

# STRUCTURE AND PROPERTIES OF COMPOSITES OF CARBON NANOTUBE FIBRES

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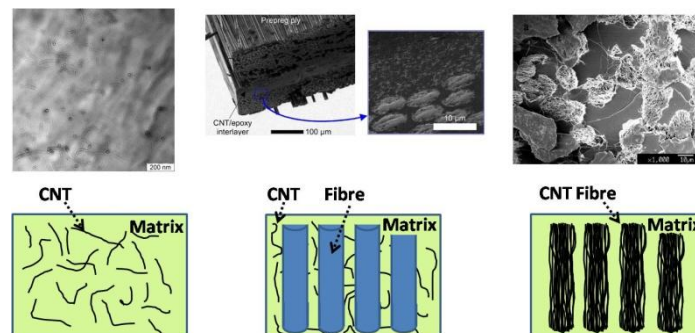
## Abstract

Fibres composed of carbon nanotubes (CNT) aligned parallel to each other and to the fibre axis have emerged as candidates for developing a new generation of composites with multifunctional properties, amongst them, mechanical properties in the high-performance range and high electrical and thermal conductivities. Furthermore, their porous yarn-like structures gives CNT fibres values of specific surface area around three orders magnitude higher than traditional “solid” fibres, as well as great resilience in bending. These two properties make them ideal for composites from the point of view of fibre-matrix adhesion and the possibility of making complex shapes.

## 1 Introduction

### 1.1 Nanocarbon composites

The appeal of CNTs and graphene arises from the combination of the outstanding properties of in-plane graphite with an exceptionally high surface area. Integrating these nanocarbons in polymer composites is one of the most promising strategies to exploit the properties of the nanobuilding blocks on a macroscopic scale. Nanocarbon composites into three kinds, each with some possible subdivisions. Examples of these composites and their schematic representations are presented in Figure 1.



**Figure 1.** Electron micrographs and schematic representation of different CNT composite routes 1.

The first type corresponds to composites where the nanocarbon is used as a filler added to a polymer matrix, the second consists of hierarchical composites with macroscopic fibres and nanocarbon in a polymer, typically thermosetting, matrix; the third type are nanocarbon-based macroscopic fibres which can then be processed to form standard fibre-reinforced polymer composites (FRPC).

One of the most promising routes to exploit the axial properties of CNTs is to assemble them into a macroscopic fibre, with the tubes aligned parallel with the fibre axis; a strategy similar to that proposed eight decades ago for the development of high-performance polymer fibres [ 2]. Carbon nanotube fibres can be produced by drawing from an array of vertically aligned CNTs [ 3]; by wet-spinning from a liquid crystalline suspension of CNTs [ 4]; 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) [ 5], the process used in this work.

Considerable attention has been devoted to optimising the structure of CNT fibres at the different stages of their production: controlling the synthesis of specific nanotubes [ 6], the assembly of CNTs into a fully dense fibre [ 7, 8] and using post-spin treatments to obtain specific properties [ 9]. However, the integration of CNT fibres into composites and the properties of these composites have received comparatively less attention, in spite of these aspects being fundamental for many potential applications of this new high-performance fibre.

## **2 Discussion**

### **2.1 CNT fibre spinning process**

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 [ 10], methane as the carbon source [ 11] and hydrogen as carrier gas. As the CNTs grow in the gas-phase they entangle due to their high aspect ratio (around 105) and the action of van der Waals forces, forming an elastic smoke, termed aerogel, which can be drawn out of the reactor continuously as a [ 5]. This diaphanous CNT material can be wound as film or densified on-line by exposure to atomised liquid to form a fibre [ 7].

This spinning process is radically different from most fibre spinning methods in that it covers both the synthesis of the building blocks and their assembly into a fibre; polymer fibres typically require production of the polymer and then fibre spinning at a separate stage. Besides any possible cost benefits from having a one stage process, another implication is that the fibre 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. Up to date, the maximum spinning rates achieved in the laboratory are around 100m/min. Another interesting feature of this process is the possibility of using methane or natural gas as carbon sources for the CNT high-performance fibre.

### **2.2 CNT fibre properties**

The current combination of properties of CNT fibres produced by the direct spinning method makes them outperform traditional high-performance fibres which have been optimised mostly for mechanical performance. Table 1 presents a comparison of CNT fibres with Kevlar 49 and AS4 carbon fibre (CF), two of the most important high-performance fibres at present. The table shows a CNT fibre 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 fibres are highly flexible and can be manipulated like a textile yarn [12]. Moreover, these properties are still under improvement by structural optimisation of the fibre and spinning process for mechanical [11] and electrical [13] performance.

Table I Composition and longitudinal properties of CNT fibres, Kevlar and AS4 CF.						
Fibre 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 fibre [b] (direct spinning)	1.5 [14]	100 [7]	0.6 [15]	$9.7 \times 10^4$ [16]	45 [17]	1.0
Kevlar 49 [c]	2.3	112	0.25	-	-	1.44
Carbon fibre AS4 [c]	2	230	0.78	$5.9 \times 10^4$	6.8	1.79

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

In addition to an outstanding combination of properties, CNT fibres have a unique structure. Unlike traditional fibres, which are 'solid', CNT fibres have a porous yarn-like structure, such as cotton or wool, but with the subfilaments being the nanotube bundles (Figure 2) [12].

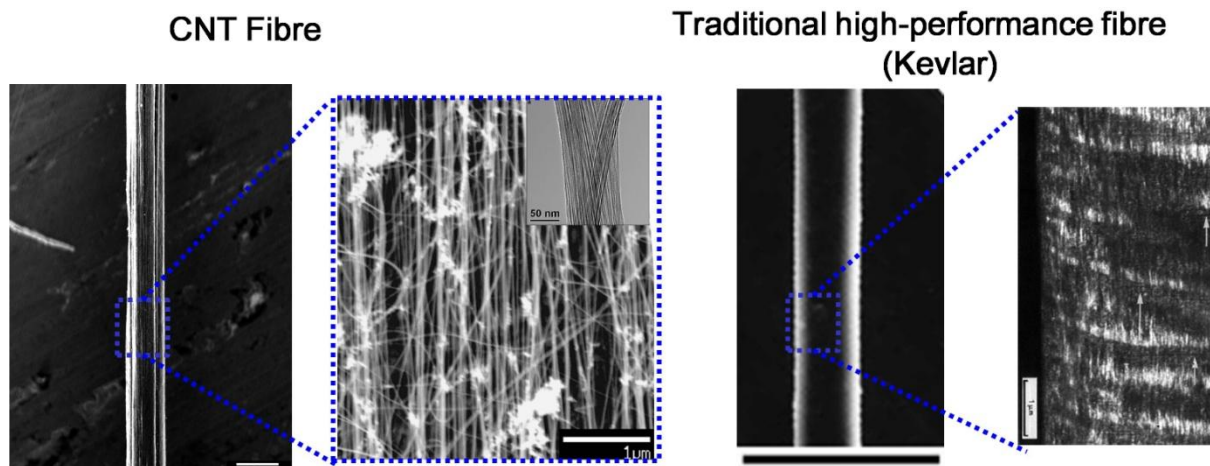
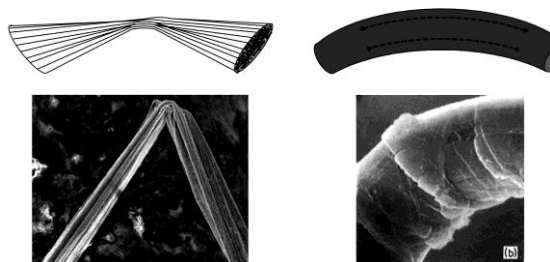


Figure 2. Scanning electron micrograph of a CNT fibre (left) and a higher magnification image (right) showing its yarn-like structure [18].

As a consequence of this yarn-like structure the CNT fibre has a high tolerance to bending and resilience to stresses perpendicular to the fibre axis. Its knot strength efficiency, which corresponds to the ratio of strength of a fibre with an overhand knot by the strength of the unknotted fibre, expressed as a percentage, is close to 100% [12]. Cotton, wool and other staple fibres have similar knot strength efficiencies; however, their tensile properties are in the low performance range. High performance fibres, on the other hand, have low knot efficiencies, with CF at 1% and aramid fibres around 15%.

In a yarn the relevant diameter determining the fibre's flexural properties is that of its fibrous subunits, which for CNT fibres is several orders of magnitude smaller than that of the fibre itself. 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 fibre are decreased by minimising the distance to the neutral plane. This difference in bending behaviour is schematically illustrated in Figure 3.

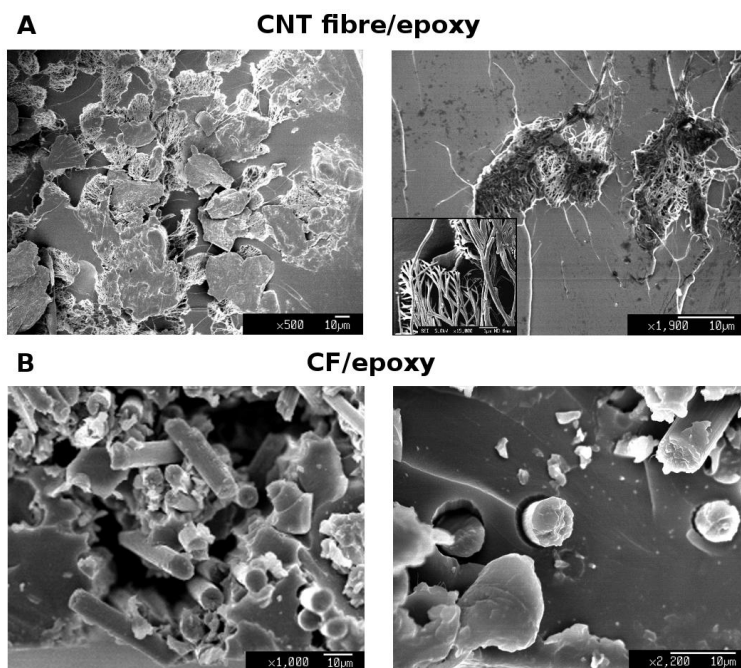


**Figure 3.** Cross-sectional change in CNT fibre with yarn-like structure (left) contrasted against ‘solid’ aramid fibre with evidence of kink damage due to compressive stresses due to bending (right) 18.

These results evidence CNT fibres’ tolerance to bending due to their hierarchically fibrous structure and therefore, point to their potential integration in complex composite shapes without a deleterious effect on its mechanical performance.

### 2.3 CNT fibre composites

The relatively open of CNT fibres means that their specific surface area is about three orders of magnitude greater than that of a traditional reinforcing fibre (200 m<sup>2</sup>/g and 0.2 m<sup>2</sup>/g, respectively). The high internal surface area of the fibres is readily accessible to polymer molecules which can infiltrate it due to capillary forces arising from the porous structure of the fibre and without the need to apply any external pressure [ 17]. Figure 6 presents an SEM micrograph example of a fibre in an epoxy matrix showing exceptional wetting by the thermoset. This infiltration mechanism, and in general the high fibre-matrix interface, provide excellent adhesion to polymer matrices when the fibre is embedded in a composite, without the need for a sizing or post-spin treatment on the fibre. 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 [ 15]. The integration of CNT fibres in polymer matrices also results in composites with high electrical (4x10<sup>3</sup> S/m) and thermal conductivity (30 W/mK), and a low coefficient of thermal expansion (~ 0) [ 17].



**Figure 4.** SEM micrographs of fracture surfaces (A) of CNT fibre/epoxy composite and (B) of a CF/epoxy composite. The high surface area of the CNT fibres results in much better wetting of epoxy, compared to the CF. The higher magnification image of the fractured CNT composite fibre (inset on top right micrograph) shows the fibre subunits, the nanotube bundles, coated with a layer of thermoset 17.

The indication so far is that the properties of the CNT fibres can be efficiently and easily exploited in polymer matrices. At high volume fractions (> 5%) the reports show composite tensile strengths around 250MPa, modulus of 19 GPa, compressive yield strength around 120MPa, and compressive modulus around 10 GPa. Most of these properties are not far off a *pro rata* relation with fibre volume fraction 15. Similarly, electrical and thermal conductivities in multiple-fibre composites as high as  $5 \times 10^3$  S/m and 30 W/mK, respectively, have been reported 17.

### 3 Conclusions

Thanks to their combination of mechanical, electrical and thermal properties, and large specific surface area, CNT fibres represent an attractive material for novel multifunctional composites. Large scale production of CNT fibres envisaged for the next couple of years will enable the development of these composite on the scale of laminate or other large FRP composite structures.

CNT fibre spinning appears to be comparatively less energy intensive than CF production, and if this is demonstrated after scale-up, CNT fibres might be positioned as a greener and cheaper alternative to CF for several applications. This spinning methods a clear example of a bottom-up process. It enables tailoring the material at different scales and therefore provides the possibility of engineering new fibres for a wide variety of applications.

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