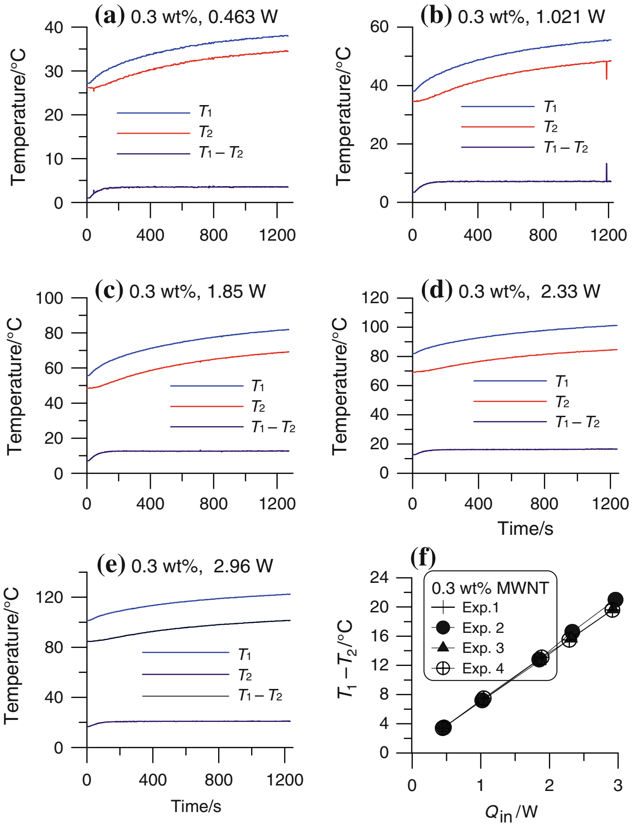


Fig. 7 **a–e** The temporal variations of the temperatures (T_1 and T_2) measured at the top and the bottom surfaces of the MWNT/epoxy composite (0.3 wt%) at five different heating rates. **f** The temperature difference ($T_1 - T_2$) as function of heating rates

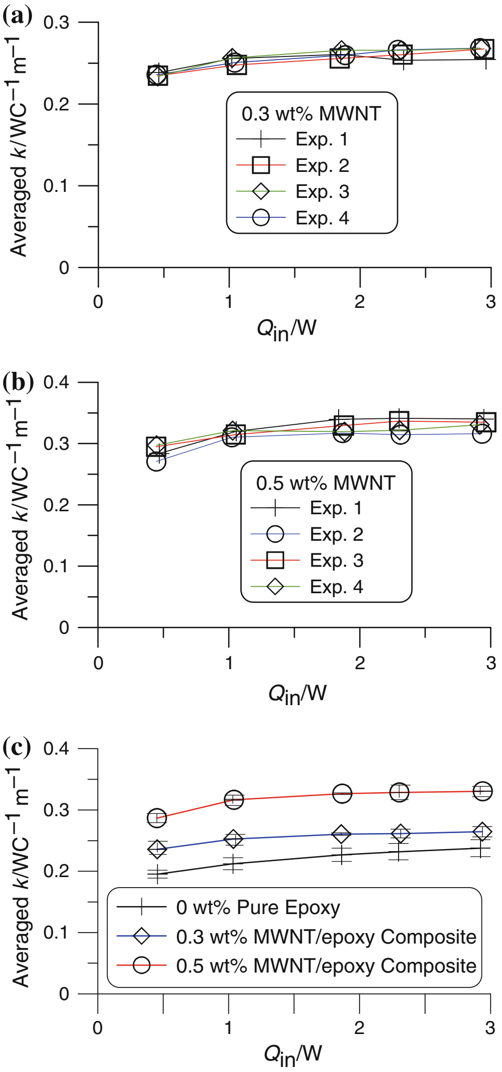


Fig. 8 **a** The thermal conductivity (k) as functions of heating rates for **a** 0.3 wt% of MWNT/epoxy composites, **b** 0.5 wt% of MWNT/epoxy, **c** The averaged thermal conductivity of the composite specimen for different weight percentage (wt%) of MWNT at various heating rates

wt% of MWNT were shown in Fig. 8c as function of heating rates. The averaged thermal conductivity is the largest for the composite with 0.5 wt% MWNT; and is the smallest for the pure epoxy resin. The thermal conductivity for the composites with 0.3 and 0.5 wt% of MWNT are higher by 15.9 and 44.9% than that of the pure epoxy. In other words, the higher the weight percentage of MWNT in the composite, the larger is the thermal conductivity of the composite. A simple theoretical matrix model is developed by Nan et al. [22] and improved by Xue [23]. Their analysis considered the influences of the anisotropic basic material, the concentration of CNT, and the interface thermal resistance on the thermal conductivities of the composites. Their results further assured the enhancement of the thermal conductivity of the composite with low wt% of MWNT. Cho et al. [18] also reported the enhancement of thermal conductivities for MWNT/copper composites with increasing wt% of MWNT. All the above-mentioned studies showed that the thermal conductivity of the composite indeed increases with the increasing wt% of MWNT. Their conclusions are in accordance with the results of the present study. Besides, at low heating rates, the variations of thermal conductivity are mild; however, the thermal conductivity is nearly constant at high heating rates.

Conclusions

In this study, the MWNT/epoxy composite with three different weight percentages of MWNT (e.g., 0, 0.3, and 0.5%) were prepared by chemical means. The temporal responses of these composites are characterized by experiment. Also, a cavity-type measuring system is designed to experimentally measure the surface temperatures on the composite specimen and calculate the thermal conductivity of the MWNT/epoxy composite. It is found that both the responding characteristics and the variation trends of the measured surface temperatures of these composites are well predicted by the lumped-heat capacity model. The composite with 0.5 wt% of MWNT has the smallest time constant, indicating the fastest response to the sudden temperature change. The temporal response becomes fast as the weight percentage (wt%) of the MWNT increases. The responses of the MWNT/epoxy composites with 0.3 and 0.5 wt% MWNT are about 25 and 47.8% faster than that of the pure epoxy. In other words, the higher the weight percentage (wt%) of MWNT in the composite, the faster is the temporal response of the composite. For the thermal conductivity, the higher the weight percentage (wt%) of MWNT in the composite, the larger is the thermal conductivity of the composite. Relative to that of the pure epoxy, the thermal conductivities for the composites with 0.3 and 0.5 wt% MWNT increase by 15.9 and 44.9%, respectively. For the weight percentages studied herein, the thermal conductivity of the MWNT/epoxy composite is found to increase mildly at low heating rates, however, it remains nearly constant at high heating rates.

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References

1. Kroto HW, Heath JR, O'Brien SC, Curl RF, Smalley RE. C_{60}: Buckminsterfullerene. Nature. 1985;318:162–3.
2. Iijima S. Helical microtubules of graphitic carbon. Nature. 1991; 354:56–8.
3. Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1-nm diameter. Nature. 1993;363:603–5.
4. Yu M, Lourie FO, Dyer M, Moloni JK, Kelly TF, Ruoff RS. Strength and breaking mechanism of multiwalled carbon nanotubes under tensile load. Science. 2000;287:637–40.
5. Demczyk BG, Wang YM, Cumings J, Hetman M, Han W, Zettl A, Ritchie RO. Direct mechanical measurement of the tensile strength and elastic modulus of multiwalled carbon nanotubes. Mater Sci Eng A. 2002;334:173–8.
6. Allaoui S, Bai H, Cheng M, Bai JB. Mechanical and electrical properties of a MWNT/epoxy composite. Compos Sci Technol. 2002;62:1993–8.
7. Gojny FH, Wichmann MHG, Fiedler B, Schulte K. Influence of different carbon nanotubes on the mechanical properties of epoxy matrix composites—A comparative study. Compos Sci Technol. 2005;65:2300–13.
8. Thostenson ET, Chou TS. Processing-structure-multi-functional property relationship in carbon nanotube/epoxy composites. Carbon. 2006;44:3022–9.
9. Wu F, He X, Zeng Y, Cheng HM. Thermal transport enhancement of multi-walled carbon nanotubes/high density polyethylene composites. Appl Phys A. 2006;85:25–8.
10. Hone J, Whitney M, Piskoti C, Zettl A. Thermal conductivity of single-walled nanotubes. Phys Rev B. 1999;59:2514–6.
11. Nan Z, Wei C, Yang Q, Tan Z. Thermodynamic properties of carbon nanotubes. J Chem Eng Data. 2009;54:1367–70.
12. Xu F, Sun LX, Zhang J, Qi YN, Yang LN, Ru HY, Wang CY, Meng X, Lan XF, Jiao QZ, Huang FL. Thermal stability of carbon nanotubes. J Thermal Anal Calorim. 2010;5. doi:10.1007/s10973-010-0793-x.
13. Zhang K, Xiao GW, Wong KY, Gu HW, Yuen MF, Chan CH, Xu B. Study on thermal interface material with carbon nanotubes and carbon black in high-brightness LED packaging with flip-chip technology. In: Electronic components and technology conference. 2005. p. 60–65.
14. Singh IV, Tanaka M, Endo M. Thermal analysis of CNT-based nano-composites by element free Galerkin method. Comput Mech. 2007;39:719–28.
15. Song YS, Youn JR. Evaluation of effective thermal conductivity for carbon nanotube/polymer composites using control volume finite element method. Carbon. 2006;44:710–7.
16. Abdalla M, Dean D, Theodore M, Fielding J, Nyairo E, Price G. Magnetically processed carbon nanotube/epoxy nanocomposites: morphology, thermal, and mechanical properties. Polymer. 2010;51:1614–20.
17. Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, Schulte K. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. Polymer. 2006;47:2036–45.
18. Cho S, Kikuchi K, Miyazaki T, Takagi K, Kawasaki A, Tsukada T. Multiwalled carbon nanotubes as a contributing reinforcement phase for the improvement of thermal conductivity in copper matrix composites. Scripta Mater. 2010;63:375–8.
19. Karippal JJ, Narashimha Murthy HN, Rai KS, Krishna M, Sreejith M. Electrical and thermal properties of twin-screw extruded multiwalled carbon nanotube/epoxy composites. J Mater Eng Perform. 2010;17. doi:10.1007/s11665-010-9604-6.
20. Liu L, Wagner HD. Rubbery and glassy epoxy resins reinforced with carbon nanotubes. Compos Sci Technol. 2005;65:1861–8.
21. Wróbel G, Rdzawski Z, Muzia G, Pawlak S. Determination of thermal diffusivity of carbon/epoxy composites with different fiber content using transient thermography. J Achiev Mater Manuf Eng. 2009;37(2):518–25.
22. Nan CW, Shi Z, Lin Y. A simple model for thermal conductivity of carbon nanotube-based composites. Chem Phys Lett. 2003; 375:666–9.
23. Xue QZ. Model for the effective thermal conductivity of carbon nanotube composite. Nanotechnology. 2006;17:1655–60.