The measurement of properties in carbon nanotube yarns

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Abstract:- The paper focuses on the importance of using specific values (values where the axial property is normalised by dividing by density) for properties of CNT yarn-like fibres to avoid the huge uncertainties introduced by the state of lateral compression of the yarn, a difficulty not only associated with the measurement of cross sectional area, but exacerbated by the influence of winding forces and indeed gripping forces while under test. Even with the disciplined use of specific parameters, there are also serious issues regarding axial mechanical tests and measurements of thermal conductivity. These are discussed as well.

Key words:- carbon nanotubes, fibre, yarn, specific properties, linear density, tensile tests, thermal conductivity

1 Introduction

Individual carbon nanotubes (CNTs) offer an exceptional range of axial properties, electrical, thermal and mechanical [1],[2],[3]. It is therefore understandable that axially oriented fibre or yarn is a natural choice for study. While the properties achieved fall short of those seen in isolated tubes [4],[5], they are none-the-less sufficiently interesting to mean that CNT yarns are likely to have very significant practical applications in the foreseeable future. A typical carbon nanotube filament fibre as spun is 10 microns in diameter, and the measurement of its axial properties can be far from straight forward. The filament consists of perhaps a million nanotubes per cross section and is essentially a yarn, an assembly of much finer fibrous elements, the nanotubes. Particularly in the case of mechanical properties there is the problem of gripping the yarn so that stress is transferred through its thickness, while for thermal conductivity the very high surface/volume ratio of the thin fibre means that the compensation for lateral heat losses is one of the central challenges of such measurements. Both these issues are discussed below. There is however, the matter of how the property measurements are expressed, their units. Measurements of materials properties as strength or conductivity (thermal or electrical) – normally require an accurate measurement of cross sectional area. This measurement is difficult, if not impossible, for any yarn like-fibre as its cross sectional area depends on how firmly it is compressed laterally, a variable, which may be considerably affected by such treatments as twisting, or indeed by the gripping processes required for property measurement. The conventional fibre industry, where yarns are an important component, overcome this difficulty by expressing the lateral size in units of linear density, that is mass per unit length instead of cross sectional area. Units often used for linear density are *tex,* which substituted for *denier* with the introduction of SI units. A property is thus expressed as a value per unit (volumetric) density which is equivalent to substituting linear density (tex) for cross sectional area.

2 The lateral size of fibres and yarns

The denier unit[1] is defined as the mass in grams per 9000m length. The reason for the irrational length, is probably because a continuous length of silk

[1] The word denier comes from an old small French coin, which in turn takes its name from the ancient Roman coin, a *denarius*. The weight of a silver denarius was also known as a 'denarius', and thus denier (= 1.18g) was adopted by the silk industry for their measure of weight per unit length.

from a silk worm's cocoon, between 600 and 900 metres, weighs of the order of 0.1 gram. Thus the linear density of silk is around 1 denier (1D). The SI compatible unit is the tex, defined as the mass in grams/1000m. Strictly the SI unit is kg/m, but this is unwieldy as the value for most fibres in this unit would be exceedingly small numbers. The transition from denier to tex for the fibre industry was a difficult one as the value for a yarn in tex would be nearly 1/10 of the value in denier. This lead to the introduction of the unit of deci tex (I tenth of a tex) so that a yarn of 1denier would be 0.9 decitex rather than 0.09 tex. In this way, if mistakes were to be made on transition to new units, the consequences would likely to be less harrowing.

If tex is related to diameter, then the question arises as to why yarns are not simply described in terms of their diameter. One reason is that a single silk filament of 0.1 tex has a diameter of the order of 10 microns, meaning that it is just visible to the naked eye. While digital callipers would register its existence, a measurement to within 10% accuracy would be demanding, although more sophisticated methods exist to measure diameter where the fibre has well defined lateral limits. Furthermore, many properties of yarns require a cross section area, so the value of diameter and thus its error has to be squared. Also, exactly round yarns are the exception rather than the rule, so there are further complications.

Another problem with diameter measurement is that a yarn such as wool or cotton which does not have clearly defined lateral limits. In any case, a yarn is likely to be very compressible laterally, so any pressure exerted by a mechanical measuring tool will affect the value obtained. Also pressures derived from reeling or twisting will also affect the diameter.

These problems do not exist if the fibre lateral size is expressed in terms of linear density as tex , dtex or denier. It is thus not surprising that they are universal in the fibre industry, and absolutely necessary where one is dealing with yarns.

3 CNT yarns

A carbon nanotube fibre consists of carbon nanotubes oriented to a greater or lesser degree with the fibre axis. It is thus a yarn consisting of an assembly of much thinner fibre elements. However, where the fibre material has been made by floating catalyst methods [6] there are often sub assemblies known as bundles, where up to 100 nanotubes are very well mutually aligned, although the bundle itself may wander from the fibre axis. Such bundles are most prevalent when the nanotubes are either single wall or double wall.

Fig1 (a) shows an SEM micrograph where the aligned elements are bundles, individual nanotubes (mainly single wall) not being visible at this resolution. The bundles form a network, not so much with classical entanglement, but through the device of swapping nanotubes, so they divide and rejoin. Fig 1(b) shows the component nanotubes of the bundles in electron transmission. The density of the fibre where would up directly from the CVD reactor is of the order of 0.01 g/cc.

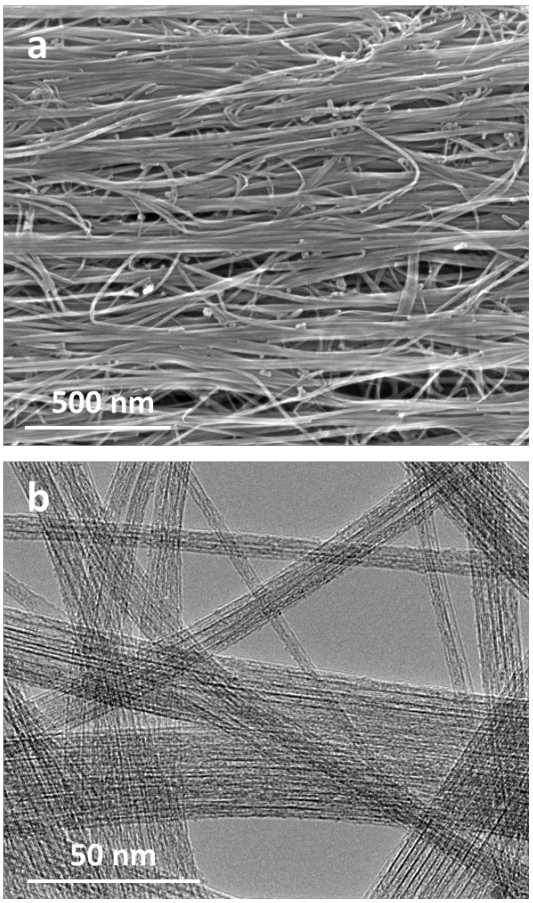


Fig 1. (a) An SEM image of a condensed carbon nanotube yarn, The fibre axis is horizontal, and the main fibrous elements visible are bundles of up to 100 nanotubes. The network points correspond to the swapping of nanotubes between the different bundles. The individual nanotubes are not resolved. (b) A high resolution TEM micrograph showing the nanotubes within the bundles. In this case the nanotubes are a mixture of single and double wall tubes. The preferred alignment of the bundles with the fibre axis has been lost in sample preparation.

However, treatment with an atomised solvent which will rapidly evaporate, such as acetone, condenses the fibre through surface tension forces to give a density of the order of 0.5 - 1g/cc. However the density is critically dependant on the nature of the solvent treatment, and indeed on other factors such as compressive pressure during winding, and generally handling thereafter. Basically density, and thus diameter for a given mass of material is a very difficult variable to pin down, and a leads to a major difficulty in comparing property values from different laboratories, where these are expressed per unit cross sectional area. As explained above, the measurement of cross sectional area is fraught with difficulty. Not only because of the intrinsic 'compressibility' of a yarn on handling, but because of possible variations in the degree of compression along the fibre length. An example of the great care required to come up with an accurate cross section area, is shown in Fig 2, which is a fibre cut by ion beam and then examined in the same instrument. However, multiple cross sections would be required to assess variability along the length, and there is the ever open question of the effect of handling, or even of the evacuation of the scanning electron microscope column, on the density and thus on area.

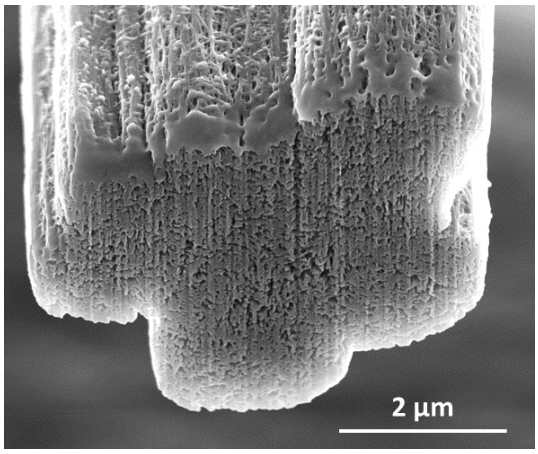


Fig 2 An SEM image of a condensed CNT fibre after sectioning using a focused ion beam. It provides a basis for a reasonably accurate measurement of cross sectional area.

Hence the lateral size of a CNT yarn is much best expressed in terms of linear density, whether as tex or dtex. The measurement of tex is comparatively straight forward assuming a significant length of fibre is available. A known cut length is simply weighed on an accurate balance.

4 The units for properties expressed using linear density

Properties which depend on cross sectional area require this parameter to be measured as accurately as possible, something very difficult with a yarn. For this reason linear density is a preferred measure. It is interesting to see the implications of expressing a stress parameter in terms of N/tex rather than N/m_A^2. (Here the subscripts, A and L are used to distinguish the length units of cross sectional area as m_A^2 and of length as m_L).

In strictly SI units, linear density (LD) has the units of kg/m_L, and the specific stress parameter, N/LD, becomes $N.m_L/kg$.

The key relationship is that the ratio of linear density to cross sectional area (LD)/A has the units of: $(kg/m_L)/m_A^2 = kg/m_L.m_A^2$ which is volumetric density.

In other words, if the cross sectional area component of stress is replaced by linear density, stress is effectively replaced by specific stress (stress/density) assuming that the units are consistent.

It follows that if the linear density is expressed in terms of g/km (tex), and the density in g/cc, then because LD (kg/m) = tex x 10^{-6} and density (kg/m^3) = density (g/cc) x 10^3, then Pa/density (g/cc) = 10^9. N/tex,

So, the Specific Stress in GPa/(g/cc) is numerically equivalent to: N/tex

Properties such as electrical and thermal conductivity do not lead to quite so neat a solution, as the measured property, unlike strength, depends also on the length of fibre or wire under test.

The SI unit of electrical conductivity (σ) is S/m, where the conductance is in Siemens (S) which is amps/volt or 1/resistance in ohms. Conductivity is thus obtained by dividing the conductance by the cross sectional area and multiplying by the length.

Hence $\sigma = S.m_L/m_A^2$ which is normally reduced to S/m. So once again the demand is made to have an accurate value for the cross sectional area, a demand not easily met for CNT yarns.

Replacing the area term in m_A^2 by linear density (LD) in Kg/m_L we obtain a specific conductivity, σ' = $S.m_L/LD$. Here the yarn length of the test specimen is effectively squared, perhaps putting more demand on what is not really a very difficult measurement, but it is still much more a

straightforward measurement than cross sectional area.

The units of thermal conductivity κ, normally written W/m.K are, in expanded form, $W.m_L/m_A^2.K$

Hence the units of specific thermal conductivity, κ', (= κ /density) are, by substituting LD for area:

$W.m_L/(LD).K$

Or in reduced form: $W.m_L^2/kg.K$

Again this value will tend to be rather small, so the equation is sometimes expressed in terms of milliwatts (mW) rather than Watts., which gives a more manageable number.

Hence the units for κ' become: mW. m^2/kg.K.

5 Problems of measuring strength parameters of CNT yarns

A conventional yarn, cotton, polyester etc., consists of shorter elements, sometimes prepared by cutting and known as 'staple', aligned with the fibre axis which share any applied load through inter filament friction. The friction is often enhanced by twisting regimes where axial tension causes the fibre to pull in on itself increasing friction by virtue of increased normal load. Enhanced normal load between the staple elements of the yarn also occurs within the grips of a tensile test, or to some extent when the yarn is attached to the testing machine by winding on capstans.

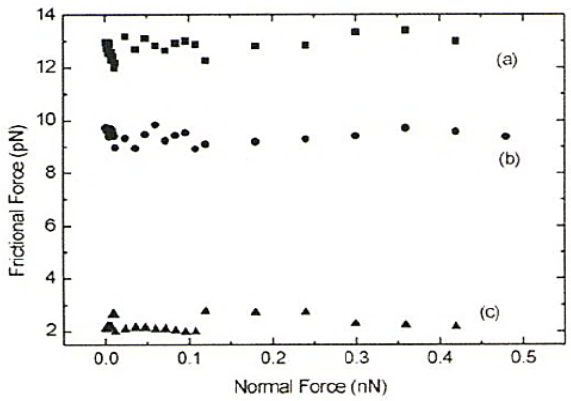


Fig 3 Normal force dependencies of friction on smooth surfaces. (a) SiO_2 (b) graphene and (c) graphite. There is very little, if any, dependence on the normal force. [7]

In the case of CNT yarns the picture is different, as frictional forces to transmit the stress from one nanotube to a neighbour are very much less – graphite being an established lubricant. The 'friction' which does occur is sometimes known as van der Waals friction and unlike conventional friction is only very weakly dependant on normal force. [Fig 3].

Early measurements of the effect of twisting on the strength of CNT yarns showed no advantage at all [Fig 4]. While these measurements suggest that twisting of CNT yarns may be of little value in terms of specific strength and stiffness enhancement, they also point to a major difficulty with the tensile test. Where the yarn is gripped using hard rubber faces, there is transfer of stress through a degree of chemical adhesion to the outer surface but the transmission of the stress to the central regions of the fibre is inefficient and not helped by the normal stress of the grips. The result is that the stress is not uniform across the cross section until a substantial distance along the gauge length.

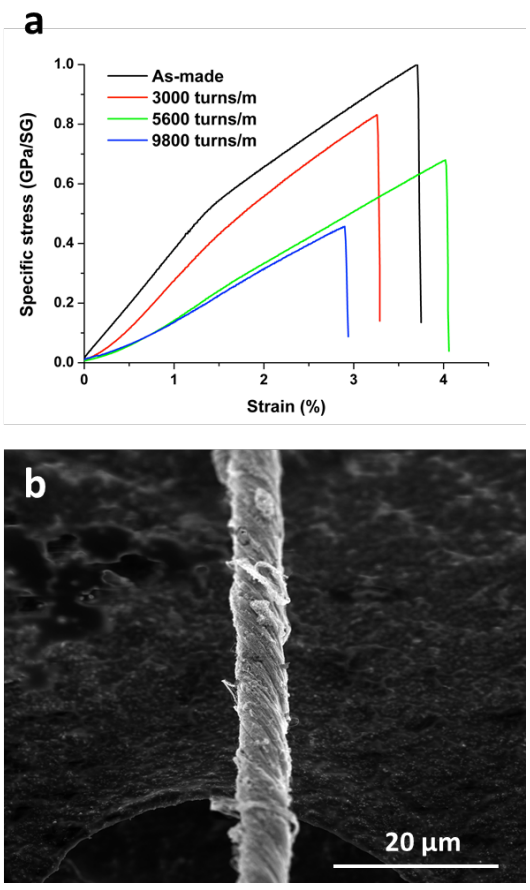


Fig 4 (a) The influence of twisting on mechanical properties. (Courtesy: Dr Juan Vilatela, [8]) (b) A twisted CNT yarn ~ 30,000 turns/metre.

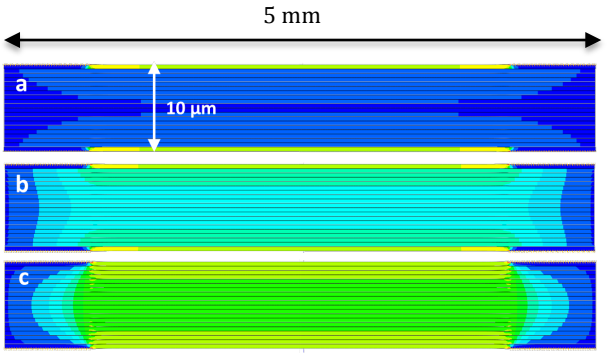


Fig 5 Finite element analysis of the stress distribution across a CNT yarn as a function of distance from testing grips with a shear stress of (a) 50 kPa, (b) 500 kPa, and (c) 5 MPa. A shear strength of 50kPa is the best estimate for graphite layers, but at this value the stress is not uniform across the sample even for a sample with a gauge length 500 x the diameter. Note that the diagrams on the left are compressed laterally by a factor of x100. [9]

Fig 5 shows models of the stress distribution in the fibre for different values of maximum shear stress. The lowest value of 50kPa is the median of literature values for the shear yield stress between graphite layers. Note, for this case, the stress concentration in the outer layers close to the grips and the considerable length of material that would be needed before the stress is at all uniform. Given that the material is a yarn, one would expect that the strength increases at short gauge lengths as an increasing proportion of the nanotubes are long enough to span the gauge length, indeed, in modelling strength v. gauge length data for conventional yarns a second term is required in the fit equations for gauge lengths small enough to approach the length scale of the individual filaments comprising the yarn [10]. For clean samples such as that in Fig 1, no increase is seen. However, if the synthesis process is run to leave a significant proportion of particulate catalyst residue between the bundles in the yarn, then an increase in specific strength is seen at short gauge lengths as shown in Fig 6.

As an unusual and more extreme example, an early fibre from the Cambridge group was tested at short gauge lengths, results which were ratified in the US [11]. Statistical data covering many tens of samples are plotted in Fig 7(a) The high strength part of the distribution seen at the shorter gauge length show values in excess of those normally realised in this material. Fig 7(b) shows SEM micrographs of the fibre which at the higher magnification shows it to have a quite exceptionally high concentration of particles which typically have an iron core coated with further carbon.

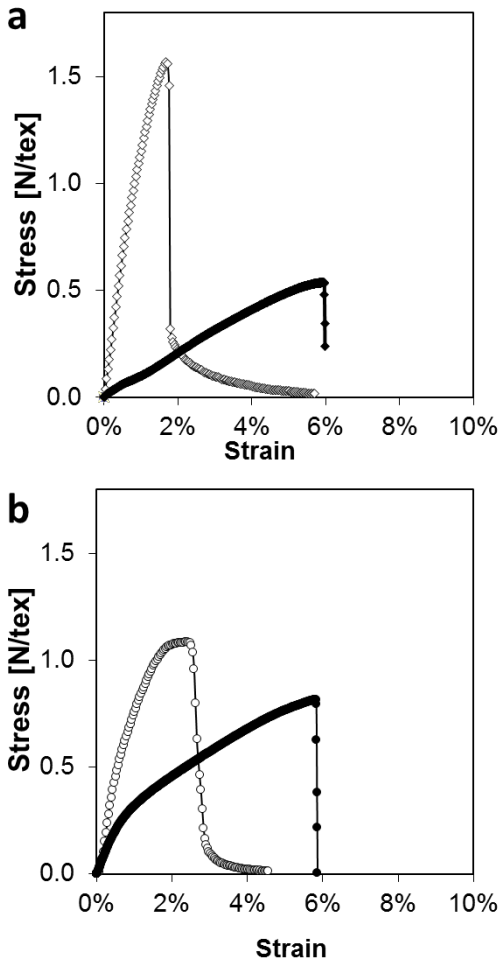
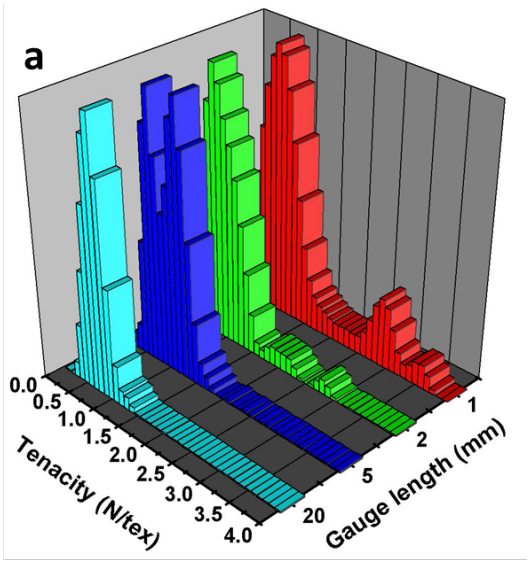
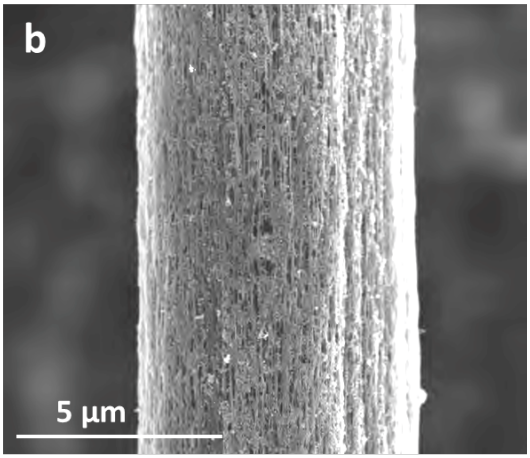


Figure 6: Specific Stress-Strain measurements on (a) impure fibre containing cluster impurities and (b) clean fibre. Filled or open symbols refer to a gauge length of 20 mm or 0.5 mm, respectively. [9]

It thus appears, tantalisingly, that the higher the impurity content the greater the strength at short gauge lengths, even though the particulate impurity must be contributing to the tex, and thus tending, in that respect, to reduce the mechanical property values. If we are to assume that the increase occurs when the gauge length approaches the length of the nanotubes, (~1mm), then it seems that the particles are in some way enhancing the through thickness stress transfer within the grips, so that all the nanotubes in the gauge length share the load rather than simply the surface ones. It is as if the particles act as *internal sandpaper* in raising the shear strength between nanotubes and their bundles [9].





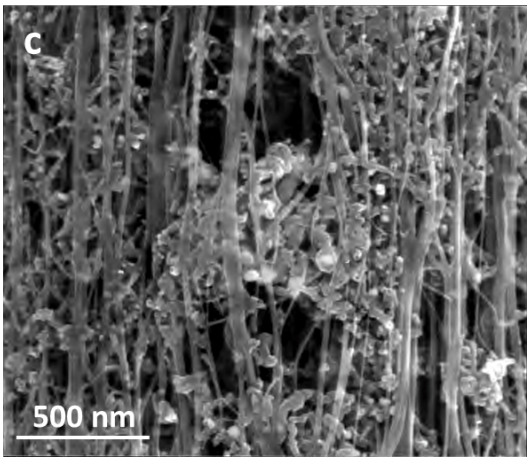


Fig 7 (a) statistical distribution of strengths as a function of gauge length. [12] (b) SEM micrographs of this unusual fibre showing that it was full of particles, mainly excess catalyst iron sometimes coated with carbon.

Another indication of the influence of extraneous material on the mechanical properties is that of a deposit of carbonaceous material sometimes seen on the surface of the nanotube bundles, but not within the bundles. It appears that when the process is run under conditions which do not produce this *goo* the fibres tend to be weaker, so it is possible that it too contributes to the strength.

6 The Challenge of Measuring the Thermal Conductivity of CNT Yarns

The very high surface to volume ratio and small mass of CNT yarns and other microfibers makes heat losses to the environment, due to radiation and convection, and in some cases to the probes, through conduction, very significant and poses a major challenge to the accurate determination of the materials' thermal conductivities. Conventional methods will use very small thermocouples to measure the temperature gradient along the test specimen and rely on insulation material to prevent heat losses at the surface; these methods are useless in the case of microfibers since their thermal mass is so small that all heat will be readily lost to the insulation and/or the thermocouples.

In all published work, [13-19] convection losses are dealt with by working under the highest possible vacuum (usually 10^{-3} mbar or lower pressure). Vacuum is a very effective way to reduce convection losses. Most methods working with thin fibers are designed in a way that all the necessary probes in contact with the sample need to work also as heatsinks or are attached to a heat source of sufficient mass [13, 15-17]. Methods requiring to measure the temperature gradient along the sample, like the dual-mode heat flow technique [18] would require the use of a thermal camera instead of thermocouples in order to work properly with microfibers. Figure 8 shows a thermal image of a CNT yarn with a nominal diameter of ~10 µm being heated by a 0.1 mA electric current.

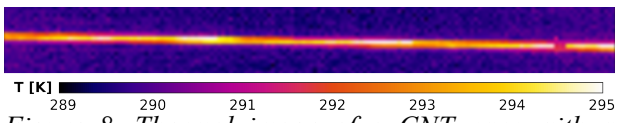


Figure 8. Thermal image of a CNT yarn with a nominal diameter of ~10 µm being heated by a 0.1 mA electric current.

Having dealt with convection and contact losses, we now need to consider radiation losses. Radiation can be minimized by working at small ΔT relative to the environment but cannot be completely

eliminated. Most researchers incorporate a simplified (either through a truncated series expansion, [17], or by using the so-called "pin-fin" approximation with a substituted coefficient, [18]) approximate form of Stefan-Boltzmann's law into their models to account for radiation, or compare expected steady-state radiation losses at the average temperature of the sample with heat conduction along it [16]. For our experiments, whether we are measuring the effects of heating a yarn by means of a laser pulse or by a sudden pulse of electric current, we use COMSOL (finite element modelling multiphysics software) to numerically solve the heat equation with the radiation term included.

A clever method that directly measures thermal losses is that of the parallel thermal conductance (PTC) [14], [15] [19]. In summary, the PTC is a steady state method that works by measuring the thermal conductances (G) between a heater and a heatsink inside a vacuum chamber in three different configurations: with no sample present in the chamber ($G_{background}$), with the sample connected to both the heater and the heatsink ($G_{connected}$), and with the sample connected to the heater only to account for radiation ($G_{disconnected}$). Each of these conductances is extracted from the inverse of the slope of a plot of the temperature difference between the heatsink and the heater (ΔT) in function of the power being inputted to the heater. The conductance of the sample (G_{sample}) is then calculated from

$$G_{sample} = G_{connected} - G_{background} - \frac{1}{2}\left(G_{disconnected} - G_{background}\right) \quad (1)$$

Finally, G_{sample} can be turned into the absolute or specific thermal conductivity of the sample with knowledge of the geometry or the linear density of the sample, respectively. Figure 9 shows a ΔT vs Pow plot for the empty vacuum chamber (black), a CNT film (red), and a Cu foil (green) used for parallel thermal conductance (PTC) measurements. At this moment, the biggest weakness of the PTC method is its sensitivity; from the figure it can be seen that the trace of the highly conductive (3.75 times more conductive than Cu in specific terms) but very thin CNT film is almost indistinguishable from the background of the empty vacuum chamber. In order to measure the thermal conductivity of yarns with this method, it is necessary to connect several (~50) in parallel to get data distinguishable from the background. This has the advantage of offering a value that averages out defective and exceptionally good yarns but requires a significant amount of material and a long time to mount all the yarns.

Nevertheless, the specific thermal conductivity for condensed CNT fibre obtained by this method, show values some 25 times that for copper, placing it in a unique position for the development of heat cables. [19].

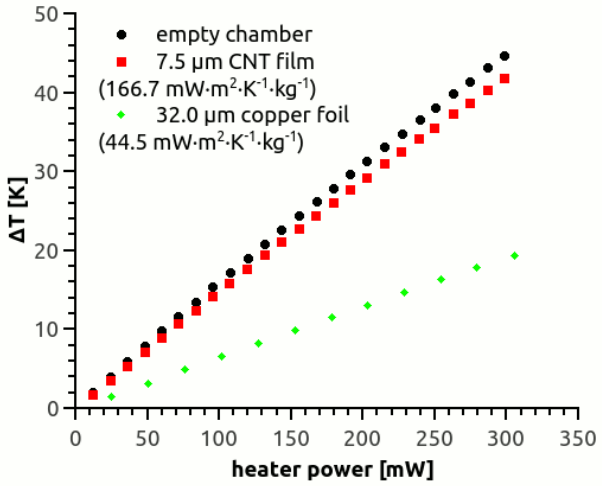


Figure 9. ΔT vs Pow plot used for parallel thermal conductance (PTC) measurements: it can be seen that the trace of the highly conductive but very thin CNT film is almost indistinguishable from the background of the empty vacuum chamber.

7 Conclusion

Carbon nanotube fibres are essentially yarns, comprising of assemblies of aligned nanotubes. Not only does a yarn-like form produce difficulties in measuring the cross section area accurately, but the value itself is highly sensitive to the handling of the fibre and could possibly be affected by clamping necessary for testing. In comparison of properties of such fibres made by the different techniques of spinning from arrays, spinning from liquid crystalline solutions or direct spinning from the CVD reactor zone, it is vital that the properties are expressed as specific values and thus not dependent on the state of lateral compression of the fibre. The use of specific values is absolutely essential where claims are made for new outstanding property values. Nevertheless, the measurement of specific values does not completely remove the challenge of accurate

property measurement. In the case of mechanical properties, it is an issue of stress transfer from the grips to obtain a uniform value across the gauge length. In the case of measurements of thermal conductivity, the very low thermal mass of the fibre coupled with its high surface to volume ratio, means that lateral heat losses need to be understood and compensated for if results of meaningful accuracy are to be obtained.

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