High thermal conductivities of carbon nanotube films and micro-fibres and their dependence on morphology

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ABSTRACT

Thermal conductivity of carbon nanotube (CNT) films and micro-fibres synthesised by floating catalyst chemical vapour deposition was measured by the parallel thermal conductance method. CNT films showed in-plane thermal conductivities of 110 W m^{-1} K^{-1}. Online condensation into a micro-fibre morphology — a two-dimensional reduction in the transverse plane, including some axial stretching during solvent evaporation — resulted in room-temperature thermal conductivity values as high as 770 ± 10 W m^{-1} K^{-1}, which is the highest thermal conductivity reported for CNT bulk materials to date. In specific terms, this matches the maximum thermal conductivity of heat-treated carbon fibre, but with a higher onset temperature for Umklapp scattering processes (300 K rather than 150 K). We selected four sample types to investigate effects of alignment, purity, and single- or multi-wall character on their thermal conductivity. For both the electrical and thermal conductivity of as-spun material, i.e. without any post-synthesis treatment, we show that the density and quality of CNT bundle alignment are still the predominant factors affecting these properties, outweighing the influence of single- or multi-walled character of the nanotubes. This raises the promise that, with optimal alignment and junction points, even higher values of thermal conductivity are achievable for macroscopic CNT fibres.

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1. Introduction

Modern technology continues to test the limits of materials science, demanding increasingly lightweight, high performance, energy-efficient and cost-effective materials. For decades, nano-scale materials have been touted as one way to meet these demands, and carbon nanotubes (CNTs) are amongst the most promising and well-studied of these at the level of individual tubes. However, in practice, bulk CNT materials are required, and their physical and microstructural properties must be understood and optimised as, overall, they are the factors inhibiting the utilization of the superlative properties of individual CNTs.

We consider floating catalyst CVD synthesis, known as direct spinning, to be intrinsically suitable for cost-effective scale-up of CNT fibre production for the following reasons: (1) amongst the main CNT production processes, namely arc discharge, laser ablation, and chemical vapour deposition, CVD processes are most promising for CNT mass production [1], (2) the single-step process is most similar to the production of carbon black [2], rather than multi-step processes employed for polymer fibre [3] or carbon fibre [4,5] production, and thus inherently inexpensive; (3) the direct spinning process is continuous and substrate-free, not a batch process. However, the disadvantages of this process lie in the large number of interdependent parameters that must be optimised in order to maximize the yield and quality of the product in terms of its mechanical, electrical and thermal properties.

Compared to their individual constituents [6–8], CNT bulk materials such as films (2D), forests (3D) or fibres (1D), suffer losses of several orders of magnitude in electrical conductivity because of (1) the presence of impurities and defects, which cause electron scattering and contact resistance, and (2) the insufficient alignment and CNT overlap length leading to increased junction resistance. An extensive review of conduction dependence on defects, nanotube packing and alignment and the state of electrical conductivity of bulk materials such as CNT fibres can be found in Ref. [9]. As for

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electrical and mechanical properties, the thermal conductivities of carbon nanotube bulk materials to date are considerably less than experimental values obtained for individual nanotubes and have provoked considerable interest particularly over the last five years.

In general, carbon-based materials are very attractive due to the combination of their exceptional thermal properties accompanied by their low densities. The best representatives of the family are diamond (with thermal conductivity up to 3320 W m^{-1} K^{-1} for nearly isotopically pure diamond [10]) and heat-treated carbon fibre (with thermal conductivity up to 2600 W m^{-1} K^{-1} [11–13]). However, both materials are expensive; in the case of carbon fibre this is due to the multi-stage and time-consuming production process. The thermal conductivity of isolated individual single-wall CNTs has been reported as among the highest measured values of any known material. With room-temperature thermal conductivities of 3500 W m^{-1} K^{-1} [14,15], individual SWCNTs experimentally show thermal conductivities greater than that of diamond. Early molecular dynamics simulations predicted values of up to 6600 W m^{-1} K^{-1} at room temperature due to the high purity and stiffness of the carbon-carbon bonds leading to long phonon mean free paths [16], with maximum values of 10,000 W m^{-1} K^{-1} at 100 K. However, Mingo et al. [17] questioned such ultra-high values and showed that the thermal conductances of SWCNTs might be smaller than previously thought, while the ballistic lengths are orders of magnitude larger. Hence, the values of thermal conductivity measured experimentally are actually in reasonable agreement with theoretical estimates.

In metals, both the thermal and electrical conductivity follow the same mechanisms of electronic conduction, and decrease with increasing temperature due to phonon scattering of the conduction electrons [18]. Pure anisotropic crystalline substances exhibit different thermal conductivities along different crystal axes, due to differences in phonon coupling in different directions. In CNTs, even metallic CNTs, both thermal conductivity and heat capacity of CNTs are dominated by the phononic modes [15] and transport is quasi-one-dimensional. At temperatures below 30 K [15], the thermal conductivity of CNTs is ballistic. The thermal conductivity, κ, increases strictly linearly with temperature ($\kappa \sim T$) and extrapolates to zero at 0 K. The ballistic regime becomes less dominant at higher temperatures as phonon-phonon, phonon-boundary, and phonon-defect scattering become more prevalent [17,19], and both heat capacity, C, and κ increase according to a power law $\kappa \sim C \sim T^{\alpha}$, with $\alpha > 1$ to 3 depending on the dimensionality of the phonon heat conduction [14,17,20–22]. The thermal conductivity then peaks near 200–300 K [14,20,23,24] due to Umklapp processes, where the excitation of high-frequency phonon modes is offset by the increased phonon scattering probability. Above that peak temperature, phonon-phonon scattering begins to dominate, and κ decreases continuously with $\sim T^{-\alpha}$, with $\alpha \sim 1$ to 2 [14]. Noteworthy, this onset for Umklapp processes occurs at significantly higher temperature than for diamond, graphite or carbon fibre (150 K) [11,13,16,23].

Defects in CNTs, including flaws in the tube wall, impurities, bends and kinks can significantly reduce κ, even at low defect concentrations, as they strongly suppress high-frequency phonon modes [25,26]. The room-temperature value of the phonon mean free path, λ_{ph}, estimated to range from 50 nm to 1.5 μm in pristine SWCNTs [15,20,27], can be as low as 4 nm in defective CNTs [14].

In MWCNTs, inter-shell forces mean that heat conduction is no longer purely one-dimensional. On one hand, the larger diameter allows for more phonon modes [28], and the thermal conductance of MWCNTs is higher than the sum of the thermal conductances of SWCNTs corresponding to each wall in MWCNTs, because the bending deformation of a tube protected by an outer tube is significantly less than that of the SWCNT without protection

[29,30]. On the other hand, the thermal conductivity of MWCNTs is smaller than that of a SWCNT corresponding to the outer tube, because the increase of cross-sectional area dominates over the increase of thermal conductance. For bundles, the thermal conductivity decreases with increasing number of CNTs associated with the quenching of phonon modes by neighbouring CNTs and the high thermal resistance at tube-tube junctions. This decrease saturates when the diameter of the bundles reaches around 150 nm [30].

For CNT bulk materials, the thermal conductivity is reduced, foremost because of their yarn-like structure: aligned bundles laterally connected by interwoven poorly oriented nanotubes lead to relatively low density, while the large surface area causes large losses due to radiation [30].

Tube-tube interactions between CNTs are dominated by van der Waals forces, which essentially vanish for CNTs separated by more than 0.4 nm [30–32]. Due to this weak interaction, heat flow between overlapping CNTs is low and the overlap length becomes highly important to determine the thermal resistance between tubes. For electrical conductivity and mechanical properties, CNT length, alignment and thus maximizing the contact between tubes [9,33–35] have been shown to be the main limiting factors to approach optimal values. Similarly for thermal conductivity, alignment is of high importance as the heat flow parallel to the CNT axis is far higher than perpendicular to it [23,36–38], however, rather than continuous contact, Baughman et al. [30] suggested that the ideal overlap length is 30–35 μm to reduce inter-tube scattering and dampen thermal vibrations, while still providing sufficient length to transfer thermal energy between the nanotubes.

CNT yarns produced by either wet-spinning or forest drawing processes typically achieve room-temperature thermal conductivities of only tens of W m^{-1} K^{-1} [39], but up to 380 or 635 W m^{-1} K^{-1}, if treated with acids or iodine-doped, respectively [24].

For heterogeneous materials such as CNT bulk material, which are effectively low-density CNT/air composites (or CNT/vacuum composites during measurements) [40], κ can vary significantly with the cross-sectional area and density of the CNT bundle network. Experimental measurements of composite materials give a value of apparent thermal conductivity, κ_{app}, averaged over the components of the composite. The value of κ_{app} can be viewed as κ for a homogeneous material with equivalent physical dimensions. Because of the high porosity of bulk CNT materials, the true cross-section through which heat can flow is significantly smaller than the overall (macroscopic) cross-sectional area. Attempts can be made to correct for the reduced density, such as normalizing the measured values to the ideal density hexagonally packed SWCNTs. However, we report the apparent thermal conductivity without correction for an ideal density, as this is the value that is most relevant to applications.

Similar to specific electrical conductivity, we report thermal conductivity in specific terms normalised by bulk density (κ/ρ), but using the linear density [41] to circumvent the necessity for measuring the thickness of films or diameter of fibres, which is the main source of uncertainty in density determination. (A detailed derivation of units can be found in Suppl. Inf.). Furthermore, κ/ρ can be directly related to thermal diffusivity, a ($a = \kappa(\rho C_s)^{-1}$ where C_s is specific heat, which is rather independent of the type of CNT).

In this paper, we describe the thermal conductivity of four samples synthesised by the same process, but from different carbon precursors and precursor concentration ratios, which were selected for their difference in bundle alignment, composition of single- or multi-wall CNTs, and amount of carbonaceous bundle coating or cluster impurities comprised of deformed CNTs. We determined the