A Multifunctional Yarn Made Of Carbon Nanotubes

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ABSTRACT
Fibers made up of carbon nanotubes (CNTs) have emerged as a new high-performance material with an exceptional combination of properties derived from those of the CNT building blocks. These fibers can be produced by spinning a CNT aerogel directly from the gas-phase during CNT growth by chemical vapour deposition. The process is continuous and can currently spin fibers at rates of 100m/min. The unique yarn-like structure of CNT fibers gives them exceptional toughness, resilience to bending stresses, extremely high surface area and good integration in polymer matrices. This work shows an overview of the production, properties and prospects of this new high-performance fiber.

INTRODUCTION
The development of high-performance fibers has been based on aligning long extended molecules with a carbon-carbon backbone parallel to each other and to the fiber axis. This strategy was proposed some eight decades ago and first demonstrated for a variety of polyesters and cellulose. [1] It resulted in a wide range of synthetic fibers that are now ubiquitous in our modern world. However, the production of high-performance fibers did not occur until stronger/stiffer building blocks were developed, such as poly (p-phenylene terephthalamide) for Kevlar, poly (p-phenylene benzobisoxazole) for Zylon and ultrahigh molecular weight polyethylene for Dyneema. *Figure 1* shows examples of polymers used for making high-performance fibers, with carbon nanotubes (CNTs) the latest addition to this list of building blocks.

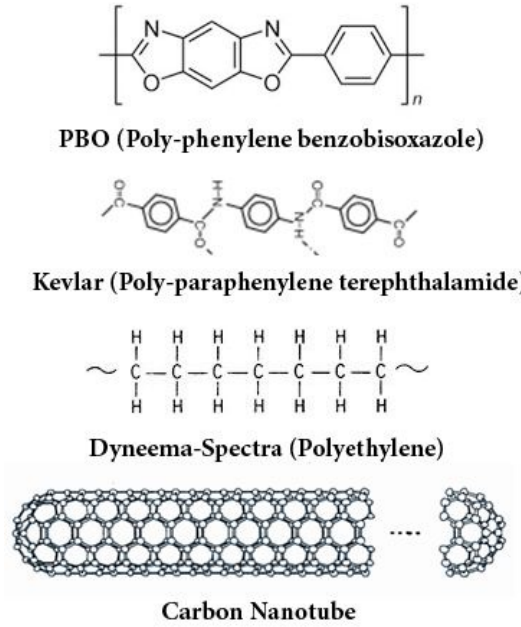

FIGURE 1. Polymers used for high-performance fibers, with a CNT as the latest addition to this group.

In addition to their low density, carbon nanotubes have a combination of outstanding mechanical, electrical and thermal properties along the tube axis [see for example 2]. These properties can be exploited in a fiber, seeking the alignment of the nanotubes parallel to each other and to the fiber axis. Morevoer, CNTs have the thermal and chemical stability of graphite and therefore do not degrade under ambient conditions, including exposure to UV radiation, and they preserve their mechanical properties up to very high temperatures.

DISCUSSION
Carbon nanotube fibers can be produced by drawing from an array of vertically aligned CNTs; [3] by wet-spinning from a liquid crystalline suspension of CNTs; [4] by coagulation spinning of a mixture of CNTs and polyvinyl alcohol (PVA); [5] or they can be spun directly from the reactor by drawing them out of the hot-zone during CNT growth by chemical

vapour deposition (CVD). [6] The last process is discussed in more detail here and a schematic presented in *Figure 2.*

CNT Fiber Spinning from the Gas-Phase

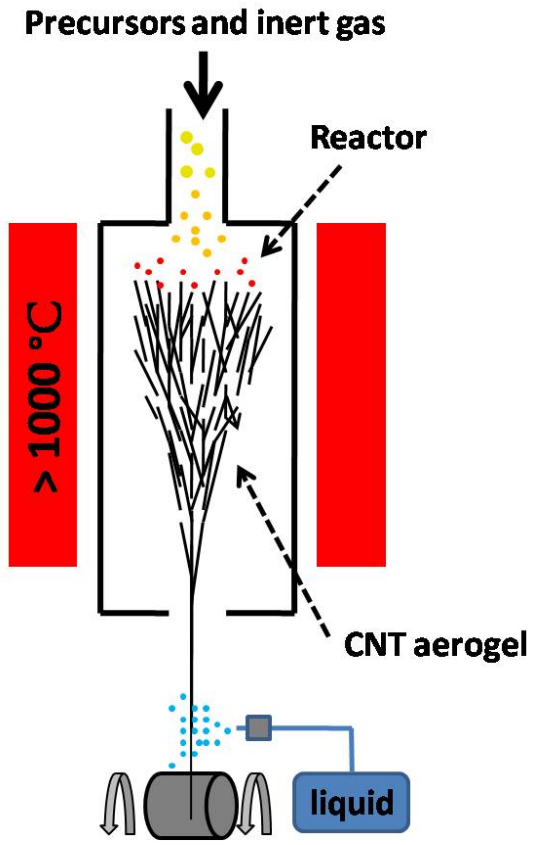

FIGURE 2. Schematic of the process for spinning CNT fibers directly from the gas-phase.

In the direct spinning method CNTs are synthesised in a vertical reactor above 1000 °C, with iron as catalyst, sulphur as a growth enhancing agent, [7] methane as the carbon source [8] and hydrogen as carrier gas. As the CNTs grow in the gas-phase they entangle due to their high aspect ratio (around 10^5) and the action of van der Waals forces, forming an elastic smoke, termed aerogel, which can be drawn out of the reactor continuously. [6] This diaphanous CNT material can be wound as film or densified on-line by exposure to atomised liquid to form a fiber. [9].

This spinning process is radically different from most fiber spinning methods, and some of its features deserve further comment. As a general observation, it is remarkable that the process covers both the synthesis of the building blocks and their assembly into a fiber; polymer fibers typically require production of the polymer and then fiber spinning at a separate stage. Besides any possible cost benefits from having a one stage process, another implication is that the fiber spinning rate is dictated by the rate at which the CNTs are synthesised. The indication so far is that in this CVD process the individual nanotubes growth at rates of at least millimetres/s and that faster spinning rates can be achieved by increasing the precursor feed rate. Indeed, spinning rates of around 100m/min have been achieved in the laboratory, being in fact currently only limited by the constraints of manual operation. Another interesting feature of this process is that amongst the possible sources of carbon that can be used are methane and natural gas; thus, effectively, this is a continuous process where natural gas is transformed into a high-performance fiber.

CNT Fiber Properties

Table I presents a summary of properties of CNT fibers produced by the direct spinning method, with Kevlar 49 and AS4 carbon fiber (CF), two of the most important high-performance fibers at present, included for comparison. The table shows a CNT fiber material with exceptional combinations of properties: mechanical properties in the high-performance range and electrical and thermal conductivity close to that of copper on a mass basis. Only special highly graphitic CF grades have a similar property combination, although they are very brittle (also expensive) and difficult to handle, whereas CNT fibers are highly flexible and can be manipulated like a textile yarn. [10] Moreover, these properties are still under improvement by structural optimisation of the fiber and spinning process for mechanical [8] and electrical [11] performance.

TABLE I. Composition and longitudinal properties of CNT fibers, Kevlar and AS4 CF.

Fiber type	Tensile strength (N/tex)	Tensile stiffness (N/tex)	Compressive yield strength (N/tex)[a]	Electrical conductivity (S/m)	Thermal conductivity (W/mK)	Density (g/cc)
CNT fiber [b] (direct spinning)	1.5 [12]	100 [9]	0.6 [13]	8×10^5 [14]	45 [15]	1.0
Kevlar 49 [c]	2.3	112	0.25	-	-	1.44
Carbon fiber AS4 [c]	2	230	0.78	5.9×10^4	6.8	1.79

[a] from composites with 1N/tex tensile strength CNT fibers.
[b] properties at 20 mm gauge length
[c] according to manufacturer´s datasheet

Fiber Structure and Yarn-Like Character

In addition to an outstanding combination of properties, CNT fibers have a unique structure. Unlike traditional fibers, which are `solid´, CNT fibers have a porous yarn-like structure, such as cotton or wool, but with the subfilaments being the nanotube bundles *(Figure 2)* [10].

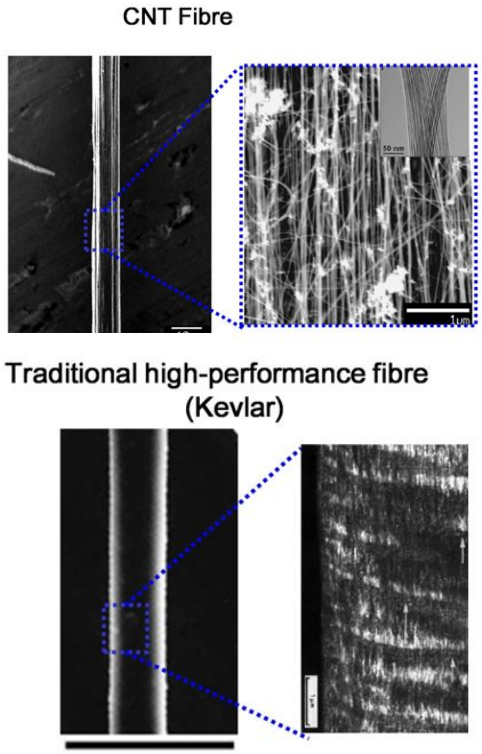

FIGURE 2. Scanning electron micrograph of a CNT fiber (top) and a higher magnification image (bottom) showing its yarn-like structure.

Implications of this yarn-like structure are their tolerance to bending and in general their resilience to stresses perpendicular to the fiber axis. The flexibility of a fiber can be quantified in terms of its knot strength efficiency, which corresponds to the ratio of strength of a fiber with an overhand knot over the strength of the un-knotted fiber, expressed as a percentage. In the case of CNT fibers spun directly from the gas-phase, their knot strength efficiency is approximately 100%. [10] Cotton, wool and other staple fibers have similar knot strength efficiencies; however, their tensile properties are in the low performance range. High performance fibers, on the other hand, have low knot efficiencies, with CF for example losing around 99% of its tensile strength when knotted. These results evidence CNT fibers' tolerance to bending due to their hierarchically fibrous structure and therefore, point to their potential as a textile that can be woven into complex fabrics without degradation of its mechanical performance.

Flexural rigidity of a fiber scales with diameter to the power of four. The advantage of a yarn over a `solid´ fiber is that the relevant diameter is that of its fibrous subunits, which is several orders of magnitude smaller than that of the diameter of the solid fiber. In addition, the low forces between subfilaments in a yarn mean that its cross-section changes when subject to a bending stress, and in the process the tensile and compressive stresses on the fiber are decreased. This difference in bending behavior is schematically illustrated in *Figure 3*.

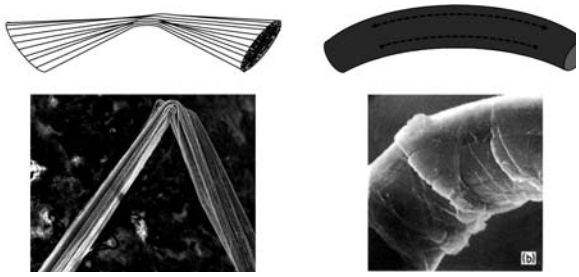

FIGURE 3. Cross-sectional change in CNT fiber with yarn-like structure (left) contrasted against `solid´ aramid fiber with evidence of kink damage due to compressive stresses due to bending (right). Aramid image from reference [16].

Factors Determining Fiber Strength

Fractography analysis of CNT fibers broken in tension indicates that the fracture surface is fibrous, with multiple bundles and other fiber subunits protruding from the fiber *(Figure 4).* Failure in tension occurs as the CNT bundles are pulled apart from each other in shear.

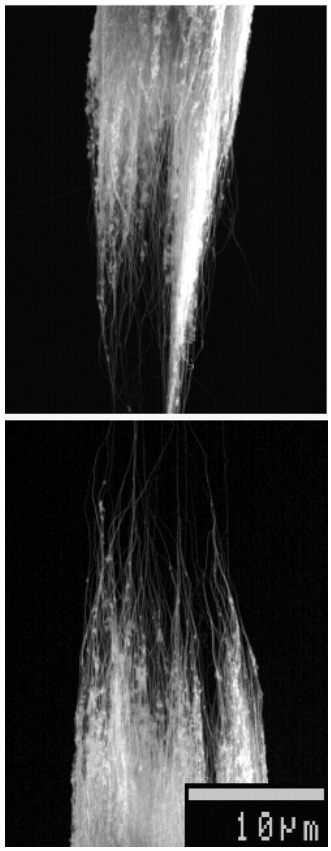

FIGURE 4. SEM micrograph of the fracture ends of a CNT fiber.

The total load bearing capacity of the fiber is determined by the total contact area of lead-bearing elements and their interfacial shear strength. Hence, fiber tensile strength scale linearly with CNT length, [17] as supported by experimental evidence from data in the literature *(Figure 5A).* A similar relationship is observed in textile yarns, such as cotton, the strength of which is proportional to the staple fiber length and frictional coefficient between fibers *(Figure 5B).* [18, 19] Because of the low shear strength of the graphitic surfaces in the fiber (graphite is a lubricant) the length of the nanotubes has to be very long in order to obtain a fiber with tensile properties in the high-performance range. Current CNT lengths in fibers are of the order of millimetres, which represents an impressive aspect ratio of almost one million.

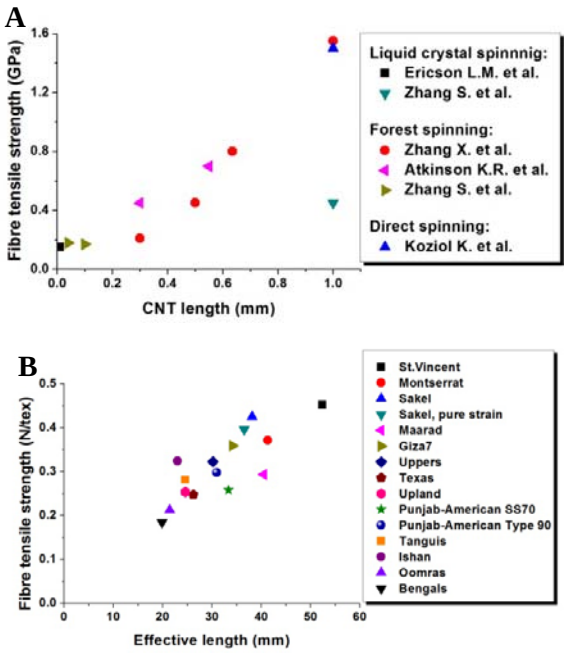

FIGURE 5. Plots of fiber strength against building block length for CNT fibers (top) and different cotton varieties (bottom). Note that the top plot is in GPa and the bottom in N/tex, as the values reported are in these units [18].

CNT Fiber Composites

The relatively open of CNT fibers means that their specific surface area is about three orders of magnitude greater than that of a traditional reinforcing fiber (200 m^2/g and 0.2 m^2/g, respectively). The high internal surface area of the fibers is readily accessible to polymer molecules which can infiltrate it due to capillary forces arising from the porous structure of the fiber and without the need to apply any external pressure. [15] This infiltration mechanism, and in general the high fiber-matrix interface, provide excellent adhesion to polymer matrices when the fiber is embedded in a composite, without the need for a sizing or post-spin treatment on the fiber. As a result, a large mechanical reinforcement is obtained resulting in composites with high strength, modulus and energy absorption both in tension and in compression. [13] The integration of CNT fibers in polymer matrices also results in composites with high electrical ($4x10^3$ S/m) and thermal conductivity (30 W/mK), and a low coefficient of thermal expansion (~ 0) [15].

CONCLUSIONS

CNT fibers, particularly those spun directly from the gas phase are an exceptional material in many ways. From the manufacturing point of view, their spinning process is very unusual in that it combines the synthesis of the fiber building blocks and the

assembly into a fiber in one stage. Virtually all fiber production processes have the two stages separate, with the possible exception of natural fibers such as spider silk. Furthermore, the possibility of using natural gas as the carbon source is another attractive feature of the direct spinning process, especially from the economic point of view.

The yarn-like structure of CNT fibers gives them mechanical properties different from those of traditional `solid´ high-performance fibers, most notably an outstanding resilience in bending and compression. This feature is particularly attractive because it could lead to complex CNT-fiber forms such as fabrics and `T´ pieces, which are normally unsuitable for traditional high-performance fibers.

Another aspect of the yarn-like structure of CNT fibers is their high surface area of a few hundred m^2/g. The porosity of this fibers means that when they are integrated in a polymer composite the polymer can infiltrate the fiber due to capillary forces, which results in good wetting, strong adhesion to the matrix and therefore high level of reinforcement. This high surface area, combined with the chemical inertness of CNTs, is also an open opportunity for membranes, electrochemical devices such as batteries, capacitors, photocatalytic, etc.

The direct spinning method for making CNT fibers is a clear example of a bottom-up process. It enables tailoring the material at different scales and therefore provides the possibility of engineering new fibers for a wide variety of applications.

ACKNOWLEDGEMENTS
This work was financially supported by the US Army International Technology Centre, London, CONACYT (Mexico) and the EPSRC (UK).

REFERENCES

[1] Carothers, W. H. & Hill, J. W., Studies of Polymerization and Ring Formation. XV. Artificial Fibers from Synthetic Linear Condensation Superpolymers. J. Appl. Chem. Soc. 54, 1579 - 1587 (1932).
[2] Jorio, A., Dresselhaus, G. & Dresselhaus, M. S. eds., Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, 1st ed. (Springer, New York, 2008).
[3] Zhang, M., Atkinson, K. R. & Baughman, R. H., Multifunctional carbon nanotube yarns by downsizing an ancient technology. Science 306, 1356 - 1361 (2004).
[4] Ericson, L. M. et al., Macroscopic, Neat, Single-Walled Carbon Nanotube Fibers. Science 305, 1447-1450 (2004).
[5] Vigolo, B. et al., Macroscopic Fibers and Ribbons of Oriented Carbon Nanotubes. Science 290, 1331 - 1334 (2000).
[6] Li, Y. L., Kinloch, I. A. & Windle, A. H., Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis. Science 304 (5668), 276 - 278 (2004).
[7] Motta, M. S., Moisala, A., Kinloch, I. A. & Windle, A. H., The role of sulphur in the synthesis of carbon nanotubes by chemical vapour deposition at high temperatures. J. Nanosci. Nanotechnol. 8, 2442 - 2449 (2008).
[8] Vilatela, J. J., Deng, L., Kinloch, I. A., Young, R. J. & Windle, A. H., Structure of and stress transfer in fibers spun from carbon nanotubes produced by chemical vapour deposition. Carbon 49, 4149 - 4158 (2011).
[9] Koziol, K. K. et al., High-Performance Carbon Fiber. Science 318, 1892-1895 (2007).
[10] Vilatela, J. J. & Windle, A. H., Yarn-like Carbon Nanotube Fibers. Adv. Mater. 22, 4959 - 4963 (2010).
[11] Sundaram, R. M., Koziol, K. k. & Windle, A. H., Continuous Direct Spinning of Fibers of Single-Walled Carbon Nanotubes with Metallic Chirality. Adv. Mater. DOI:10.1002/adma.201102754 (2011).
[12] Zhang, X. et al., Ultrastrong, Stiff, and Lightweight Carbon-Nanotube Fibers. Adv. Mater. 19, 4198 - 4201 (2007).
[13] Mora, R. J., Vilatela, J. J. & Windle, A. H., Properties of composites of carbon nanotube fibers. Comp. Sci. Tech. 69, 1558 - 1563 (2009).
[14] Stano, K. L. et al., Direct spinning of carbon nanotube fibers from liquid feedstock. Int. J. Mater. Form. 1, 59 - 62 (2008).
[15] Vilatela, J. J., Khare, R. & Windle, A. H., Multifunctional Carbon Nanotube Fiber Composites: Hierarchical Structure and Properties. Carbon 50, 1227 - 1234 (2011).
[16] Greenwood, J. H. & Rose, P. G., Compressive behaviour of Kevlar 49 fibers and composites. J. Mater. Sci. 9, 1809 - 1814 (1974).
[17] Vilatela, J. J., Elliott, J. A. & Windle, A. H., A Model for the Strength of Yarn-like Carbon Nanotube Fibers. ACS Nano 5, 1921 - 1927 (2011).

[18] Gregory, J., Cotton Yarn Structure Part IV - The Strength of Twisted Yarn Elements in Relation to the Properties of the Constituent Fibers. J. Text. Inst. 44, T499 - T514 (1954).
[19] Morlier, O., Orr, R. & Grant, J., The Relation of Length to Other Physical Properties of Cotton Fibers. Text. Res. J. 21, 6 - 13 (1951).
[20] Pick, M., Windle, A. H., Vilatela, J. J. & Koziol, K. K., UK Patent No. EP2145043 (2007).
[21] Dobb, M. G. & Robson, R. M., Structural characteristics of aramid fiber variants. J. Mat. Sci. 25, 459 - 464 (1990).

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