Enhanced thermal conductivity of carbon fiber/phenolic resin composites by the introduction of carbon nanotubes

Y. A. Kim, S. Kamio, T. Tajiri, T. Hayashi, S. M. Song and M. Endo
Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano-shi 380-8553, Japan

M. Terrones
Advanced Materials Department, IPICyT, Camino a la Presa de San José 2055, Col. Lomas 4a. Secc., 78216 San Luis Potosí, S. L. P., México

M. S. Dresselhaus
Massachusetts Institute of Technology, Cambridge, MA 02139-4307, USA

Abstract

We report a significant enhancement in the thermal conductivity of a conventional carbon fiber/phenolic resin composite system when adding highly crystalline multi-walled carbon nanotubes. We demonstrate that 7 wt% of carbon nanotubes dispersed homogeneously in a phenolic resin acted as an effective thermal bridge between adjacent carbon fibers and resulted in an enhancement of the thermal conductivity (e.g. from 250 to 393 W/m-K). These results indicate that highly crystalline carbon nanotubes can be used as a multifunctional filler to enhance simultaneously the mechanical and thermal properties of the carbon fiber/phenolic resin composites.

Keywords: Carbon nanotubes, Polymer composite, Thermal management

Corresponding author: Tel: +81-26-269-5212; fax: +81-26-269-5208
E-mail: yak@endomoribu.shinshu-u.ac.jp

The development of light-weight and non-metallic composites, exhibiting high thermal conductivity and a low coefficient of thermal expansion, have been critically needed for achieving an effective heat conduction that could be used in numerous industrial processes. For this type of applications, carbon nanotubes, which consist of concentric graphene cylinders built from sp^2-bonded carbon atoms, have been intensively studied as an ultimate filler in polymer composites for thermal management[1-4]. This approach is taken because theoretical calculations [4, 5] and experimental results [6-9] have demonstrated that individual carbon nanotubes could exhibit very high thermal conductivity values. Both the limited amount of suitable carbon nanotubes that are currently available and their complex processing techniques (e.g., dispersion and alignment) within a polymer are thought to be the main factors limiting their effective usage in this field. Because the viability of carbon nanotubes in the long term strongly depends on their commercialization, the alternative end-use of carbon nanotubes in thermal management is suggested.

Here we report a simple and effective way of using highly crystalline multi-walled carbon nanotubes (MWNTs) as fillers in conventional carbon fiber/phenolic resin composites for thermal management applications. Our results indicate that crystalline carbon nanotubes are able to create effective thermal paths between adjacent carbon fibers and thereby contribute to a significant increase in the thermal conductivity of the carbon fiber/phenolic resin composite (from 250 to 393 W/m-K).

In order to fabricate conventional continuous carbon fiber/phenolic resin composites, we selected high modulus pitch-based carbon fibers with a thermal conductivity of ca. 500 W/m-K (Nippon Graphite Fiber Co.) (Fig. 1 (a)) and a resol-type phenolic resin (BLS-341, Showa Highpolymer Co.). In addition, we selected an additional filler consisting of high crystalline MWNTs with an average diameter of 80 nm, that were prepared on an industrial scale by a combination of a chemical vapor deposition (CVD) method, and subsequent high-temperature treatment at 2800 °C in argon[10, 11]. Since acoustic phonons dominate the transport properties of conventional carbon materials, high-temperature thermal treatment is critical to increase the structural integrity of carbon nanotubes. As shown in inset of Fig. 1 (b), thermally treated tubes display straight graphitic fringes over a short length range, but in the aggregate, the MWNTs appear to be un-aligned in the bulk (Fig. 1 (b)). As summarized in Table 1, a large decrease in the interlayer spacing from 0.342 to 0.3389 nm and a large decrease in the R value (the intensity of the D band over the intensity of the G band) from 0.8950 to 0.1342 and an increase in the real density from 1.85 to 2.08 g/cm^3 indicated that a high-temperature thermal treatment is the effective way of converting the relatively defective as-synthesized tubes to highly crystalline nanotubes.[11]

In order to understand the role of as-synthesized MWNTs (not heat treated) as fillers in the carbon fiber/phenolic resin composites, we performed a comparative study using thermal treated tubes and as-produced nanotubes. Very recently, it was demonstrated that shortened carbon nanotubes[12] were effective to prevent crack propagation when they were used as a hybrid filler in conventional carbon fiber/polymer composites.[13] Therefore, the present account deals with the use of highly crystalline MWNTs as fillers in the fabrication of high thermal conducting composites using the route described in Fig. 1 (c).

For the use of carbon nanotubes as fillers in polymer composites, the generation of a homogeneous dispersion of the tubes is a critical issue for exploiting their intrinsic properties. In order to solve the dispersion problem, we prepared a homogeneously dispersed carbon nanotube/resin suspension in ethanol with the help of ultra-sonication (Kubota UP50H). Subsequently, we impregnated the pitch-based carbon fibers with the nanotube/resin suspension and dried the resultant material in vacuum to remove ethanol and air (Fig. 1 (d)). As a result, we obtained a hybrid-type carbon fiber/carbon nanotube/resin composite (Fig. 1 (e)) after pressing the dried mixture into a mold (25 × 25 mm^2) using a hot press (180 °C, 80 MPa, 30 min) (Marumoto Struers K.K.). In preparing composite samples, we fixed the ratio of carbon fiber/phenolic resin to 1 wt% and varied the incorporated amount of MWNTs from 5, 7 and 10 wt%. Finally, we sliced the sample and obtained pallets with a diameter of 10 mm and a thickness of 2 mm (Fig. 1 (f)), so that thermal conductivity measurements could be performed at room temperature using the Argon flash diffusivity testing procedure (Laser flash TC-7000, Ulvac-Riko Co.).[14, 15] The thermal diffusion can be calculated using the following equation $\alpha = 1.37L^2 / t_{1/2}$, where L is the thickness of the sample, $t_{1/2}$ is the time at which the rear surface of the sample reaches half of its maximum temperature, and α is the sample's thermal diffusivity. In addition, the density was also determined using the Sartorius technique (Genius). We finally obtained the thermal conductivity (k, W/cm-K) for our samples using the following equation; $k = \alpha \cdot c \cdot d$, where α = thermal diffusivity (cm^2/s), c = specific heat (J/g-K), d = density (g/cm^3).

In order to examine the dispersion of carbon nanotubes in the carbon-fiber polymer composite, FE-SEM observations on the fractured surface of the composites were carried out (Fig. 2). From these images, we can clearly identify randomly distributed carbon fibers with diameters of ca. 7 μm and bright colored nanotubes, which are likely to protrude from the fractured polymer. The absence of aggregated carbon nanotubes provides indirect evidence of the homogeneous dispersion of the carbon nanotubes within the polymer. The basic reason for choosing a phenolic resin for the composite material is that this type of resin has been used as a polymeric adhesive due to its excellent bonding strength and other physical properties.

Figure 3 shows the variation of the thermal conductivities for the carbon fiber/phenolic resin/MWNTs composites. In the case of thermally treated crystalline MWNTs, the thermal conductivity of the carbon-fiber-phenolic composite increased with an increase in the amount of MWNTs, and the thermal conductivity reached a maximum value of ca. 396 W/m-K when 7 wt% of crystalline MWNTs were added; note that the thermal conductivity of copper is 390 W/m-K. Interestingly, we observed an abrupt reduction in the thermal conductivity by increasing the amount of highly crystalline tubes to 10 wt% (see Fig. 3). We found that the best experimental conditions, occurred when 7 wt% of carbon nanotubes were added to the fiber/phenolic composites. This could be explained by the uniform dispersion of nanotubes (avoiding formation of agglomerates) in the phenolic resin, which created effective thermal paths between adjacent carbon fibers embedded in the composite, because the phenolic resin with the incorporation of 10 wt% of crystalline MWNTs exhibited an increase in the thermal conductivity from 0.2878 to 1.0717 W/m-K.

In contrast, as-produced MWNTs (not heat treated) resulted in reduced thermal conductivity values for the composites, thus indicating that catalytically grown MWNTs possessing intrinsic structural defects are not adequate for the fabrication of highly thermal conducting composites, and MWNTs require high-temperature thermal treatments (above 2500 °C) for improving their structural integrity.[16] In other words, by converting the short, and defective graphene cylinders into more crystalline concentric tubes (longer and straighter), it is expected that the transport properties of an individual MWNT will increase significantly because the presence of defects on the sidewalls of carbon nanotubes obstructing the propagation of phonons is annealed out during the high-temperature thermal treatment. For further work, it will be very important to evaluate the thermal conductivity of individual MWNTs as a function of the defect concentration (or thermal treatment temperature).

In summary, we have found a route to fabricate highly thermally conductive carbon-fiber based composites by the introduction of highly crystalline carbon nanotubes into the phenolic resin. We have demonstrated that the high degree of crystallinity in the tubes makes the composite more thermally conducting. It was demonstrated that 7 wt% of carbon nanotubes were necessary to show the best thermal conduction performance of the composite (ca. 393 W/m-K). Therefore, it is envisaged that carbon nanotubes could find their way into the composite industry as a hybrid filler in conventional composites, where the enhancement of both the thermal and mechanical properties, are critically needed.

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Table 1 Basic properties of the multi-walled carbon nanotubes used in this study

Terms	Pristine defective tube	Thermally treated crystalline tubes	Testing method
Diameter (nm)	80	80	FE-SEM
Length (nm)	10-20	10-20	FE-SEM
d_{002} (nm)	0.342	0.3389	X-ray diffraction
Real density (g/cm^3)	1.85	2.08	Helium pycnometer
R value (R = ID/IG)	0.8950	0.1342	Raman spectroscopy (532 nm)

Figure Captions

Figure 1 (a) FE-SEM image of pitch-based carbon fibers, (b) FE-SEM image of crystalline carbon nanotubes (inset is a high resolution TEM image), and (c) schematic image describing the role of a thermally conductive filler of carbon nanotubes between adjacent carbon fibers and (d) the preparation procedure; impregnation, hot press molding and shaping.

Figure 2 FE-SEM images of the fractured carbon fiber/phenol composites containing 5 wt% (a, b), 7 wt% (c, d) and 10 wt% (e, f) of carbon nanotubes, respectively.

Figure 3 Thermal conductivities of carbon fiber/phenolic resin composites containing either highly crystalline MWNTs or defective MWNTs as a function of the amount of the added MWNTs, respectively. Note that the maximum value of the thermal conductivity for the composite with the crystalline MWNTs is exactly the same as that of copper.