Limiting Mechanisms of Thermal Transport in Carbon Nanotube-Based Heterogeneous Media

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Abstract: The outstanding thermal properties of carbon nanotubes (CNTs) have generated considerable interest and research activity. A very promising application is the use of vertically aligned arrays of CNTs as thermal interface materials (TIMs) for electronic systems. TIMs require a high thermal conductivity, a low thermal interface resistance with the adjacent microprocessor and heat sink, and significant mechanical compliance to help minimize the impact of mismatched thermal expansion coefficients. However, due to high thermal interface resistances of CNT films, more detailed measurements and improved fabrication methods are needed. This review paper presents current patents and last experimental/computational techniques investigating heat transfer and limiting mechanisms of CNTs, CNT-thermal interface structures, CNT-polymer nanocomposites (PNCs), and thermal boundary resistance (TBR) of the CNTs and different surrounding matrices (metals, nanofluids and polymers). Effects on directional thermal conductivities of aligned CNTs in PNCs/TIMs are predicted using a random walk simulation. The TBR of CNT-matrix and inter-CNT contact significantly affect the effective thermal transport properties including anisotropy ratios. When CNT-CNT contact is significant or CNT-CNT TBR is low (relative to the CNT-matrix TBR), then heat transport is dominated by CNT-CNT contact effects, rather than CNT-matrix interfacial effects. The effects of CNT orientation, type (single-versus multi-wall), inter-CNT contact, volume fraction and TBR on the effective thermal conductivities of CNT-PNCs/TIMs are quantified. The simulation results agreed well with reported experimental data for randomly-oriented SWNT-epoxy and polymethyl methacrylate nanocomposites. These simulation results can be very useful for developing techniques to enhance the effective thermal conductivity of composites using conductive nanomaterials embedded in matrices, and assist experimentalists in interpreting heat conduction measurements.

Keywords: Carbon nanotube (CNT), thermal conductivity, thermal interface material (TIM) composite, thermal boundary resistance, random walk algorithm.

1. INTRODUCTION

State-of-the-art integrated circuits (ICs) for microprocessors routinely dissipate power densities on the order of 50Watts/cm² [1]. This large power is due to the localized heating of ICs operating at high frequencies, and must be managed for future high-frequency microelectronic applications. When the size of components/devices for ICs and other appliances are smaller, heat dissipation and transport for such components/devices are more difficult. Due to microscaling problems, a thermal conductor for a macro size is not relevant for use with a micro size component/device. The need for addressing this problem is imperative for next-generation IC packaging technology. One potential solution is to fabricate new packaging materials having high thermal conductivity that can transfer heat from a local hot spot to a larger heat sink [1-4].

The heat transfer rate between a target object and a cold reservoir is limited by the interface morphology. Practical objects have only a very small portion of surface in contact with other solid surfaces. Eutectic bonding materials or thermal conducting pastes/films are normally applied at the interface to increase the contact area. However, the thermal conductivities of these bonding materials are normally orders of magnitude lower than those of solid materials such as Cu and Si. So the interface remains the bottleneck for heat dissipation. Metal film can be used to improve the thermal conductivity but is only applicable for high-pressure loading [1].

It is essential to develop a compliant TIM that efficiently and promptly dissipates or conducts heat from a micro size component/device, preferably down to nanometer scale systems, to a heat sink with a heat transfer rate that is comparable to rates for macro size components and devices. Preferably, the thermal conductor should be reusable and should work with any surface, rough or smooth.

A variety of TIMs have been used in the past to reduce TBR between a die and a cooling solution [5]. Thermal greases are also used for the TIM since such materials have high bulk thermal conductivity and readily conform to surface irregularities in the heat sink and the device. Use of thermal greases, however, have the disadvantage of possible pump out and phase separation of the grease as the die is heated and undergoes thermal warping due to differences in the coefficient of thermal expansion between die and organic
substrate. Other adhesives such as epoxy are used as TIMs but requiring a cure process after their application. Various thermal gels such as silicones or olefins may also be used as TIMs but they also require curing after application and have low thermal conductivity. Elastomers such as urethane rubber have high bulk conductivity but suffer from high contact resistance and require that high pressure of at least 100 psi be applied at the thermal junction to provide adequate thermal coupling. Finally, phase change materials such as low molecular weight polyesters have been used but still have the lower thermal conductivity than that of thermal grease. The thermal conductivity of TIMs commonly used is 10W/m.K as shown in Fig. (1) [4, 5].

![Thermal conductivities of different materials.](image)

A thermal interface structure is formed from an array of aligned CNTs in a polymeric interstitial material [1-3, 5]. CNTs with high thermal conductivity and stability have high potential as components in structures that require high heat dissipation and thermal transport control. Applications vary from micro-scale thermal tapes in electric circuits [6, 7] to macro-scale aerospace structural composites [8, 9] that benefit also from lightweight and other multi-functional (mechanical and electrical) property enhancements due to the CNTs. Since the thermal conductivity of the CNTs is about 2000-3000W/m.K [10-15], using them in a thermal interface structure will substantially increase its thermal conductivity.

Electron and phonon scattering occurring at their interfaces, leading to high electrical and thermal resistances limits semiconductor packages using the CNTs. A major challenge in overcoming such limitations lies in tailoring the interface to control interface resistance. Typically it is proposed that the CNT surface should be functionalized with low interface resistance materials such as titanium or nickel should be sputtered onto the ends of a CNT. However, functionalization introduces defects in the CNT structure and may deteriorate its intrinsic thermal and electrical properties, while sputtering with low contact resistance materials may not always achieve good bonding with CNTs, especially if the sputtered metal is not a carbide former. So alternate methods of tailoring the CNT interface and forming good interfacial adhesion (lower contact resistance) at CNT surfaces without compromising the CNTs’ desirable intrinsic properties are developed [16].

Functionalization of CNTs can enhance their applicability. Functionalization may lead to more efficient purification/separation techniques, such as, those based on chirality or the separation of metallic SWNTs from semi-conducting ones. Functionalization also leads to the development of new classes of material with different advanced physical and chemical properties. For different functionalization purposes, CNTs are usually treated in different solvents by refluxing, heating and stirring over a long period of time. Acid treatment has been the most commonly used functionalization approach. It separates the CNT bundles, and is the first step towards amidation, esterification and other applications. But conventional acid treatment is a long process requiring up to several days depending upon the requirements of the final product [16]. So the developments of a fast, efficient and controllable technique for CNT functionalization can dramatically speed-up their real world applications.

Mitra et al.’s invention [17] is using the microwave to functionalize SWNTs. Microwaves are electromagnetic radiation in the 0.3-300 GHz frequency range (corresponding to 0.1-100 cm wavelength). The energy at this wavelength is 0.3 cal/mol (Planck’s law), and is therefore not enough for molecular excitation. Thus most of the energy is used in substrate heat-up. In microwave heating, electromagnetic energy is transformed into heat through ionic conduction and the friction due to rapid reorientation of the dipoles under microwave radiation. The larger the dipole moment of a molecule, the more vigorous is the oscillation in the microwave field, consequently more heating. This microwave heating is fast, no inertia, and in situ without heating the surroundings. Chemistry under microwave radiation is known to be quite different, fast and efficient. The microwave heating is also eco-friendly due to less solvent usage. It has been exploited in various organics synthesis including heterocyclic, organometallic, and combinatorial chemistry. The reported advantages are rapid reactions under controlled temperature and pressure (especially in a closed system), higher purity products achieved due to short residence times at higher temperatures, and better yields at even very short residence times.

2. HEAT TRANSFER OF CARBON NANOTUBES

Heat transfer within an individual SWNT has been rigorously investigated to identify lattice vibration modes and their allowed energy levels, which are different from other carbon structures (graphenes, graphites) due to the periodic

![Fig. (1). Thermal conductivities of different materials.](image)
boundary conditions along the CNT circumference [18, 19]. SWNT thermal conductivity has been estimated to be as high as 300-3000 W/m.K at room temperature by molecular dynamics (MD) models [20].

The length dependence of thermal conductivity and ballistic-diffusive features of heat conduction have also been presented [21-23]. Experimentally obtained thermal conductivities in the literature were comparable with these theoretical values for both SWNTs with 1.7nm diameter and 2.6 mm length [24], and multi-walled CNTs (MWNTs) with 14nm diameter and 2.5 mm long measured using a microfabricated suspended device [25]. However, the effective thermal conductivities of SWNT and MWNT bundles (the averaged value of CNTs and their surrounding media, normally air) were experimentally measured [26-31] to show large variation and deviation from the estimated values using rules of mixture based on individual component values. These differences possibly originate from the type of CNTs themselves (quality, defects, diameter, length, chirality, and number of walls), CNT morphology (alignment, waviness, CNT-CNT contacts, etc.), the inter-wall or inter-tube interactions and phonon transportation inside CNTs (mean free path). An experimental study [32] demonstrated high thermal conductivities of SWNTs at room temperature and phonon mean free path is discussed to be <1.0 mm. CNT thermal conductivity is certainly affected when the CNT array length is much longer than the phonon mean free path due to phonon scattering.

The thermal properties of the CNT arrays were measured using a standardized ASME procedure for flash diffusivity infrared detection [4]. Long, continuous vertically aligned CNT arrays with over 400-μm height were measured. Following application of an approx.7 ms heating pulse from a Xe flash lamp, a fast InSb detector records the arrival of infrared radiation through the sample. Known calibration standards ensured accurate system response. Fig. (2) shows the heat pulse arriving through 2 mm of pure epoxy (peak of pulse approx.15 seconds), through 2 mm of epoxy containing 4.7 vol% vertically aligned CNT (peak of pulse approx. 0.12 seconds), and through as-grown vertically aligned CNTs on Si in air (peak of pulse approx. 0.06 seconds). From the waveforms measured by this technique, the thermal diffusivity of the vertically aligned CNT array is determined.

Other investigations showed that creating vertically aligned CNT arrays better utilizes the outstanding thermal conductivity of individual CNTs. Hu et al. [33] used the 30 method to measure the room temperature thermal conductivity of a 13 μm thick vertically aligned MWNT grown on silicon to be 75 W/m.K, which outperforms that of randomly oriented tube samples. However, the total thermal resistance of the aligned CNT TIM was found to be 16 m².K/MW, which still falls well short of theoretical expectations. Yang et al. [34] found the effective thermal conductivities of the similar MWNT arrays using a thermoreflectance technique to be around 15 W/m.K, with total thermal resistances of 0.8-2.9 m².K/MW. Even taking account porosity effects, the reduced performance of these aligned MWNT arrays indicates that the TBR between the CNT and the substrate is significant.

Other techniques have been developed to characterize the thermophysical properties of micro-/nanoscale wires/tubes including the CNT arrays, like microfabricated device method [35, 36]. At present, an optical heating and electrical thermal sensing technique [37-39], a transient electrothermal (TET) technique [40, 41], and a transient photoelectrothermal (TPET) technique [42, 43] have been developed to measure the thermophysical properties of individual one-dimensional wires/tubes at micro/nanoscales. Guo et al. [44] developed a pulse laser-assisted thermal relaxation (PLTR) technique to overcome the drawbacks of the TET and TPET techniques (a relatively long measurement time and suffers from a low signal level) while providing comparable fast experiment implementation and high signal/noise ratio. This technique can be applied to metallic, nonconductive, and semiconductive micro- and nanoscale wires. The PLTR technique can be used to measure more accurately short wires with high thermal conductivity/diffusivity. The thermal diffusivities of MWNTs (with diameters from 30 to 50 nm inside bundles; bundle diameter varies 30-200 μm) measured by the TET and PLTR techniques are 1.09x10⁻³ and 1.50x10⁻³ m²/s. The random alignment of the CNTs in the bundle causes low thermal diffusivity. However, there currently no previous experimental or computational work in previous work [40-44] studying comprehensively the thermal conductivity of CNTs by taking into account effects of CNT morphology and heat loss to the experimental ambient. Duong et al. [45] developed numerical (finite difference) study of the thermal conductivity of the CNT fibers has been carried out by taking into account the effects of various morphologies (different length, different diameter and various aspect ratios of CNT fibers), anisotropic heat conduction (radial and axial heat conduction along the CNT fibers) and heat lost to the CNT fiber ambient (heat radiation from the CNT fiber surface). This computational work based on the TET and PLTR techniques is more realistic and useful for helping experimentalists understand better the heat conduction mechanism within the CNTs, as well as improving the
thermal conductivity measurement by choosing relevant experimental conditions.

Panzer et al. [30] used a thermoreflectance technique to measure the volumetric heat capacity, TBR and to place a lower bound on the internal volume resistance of a vertically aligned SWNT array capped with an aluminum film and palladium adhesion layer. The total structure TBR, including volume and interface contributions, is 12 m².K/MW. The experimental data show that the top and bottom interfaces of the CNT array strongly reduce its effective vertical thermal conductivity. A low measured value for the effective volumetric heat capacity of the CNT arrays shows that only a small volume fraction of the CNTs participate in thermal transport by bridging the two interfaces. As only a subset of the CNTs is actually responsible for the thermal transport, the effective volume fraction of SWNTs contributing to thermal transports is 0.35 vol%, which is much less than 12 vol% SWNTs estimated from the catalyst deposition process. A thermal model of transport in the array exploits the volumetric heat capacity to extract an individual CNT-metal contact resistance of 10 m².K/GW (based on the annular area), which is equivalent to the volume resistance of 14 nm of thermal SiO₂.

3. CARBON NANOTUBE THERMAL INTERFACE STRUCTURES

Electronic components are becoming smaller and smaller while their heat dissipation requirements are increasing due to the improved capacity to process data faster. Thermal management becomes important for high power ICs such as microprocessors or pumped laser diodes to improve their performance and working life. Thermal management includes dissipating the heat generated by an electronic device away from the device and allowing the generated heat to disperse to its surroundings, while maintaining the semiconductor device at a low temperature. Poor heat dissipation can result in performance and reliability degradation of the electronic devices/circuit due to an unacceptably high operating temperature. So TIMs play a big role in the thermal management. Typical thermal management solutions use some combination of aluminum or copper heat sinks, fans, thermal spreaders/heat pipes, thermal pastes or adhesives to form a low thermal resistance path between the semiconductor chip and the ambient.

In order to achieve a low operating temperature for the chip, it is necessary to minimize the total thermal resistance (°C/W) from the chip to the ambient. The TIM, the interface media between chip and heat sink, is one of the bottle necks in thermal management. The TIM layers provide mechanical compliance to relieve the thermal expansion mismatch stress between the components that are constructed of different materials, but they also represent a significant portion of the total thermal resistance. Thermal paste is one of the most common TIMs. It is a thick paste of conducting particles in oil or other low thermal conductivity media. Due to the interface resistance, the thermal conductivity of the paste is in the order of 1.0 W/m.K. The thermal adhesive can be used as a TIM as it serves both functions of thermal conduction and adhesion. Silicone and thermal epoxy are commonly used thermal adhesives. Metal or ceramic fillers are dispersed within a polymer binder to increase the thermal conductivity. Typical fillers are aluminum, silver, aluminum nitride, boron nitride, magnesium oxide, and zinc oxide. The typical polymer binder materials include silicone, urethane, thermoplastic rubber, and other elastomers. However, the thermal conductivity of the thermal adhesives is less than a few tens of W/m.K. The heat conduction coefficient of the conventional TIM is now considered to be too low for many contemporary applications, because it cannot adequately meet the heat dissipation requirements of modern electronic components. Therefore, the new TIMs with better thermal conductivity are invented.

Montgomery et al., 2005 invented a process to produce a thermal interface structure by combining aligned CNTs with a polymer [5]. This product can be used to reduce the TBR between an electronic device and a cooling solution. In this structure, CNT bundles are oriented parallel to each other and to the heat transfer axis of the thermal interface. A polymer, such as polycarbonate, polypropylene, polycetal, polyoxyethylene or polyformaldehyde, is added between the CNT bundles. This composite structure has two planar surfaces, which are perpendicular to the aligned CNTs. These two surfaces will be coupled with an integrated circuit die and a heat sink, respectively, to facilitate the heat transfer from the die to the heat sink.

In another invention, Hsiao used two substrates and put them in parallel facing positions [46]. The substrates can be made of glass, silicon or metal. An array of CNT was formed on one of the two facing surfaces of the two substrates by a chemical vapor deposition method. The CNTs were parallel to each other and perpendicular to the surfaces of the substrates. The CNTs were grown until they were close or met the surface of the opposite substrate. Then a liquid state base was filled into the interstices between the CNTs. A hardener was also added into the base. The base can be silicone, polyester, polyvinyl chloride, polyvinyl alcohol, polyethylene, polypolypylene, epoxy resin, polycarbonate, polyoxyethylene, or a polycetal. The composite was heated for 5 min at 175°C under a pressure of 50 kg/cm². Then it was treated in vacuum at 180°C for hardening for about 6h to form the TIM. Then the substrates were removed. The TIM can be treated further by etching to ensure that tips of the CNTs are exposed from the two opposite surfaces.

The CNTs have high current carrying capacity as well as high thermal conductivity. However, their use in semiconductor packages is limited due to electron and phonon scattering occurring at their interfaces, leading to high electrical and thermal resistances. A major challenge in overcoming such limitations lies in tailoring the interface to control interface resistance. Typically it is proposed that the CNT surface should be functionalized with low interface resistance materials, or that a low contact resistance material such as titanium or nickel should be sputtered onto the ends of a CNT. Functionalization, however, introduces defects in the CNT structure and may deteriorate its intrinsic thermal and electrical properties, while sputtering with low contact resistance materials may not always achieve good bonding with CNTs, especially if the sputtered metal is not a carbide former. Alternate methods of tailoring the CNT interface are therefore necessary, methods that form good interfacial adhesion and
lower contact resistance at CNT surfaces without compromising the CNTs’ desirable intrinsic properties. In Shekhawat et al. ’s invention [16], a thermally and electrically conductive structure comprises a CNT (110) having an outer surface (111) and a carbon coating (120) covering at least a portion of the outer surface of the CNT. The carbon coating may be applied to the CNT by providing a nitrile-containing polymer, coating the CNT with the nitrile-containing polymer, and pyrolyzing the nitrile-containing polymer in order to form the carbon coating on the CNT. The CNT may further be coated with a low contact resistance layer (130) exterior to the carbon coating and a metal layer (140) exterior to the low contact resistance layer.

In Taya and Park’s invention [47, 48], a method for preparing a very thin TIM was developed. The TIM consists of a matrix and a thermally-conductive filler. The matrix was made from silicone thermal grease and chloroform. Single walled CNT was used as the filler. Chloroform was used as a solvent to dissolve the grease. The material was formed by the dispersion of CNT in the matrix. In the material synthesis, CNT was mixed and dispersed well in the silicone thermal grease and chloroform at room temperature by ultrasonic power to obtain a uniform mixture. Then chloroform was evaporated and the composite was formed. In order to reduce the thermal resistance and thermal impedance, the authors tried to reduce the thickness and increase the thermal conductivity of the TIM.

Recently, Chiou and Lee [49] have showed a new TIM in their patent. The deficiencies of low thermal conductivity and high thermal resistance in the conventional TIMs were resolved. The TIM composite structure was formed by using CNT with high thermal conductivity and liquid crystal polymer with the well-ordered structure. The TIM thereby has a high thermal conductivity. The TIM was composed of a phase change thermoplastic resin, wherein a percentage of the phase change thermoplastic resin in the composition is about 30-89 by weight, wherein a melting point of the phase change thermoplastic resin is lower than 100°C, a liquid crystal polymer, wherein a percentage of the liquid crystal polymer in the composition is about 10-50 by weight; and a CNT, wherein a percentage of the CNT is about 1-25 by weight. The added amount of CNT is less than the added amount of metal or ceramic powders in the prior art for improving the dispersion process. The CNT-LC thermal composite structure and the phase change resin are compatible without phase separation. The TEM has a phase change temperature about 45-75°C. Any holes, gaps and dents on the surface of device are filled at the normal operating temperature of device to reduce the thermal resistance of the entire device.

In 2010, Huang et al. [50] proposed a method for manufacturing a TIM comprising the steps of: providing a CNT array comprising a plurality of CNTs each having two opposite ends; forming a composite phase change material by filling clearances in the CNT array with a phase change material; forming a section with predetermined thickness by cutting the composite phase change material along a direction cross to an alignment direction of the CNTs; and heating up the section to a temperature higher than a phase change temperature of the phase change material and cooling down after the two opposite ends of the CNTs protruding out of the section.

Dubin et al. [51] proposed a method of constructing an electronic assembly to enhance heat dissipation through a thermal interface. In this structure, a layer of metal was formed on a backside of a semiconductor wafer having integrated formed thereon. Then, a porous layer was formed on the metal layer. A barrier layer of the porous layer at the bottom of the pores was thinned down. Then, a catalyst was deposited at the bottom of the pores. The CNTs were then grown in the pores. Another layer of metal was then formed over the porous layer and the CNTs. The semiconductor wafer was then separated into microelectronic dies. The dies were bonded to a semiconductor substrate, a heat spreader was placed on top of the die, and a semiconductor package resulting from such assembly was sealed. A thermal interface was formed on the top of the heat spreader. Then a heat sink was placed on top of the thermal interface.

In Jewram et al.’s patent [52], a method for producing a thermally and electrically conductive interconnect structure for operable placement between a first body and a second body was described. The interconnect structure included a first surface for operable juxtaposition with the first body, a second surface for operable juxtaposition with the second body, and a thickness dimension defined between the first and second surfaces. The interconnect structure included a first thermally conductive material and a second electrically conductive material, wherein the second electrically conductive material was formed in one or more distinct structures, with the structures forming at least one substantially continuous pathway of the second material through the thickness dimension. The interconnect structure exhibited a compressive modulus along a thickness axis of less than about 100 psi.

In 2011, Hua et al. [53] showed a new TIM preparation from CNTs and particles. Advantages include increased thermal conductivity and improved mechanical properties such as lower viscosity. In selected embodiments, free particles such as metallic particles or CNTs were included in a TIM along with composite particles. An advantage of including free particles along with composite particles includes improved packing density within selected embodiments of TIMs.

4. CARBON NANOTUBE NANOCOMPOSITES

The thermally conductive material formed by injection molding is relatively thick, which increases a bulk of the thermally conductive material and reduces its flexibility. Furthermore, CNTs are dispersed randomly in the matrix material, which results that heat tends to spread uniformly and retaining much of the heat within the heat transfer material. The heat does not spread efficiently from the first surface engaged with the electronic device to the second surface engaged with the heat sink. Therefore, a thin CNT-PNC, with controlled CNT orientation within one or more desired patterns and with good thermal/electrical conductivity, is developed as below.

The CNT arrays are used to provide one or more high performance thermal conductors for applications that require
large heat dissipation [2]. The innovation uses vertically oriented CNT arrays to increase the effective contact area (particularly for a rough surface) while providing an extremely large thermal conductivity along a CNT axis and across the interface. This approach also improves the mechanical strength of CNTs so that the CNT arrays can remain stable and can make good contact to the target surface. Copper and other high thermal conductivity materials are deposited to fill interstitial regions or gaps in a first part of the CNT arrays. This composite structure provides mechanical strength to maintain the CNTs in position and also serves as an efficient heat transfer material to improve diffusion of heat flux from an individual CNT to a larger surrounding volume.

The fabrication involves four steps: (1) substantially vertically aligned CNT arrays with 1 - 50 micron length are grown on a solid substrate such as Si wafers and metal blocks/films (serving as a heat sink and having good thermal conductivity); (2) a first portion of interstitial spaces between adjacent CNTs is filled with highly thermally conductive materials such as Cu, Ag, Au, Pt or doped Si by chemical vapor deposition, physical vapor deposition, plasma deposition, ion sputtering, electrochemical deposition, or casting from liquid phase; (3) filler materials are removed from a second portion of the interstitial spaces by mechanical polishing, chemical mechanical polishing, wet chemical etching, electrochemical etching, or dry plasma etching so that the top portion of the CNT arrays is exposed, with the bottom part remaining embedded in the filler materials; and (4) the CNTs can reversibly buckle or bend one by one under low loading pressure so that the CNTs can make maximum contact with the object to be cooled, even an object with a very rough surface.

Yao et al. [54] claimed that aligned CNTs grow readily from catalyst patterns into well-defined vertical bundles. However the CNT bundles have poor adhesion to the substrate. Therefore, when CNT bundles reach more than 100 micrometers in length, they have difficulty in remaining upright. These difficulties have prevented the application of the CNT bundles to macroscopic thermal management such as silicon chip for high power device applications. Their invention is directed to a composite plate comprising CNT bundles with high thermal conductivity. The method of forming the composite plate comprising CNT bundles with high thermal conductivity comprises preparing a CNT growth substrate, depositing a CNT growth catalyst on the CNT growth substrate, preparing a wafer with etched through via arrays, placing the wafer with the etched through via arrays over the CNT growth substrate with the CNT growth catalyst, growing CNT bundles in the etched through via arrays on the wafer over the CNT growth substrate with the CNT growth catalyst in a CVD chamber to form a wafer matrix CNT-PNC structure; and removing the CNT growth substrate from the wafer matrix CNT-PNC structure. The formed composite plate comprising CNT bundles with high thermal conductivity provides and improved CTE silicon match, provides a more effective thermal conductivity than a silicon matrix or Cu or Cu alloy substrate, and contains CNTs that remain vertical.

Cecelbi et al. [55] reported novel fabrication techniques yield controlled-morphology aligned CNT-PNCs with measured non-isotropic properties and trends consistent with standard composites theories. First, continuous and aligned MWNTs were grown using the thermal chemical vapor deposition (CVD) method on silicon wafers with a thin catalyst layers of Fe(catalyst)/Al2O3(diffusion barrier)(1/10 nm) deposited by electron beam evaporation. The as-grown (1.0vol%) CNT forests were released from the growth substrate and the freestanding forests were compressed using a mechanical biaxial densification instrument to desired volume fractions (1, 8, and 20 vol%) [56]. The compressed forests (surfaces unmodified, unfunctionalized) were then transferred to a z-stage and lowered into an uncured epoxy pool just touching the top surface of epoxy. An aerospace-grade epoxy, RTM 6 (Hexcel), having viscosity of approximately 80 cP at 90 °C was used. Infiltration of polymer into CNT forest was driven by capillary action, which is strongly affected by inter-CNT spacing (volume fraction effect) and polymer viscosity. CNTs preserve their alignment during polymer infiltration to forest, and the epoxy is cured following the recommended procedure from the manufacturer as 1 hour at 160 °C and 2 hours at 180 °C, yielding the desired nanocomposites. The cured samples were machined and mechanically polished to achieve a smooth surface for characterization. Modulus and electrical conductivity are maximal along the CNT axis, and are the highest reported in the literature due to the continuous aligned-CNTs and use of an unmodified aerospace-grade structural epoxy. Rule-of-mixtures predictions are brought into agreement with the measured moduli when CNT waviness is incorporated. Waviness yields a large (~10×) reduction in modulus, and therefore control of CNT collimation is seen as the primary limiting factor in CNT reinforcement of composites for stiffness. Anisotropic electron transport (conductivity and current-carrying capacity) follows expected trends, with enhanced conductivity and Joule heating observed at high current densities.

Marconnet et al. [57] reported the impact of CNT density on the thermal conductivity of PNCs consisting of mechanically-densified, aligned MWNT arrays infiltrated with an unmodified aerospace-grade thermostet epoxy. To better understand factors limiting thermal conductivity enhancement with the inclusion of CNTs, both the axial and transverse thermal conductivities are compared with predictions from effective medium theory. The conduction mechanisms within the composites are considered to explain the observed non-linear increase in thermal conductivity with volume fraction. Unlike unaligned, randomly oriented CNTs, aligned MWNT arrays can potentially provide more direct thermal conductivity pathways across the entire composite thickness, which can yield significant thermal conductivity improvements [58-60]. The present manuscript offers the first benchmark data of CNT-PNCs with controlled CNT density allowing correlation between CNT density and composite thermal conductivity. These data complement previous work characterizing the mechanical and electrical properties of these mechanically densified aligned CNT composites (up to 20 vol% CNTs), which showed promise for use in multifunctional applications with a factor of 3 enhancement in elastic modulus at 17 vol% CNTs and a significant reduction in electrical resistance with increasing CNT density [55,61]. Comparative infrared (IR) microscopy (Fig. (3)) characterizes
the axial and transverse thermal conductivities of aligned CNT-PNCs of varying volume fraction. The measured thermal conductivities are comparable with or greater than those reported previously for other aligned CNT-PNCs [58,59], but the data fall well below the best data for CNT films without an epoxy matrix [30,62-64]. The axial thermal conductivity of the composites ranges from 0.46 to 4.87 W/m.K as the CNT density increases from 1.0 vol% to 16.7 vol%. The axial thermal conductivity of the composites is comparable to the thermal conductivity of unfilled, aligned, densified MWNT films which ranges from 0.29 to 3.60 W/m.K as shown in Fig. (4). The unfilled arrays were fabricated in the same manner as the composites and measured with a similar comparative infrared microscopy technique as the composites with minor differences. The axial and transverse thermal conductivities of CNT PNCs and unfilled CNT films as a function of volume fraction are shown in Fig. (5).

There are several possible explanations for the lower thermal conductivities reported here for composites than expected for CNT-based materials and reported for thin, unfilled and uncompressed CNT arrays. First, the quality of the CNT film used for composites strongly impacts the composite performance. Measurements and simulations of individual CNTs and simulations highlight the impressive thermal conductivity of pristine CNTs leading to impressive predictions of the behavior of bulk materials fabricated from CNT films. Second, contact regions between CNTs, which occur even in the best aligned CNT films, can impact thermal performance of any CNT-PNC. Third, CNT-polymer boundary resistance impacts the effective thermal conductivity of CNT-PNCs. In unaligned CNT-PNCs, the individual CNTs do not bridge the entire thickness of the composite and the CNT-polymer boundary resistance is critical. In theory, for these well aligned CNT-PNCs, the CNT-polymer boundary resistance is only important for the conductivity transverse to the CNT axis. However, if some of the CNTs fail to extend to the surface of the polymer, the CNT-polymer thermal boundary resistance will impact the axial conduction as well as the transverse conduction. Furthermore, phonons within CNTs can be damped and scattered by the polymer matrix reducing the thermal conductivity of the CNTs themselves.

In the vertically aligned CNT-PNC, the CNTs are parallel to one another and perpendicular to surfaces of the CNT-PNC. However, the CNTs do not contact one another. The...
configuration limits a thickness of the CNT-PNC to be equal to a length of the CNTs, i.e., a several hundred microns, and limits a direction for thermal and/or electrical conduction. Furthermore, a range of thermal and/or electrical conduction is restricted to the length of the CNTs. Therefore, a CNT-PNC with good thermal/electrical conductivity in a direction parallel to a surface of the CNT-PNC and perpendicular to a growing direction of the CNTs and, a method for manufacturing such a composite are developed [72]. The manufacturing the horizontally-aligned CNT-PNC includes: (1) providing a number of CNTs distributed in a number of parallel strip-shaped areas of a substrate, (2) immersing the CNTs into a liquid matrix in order to introduce the liquid matrix into clearances among the CNTs, (3) taking the CNTs with the matrix bound thereto out of the liquid matrix, (4) pressing the CNTs down along a consistent direction, (5) solidifying the matrix bound to the CNTs; and peeling off the matrix bound with the CNTs from the substrate, thereby obtaining a CNT-PNC.

5. THERMAL BOUNDARY RESISTANCE OF CNT AND SURROUNDING MATRICES

Aligned arrays of CNT films potentially offer the unique combination of low thermal resistance and controllable elastic modulus due to the high thermal conductivity [24, 73] and flexibility of individual CNTs [74, 75]. However, integrating these materials into devices and structures creates additional interfaces (causing thermal boundary resistance) often with metals that inhibit heat conduction e.g., it was found that the effective thermal conductivities of CNT-PNCs are much lower than those calculated from the modified Maxwell theory. The effect of the thermal boundary (Kapitza) resistance becomes important when the surface area of the CNTs and their aspect ratios are small. Measurements with various CNT-substrate interface combinations such as pressed metal and dielectric interfaces [64, 76, 77] growth interfaces [30, 64, 78, 79] and physically deposited metals [30, 79], yield large CNT-substrate thermal interface resistances in the range of 0.3-50 mm².K/W. These large resistances are due to incomplete CNT-substrate contact amplifying the nanoscale conduction resistances of individual CNT-substrate interfaces [30, 79].

5.1. Thermal Boundary Resistance of CNT and Metals

Such individual nanoscale metal-tube interfaces often dominate the conduction resistances for film thicknesses below 50 μm. The nanoscale features of the contact further complicate the interface resistance by modifying the phonon transport physics for which there are no established models [80]. The structure of these interfaces at the nanoscale is highly dependent on the interaction, adhesion, and wet ability of the CNT and substrate materials. Previous data yield no clear relation between interface resistance and interface structure. Better understanding the contribution of the interface materials on the conduction physics and effective CNT contact area at the interface are necessary to improve the thermal performance of CNT films. Panzer et al. [81] directly measures the contribution of interface metallization on the SWNT engagement efficiency and thermal interface resistances via the composition dependence of the interface resistances and effective heat capacities of metal coated SWNT films using nanosecond thermoreflectance thermometry. The temperature dependence of these properties provides a means to study phonon transmission at the interface.

Duong et al. [82] present a detailed SEM analysis of the dependence of the metal-SWNT morphology on material and deposition conditions. The microstructure of the interface is illustrated by a representative TEM cross-section of an Al (160 nm)/Pd(20 nm)-SWNT interface from previous work [30] showing many voids and a lower SWNT density near the interface compared to deeper within the sample. This incomplete contact leads to partial engagement between the SWNTs and the metal, increasing thermal conduction resistances. The apparent effective heat capacity can deviate from the heat capacity based on the nominal density if there is poor SWNT-metal contact and if large intertube thermal resistances cause the partial intertube thermalization of the SWNTs during the time scales of the measurement [30]. A detailed model of intertube heat transfer within the array at the nanoscale developed in previous work [30] suggests that intertube thermal transfer within the array is weak during the time scales of the measurement due to the large intertube thermal resistances. These results also suggest that the effective volume fraction contributing to the heat capacity is a reasonable measure for the volume fraction that makes good thermal contact with the metal film [30].

Fig. (6a) plots $R_{\text{met-SWNT}}$, $R_{\text{sys}}$, and their sum total, $R_{\text{tot}}$, versus the measured effective heat capacity volume fraction for the five metallizations. The error bars capture the uncertainty due to variations in measurement data taken at four different locations on each sample, variations in film physi-
cal properties (e.g., film thickness), and the sensitivity to the uniqueness of the fit parameter combinations. While $R_{\text{met-SWNT}}$ falls in the range of 3.5-9.2 mm$^2$.K/W, $R_p$ is much larger, ranging between 33-46mm$^2$.K/W. The larger values of $R_p$ compared to $R_{\text{met-SWNT}}$ may be due to a variety of contributions including large SWNT-substrate interface resistances, large SWNT volumetric resistances, or an artifact of the effective heat capacity increasing over the longer time scales of the measurement (approx. 10 μs) for which $R_p$ is sensitive. The observations that the effective SWNT volume fractions are much less (0.5-0.9 vol%) than the nominal 3 vol%, and the trend in the data of decreasing $R_{\text{meta-SWNT}}$ with increasing volume fraction suggest that the large interface resistance in SWNT arrays are due to a low SWNT engagement efficiency with the metal. Sample-dependent nanoscale surface morphologies and differences between the metals' abilities to coat the SWNTs may explain their relative engagement efficiencies. Previous observations [83, 84] showed that the metal-SWNT coating behavior can be strongly dependent on metal-SWNT interaction energies [83] with Ti, Ni, Pd, and Al demonstrating an increasing tendency to cluster on the individual SWNTs. Metals that effectively coat the SWNTs can show reduced engagement due to the lower tendency of the metal to form interpulse clusters that can bridge multiple tubes and bundles. This effect can explain the low value of volume fraction for Ti compared to other metals since Ti has an excellent ability to coat SWNT and a low tendency to form clusters. Fig. (6b) shows the relation between $R_{\text{met-SWNT}}$ and $\varphi$, along with the results of molecular dynamics simulations for the resistance of an individual (10,10) SWNT-Si interface [84, 85]. Fig. (2b) also shows theoretical predictions of individual metal-SWNT interface resistances based on a modification of the acoustic mismatch model (AMM) in an approximation treating the SWNT as a graphene metal 2D-2D interfaces [30]. The trend of decreasing $R_{\text{met-SWNT}}$ with increasing $\varphi$ suggests that the same physical properties that govern the interface resistance (e.g., interface adhesion energies, Debye temperatures, etc.) may be related to the mechanisms that govern the engagement of the metal with the SWNTs. $R_{\text{met-SWNT}}$ is about an order of magnitude larger than the theoretical predictions. Nonideal metal-SWNT interface geometries may explain this discrepancy. The bundle structure of the CNTs can reduce the ratio of the metal-SWNT interface area to the SWNT volume and consequently increase the apparent individual metal-SWNT interface resistance.

The large thermal interface resistances in SWNT films are related to the degree of engagement of the SWNT films and the interface resistances of individual contacts at the nanoscale. The metallization dependence of the SWNT engagement suggest that engineering the CNT interfaces contacts offers a possible approach to reduce the total thermal resistance of CNT films, potentially below 1.0 mm$^2$.K/W.

5.2. Thermal Boundary Resistance of CNT and Nanofluids

Few investigations have focused on the thermal conductivity of fluids containing dispersed SWNTs. Traditional models of the effective thermal conductivity of suspensions are based on microscopic rather than nanoscale considerations. They have been derived assuming that the continuum approximation holds, and they do not account for ballistic heat transfer. The variables that determine the effective conductivity in traditional models are the particle shape and the volume fraction [86, 87]. However, the thermal conductivity of nanofluids also depends on possible epitaxial layering of the fluid molecules in the molecular layers adjacent to the suspended nanoparticles [88] and on the temperature. The existence of a thermal resistance [32, 89-91] to the transfer of heat between the nanoscale inclusions (SWNTs) and the surrounding matrix (suspending liquid) can also result in anomalous heat transfer behavior. As there are no accurate and reliable theoretical formulas currently available to predict the thermal conductivity of nanofluids satisfactorily, it is important to systematically explore the thermal properties of SWNT-in-fluid suspensions by a numerical method.

Fig. (6). (a) Measured area-averaged metal-SWNT, SWNT-substrate, and total thermal resistance plotted as a function of the measured effective SWNT heat capacity volume fraction, $\varphi$, calculated by dividing the measured effective SWNT volumetric heat capacity $C_v$ by the volumetric heat capacity of an individual SWNT, $C_v$. (b) Estimated resistance of individual metal-SWNT contact extracted by multiplying the area-average metal-SWNT interface resistance by $\varphi$.

Previous studies of the thermal conductivity of SWNT suspensions and the thermal resistance of the SWNT-matrix interface include the work of Maruyama et al., [32] who studied the thermal conductance between a SWNT and confined water by molecular dynamics (MD) simulations. A (10, 10) SWNT with a length of 20.1 nm and a diameter of ap-
approximately 1.0 nm was simulated in a 20.1 \times 10 \times 10 \text{ nm} fully periodic simulation cell. The SWNT contained 192 water molecules in its hollow space. Initially, water molecules and the SWNT were equilibrated at 300 °C, and then the SWNT was suddenly heated to 400 °C. By observing the heat transfer from the heated SWNT to the water, and using the lumped capacity method, Maruyama et al. [32] found that the thermal boundary resistance \( R_{bd} \) between the SWNT and the water was \( 2.0 \times 10^{-7} \text{ m}^2\text{K/W} \) (thermal boundary conductance, \( K_{bd} = 1/R_{bd} = 5 \text{ MW/m}^2\text{K} \)). Huxtable et al. [92] used picosecond transient adsorption to measure the interface thermal conductance of CNTs suspended in surfactant micelles in water. Their experimental results showed that the interface thermal conductance did not depend critically on the surfactant as long as the surfactant was not covalently bonded to the CNT. The thermal boundary resistance was measured to be \( 0.83 \times 10^{-7} \text{ m}^2\text{K/W} \) (\( K_{bd} = 12 \text{ MW/m}^2\text{K} \)).

5.3. Thermal Boundary Resistance of CNT and Composites

Like CNT-nanofluids, as there are also no accurate and reliable theoretical formulas currently available to predict the thermal boundary resistance of CNT-PNCs satisfactorily, it is important to systematically explore their thermal resistance through comparing computational models and experimental data. The simulation results have been validated by comparison with experimental data of randomly oriented SWNT-PNCs as shown in Fig. (7) [65]. Duong et al. [80, 93] predicted the effective thermal conductivities of the PNCs having CNTs randomly dispersed with and without CNT contact under a wide range of CNT volume fractions. However, only a single large value of the CNT-CNT TBR was used, and the possibility of better CNT-CNT interaction that can decrease the CNT-CNT TBR has not been considered.

The simulation results were compared with the experimental data of Bryning et al. [65] for the SWNT–epoxy composites having the SWNTs dispersed randomly Figs. (6a and 6b). For each value of thermal boundary resistance and weight fraction of SWNTs, the thermal conductivity is the average of three simulations with different initially SWNT distributions. The weight boundary error of the experimental data of Bryning et al. [65] was reported to be \( \pm 10\% \). The simulations are conducted with different values of the average probability for transmission of phonons across the interface into the SWNTs, \( f_{m-CN} \). We found that the value of \( f_{m-CN} \) giving the best fit between the simulation results and the experimental data for this experimental work is 0.02. Applying the acoustic theory, the thermal boundary resistance can then be calculated by equation (3) to be \( 4.01 \times 10^{-8} \text{ m}^2\text{K/W} \), very close to \( 4.27 \times 10^{-8} \text{ m}^2\text{K/W} \), the average thermal boundary resistance estimated by the effective medium theory [65, 94]. As can be seen in Fig. (6b), the simulation results fit very well with the experimental data using this specific value of \( f_{m-CN} \). The upper and the lower dashed curves indicate the maximum and minimum possible values of the thermal conductivity, respectively, as a function of the weight fraction of SWNTs dispersed in epoxy for the conditions reported in the experiments. The maximum thermal conductivity was obtained when all SWNTs were arranged with their axes parallel to the direction of the heat flux (the \( x \) direction) and the minimum thermal conductivity was obtained when all SWNTs were arranged with their axes perpendicular to the direction of the heat flux (the \( z \) direction). The simulation results are also compared to the experimental data of Du et al. [66] for the SWNT–PMMA composites as a
function of the weight fraction of SWNTs dispersed in PMMA. The thermal boundary resistance calculated by the computational model is $9.53 \times 10^{-9}$ m$^2$.K/W. The thermal conductivity error of this work was reported to be ±15%. The difference in thermal boundary resistance in the SWNT-epoxy and SWNT–PMMA composites is perhaps the result of CNT type, dispersion quality, CNT purity and length, or the composite preparation procedure [65, 66]. For example, raw SWNT material, not highly purified SWNTs, often contains significant carbonaceous and metallic impurities on the SWNT surface, which can adversely affect the composite performance and complicate the quantitative analysis of composite properties [65].

6. EFFECTS ON THERMAL CONDUCTIVITIES OF CARBON NANOTUBE NANOCOMPOSITES

Based on the predictions of Maxwell’s formula [95] or of the simple “mixture law”, one would expect CNT-PNCs with low conductivity polymers (i.e., conductivity less than 0.5 W/m.K) to demonstrate an effective conductivity tens of times higher than the conductivity of the polymer matrix, even for 1.0 wt% CNT. However, experimental evidence has shown that the addition of up to 2.0wt% of CNTs into industrial epoxy composites increases their thermal conductivity by up to 125% [96]. As the modified effective medium theory (EMT) [94, 97] is limited to simple, non-interacting geometries, the effect of some of these above factors on CNTs in a media have so far been investigated solely with MD [32, 98], or Monte-Carlo [73] simulations. The EMT is a macroscopic analysis that may reach its limits with the CNT-matrix interface [81, 82] and using Monte Carlo-walk algorithm, has been developed by introducing the TBR function of the weight fraction of SWNTs dispersed in PMMA. The thermal boundary resistance calculated by the computational model is $9.53 \times 10^{-9}$ m$^2$.K/W. The thermal conductivity error of this work was reported to be ±15%. The difference in thermal boundary resistance in the SWNT-epoxy and SWNT–PMMA composites is perhaps the result of CNT type, dispersion quality, CNT purity and length, or the composite preparation procedure [65, 66]. For example, raw SWNT material, not highly purified SWNTs, often contains significant carbonaceous and metallic impurities on the SWNT surface, which can adversely affect the composite performance and complicate the quantitative analysis of composite properties [65].

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A different and meshless approach, based on a random walk algorithm, has been developed by introducing the TBR at the CNT-matrix interface [81, 82] and using Monte Carlo-based models [99,100] to predict the thermal conductivities of MWNT-PNCs [66] and SWNT-PNCs [65]. This method simulates the quasi phonon particle at an intermediate physical scale that allows CNT morphology, anisotropy, and interfacial CNT-CNT or CNT-matrix effects [65, 66, 99] to be considered. Prior work in the area of CNT-matrix and CNT-CNT TBR is not extensive, neither theoretical nor experimental [100, 101]. Maruyama et al. [32] applied MD simulations to estimate the TBR between SWNTs in a bundle. Zhong et al. [98] reported systematic MD studies of the effect of contact morphology on the TBR. The reported values of the CNT-CNT TBRs range between $8 \times 10^{-8}$ and $25 \times 10^{-8}$ m$^2$.K/W. This value range is slightly higher than reported CNT-polymer matrix TBRs (i.e., $1.0 \times 10^{-8}$ m$^2$.K/W for SWNT-PMMA [66] and $4.3 \times 10^{-8}$ m$^2$.K/W for SWNT-epoxy [65]), and it is also higher than the range of SWNT-matrix TBRs ($0.1-4.4 \times 10^{-8}$ m$^2$.K/W) used for simulations in the work of Duong et al. [73]. Later Duong et al. [102] used the simulation methodology to explore CNT-CNT interactions more appropriately, particularly the effects of a wide range of the CNT-CNT TBRs, CNT isolation degree, and the distribution of aligned CNTs in aligned-CNT PNCs. Non-isotropic (along the CNTs vs. perpendicular to the CNT alignment axis) heat conduction is the focus herein, noting that thermal anisotropic ratios are strongly affected by CNT morphology.

Different interfaces (and TBRs) such as CNT-CNT, CNT-heat source and CNT- matrix TBRs are shown in Fig. (8). CNT line contact is assumed and the CNT-heat source TBR is assumed to be equal to the CNT-matrix TBR for simplicity. As the CNT-CNT TBR can be decreased by functionalizing the CNTs to achieve better contact between the CNTs, a wider CNT-CNT TBR range, which includes a CNT-CNT TBR lower than that of CNT-matrix TBR were employed. The functionalizing of the CNTs can be beneficial when considering improvements to the effective thermal conductivities of CNT- PNCs by increasing the CNT volume fraction or by keeping the same CNT volume fraction, but increasing better CNT interaction with other components. Several authors [103,104] have predicted that the wavy shape and spatial agglomeration of CNTs have a large detrimental influence on the effective elastic moduli of CNT-reinforced PNCs, and recent work addresses waviness effects on electrical conductivity [105]. Such effects could potentially modify the thermal properties of CNT-PNCs, but the case of curved CNT shapes that results in intermittent CNT contact is not examined. Through the CNT isolation degree study, the model allows consideration of spatial CNT agglomeration, a significant parameter that helps to evaluate and select appropriate matrix materials and fabrication procedures in PNC design. The CNT isolation degree is defined as the ratio of the number of isolated CNTs to the total number of CNTs in a computational cell (see illustrations in Fig. (9)). Previous experimental work [106] has showed that uniform CNT distribution plays an important role in improving the multifunctional properties of the CNT-PNCs. The major challenge in fabricating the CNT-PNCs is to avoid agglomeration and (if possible) control the PNC morphology via aligned CNTs Figs. (8, 9). As there is no experimental data available showing systematically the CNT distribution effect on the effective thermal conductivities of the CNT-PNCs, this topic can be investigated through computations. Here the effects of the CNT-CNT and CNT-matrix TBR Fig. (8), CNT isolation degree, and the CNT distribution uniformity see Fig. (9a-9d) on both SWNT- and MWNT-PNCs with various CNT volume fractions (1-20 vol%) and orientations (heat flux is parallel and perpendicular to the CNT axis) are considered. The anisotropy of heat conduction related to the CNT direction and the CNT diameter (SWNT vs. MWNT) influences are also discussed. Duong et al. [73] reported that with CNT-CNT contact effects, high CNT-CNT TBR can have an adverse affect on effective thermal conductivities of the CNT-PNCs assuming a single CNT-CNT TBR value and using a random CNT distribution. CNT distribution effects were studied previously only for CNT-PNCs having no CNT-CNT contact. Comparison of the simulated results with experiments would enable extraction of the TBR values and the CNT isolation degree values that would help experimentalists in selecting an appropriate fabrication process. The results can also be used with a representative volume element (RVE) Fig. (10) approach to design optimized heat conduction materials using CNTs [56], including complex
3D hybrid fiber-matrix composites reinforced with aligned CNTs currently under development [107-109]. Heat distribution of the MWNT-epoxy PNCs at 20 vol% of the MWNTs parallel to the heat flux is shown in Fig. (11).

As there is no experimental data and ideal theoretical analysis to study comprehensively all effects on the thermal conductivities of the CNT-PNCs, the off-lattice Monte Carlo algorithm is developed [102]. The simulation results of the effects on the effective thermal conductivities of the CNT-PNCs are discussed next. Table 1 shows material properties and parameters used in the simulations.

6.1. Effects of CNT Morphology, and of Thermal Boundary Resistance on the Effective Thermal Conductivity of the CNT–Polymer Composites

Heat flow was studied in a $300 \times 100 \times 100$ nm$^3$ computational epoxy cell containing CNTs with $300$ nm in length; $2.4$ nm diameter SWNTs or $8.0$ nm diameter MWNTs [97]. The CNTs were parallel or perpendicular to the direction of heat flux and extended from one end of the computational domain to the other; in all cases the locations of the CNTs were random. The number of CNTs in the computational cell varied from 22 to 448 (SWNTs) and from 2 to 40 (MWNTs), depending on the volume fraction of CNTs in the epoxy (1–20 vol%). The heat distribution of a MWNT-epoxy composite is shown in Fig. (11) with MWNTs parallel to the heat flux at 20% volume fraction at different positions in the computational cell. The heat distribution in steady-state is shown for three orthogonal slices in the Z direction; CNT-CNT contact can be observed in the top slice and CNTs without contact can be observed in the bottom slice. The simulations were conducted with different thermal resistances ($f_{CN}=1.00, 0.50, 0.20, 0.02$, i.e., $R_{bd}=0.09, 0.17, 0.44, 4.36(\times 10^{-8} \text{ m}^2 \text{K/W})$, respectively) and with different CNT volume fraction (1, 8 and 20 vol%). The CNT epoxy thermal boundary resistance values used in this work are less than that of the CNT-CNT boundary resistance of $24.8 \times 10^{-8}$ m$^2$K/W [32] and fall within the wider range of boundary resistance values considered by Clancy et al. [110].
Table 1. Material Properties and Parameters Used in the Simulations.

<table>
<thead>
<tr>
<th>CNT - Composites</th>
<th>SWNT</th>
<th>MWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Geometry</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Computational cell size (nm³)</td>
<td>300 x 100 x 100</td>
<td>300 x 100 x 100</td>
</tr>
<tr>
<td>CNT diameter (nm)</td>
<td>2.4</td>
<td>8.0</td>
</tr>
<tr>
<td>CNT length (nm)</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>CNT volume fraction (%)</td>
<td>1, 8, 20</td>
<td>1, 8, 20</td>
</tr>
<tr>
<td>Number of CNTs in a cell</td>
<td>22, 179, 448</td>
<td>2, 16, 40</td>
</tr>
<tr>
<td><strong>Thermal Property</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal boundary resistance at the CNT-matrix Interface, $R_{bd-m-CN}$ ($\times 10^{-8}$ m²K/W)</td>
<td>174, 4.36, 0.44, 0.17, 0.09</td>
<td>174, 4.36, 0.44, 0.17, 0.09</td>
</tr>
<tr>
<td>Thermal boundary resistance at the CNT-CNT Interface, $R_{bd-CN-CN}$ ($\times 10^{-8}$ m²K/W)</td>
<td>24.8, 8.67, 1.73</td>
<td>24.8, 8.67, 1.73</td>
</tr>
<tr>
<td>Probability for phonon transmission from matrix to CNT, $f_{m-CN}$</td>
<td>0.0005, 0.02, 0.20, 0.50, 1.00</td>
<td>0.0005, 0.02, 0.20, 0.50, 1.00</td>
</tr>
<tr>
<td>Probability for phonon transmission from CNT to CNT, $f_{CN-CN}$</td>
<td>0.0024, 0.2000, 1.0000</td>
<td>0.0024, 0.2000, 1.0000</td>
</tr>
<tr>
<td>Thermal conductivity of matrix, $K_m$ (W/(m.K))</td>
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<td>0.2</td>
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<tr>
<td>Thermal equilibrium factor, $C_f$</td>
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<tr>
<td>Without CNT-CNT contacts</td>
<td>0.248</td>
<td>0.319</td>
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<tr>
<td>With CNT-CNT contacts</td>
<td>0.23</td>
<td>0.295</td>
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<tr>
<td><strong>Simulation Conditions</strong></td>
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<tr>
<td>Number of walkers</td>
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<td>9000</td>
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<tr>
<td>Time increment, $\Delta$ (ps)</td>
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<td>0.25</td>
</tr>
<tr>
<td>Heat flux direction</td>
<td>Parallel and perpendicular to the CNT axis</td>
<td></td>
</tr>
<tr>
<td>CNT-CNT contacts</td>
<td>Set by placing the aligned CNTs randomly in the volume and if they overlap, the CNTs are placed in contact</td>
<td></td>
</tr>
</tbody>
</table>

Two MWNTs are forced to be in contact in this case rather than a random assignment.

Thermal boundary resistance $R_{bd}$ is calculated from [102]; epoxy specific heat is 0.97 J/(g.K) [112]; epoxy density is 1.97 g/cm³ [112]; sound velocity in epoxy is 2400 m/s [113]; SWNT density is 1.30 g/cm³ [114]; sound velocity in SWNTs is 8000 m/s [115]; and SWNT specific heat is 0.625 J/(g .K) [116]. The same $f_{CN-CN}$ is assumed for the MWNTs due to unavailable values in the literature to calculate $f_{CN-CN}$ [102].

The matrix used for the simulations was epoxy with thermal conductivity $K_{epoxy}= 0.2$ W/m.K. With and without the inter-CNT contact effects, the thermal conductivities of both the SWNT- and MWNT-epoxy composites having the CNT axis parallel to heat flux are, as expected, much higher than those having CNTs perpendicular to the heat flux, see Fig. (12). Similarly, an increased volume fraction of CNTs enhances all the effects of transport whether in the parallel or perpendicular direction with the small thermal boundary resistance. The CNTs span the PNC volume and therefore the PNC conductivity parallel to the CNT axis is dominated by the CNT conductivity, and is only limited by the thermal boundary resistance. Importantly, the $R_{bd}$ of the CNT-matrix interface is the same as that for the ends of the CNTs located at the end of the computational cell. This represents the simplest case and the CNT-domain interface resistance should be further studied and quantified for different thermal interface materials. This explains why the conductivity in Fig. (12a) (along the CNT axis) is enhanced at low $R_{bd}$ by the CNTs, but has little effect at high $R_{bd}$ where heat transferred into the CNTs from the matrix becomes vanishingly small and the CNTs act like an excluded volume from a thermal transport perspective. It follows that for the CNT-epoxy composite having CNTs perpendicular to the heat flux, with the CNT volume fraction fixed, the thermal conductivities increase with decreasing thermal boundary resistance. As the boundary resistance decreases, the walkers (i.e., heat) also have higher probability of entering the CNTs and traveling (more quickly) along the radial axis of the CNTs. As the thermal boundary resistance increases see Fig. (12b), it can dominate the perpendicular transport and a critical value is reached ($\sim 0.5 \times 10^{-8}$ m²K/W) where the CNTs do not en-
hance thermal conductivity in the composite; and at higher $R_{bd}$, the CNTs reduce conductivity significantly. A decrease in thermal conductivity below that of the epoxy in the transverse direction may be advantageous from a thermal tailoring perspective.

Note that the thermal conductivity of the PNCs is lower than that calculated from continuum theories that ignore thermal boundary resistances, e.g., the Maxwell theory modified by Rayleigh [95]. According to the simulation results, the maximum thermal conductivity of the MWNT-epoxy composites with 20 vol% is 7.62 W/m.K, while the Maxwell theory gives a thermal conductivity of ~600 W/m.K (assuming the thermal conductivity of the MWNTs of 3000 W/m.K). The trend in Fig. (12b) of decreased perpendicular conductivity with increased CNT volume fraction at high $R_{bd}$ is contrary to predictions by such continuum theories. Thus, depending on the values of the boundary resistance, the trend can agree or disagree with the classical theories, indicating the importance of the thermal boundary resistances and underscoring the need for better experimental quantification of these parameters.

6.2. Effects of Inter-CNT Contact

The effects of the inter-CNT contact on the effective thermal conductivity of MWNT-epoxy in Fig. (12a and 12b) and SWNT-epoxy in Fig. (15a and b) are discussed here. When CNTs are parallel to the heat flux, the effective thermal conductivities predicted from the simulations that account for the inter-CNT contact are smaller than those from the model without the inter-CNT contact effect, as shown in Fig. (12a). The reasons for this finding are: (1) walkers in the matrix do not see as much CNT surface area to go into when CNTs are touching, and therefore the walkers stay in the matrix longer; and (2) relatively more walkers travel along the CNT radius and cross into adjacent CNTs rather than along the CNT axis, reducing the dispersion of heat in the direction of the heat flux. This is an interesting result that needs to be validated with experimental measurements. Very recent results by Peters et al. [111] indicate that the thermal conductivity of SWNT-polystyrene composites does not increase with the volume fraction of the CNTs as much as predicted. The reason might very well be the increase of the SWNT-SWNT contact points in the composite, or the value of the CNT-polymer or CNT-CNT thermal boundary resistance. As the CNT-CNT thermal boundary resistance is larger than the CNT-polymer resistance, most of the heat is transferred through CNT-polymer-CNT. Once the CNT-CNT contact is improved, the CNT-CNT thermal boundary resistance is much smaller and the heat transfer through CNT-CNT becomes more important. When CNT-CNT contact is considered in our model, the effective thermal conduc-
Thermal Transport Limitation of Carbon Nanotube Heterogeneous Media

Recent Patents on Engineering 2011, Vol. 5, No. 3 223

...tivity decreases at a higher rate when the volume fraction of the CNTs increases, or when the thermal boundary resistance decreases, as can be seen, for example, at the point for 20% volume fraction in Fig. (12a) (a X2.1 decrease when CNT-CNT contact is considered).

For the CNTs perpendicular to the heat flux as shown in Fig. (12b), with the same thermal boundary resistance and volume fraction of the CNTs, the effective thermal conductivities of the CNT-PNCs when the inter-CNT transfer is taken into account is slightly higher than those without the inter-CNT contact. This is because thermal walkers can now enter through the interface region of the CNT contact and transfer faster along the CNT radius, cross into the next CNTs in contact, and continue along the CNT radius (perpendicular) direction. The inter-CNT contact effect causes significant enhancement of the effective thermal conductivity when the volume fraction of the CNTs increases and the polymer-CNT thermal boundary resistance is low. When the thermal boundary resistance is high, the inter-CNT contact effect causes a significant decrease of the effective thermal conductivity with higher CNT volume fraction. At 20 vol% of the MWNTs and the minimum thermal boundary resistance ($f_{\text{m, CN}} = 1.0$), the effective thermal conductivity of the MWNT-epoxy composites with inter-CNT contact is X1.1 times higher than that without the CNT contact effect for heat flux perpendicular to the CNTs. It is hypothesized that the effect of CNT-CNT contact is similar to effectively increasing the radius of the CNT: the trends considering CNT-CNT contact in both the parallel and perpendicular directions are directly comparable to the trends observed between SWNT versus MWNT-PNCs as discussed subsequently.

6.3. Effects of Anisotropic Heat Transfer

The anisotropy ratio of the effective thermal conductivities ($K_{\text{eff, parallel}}/K_{\text{eff, perpendicular}}$) of MWNT- and SWNT-epoxy composites, with CNTs parallel and perpendicular to the heat flux without and with the inter-CNT contact, are shown in Fig. (13a and 13b), respectively, as a function of CNT volume fraction and thermal boundary resistance. This anisotropy ratio represents the ratio of the largest to the smallest eigen value of the effective thermal conductivity tensor, sometimes called the condition number of the tensor. With the same CNT volume fraction as shown in Fig. (13a), the ($K_{\text{eff, parallel}}/K_{\text{eff, perpendicular}}$) ratios of the MWNT-epoxy composites with and without the inter-CNT contact increase at lower values of CNT-epoxy thermal boundary resistance as expected. This trend is significant with higher volume fraction. In all cases the anisotropy ratio is larger than unity, but approaches unity at high values of $R_{bd}$, where the CNTs act more and more like non-contributing inclusions. CNT-CNT contact effects are noted to follow the same trend in Fig. (13) as that of increasing CNT diameter. Consider the trend at the lowest value of $R_{bd}$ at 20 vol% fraction where the SWNTs have the highest anisotropy ratio Fig. (13b), which is reduced substantially if CNT–CNT contact is considered. A similar decrease is noted for MWNTs. The anisotropy ratio also decreases as CNT–CNT contact is allowed for the MWNT in Fig. (13a). The effect of CNT–CNT contact is thus noted to be similar to increasing the effective radius of the CNT, diminishing the surface-to-volume ratio of the conductive CNT phase.

6.4. Comparison of Effective Thermal Conductivities of SWNT– and MWNT–Composites with and Without Inter-Carbon Nanotube Contact

The ratio of the effective thermal conductivities without the inter-CNT contact effects for SWNT- and MWNT-epoxy composites, normalized by the thermal conductivity of the pure epoxy, is shown in Fig. (14). Both cases of CNTs oriented parallel and perpendicular to the heat flux are also shown in Fig. (14). The same type of data, but taking into account the inter-CNT contact, is presented in Fig. (15).

![Fig. (13). Thermal conductivity ratio ($K_{\text{eff, parallel}}/K_{\text{eff, perpendicular}}$) of (a) MWNT- and (b) SWNT-epoxy composites without (solid dots) and with (open dots) the inter-CNT contact effects as a function of thermal boundary resistance with different volume fraction of CNTs.](image-url)
As the CNT volume fraction increases, the thermal conductivity enhancement in the direction parallel to the CNTs is more significant for SWNT-epoxy composites than MWNT-epoxy composites, as seen in Fig. (15a and 15b). The maximum thermal conductivity of the SWNT-polymer composite is ~3.5 times and ~2.0 times higher than that of the MWNT-epoxy composite at 20 vol% CNT without and with the inter-CNT contact, respectively. This can be explained because at the same CNT volume fraction, the surface to volume ratio of the SWNTs is higher than that of the MWNTs, and, therefore, the area available for heat transfer between the matrix and the CNTs is higher for SWNTs. Considered in Lagrangian terms, the heat walkers are allowed more chances to come into the CNTs with the same matrix probability and therefore they can move more rapidly along the direction of the CNT axis. It is apparent that the CNT size plays an important role in the thermal conductivity enhancement. The same reasoning applies for enhanced thermal conductivity with increasing CNT volume fraction. For the CNTs perpendicular to the heat flux as seen in Fig. (14b and 15b), with the same volume fraction and thermal boundary resistance, the thermal conductivity of the MWNT-epoxy composites is higher than that of the SWNT-epoxy ones. This happens because the larger MWNTs allow more heat to be transferred along their radius. For a relatively small thermal boundary resistance, MWNT-epoxy composites have enhanced conductivity in the perpendicular direction relative to SWNT-epoxy composites. The above observations are consistent with the results both with and without the inter-CNT contact.

The ratio of effective thermal conductivities, with and without the inter-CNT contact of the MWNT and SWNT composites, as a function of the relative value of the thermal boundary conductances expressed as the ratio \( \frac{K_{bd\text{-CNT}}}{K_{bd\text{-epoxy}}} \) at different CNT volume fractions is shown in Fig. (16). The CNTs are parallel to the direction of the heat flux, which is the case that yields the maximum effective thermal conductivity. All values of the effective thermal conductivity ratio are less than one, indicating that the resistance to heat transfer at the CNT-CNT contact is reducing \( K_{\text{eff}} \) for both SWNT and MWNT composites. Furthermore, the higher the difference between the resistance at the CNT-CNT contact and the resistance at the CNT-matrix interface, the larger the reduction of \( K_{\text{eff}} \). A high \( K_{\text{bd\text{-CNT}}} \) effectively prohibits inter-CNT heat exchange, or equivalently, heat transfer is blocked around part of the equivalent radius of the non-contacting CNTs, thereby reducing transport in and out of the CNT relative to the case without CNT contact.

### 6.5. Effects of CNT Isolation Degree and Uniform Dispersion on the Thermal Conductivity of the PNCs

Here, we consider the effect of CNT-CNT contact degree by controlling (forcing) different degrees of CNT contact considering randomly-dispersed CNTs as summarized in Table 2. Thermal conduction anisotropy \( \frac{K_{\text{eff\text{-parallel}}}}{K_{\text{eff\text{-perpendicular}}}} \) of MWNT-epoxy composites with and without CNT-CNT contact (largest CNT-CNT TBR, \( R_{\text{bd\text{-CNT-CN-CN}}}=24.8 \times 10^{-8} \text{ m}^2\text{K/W} \)) are compared in Fig. (17). CNT contact...
has a significant effect on the anisotropy ratio at high CNT loading, and low CNT-matrix TBR for this case Fig. (17) when the CNT-CNT TBR is very large (largest in the range considered in this work). In Table 2, with lower CNT-matrix TBR and higher CNT volume fraction, the reduction of $K_{\text{eff-parallel}}/K_{\text{eff-perpendicular}}$ ratios of the CNT-PNCs without and with the CNT-CNT contact is greater. At 20 vol% of MWNTs and the lowest CNT-matrix TBR (0.09 x 10^{-8} m^2.K/W), the anisotropic heat conduction of the CNT-PNCs with the CNT-CNT contact decreases 2.3X compared with that without the CNT-contact.

The simulation results of this part could be also very helpful interpreting experimental work. The effective thermal conductivities of the SWNT- and MWNT-PNCs having 20 vol% and the CNT-CNT TBR, $R_{bd-CN-CN} = 24.8 x 10^{-8} m^2.K/W$ were studied over a wide range of the CNT isolation degree, from no isolated CNT (0.0%) to completely isolated CNTs (100.0%). Different isolation degree values (Table 3) are used to calculate the thermal conductivities of directional PNCs having the CNTs parallel and perpendicular to the heat flux.

When the CNTs were randomly placed, 40.0% were in isolation for MWNT and 32.5% for SWNT. For the case of heat flux parallel to the CNT axis Fig (18a) and Table 3, the effective thermal conductivities of SWNT- and MWNT-PNCs decrease when the CNT isolation degree decreases. When the CNT-CNT TBR is larger than the CNT-matrix TBR, the more isolated CNTs provide larger the effective thermal conductivity. The effective thermal conductivities of the CNT-PNCs are highest with completely isolated CNTs (100.0%) and lowest with 0.0% isolated CNTs. With the
Table 2. Summary of CNT-CNT TBR Effects on Simulated Normalized Thermal Conductivities ($K_{eff}/K_m$) of SWNT- and MWNT-PNCs for 40% Isolated Randomly Distributed CNTs, Randomly Distributed CNTs (No CNT-CNT Contact), and CNTs with 1--% Isolated Uniformly Distributed (Square Packing)$^a$.

<table>
<thead>
<tr>
<th>Vol % (wt of CNTs)</th>
<th>CNT – CNT Contact Random CNT Distribution</th>
<th>No CNT – CNT Contact, Random CNT Distribution</th>
<th>No CNT – CNT Contact, Uniform CNT Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\text{CN-CN}}$ [x10$^{-8}$ m$^2$ K/W] ($f_{\text{CN-CN}}$)</td>
<td>$R_{\text{CN-CN}}$ [x10$^{-8}$ m$^2$ K/W] ($f_{\text{CN-CN}}$)</td>
<td>$R_{\text{CN-CN}}$ [x10$^{-8}$ m$^2$ K/W] ($f_{\text{CN-CN}}$)</td>
</tr>
<tr>
<td></td>
<td>24.8 (0.0024)</td>
<td>8.67 (0.2000)</td>
<td>1.73 (1.0000)</td>
</tr>
</tbody>
</table>

Table 3. Effects of CNT Isolation Degree on Thermal Conductivities of the 20 vol % SWNT- and MWNT-PNCs with Highest CNT-CNT TBR and Randomly Distributed CNTs$^a$.

<table>
<thead>
<tr>
<th>CNT Isolation Degree (%)</th>
<th>$K_{\text{eff}}/K_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_{\text{CN-CN}}$ [x10$^{-8}$ m$^2$ K/W] ($f_{\text{CN-CN}}$)</td>
</tr>
<tr>
<td>SWNTs Heat Flux</td>
<td>4.36 (0.02)</td>
</tr>
<tr>
<td>MWNTs Heat Flux</td>
<td>3.48 (0.02)</td>
</tr>
</tbody>
</table>
same CNT isolation degree and volume fraction, the effective thermal conductivities of the SWNT-PNCs are larger than those of the MWNT-PNCs due to the larger SWNT-matrix interfacial area. When CNT-matrix TBR increases, fewer walkers can cross into the CNTs to take advantage of the CNT high thermal conductivity. This makes the effective thermal conductivities of both SWNT- and MWNT-PNCs decrease with the same CNT isolation degree. In Fig. (18a) (parallel cases), with the same CNT volume fraction and the CNT isolation degree, the effect on the effective thermal conductivity of the SWNT-PNCs is larger than those for MWNT-PNCs. This can be explained because the SWNT-matrix interface reduces significantly more than the MWNT-PNCs as the contact between CNTs increases.

**Fig. (17).** Comparison of ratio ($K_{\text{eff-parallel}}/K_{\text{eff-perpendicular}}$) of MWNT-epoxy composites with (open dots, highest $R_{bd-CN-CN}$ $24.8 \times 10^{-8}$ m$^2$K/W) and without (solid dots) the CNT-CNT contact as a function of CNT-matrix TBR with different volume fractions of CNTs.

**Fig. (18).** Comparison of effective thermal conductivity of MWNT-epoxy (solid dots and solid lines) and SWNT-epoxy (open dots and dashed lines) composites having 20 vol% and highest CNT-CNT TBR, $R_{bd-CN-CN}$ $24.8 \times 10^{-8}$ m$^2$K/W as a function of CNT-matrix TBR with different CNT isolation degree and the CNTs oriented (a) parallel and (b) perpendicular to the heat flux.
For the case of heat flux perpendicular to the CNT axis Fig. (18b) and Table 3, with same CNT isolation degree, effective thermal conductivities of MWNT-PNCs are larger than those of SWNT-PNCs. Again this is because walkers can travel faster along the MWNT diameter (8.0nm), which is larger than the SWNT diameter (2.4nm). The effective thermal conductivities of the SWNT- and MWNT-PNCs decrease when CNT-matrix TBRs increase. When decreasing the CNT isolation degree (100.0% down to 32.5% for SWNT-PNCs and 100.0% down to 40.0% for MWNT-PNCs), the effective thermal conductivities increase slightly (Table 3). Walkers can travel faster along the CNT diameter, cross the CNT-CNT interface, and move faster along next contacting CNT diameter. Especially, with higher CNT volume fraction 20 vol%, Fig. (18b), larger MWNT diameter and the smallest CNT isolation degree (0.0%), walkers can move faster along the CNT radius and come out the computational cell quickly.

Here the effects of a uniform CNT distribution on the effective thermal conductivities of SWNT- and MWNT-PNCs without CNT-CNT contact Table 2 and Figs. (19 and 20) are also studied. For uniformly distributed CNTs in the computational cell, the distance between two nearby CNTs in the same row or column was equal. As random distribution of the CNTs cannot preclude local CNT agglomeration in the PNCs, distributing the CNTs uniformly avoids this issue in the modeling. For the CNTs parallel to the heat flux Fig. (19a), distribution (random vs. uniform) has very little effect on effective thermal conductivities when CNT-CNT contact is not considered. These local CNT agglomerations prevent phonons from coming into the CNTs from the matrix. The effect of the CNT agglomeration increases with the CNT volume fraction. In Fig. (20a), with the same CNT volume fraction and the same CNT-matrix TBR, the thermal conductivities of the SWNT-PNCs are significantly larger than those of the MWNT-PNCs. In Table 2, this is shown for both CNT random and uniform distributions effects due to the larger interfacial area. At 20 vol% and the CNT-matrix TBR, \( R_{\text{eff-m-CN}} = 0.09 \times 10^{-8} \text{m}^2\text{K/W} \), the uniform distribution effect can enhance X1.6 and X1.1 the effective parallel thermal conductivities of the SWNT- and MWNT-PNCs, respectively, relative to those with random distribution.

For the CNTs perpendicular to the heat flux Table 2 and Fig. (19b), CNT distribution effects also do not play an important role on the thermal conductivities of MWNT-PNCs. This is true for SWNT-PNCs with low CNT volume fractions (1-8 vol%). For the SWNT-PNCs with CNT uniform distribution at the 20 vol% (Table 2), phonons have an increased chance of contacting a CNT, and there is a small effect. So with the higher CNT-matrix TBR, the CNTs block the phonons/walkers and make them travel slower in the matrix. Localized agglomeration can now have the opposite effect, i.e., when the SWNTs are agglomerated, the excluded area for heat transfer is smaller than when the SWNTs were well distributed in the PNCs. This makes the effective thermal conductivities of the CNT-PNCs with the uniform CNT distribution smaller. In Table 2 and Fig. (20b), the ratio \( K_{\text{eff}}/K_m \) for MWNT- and SWNT- PNCs with the CNT uniform distribution at 20 vol% decreases below one when the CNT-matrix TBRs are larger than a critical CNT-matrix TBR \( (0.5 \times 10^{-8} \text{m}^2\text{K/W} \text{ for the MWNT-PNCs and 0.2} \times 10^{-8} \text{m}^2\text{K/W for the SWNT-PNCs}) \). With the same CNT-matrix TBR and the same CNT volume fraction, the thermal conductivities of the MWNT-PNCs are always larger than those of the SWNT-PNCs with the uniform CNT distribution due to larger MWNT diameter and less interfacial area.

![Fig. (19). Comparison of effective thermal conductivity of MWNT-epoxy having no CNT-CNT contact with uniform CNT distribution (solid dots) and with random CNT distribution (open dots) effects with as a function of CNT-matrix thermal boundary resistance with different volume fractions of CNTs and the CNTs oriented (a) parallel and (b) perpendicular to the heat flux.](image-url)
The effective thermal conductivities of CNTs dispersed in a continuous matrix were computed over a wide range of thermal resistance, CNT volume fraction, and CNT aspect ratio. A random walk algorithm was used to simulate heat transfer through such a material under different boundary conditions and after taking into account the effects of thermal resistance. The algorithm was efficient in that it removed the need to perform random walks within the CNTs. The simulation consumes much less time than MD and finite element methods. This model can be applied to any polymer and any solid materials with a very wide range of volume fraction of CNTs in the matrix. It was found that the effective thermal conductivities of CNT-PNCs are much lower than those calculated from the modified Maxwell theory. The effect of the thermal boundary (Kapitza) resistance becomes important when the surface area of the CNTs and their aspect ratios are small.

7. CURRENT & FUTURE DEVELOPMENTS

Oriented CNT arrays are used to increase the effective contact area (particularly for a rough surface) while providing an extremely large thermal conductivity along a CNT axis and across the interface. Embodiments of the current patents can be cost effective and advantageous for at least the following reasons. The benefits of the invention are a new class of nanostructured TIMs for high value-added applications. These benefits should accrue in the microelectronics and aerospace sectors. The main advantages of the patents are (a) high native thermal diffusivity, (b) ability to be infiltrated with conductive pastes or polymers or resins, (c) conformable top and bottom surfaces for good thermal contact to surfaces with micro-protrusions (areas which normally yield gaps and poor thermal interfaces), (d) very small thermal expansion coefficient, for multiple thermal cycles without losing contact to the surfaces it is interfacing. Embodiments of the invention have the additional advantage of being nanostructured and are, therefore, capable of being fabricated into specific shapes and heights directly during manufacturing. In addition, the thermal interface to the mating surface can be provided by many conformable contact points instead of a machined surface, providing additional advantages for better thermal Interfaces. Embodiments of the invention improve quality and/or reduce costs compared to previous approaches.

The effective thermal conductivities of CNTs dispersed in a continuous matrix were computed over a wide range of thermal resistance, CNT volume fraction, and CNT aspect ratio. A random walk algorithm was used to simulate heat transfer through such a material under different boundary conditions and after taking into account the effects of thermal resistance. The algorithm was efficient in that it removed the need to perform random walks within the CNTs. The simulation consumes much less time than MD and finite element methods. This model can be applied to any polymer and any solid materials with a very wide range of volume fraction of CNTs in the matrix. For thermal conductivity prediction of CNT-PNCs, A Monte Carlo model was applied to study the effects of aligned CNT array morphology on the effective thermal conductivities of the CNT-PNCs for a wide range of CNT-CNT and CNT-matrix TBRs, CNT distributions (random or uniform), CNT isolation degree, and CNT volume fractions. Since currently available calculations suggest that the CNT-CNT TBR is higher than the CNT-matrix TBR, it appears that there should be an effort to improve the quality of the CNT-CNT interface by reducing the thermal resistance at this interface, rather than focusing exclusively on increasing the volume fraction of the CNTs. The current model does not take into account the CNT wavy shapes that give intermittent CNT-CNT contact. In addition, to validate the simulation results with experiments, future work should include exploration of a wider range of CNT-matrix interface resistance and quantification for different TIMs like CNT-
metal composites. The effects on TBRs of other molecules existing on the surface of synthesized CNTs and the possibility that the CNTs cause a local polymer interphase different than the neat polymer should also be considered. Uneven CNTs topography due to the variation of CNT heights causing uneven contact with heat source and contact in length direction for shorter CNTs than film thickness seems to be the critical problems for at least SWNTs.

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CONFLICT OF INTEREST

Authors do not have any conflict of interest to declare.

REFERENCES


