Non-Linear Thermal Conductivity Enhancement in Nanocomposites with Aligned-Cnt Implementation

NON-LINEAR THERMAL CONDUCTIVITY ENHANCEMENT IN NANOCOMPOSITES WITH ALIGNED-CNT IMPLEMENTATION

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Keywords: *Carbon Nanotubes, Hybrid Composite, Thermal Conductivity*

1 Introduction

Carbon nanotubes (CNTs) have been expected to enhance thermal conductivity in various materials including composites, for applications such as thermal interface materials. However, the thermal properties of bulk CNTs and CNT composites tend not to achieve the high values of individual nanotubes. Factors that cause such scaling effects include CNT morphology (length, alignment, entanglement, etc.), and inter-CNT/CNT-medium boundary properties. It is critical to evaluate and minimize these effects. However, structure-property relationships are not yet well understood, and thus effective use of CNTs has not been achieved for the majority of currently existing CNT polymer composites.

In this work, consistent CNT samples with well-controlled morphology were fabricated by embedding aligned CNTs in polymer to create aligned CNT polymer nanocomposites (A-CNT-PNCs), as shown in Figure 1. A-CNT-PNCs were thoroughly evaluated for their anisotropic thermal properties, and a non-linear increasing trend of thermal conductivity has been observed with increasing CNT volume fraction (v_{CNT}). This newly identified trend was understood through comparison with both analytical and numerical models of the transport behavior. Such understanding can help utilize CNTs in the most effective ways for tailoring thermal conductivities for bulk composite and other applications.

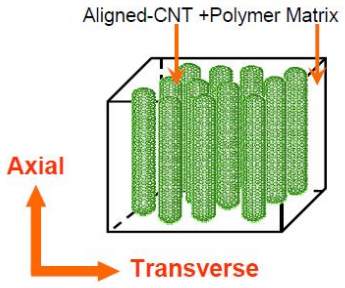

Fig.1. Schematic of aligned CNT polymer nanocomposite (A-CNT-PNC).

2 Materials and Methods

The fabrication of A-CNT-PNCs consists of growth of vertically aligned multi-walled carbon nanotube (MWNT) forests [1], mechanical densification of the forests, and finally wetting of the forests with a polymer [2] (an unmodified aerospace-grade thermoset epoxy, HexFlow RTM6, Hexcel Corp.). Chemical vapor deposition (CVD) growth of vertically aligned MWNTs is repeatable and allows easy detachment of mm-long intact MWNT forests from the substrate. The CNT volume fraction, v_{CNT}, can be independently varied from 1 to 20% by the mechanical densification. Capillarity-driven epoxy infiltration enables facile and complete wetting of the aligned MWNTs even with high v_{CNT}.

Fabricated samples were characterized for CNT alignment and voids, to control sample quality. After every major fabrication step, CNT morphologies were inspected visually using scanning electron microscopy (SEM). CNT waviness was quantitatively characterized from these SEM images, as their mean square cosines of the azimuthal angle.

A-CNT-PNCs were tested in the directions along the CNTs (axial) and perpendicular to CNTs (transverse), based on ASTM standard E1225, the comparative method for thermal conductivity [3, 4]. An A-CNT-PNC sample was stacked with reference (Quartz or Pyroceram 9606) layers. After placing the stack between a heater and a heat sink, the resulting temperature gradients within each layer of the stack

were measured using infrared (IR) microscopy (Infrascope, Quantum Focus Instruments Corporation, up to 0.1 K temperature sensitivity, and 2 μm spatial resolution). Assuming one-dimensional heat transport through the stack, with minimum heat losses to the environment, the thermal conductivity is inversely proportional to the temperature gradient according to Fourier's law. A-CNT-PNC conductivities were calculated in comparison with the reference layers with a known thermal conductivity, without requiring an estimation of heat flux. IR microscopy temperature measurement is non-contact, minimizing conductive heat dissipation. In addition, 2D surface temperature mapping of the sample and neighboring layers (reference and heater/cooler) uniquely enable identification, elimination, and evaluation of thermal resistances at interfaces that can be dominant. Details about the measurement set-up can be found in [4].

3 Results

Measured thermal conductivities of A-CNT-PNCs are summarized in Figure 2 [4], for both the axial and transverse directions. Thermal conductivity of pure RTM6 epoxy (0% v_{CNT}) was measured to be ~0.27 W/mK. With 16% v_{CNT}, thermal conductivity in the axial direction is ~4 W/mK (×13 increase over pure polymer). The measured thermal conductivity and enhancement degree are consistent with other A-MWNT-PNCs [5, 6]. When compared with the electrical transport enhancement, the thermal conductivity enhancement due to the CNTs is small. This is likely because, in practice, the thermal property contrast between CNT and polymer is smaller, and because the thermal boundary resistance is expected to be high when compared with electrical boundary resistance [7]. Thermal transport within CNTs is dominated by phonons (lattice vibrations). At boundaries, high-frequency phonon modes in a CNT need to be transferred to low-frequency modes through phonon-phonon coupling in order to be transported to the surrounding medium (epoxy or neighboring CNTs). This acoustic impedance mismatch results in large thermal resistance. The number of these boundaries is expected to be large for a nanocomposite packed with high v_{CNT} of nm-diameter CNTs, especially in the transverse direction. Nano-scale transport, especially ballistic conduction, can be drastically

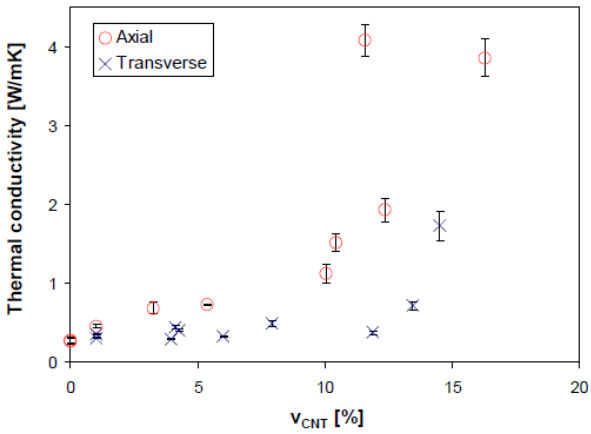

Fig.2. A-CNT-PNC thermal conductivity (axial and transverse) variation measured as a function of v_{CNT} via the comparative method using an IR microscope. Error bars represent upper and lower bounds. The data appears in [4].

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suppressed by inter-tube interactions, impurities, and/or defects.

Meanwhile, a unique trend has been observed. The thermal conductivity increases non-linearly with v_{CNT} both in the axial and transverse directions; the axial and transverse thermal conductivity slope *increases* with v_{CNT}. A similar non-linear trend has been experimentally observed with CNT nanocomposite, but without CNT continuity or alignment [5, 8]. In models, such non-linear behavior was observed only in numerical models that include inter-CNT interactions, and at high concentrations, where inter-particle conduction participates significantly in the thermal transport within the composites [9].

4 Discussions

Measured conductivities were compared with both an analytical effective medium approach (EMA) and a numerical Monte Carlo simulation to study the effects of two major hypothesized controlling factors of thermal transport: CNT-polymer boundary resistance, $R_{bd\text{-}m}$, and inter-CNT boundary resistance, $R_{bd\text{-}CNT}$.

4.1. Comparison with Analytical Effective Medium Approach

The EMA model allows modeling of complex geometries of CNTs (diameter, aspect ratio, orientation, and non-homogeneous distribution) and CNT-polymer boundary resistance [10], but to date not inter-CNT conduction. The measured data were curve-fit by varying the unknown parameter, CNT-polymer boundary resistance, with the available literature value, ~10×10^{-8} Km^2/W (at SWNT-fluid boundary [11]) as a starting point.

As shown in Figure 3, the non-linear thermal conductivity behavior with v_{CNT} was observed both in the axial and transverse directions. The $R_{bd\text{-}m}$ effect is larger with high v_{CNT} since more CNT-polymer interfaces are introduced. As $R_{bd\text{-}m}$ decreases, the non-linearity type was observed to shift. With $R_{bd\text{-}m}$ on the order of 10×10^{-8} Km^2/W, the thermal conductivity increases but reaches a plateau in the high v_{CNT} range (convex curvature), since CNT-polymer boundaries, introduced together with CNTs, interfere with thermal transport. However, when $R_{bd\text{-}m}$ is smaller (< 1×10^{-8} Km^2/W), CNT-polymer boundaries also act as effective thermal

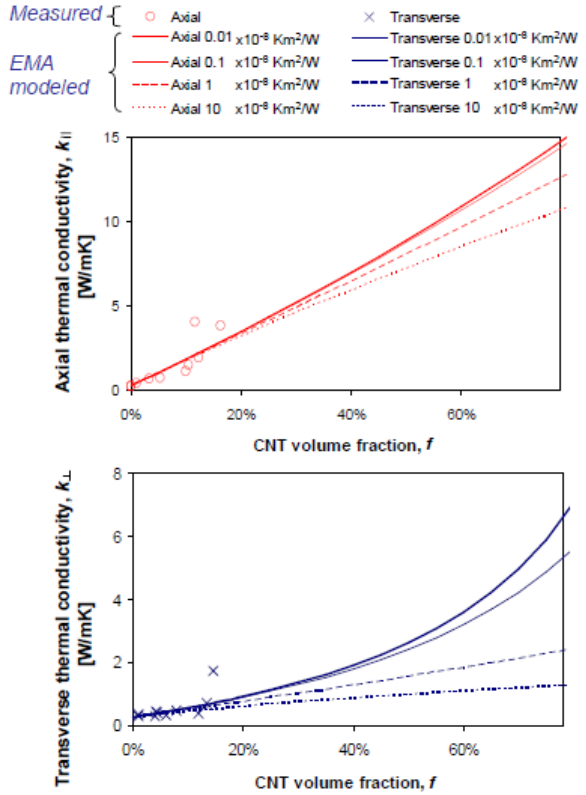

Fig.3. Comparison of experimentally measured thermal conductivities of A-CNT-PNCs with the EMA model.

conductive pathways trough the polymer between conductive CNTs, and thus A-CNT-PNC conductivity rapidly increases in the high v_{CNT} range (concave curvature). Such effect of $R_{bd\text{-}m}$ is more significant with conduction in the transverse direction since CNT-polymer interfaces are dominant. This concave non-linear behavior modeled with the small $R_{bd\text{-}m}$ values is comparable with the experimentally observed trends with the axial and transverse conductivity. However, such small $R_{bd\text{-}m}$ (< 1×10^{-8} Km^2/W) deviates, ×10 smaller, from experimentally and theoretically estimated $R_{bd\text{-}m}$ of nano-particles in polymer [11].

4.2. Comparison with Numerical Monte Carlo Simulation

While the non-linear trend was explained by the EMA analytical model as the $R_{bd\text{-}m}$ effect, the curve-fit of measured thermal conductivities was not successful with reasonably chosen parameter inputs. Such deviation can be explained by the effect of inter-CNT boundary resistance, which was not considered in the above EMA model. Effects of the inter-CNT boundary resistance should be more significant with higher v_{CNT}, where conductivity behavior deviates from the EMA model. Thus, a numerical method, specifically a Monte Carlo simulation with the random walk algorithm [12], was introduced to simulate nano-scale transport and inter-CNT contact effects. In an off-lattice Monte Carlo (MC) simulation, a large number of walkers (heat carriers) were simulated to travel in a computational cell until steady-state was achieved. Governing principles for walker motion were set to model microscopic heat transfer within a polymer matrix, within CNTs, and across CNT-matrix and inter-CNT boundaries, respectively. Within the polymer matrix, walkers were assumed to execute random jumps in terms of distance and direction after each time step (the Brownian motion). Across inter-CNT and CNT-polymer boundaries, walkers were set to move probabilistically using the acoustic theory. $R_{bd\text{-}CNT}$ of 24.8×10^{-8} m^2K/W was chosen because it was the only available $R_{bd\text{-}CNT}$ value in the literature, extracted from simulation of a SWNT using molecular dynamics [13].

As shown in Figure 4, the non-linear behavior of A-CNT-PNC thermal conductivity was successfully simulated within the expected v_{CNT}

range. Boundary resistances, both inter-CNT and CNT-polymer, were extracted to be ~10^{-8} m^2K/W, an order of magnitude smaller than the expected values based on previous work. Although non-linearity in the experimental data were explained, further model development is necessary for better comparison with experimental data, including factors such as CNT waviness, or parameter variation with v_{CNT} (inter-CNT boundary resistance, the isolation factor, etc.).

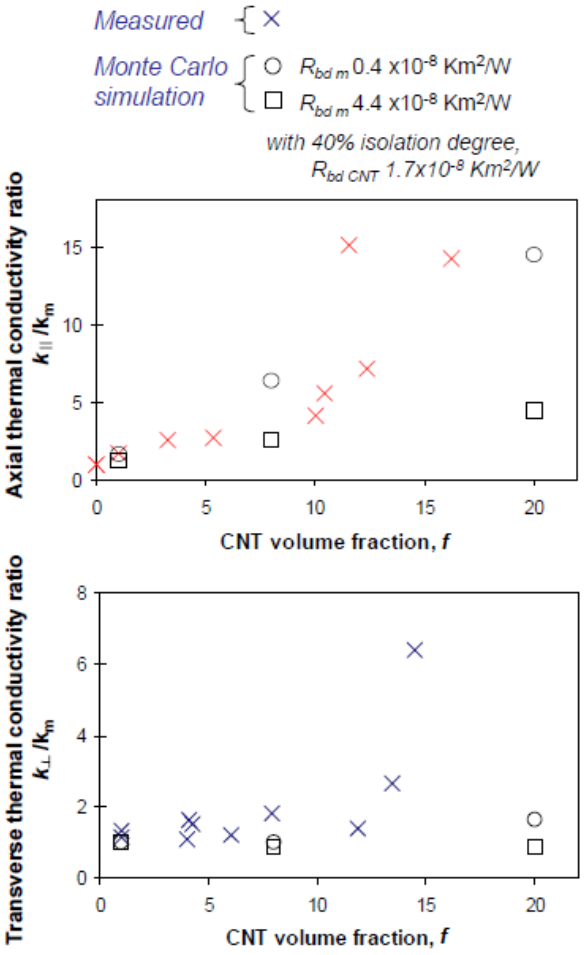

Fig.4. Comparison of experimentally measured thermal conductivities of A-CNT-PNCs with the Monte Carlo simulation.

5 Conclusions

MWNTs are expected to improve thermal conductivity of polymer composites because of the shielded internal tube layers. In order to achieve such optimized use of MWNTs in A-CNT-PNCs, minimization of both the inter-CNT and CNT-polymer boundary resistances are required. Purification of the nanotubes or functionalization of the CNT surfaces might improve the boundary resistances and the composite thermal conductivity. Experimentally, the sample-substrate boundary resistance was accounted for in the measurements of thermal conductivity. But in practice, the interface resistance needs to be minimized for successful implementation of CNT-PNCs in applications including as thermal interface materials.

References

[1] A.J. Hart and A.H. Slocum "Rapid growth and flow-mediated nucleation of millimeter-scale aligned carbon nanotube structures from a thin-film catalyst." *J. Phys. Chem. B*, 110(16), 8250–8257, 2006.

[2] B.L. Wardle, et al. "Fabrication and characterization of ultra high volume fraction aligned carbon nanotube-polymer composites." *Adv. Mater.*, 20(14), 2707–2714, 2008.

[3] X.J., Hu, M.A. Panzer, and K.E. Goodson "Infrared microscopy thermal characterization of opposing carbon nanotube arrays." *J. Heat Trans.*, 129(1), 91–93, 2007.

[4] A. Marconnet, N. Yamamoto, M. A. Panzer, B.L. Wardle, and K.E. Goodson, "Thermal conduction in aligned carbon nanotube-polymer nanocomposites with high packing density." *ACS Nano*, online May 2011.

[5] H. Huang, C.H. Liu, Y. Wu, and S. Fan, "Aligned carbon nanotube composite films for thermal management." *Advanced Materials*, 17(13):1652–1656, 2005.

[6] I. Ivanov, A. Puretzky, G. Eres, H. Wang, Z. Pan, H. Cui, R. Jin, J. Howe, and D. B. Geohegan, "Fast and highly anisotropic thermal transport through vertically aligned carbon nanotube arrays." *Applied Physics Letters*, 89(22):223110–3, 2006.

[7] K. I. Winey, T. Kashiwagi, and M. Mu, "Improving electrical conductivity and thermal properties of polymers by the addition of carbon nanotubes as fillers." *MRS Bulletin*, 32:348–353, 2007.

[8] C. Guthy, F. Du, S. Brand, K. I. Winey, and J. E. Fischer, "Thermal conductivity of single-walled carbon nanotube/PMMA nanocomposites." *Journal of Heat Transfer*, 129(8):1096–1099, 2007.

[9] S.U.S. Choi, Z.G. Zhang, W. Yu, F. E. Lockwood, and E. A. Grulke, "Anomalous thermal conductivity

enhancement in nanotube suspensions." *Applied Physics Letters*, 79(14):2252–2254, 2001.

[10] C.W. Nan and R. Birringer "Effective thermal conductivity of particulate composites with interfacial thermal Resistance. *J. Appl. Phys.*, 81(10), 6692–6699, 1997.

[11] S. T. Huxtable, D. G. Cahill, S. Shenogin, L. Xue, R. Ozisik, P. Barone, M. Usrey, M. S. Strano, G. Siddons, M. Shim, and P. Keblinski, "Interfacial heat flow in carbon nanotube suspensions." *Nature Materials*, 2(11):731–734, 2003.

[12] H. M. Duong et al. "Morphology effects on nonisotropic thermal conduction of aligned single-walled and multi-walled carbon nanotubes in polymer nanocomposites". *J. Phys. Chem. C*, 114(19), 8851–8860, 2010.

[13] S. Maruyama, Y. Igarashi, Y. Taniuchi, and J. Shiomi, "Anisotropic heat transfer of single-walled carbon nanotubes." *Journal of Thermal Science and Technology*, 1(2):138–148, 2006.