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

Y. A. Kim,^{a)} 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, San Luis Potosí, México

M. S. Dresselhaus

Massachusetts Institute of Technology, Cambridge, Massachusetts 02139-4307

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The authors report a significant enhancement in the thermal conductivity of a conventional carbon fiber/phenolic resin composite system when adding highly crystalline multiwalled carbon nanotubes. They 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. © 2007 American Institute of Physics. [DOI: 10.1063/1.2710778]

The development of lightweight and nonmetallic composites, exhibiting high thermal conductivity and a low coefficient of thermal expansion, has 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 results⁶⁻⁹ 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 multiwalled carbon nanotubes (MWCNTs) 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 approximately 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 highly crystalline MWCNTs with an average diameter of 80 nm, that were prepared on an industrial scale by a combination of a chemical vapor deposition 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 the inset of Fig. 1(b), thermally treated tubes display straight graphitic fringes over a short length range, but in the aggregate, the MWCNTs appear to be unaligned in the bulk [Fig. 1(b)]. As summarized in Table I a large decrease in the interlayer spacing from 0.342 to 0.3389 nm, 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/cm³ indicate that a high-temperature thermal treatment is the effective way of converting the rela-

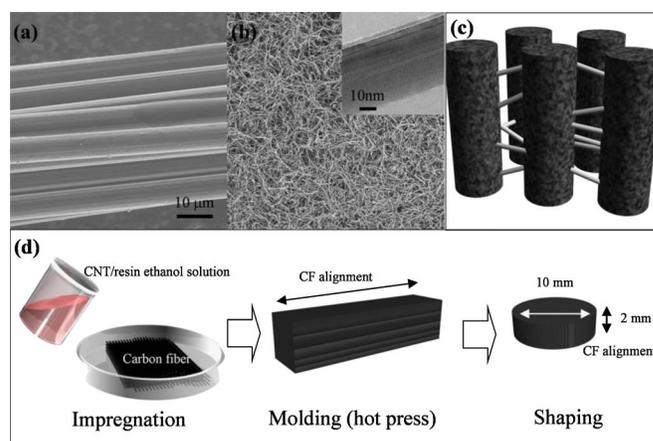


FIG. 1. (Color online) (a) FE-SEM image of pitch-based carbon fibers, (b) FE-SEM image of crystalline carbon nanotubes (inset is a high resolution TEM image), (c) schematic image describing the role of a thermally conductive filler of carbon nanotubes between adjacent carbon fibers, and (d) the preparation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

^{a)} Author to whom correspondence should be addressed; FAX: +81-26-269-5208; electronic mail: yak@endomoribu.shinshu-u.ac.jp

TABLE I. Basic properties of the multiwalled 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 ($R=I_D/I_G$)	0.8950	0.1342	Raman spectroscopy (532 nm)

tively defective as-synthesized tubes to highly crystalline nanotubes.¹¹

In order to understand the role of as-synthesized MWCNTs (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 nanotubes¹² were effective in preventing 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 MWCNTs as fillers in the fabrication of highly 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 ultrasonication (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 ($25 \times 25 \text{ mm}^2$) using a hot press (180°C , 80 MPa , and 30 min) (Marumoto Struers K.K.). In preparing the composite samples, we fixed the ratio of carbon fiber/phenolic resin to 1 wt % and varied the incorporated amount of MWCNTs 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 , $\text{W}/\text{cm K}$) for our samples using the following equation: $k = \alpha cd$, where α is the thermal diffusivity (cm^2/s), c the specific heat ($\text{J}/\text{g K}$), d and the density (g/cm^3).

In order to examine the dispersion of carbon nanotubes in the carbon fiber polymer composite, field emission scanning electron microscope (FE-SEM) observations on the

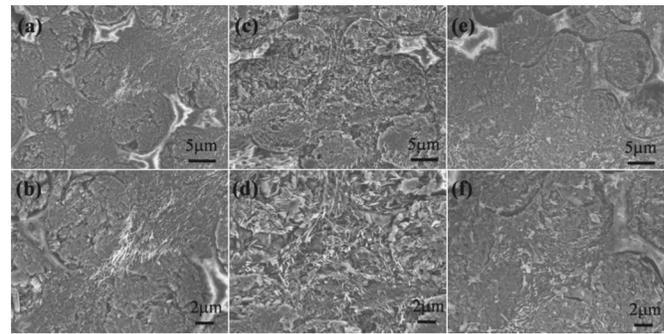


FIG. 2. FE-SEM images of the fractured carbon fiber/phenol composites containing 5 wt % [(a) and (b)], 7 wt % [(c) and (d)], and 10 wt % [(e) and (f)] of carbon nanotubes, respectively.

fractured surface of the composites were carried out (Fig. 2). From these images, we can clearly identify randomly distributed carbon fibers with diameters of approximately $7 \mu\text{m}$ 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/MWCNT composites. In the case of thermally treated crystalline MWCNTs, the thermal conductivity of the carbon fiber/phenolic composite increased with an increase in the amount of MWCNTs, and the thermal conductivity reached a maximum value of approximately $396 \text{ W}/\text{m K}$ when 7 wt % of crystalline MWCNTs were added; note that the thermal conductivity of copper is $390 \text{ W}/\text{m K}$. 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

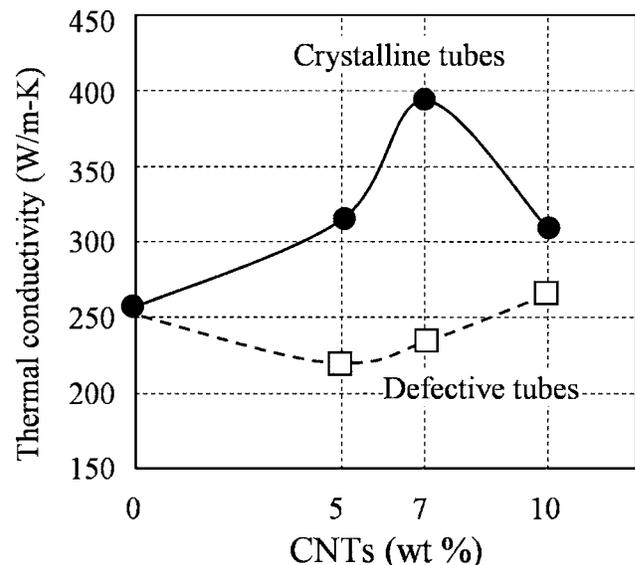


FIG. 3. Thermal conductivities of carbon fiber/phenolic resin composites containing either highly crystalline MWCNTs or defective MWCNTs as a function of the amount of the added MWCNTs, respectively. Note that the maximum value of the thermal conductivity for the composite with the crystalline MWCNTs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

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 MWCNTs exhibited an increase in the thermal conductivity from 0.2878 to 1.0717 W/m K.

In contrast, as-produced MWCNTs (not heat treated) resulted in reduced thermal conductivity values for the composites, thus indicating that catalytically grown MWCNTs possessing intrinsic structural defects are not adequate for the fabrication of highly thermal conducting composites, and MWCNTs 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 MWCNT 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 MWCNTs 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 (approximately 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 enhance-

ment of both the thermal and mechanical properties are critically needed.

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