Composites Part B 79 (2015) 505–512

Contents lists available at ScienceDirect

Composites Part B

journal homepage: www.elsevier.com/locate/compositesb

Thermal conductivity of polymer composites based on the length of multi-walled carbon nanotubes

Hyun Su Kim [a], Ji-un Jang [a], Jaesang Yu [a], Seong Yun Kim [a, b, *]

[a] Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk, 565-905, Republic of Korea
[b] Nanomaterials Science and Engineering, Korea University of Science and Technology (UST), 217 Gajeong-ro, Yuseong-gu, Daejeon, 305-350, Republic of Korea

ARTICLE INFO

Article history:
Received 27 December 2014
Received in revised form
5 May 2015
Accepted 6 May 2015
Available online 14 May 2015

Keywords:
A. Polymer-matrix composites (PMCs)
B. Thermal properties
C. Micro-mechanics
D. Thermal analysis

ABSTRACT

The anisotropic development of thermal conductivity in polymer composites was evaluated by measuring the isotropic, in-plane and through-plane thermal conductivities of composites containing length-adjusted short and long multi-walled CNTs (MWCNTs). The thermal conductivities of the composites were relatively low irrespective of the MWCNT length due to their high contact resistance and high interfacial resistance to polymer resins, considering the high thermal conductivity of MWCNTs. The isotropic and in-plane thermal conductivities of long-MWCNT-based composites were higher than those of short-MWCNT-based ones and the trend can accurately be calculated using the modified Mori-Tanaka theory. The in-plane thermal conductivity of composites with 2 wt% long MWCNTs was increased to 1.27 W/m·K. The length of MWCNTs in polymer composites is an important physical factor in determining the anisotropic thermal conductivity and must be considered for theoretical simulations. The thermal conductivity of MWCNT polymer composites can be effectively controlled in the processing direction by adjusting the length of the MWCNT filler.

1. Introduction

The large surface area of nanofillers generates a large matrix-nanofiller interface in nanocomposites, and the number of contact points between nanofillers in the percolation networks increases with decreasing nanofiller size. The interface between the polymer matrix and nanofillers plays a major role in determining the thermal conductivity of the polymer nanocomposites. In polymer-CNT nanocomposites, the contact resistance between the nanotubes and the interfacial resistance between the polymer matrix and the CNTs can be regarded as interfacial effects. The interfacial effects result in disappointing thermal conductivities in the polymer-CNT composites which are lower than expected despite the high thermal conductivity of CNTs of 2800–6000 W/m·K [1–3].

The thermal resistance at these interfaces indicates a heat flow barrier associated with a weak contact at the interface, and differences in phonon spectra based on the atomic arrangements and densities of the two phases. The interfacial thermal resistance between the polymer matrix and CNTs was theoretically and experimentally quantified in units of 10^{-8} m^2 K/W, which is consistent with that of a 10 nm thick polymer layer. From a theoretical point of view, phonon scattering in composites is mainly due to acoustic mismatch arising from the interfacial thermal barrier [4,5]. Polymer-CNT composites are known to form percolation networks at a very low concentration of nanotubes based on their electrical conductivity, which can be used as a percolation threshold: this suggests that CNTs are in contact with one another when including the tunneling length of electrons [6–8]. However, the relationship between thermal conductivity and such CNT–CNT contacts is not well understood. Hone et al. [6] investigated thermal conductivity in networks of free-standing single-walled CNTs (SWCNTs) and reported far greater thermal conductivity than in the networks of non-aligned SWCNTs.

The diameter and length of CNTs have an important impact on their own thermal conductivity, in addition to the interfacial effects, i.e., interfacial resistance and contact resistance, in polymer-

* Corresponding author. Carbon Composite Materials Research Center, Institute of Advanced Composite Materials, Korea Institute of Science and Technology (KIST), 92 Chudong-ro, Bongdong-eup, Wanju-gun, Jeonbuk, 565-905, Republic of Korea. Tel.: +82 63 219 8142; fax: +82 63 219 8239.
E-mail address: sykim82@kist.re.kr (S.Y. Kim).

http://dx.doi.org/10.1016/j.compositesb.2015.05.012
1359-8368/

CNT composites. The mean free path of phonons in CNTs is estimated to be 500 nm for MWCNTs and longer for SWCNTs. The structure of CNTs is typically characterized by a large aspect ratio and surface area, which can be explained by their diameter and length. The effect of the diameter and length of CNTs on the thermal conductivity of the material has been studied [2,9–11]. Cao et al. [12] reported that the thermal conductivity of SWCNTs theoretically increases with decreasing diameters. The thermal conductivity was inversely proportional to the diameters. Similarly, Fujii et al. [13] reported that the thermal conductivity of a SWCNT varied from 500 W/m at a diameter of 28 nm–2069 W/mK at the diameter of 10 nm. The thermal conductivity of SWCNTs estimated by a molecular dynamics simulation increased with the increase in tube length from 6 nm to 404 nm. These results can be explained by a variable ratio between the length of the CNT and the phonon mean free path in them. It is therefore reasonable to expect that the thermal conductivity of the tube will be saturated if the CNT length is longer than the phonon mean free path [14,15].

There is little information on the effect of the CNT length on the anisotropic thermal conductivity of thermally conductive polymer composites though the effect of the CNT length on the thermal conductivity of composites was previously reported [16]. The present study evaluated the effect of the CNT length on the anisotropic thermal conductivity of composites. We fabricated MWCNT composites from commercial length-adjusted MWCNTs based on a typical melt-mixing process. The thermal conductivities of the samples were measured according to the weight fraction of MWCNTs at contents within 2 wt%, at which a uniform dispersion of MWCNTs is known to be achievable [17]. Furthermore, the anisotropic thermal conductivity of the polymer composites was calculated based on the Mori-Tanaka theory, and the theoretical estimates were compared with experimental findings to clarify the effect of MWCNT length on the anisotropic thermal conductivity of the polymer composites.

2. Experimental

2.1. Materials

MWCNTs, CM-130 (short MWCNT) and CM-280 (long MWCNT), were obtained from Hanwha Chemical Corporation in South Korea. Each of these CNTs was fabricated by the chemical vapor deposition method. Table 1 lists the basic properties of the individual MWCNTs provided from the supplier. A linear polycarbonate (PC) resin (LUPOY PC 1300-03, LG Chemistry Co., Gyeonggi-do, Korea) designed for extrusion and injection molding was used as the matrix of the composites. The melt flow rate was measured to be 3 g per 10 min according to ASTM D-1238, and the resin density was 1200 kg/m^3, as determined by ASTM D-792. The Vicat softening point was 151 °C when measured according to ASTM D-696 under 50 °C/h and 50 N load conditions.

Table 1
Properties of MWCNTs and through-plane thermal conductivity of composites filled with short and long MWCNTs.

	Bulk density (g/cm^3)	Diameter (nm)	Length (μm)
Short MWCNT	0.04	20–100	~20
Long MWCNT	0.01	20–100	~200

MWCNT loading (wt%)	Short MWCNT composites (W/m·K)	Long MWCNT composites (W/m·K)
0	0.21	0.21
0.5	0.26	0.28
1.0	0.30	0.31
1.5	0.31	0.32
2.0	0.32	0.33

2.2. Preparation of nanocomposites

MWCNTs and PC resin were prepared at their respective content levels and mixed using a Haake Rheomix internal mixer (HAAKE™ Rheomix 600R OS Mixer, Thermo scientific Inc., Marietta, GA, USA) at a temperature of 250 °C and a screw speed of 60 rpm for approximately 4 h until the torque became stable at 1.5 N m. The content of MWCNTs was determined to be lower than 2.0 wt%, at which uniform composites are known to be fabricable without using any dispersant [17]. The fabricated composites were pelletized and the pellets were placed in a rectangular mold of 2 mm thickness and 4 cm^2 area. Thermally-conductive composite samples were prepared by hot pressing using a heating press (D3P-30J, Daheung Science, Incheon, Korea) at a pressure of 15 MPa for 10 min at 250 °C and were then quenched to 30 °C.

2.3. Characterization

2.3.1. Functionality and defect level of MWCNTs

In order to analyze the functionality of the two types of MWCNTs, we assessed their surfaces using Fourier transform infrared spectroscopy (FT-IR, Nicolet iS 10, Thermo Fisher Scientific., USA) with a resolution of 1 cm^{-1} in a wavenumber range of 1000–4000 cm^{-1} and X-ray photoelectron spectroscopy (XPS, AXIS-HSi, Kratos, Kyoto, Japan) with a Mg X-ray source with a power of 150 W under a pressure of 1×10^{-8}Torr. In addition, the defect levels of the MWCNTs were observed in the wavenumber range of 1000–3000 cm^{-1} at a magnification of 50 using a Raman spectroscope (LabRAM HR 800, HORIBA jobin Yvon, Japan) with a 514 nm Ar-ion laser.

2.3.2. Morphology

The wall thickness of the MWCNTs was observed with a transmission electron microscope (TEM, Tecnai F20, FEI Corp., OR, USA). The MWCNTs were dispersed in ethanol and sonicated for 5 min, and subsequently the dispersion was dropped on a lacey carbon coated film on a Cu grid. The TEM observations were performed at 120 kV and the exposure time to accelerated electrons was minimized to avoid electron radiation damage. A field emission scanning electron microscope (FE-SEM, Nova NanoSEM 450, FEI Corp., OR, USA) was used to observe the length and diameter of the MWCNTs and fracture surface of the composites. To observe the MWCNTs, MWCNTs of 0.5 mg were dispersed for 10 min in 10 ml of ethanol using an ultrasonic bath (JAC-2010P, Kodo Technical Research Co. Ltd, Gyeonggi-do, Hwaseong, Korea) and then coated onto a silicon wafer for 30 s at 3000 rpm using a spin coater (spin process controller, MIDAS, Daejeon, Korea). The compression molded composite samples were fractured after freezing in liquid nitrogen. Both samples were surface-coated with platinum for 120 s in a vacuum using a sputter coating machine (Ion Sputter E-1030, Hitachi High Technologies, Tokyo, Japan). The prepared samples of MWCNTs and composites were observed using the FE-SEM with a voltage of 10 kV applied under a nitrogen vacuum.

2.3.3. Thermal conductivity

The anisotropic thermal conductivity of the fabricated composites was measured. The isotropic (three-dimensional randomly oriented), and in-plane (two-dimensional (2D) randomly oriented in the plane direction of the rectangular composite samples), thermal conductivities of the composites were measured at room temperature and ambient pressure conditions using a thermal conductivity analyzer (TPS 2500 S, Hot Disk AB, Gothenburg,