Institution:	**UNIVERSITY OF CAMBRIDGE**
Unit of Assessment:	**B13** Electrical and Electronic Engineering, **Metallurgy and Materials**
Title of case study:	**Carbon nanotubes and carbon nanofibres**

1. Summary of the impact

Viewing carbon nanotubes (CNTs) as very rigid polymer molecules led to research on turning them into useful materials. Strategic investments to develop different aspects of this research have been made by two separate companies. A process for the synthesis of CNTs was transferred to *Thomas Swan Ltd* who have made significant investment, and are now Europe's leading supplier of high-quality CNTs. In 2003 a process was invented to spin CNT fibres directly from a synthesis reactor. The process is intrinsically cheaper than the conventional process for carbon fibre and it produces a tougher and more versatile product. The University of Cambridge (**UCAM**) spin-out company *Q-Flo Ltd* (created in 2004 to achieve focus on transfer of this technology) and *Plasan* (multinational manufacturer of vehicle defensive armour) formed a joint venture in 2010 which has enabled the first-stage scale-up of manufacture.

2. Underpinning research

Alan Windle (Professor of Materials Science, Dept of Materials Science & Metallurgy, UCAM, 1992 to date) has led the research on carbon nanotubes (CNTs) and CNT fibres. His polymer-science research spanned from flexible polymers (e.g. polyethylene) through to the most rigid liquid-crystalline polymers. He perceived CNTs as the ultimate rigid polymer molecule, fuelling new ideas for their processing into useful materials such as fibres. Windle's group undertook some of the first work on CNT composites, studying their liquid suspensions, and measuring the influence of entanglements on properties. Work with Shaffer (PDRA, left 2006, now Professor at Imperial) led to several research papers, e.g. [1], and later the first report of liquid crystallinity in CNT suspensions [2].

Research into CNT synthesis led to a patent set which was licensed to *Thomas Swan & Co Ltd*, a specialist chemical manufacturer of Consett, Co Durham, which based a new business on it. Specifically, the problem of catalyst particle-size control was solved by forming from a precursor deposited on a magnesium-oxide substrate, which was removed by dissolution after CNT growth. The products now on sale (see Section 4a) consist of highly characterized single-wall CNTs.

Windle's subsequent research explored much higher synthesis temperatures, up to 1300°C, and moved from substrate to floating catalyst (gaseous suspension) methods. The CNTs form a smoke; their entanglement means the smoke is elastic and can be continuously withdrawn from the reactor as a fibre, as fast as it is produced. Work with two PDRAs, Ian Kinloch (2002-06, now Professor at Manchester) and Ya-Li Li (2001-04), led to a high-profile publication [3] and to a patent, now granted in the US and Korea, with Europe and Japan pending. The invention is essentially an aerogel version of the (liquid) gel-drawing process for making the polyethylene high-tech fibre marketed by DSM as *Dyneema*.

Process development 2004 to 2008, funded by an EPSRC grant (EP/E04218X/1, £890,000, with Windle as PI), included fibre condensation, external reeling, control of injection and process modelling using advanced CFD packages, the latter work in collaboration with UCAM's Dept of Chemical Engineering [4]. This work led to two supporting patents. The grant also involved collaboration with Vicki Stone (Napier University, now Professor of Toxicology and Director of Nano-Safety Research Group, School of Life Sciences, Heriot-Watt University). Thus health issues with the production of CNT materials were addressed as the research developed, not as an afterthought. A collaboration with *US Army Natick Soldier Research Development and Engineering Center* examined the relationship between structure and strength [5]: in short gauge lengths, the fibre had exceptional strength and stiffness [6], clearly exceeding those of conventional high-performance fibres. One sample measured is possibly the strongest fibre ever seen [6].

Since 2008, the research has continued unabated, particularly in process control and in understanding mechanical properties, with a simple model introduced for predicting strength. Unlike conventional carbon fibre, the CNT fibre is exceptionally tough and weavable, largely because it is yarn-like, illustrated particularly by the fibre's ability to take knots without reduction in strength (Fig. 1). A further breakthrough (2011) by Windle's group has been the creation of fibres

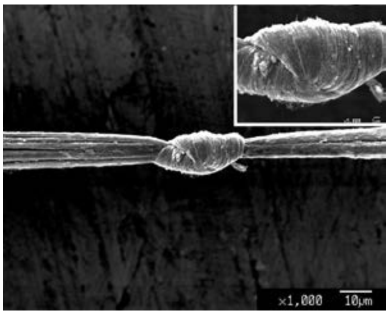

Figure 1. A tight knot in the tough CNT fibre. The knot does not fail prematurely under tension.

containing only single-wall CNTs with chiralities which lead to metallic rather than semiconducting behaviour [7]. This advance stems from recognition that small amounts of sulfur added to the process to promote CNT detachment from the floating catalyst particles are also effective in limiting the growth of these particles by collision, so they can be kept to sizes of order 1 nm until the carbon necessary for CNT growth becomes available. The reason for the very useful selectivity for tubes of metallic chirality is not yet completely understood and work in collaboration with the global modelling community is addressing this key issue. Work towards composites has shown that when the fibres are embedded in a resin matrix, the resin infiltrates the fibre, giving excellent keying and thus interfacial shear strength on curing.

The major commercial investment now occurring reflects the vision that CNT fibre of this kind might replace carbon fibre in the structural domain, and replace copper for electrical conductors, while being less expensive on both counts.

3. References to the research

1. MSP Shaffer & AH Windle: Fabrication and characterization of carbon nanotube/poly(vinyl alcohol) composites, *Advanced Materials* **11** (1999) 937; DOI: 10.1002/(SICI)1521-4095(199908)

2*****. W Song, IA Kinloch & AH Windle: Nematic liquid crystallinity of multi-wall carbon nanotubes, *Science* **302** (2003) 1363; DOI: 10.1126/science.1089764

3*****. Y-L Li, IA Kinloch & AH Windle: Direct spinning of carbon nanotube fibers from chemical vapor deposition synthesis, *Science* **304** (2004) 276; DOI: 10.1126/*science*.1094982

4. D Conroy, A Moisala, S Cardoso, AH Windle & J Davidson: Carbon nanotube reactor: Ferrocene decomposition, iron particle growth, nanotube aggregation and scale-up, *Chemical Engineering Science* **65** (2010) 2965; DOI: 10.1016/j.ces.2010.01.019

5. JJ Vilatela & AH Windle: Yarn-like carbon nanotube fibers, *Advanced Materials* **22** (2010) 4959; DOI: 10.1002/adma.201002131

6*****. KKK Koziol, JJ Vilatela, A Moisala, MS Motta, P Cunniff, M Sennett & AH Windle: High-performance carbon nanotube fiber, *Science* **318** (2007) 1892; DOI: 10.1126/science.1147635

7. RM Sundaram, KKK Koziol & AH Windle: Continuous direct spinning of fibers of single-walled carbon nanotubes with metallic chirality, *Advanced Materials* **23** (2011) 5064; DOI: 10.1002/adma.201102754

*****<u>references best indicating the quality of the underpinning research</u>. (All 7 papers are in journals subjected to rigorous peer review and, as of October 2013 they had attracted, in total, more than 1600 citations.)

Aspects of the work have frequently been presented as Plenary Lectures by Windle, the most recent being at the *Polymer Processing Society Meeting* at Nuremberg, July 2013. The spinning process and its potential in different applications have featured in several TV programmes; in particular, the potential of the fibre for making the space-elevator cable was the closing feature of the *Royal Institution Christmas Lectures* by Mark Miodownik, broadcast on BBC1 in 2010.

4. Details of the impact

(a) Technology transfer to *Thomas Swan & Co Ltd*

Windle's underpinning research, involving modification to synthesis routes, was vital in that it overcame existing problems with scale-up, where the planar substrate carpet process was ineffective. Windle's work led to higher-temperature synthesis routes, the use of powdered substrates as a catalyst bearer, and the production of the transition-metal catalysts in-situ from the thermal decomposition of their salts. During the REF impact period, following UCAM's transfer of IP to *Thomas Swan*, the company sells worldwide and has become Europe's leading manufacturer of single-wall CNTs, specializing in high-quality, mainly single-wall material (the *Elicarb*® CNT

Figure 2. Carbon nanotube product from the Thomas Swan *Elicarb®* range.

product range, Fig. 2), in particular for the energy-storage and advanced-electronics sectors. The patent licensing and transfer of research outputs to *Thomas Swan* led to a strategic shift for the company to set up their Advanced Materials Division. [text removed for publication]

. User companies have benefited from a supply of materials with consistent and reproducible properties as a result of *Thomas Swan*'s development of the technology during these early stages of adoption of CNT technologies by industry. [text removed for publication]

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(b) The fibre invention and technology transfer

Windle's research which led to the new process for spinning fibre, consisting wholly of CNTs, directly from the CVD reactor zone has resulted in three patents licensed so far (PCT/GB04/002969, PCT/GB2008/001473, PCT/GB2011/050798) with others more recently filed. The head patent, which describes the new process, was invented by Windle, Kinloch and Li (then all at DMSM). The fourth inventor was Mr S Cash, a visitor from the sponsor *Thomas Swan* present at the brainstorming session which created the new idea.

The mechanism of technology transfer has been through a spin-out company *Q-Flo Ltd*. Windle is both a Founder and a Director, and UCAM is a significant share-holder. The role of this company is to market the IP worldwide with the objective of establishing an international business to manufacture and exploit the radically new type of carbon fibre. UCAM, as owner of the patents, has licensed these to *Q-Flo*, which has achieved its first major success through partnership with *Plasan Ltd* to form a joint-venture company, *TorTech Nano Fiber Ltd*. Plasan is an Israel-based company making protective armour, with plants in the US and in France. *TorTech* was created in 2010 to develop, manufacture and scale-up the process to the point where as a disruptive technology it can challenge the existing world leaders: carbon, aramid (*Kevlar*) and UHMW polyethylene (*Dyneema*). Not limiting its interests to the mechanical properties of the fibre, *TorTech* is trying to develop the fibre for electrical conductivity as it seeks a product that will replace copper and aluminium in electrical cables and wires. A parallel study has shown equal promise for the fibre's thermal conductivity which, measured to be greater than 1200 W/m.K, is far beyond silver, especially impressive given the far lower density of the CNT fibre.

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Main types of impact

Economic — Performance of existing business improved through new products & processes (*Thomas Swan*, establishing a new Advanced Materials Division, with new CNT-based product range); Spin-out business created (*Q-Flo*, with joint venture *TorTech*, bringing benefits for businesses and investors); Business sector adopted new or significantly changed technology or process (*Plasan*, through *TorTech* for armour production); Performance improved through highly skilled people taking up specialist roles that draw on their research (eg two members of Windle's group joined the new Advanced Materials Division in *Thomas Swan*: Dr M Motta in 2008 and Dr K Paton in 2010); Licensing income for UCAM.

Public policy & services — Risks to the security of nation states reduced (*Plasan* lightweight CNT-based armour for vehicles, improving safety and performance of security personnel).

Society — Research has contributed to community regeneration (*Thomas Swan* investment, safeguarding and creating jobs in Co Durham).

5. Sources to corroborate the impact

1. Commercial Director, Advanced Materials, *Thomas Swan & Co Ltd* (Claims 1 and 2)
2. CEO, *Q-Flo Ltd* (Claim 3)
3. Head of Physical Sciences, Cambridge Enterprise, UCAM (Claim 4)

Companies (for verification of areas of activity):

Thomas Swan & Co Ltd (http://www.thomas-swan.co.uk/)

Q-Flo Ltd (http://www.q-flo.com/)

Plasan Ltd (http://www.plasansasa.com/)

Patents:

Patents licensed to *Thomas Swan & Co Ltd*

1. US Patent Number 7,135,159, European Patent Number 1390294, and Japanese Patent Number 3930810 (National Phase of PCT/GB02/02239, priority date 15th May 2001)
Title: Synthesis of Nanoscaled Carbon Materials
Inventors: MSP Shaffer, IA Kinloch & AH Windle

2. US Patent Number 8,173,211, European Patent Application Number 03764020.8, and Japanese Patent Number 4703182 (National Phase of PCT/GB03/003086, priority date 17th July 2002)
Title: CVD synthesis of carbon nanotubes
Inventors: MSP Shaffer, AH Windle, BFG Johnson, J Geng, D Shephard & C Singh

3. US Patent number 7,767,615, and European Patent Application Number 03775549.3 (National Phase of PCT/GB03/04925, priority date 13th December 2002)
Title: Method for producing carbon nanotubes and/or nanofibres
Inventors: IA Kinloch, AH Windle, C Singh, MSP Shaffer & KKK Koziol

Patents licensed to *Q-Flo Ltd*

1. US Patent Number 7,323,157, European Patent Application Number 04743311, and Japanese Patent Application Number 2011091872 (National Phase of PCT/GB04/002969, priority date 11th July 2003)
Title: Production of agglomerates from the gas phase
Inventors: IA Kinloch, Y-L Li, AH Windle & SL Cash

2. US Patent Application Number 12/597,837, and European Patent Application Number 08737118 (National Phase of PCT/GB2008/001473, priority date 28th April 2007)
Title: Enhancement of the structure and properties of carbon nanotube fibres and films
Inventors: KKK Koziol, J Vilatela Garcia, AH Windle & M Pick.

3. US Patent Application 13/696,582, and European Patent Application EP117718769.0 (National Phase of PCT/GB2011/050798, priority date 6th May 2010)
Title: Chemical Treatment of Carbon Nanotube Fibres
Inventors: KKK Koziol, AH Windle, S Boncel & R Sundaram