# Investigations into the Potential of Constructing Aligned Carbon Nanotube Composite Materials through Additive Layer Manufacture

Robert J. A. Allen

College of Engineering, Mathematics and Physical Sciences

University of Exeter

A thesis submitted for the degree of

*Doctor of Philosophy*

June 2013

# Investigations into the Potential of Constructing Aligned Carbon Nanotube Composite Materials through Additive Layer Manufacture

Submitted by Robert James Anthony Allen to the University of Exeter

as a thesis for the degree of

Doctor of Philosophy in Engineering

In June 2013



I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

Signature: …………………………………………………………..

## Acknowledgements:

The undertaking of the works contained in this thesis has been a privilege and a pleasure and I am extremely grateful to all who have made this possible. It is only through the help of many people that this thesis has come to completion and although clearly not extensive the following provides a list of those who have extended significant and invaluable aid over the past three years:

- Firstly I would like to thank the late Prof. Alexander Savchenko, his excellent tuition was invaluable during the final years of my undergraduate studies and without his guidance and belief it is unlikely that I would have chosen to pursue the course of this PhD.

- I extend many thanks to my supervisors, Prof. Kenneth Evans, Dr Oana Ghita, Dr Benjamin Farmer, and Dr Mark Beard who have all provided extensive assistance and support throughout.

- Much gratitude is given to the Engineering and Physical Sciences Research Council (EPSRC) and EADS Innovation Works for providing the financial support necessary to undertake these investigations.

- Much credit is owed to the Engineering Workshop and its Staff, in particular Pete Gerry, Martin Simpson, Roger Perret, and Dave Baker. Their help in producing custom equipment has been crucial.

- Thanks to the Engineering Instrument Pool (EIP) for the loan of a high speed camera to conduct the experiments detailed in **Chapter 6**.

- Thanks as well to the many staff and students at the university who have made the last few years so enjoyable, Thanks to: Lesley Wears, Tom Hughes, Will Newby, Nunzio Palumbo, Chris Taylor, David Barnes, Wayne Miller, Stephen Mellor, Mathew Johns, Marc-Antoine Boucher, Giovani Stranno, Asmi Rizvi, Pierre Aumjaud, Paul BrookBank, Monica Craciun, Yat-Tarng Shyng, Linda Urlu and Pete Jerrard.

- Thanks to my friends for being so adventurous, and providing relief from my studies by exploring everywhere from Lands' End to the French Alps, Thanks to: Freddie Withers, Tom Bointon, Edward Halliday, Lucy Sainsbury, Ellis Woods, Lucy Halliday, Tom Bonning-Snook, Greg Simpson, Jim Hirst, Tom Bailey, Ben Goddard, Chris White, Nathan Shumoogum, and Jack Dyer to name but a few.

- Extended thanks to all of my family who have always been invaluably supportive in many different ways throughout my studies to date.

- Finally, Many many thanks to my partner Laura Taylor for all her support throughout these past few years.

## Publications:

[1] **R. J. Allen**, O. Ghita, B. Farmer, M. Beard, and K. E. Evans, 'Mechanical testing and modelling of a vertically aligned carbon nanotube composite structure', *Compos. Sci. Technol.*, vol. 77, pp. 1–7, Mar. 2013.

[2] **R. J. Allen**, O. R. Ghita, B. L. Farmer, M. A. Beard, and K. E. Evans, 'Wetting Mechanisms of Vertically Aligned Carbon Nanotube (VACNT) Composite Structures in readiness for Additive Layer Manufacture', *15th Eur. Conf. Compos. Mater. ECCM15*, June 2012

[3] B. L. Farmer, **R. J. Allen**, O. R. Ghita, M. A. Beard, and K. E. Evans, 'Strategies to combine nanocomposite and additive layer manufacturing techniques to build materials and structures simultaneously', *15th Eur. Conf. Compos. Mater. ECCM15*, June 2012

[4] B. L. Farmer, M. A. Beard, O. Ghita, **R. J. Allen**, and K. E. Evans, 'Assembly Strategies for Fully Aligned and Dispersed Morphology Controlled Carbon Nanotube Reinforced Composites Grown in Net-Shape', *MRS Online Proc. Libr.*, vol. 1304, 2011.

# Investigations into the Potential of Constructing Aligned Carbon Nanotube Composite Materials through Additive Layer Manufacture

## Abstract

Since their discovery Carbon Nanotubes (CNTs) have attracted much interest from many fields of the scientific community owing to their range of unique and impressive properties. Measurements of the mechanical properties of these nanoscale molecules have shown strengths up to five times greater than that of steel at only a quarter of the density. Consequently many have attempted to unlock these remarkable properties by creating nano-composite structures where CNTs effectively reinforce materials with little increase in density. Unfortunately the tendency of CNTs to form agglomerations when allowed to disperse in fluid suspensions has made this process non trivial, and led to difficulties in achieving effective reinforcement when simply mixing CNTs into a matrix material. As a result it has become clear that new approaches to composite construction will be required if effective composite reinforcement using CNTs is to be achieved.

Recent advances in CNT synthesis using Chemical Vapour Deposition (CVD) where tall forests of these nanoparticles are grown from the vapour phase have begun to solve the agglomeration problem. These forests are produced in aligned and dispersed arrays, and wetting of these structures with polymer matrices has demonstrated improvements in modulus of several hundred percent. These improvements arise as the CNTs retain both the dispersion and alignment of the forest when incorporated into the matrix thus overcoming the difficulties observed using traditional manufacture methods. New complications arise when attempting to extend these promising results to larger scale composite components owing to the typically millimetre size of CVD grown vertically aligned CNT (VACNT) forests. From these results it follows that to create large composite parts it will be required to incorporate many individually CVD grown VACNT forests into a single composite structure.

Strategies to achieve such a composite are being developed, with a range of ideas extending from knowledge gained from the emerging technology of additive manufacture (AM) described as '...the process of joining materials to make objects from 3D model data, usually layer upon layer....'. Indeed it is desirable to reinforce materials used in AM processes and the nano scale diameter of CNTs makes them the perfect choice owing to their high aspect ratios at the micron scale. In this thesis

investigations are conducted into the feasibility of manufacturing CNT composite structures using CVD grown forests and AM techniques. These investigations include measurement of the anisotropic mechanical properties of composite samples, and studies of the wetting interactions that occur between CNT forests and polymer materials. Composite samples are constructed and tested mechanically in the transverse orientation and results compared to traditional fibre composite reinforcement models in order to understand the material properties that can be expected if such an AM process is achieved. Results show greater mechanical improvements in transverse modulus than expected, and these results are attributed to the wavy nature of individual CNTs within forest structures providing multi directional reinforcement to the matrix material. Further studies are conducted to investigate the flow of molten thermoplastic materials into CNT forest structures under capillary driven flow. Thermoplastics were allowed to flow into VACNT forests before being cooled and inspected using micro x-ray computed topography (μ-CT) to gain an understanding of the wetting mechanism. Results from μ-CT scans show that the polymer flows into the structure in peaks of similar radius. Finally dynamic investigations were conducted into the fast capillary driven flow of a low viscosity thermoset resin into VACNT forests using a high speed camera. Results are fitted to traditional models for dynamic capillary driven flow in porous media and an effective radius and porosity is calculated for VACNT forests. Experimental values illustrate that these nanoscale structures still fit to traditional flow models of fluids where the height of capillary rise is proportional to the square of the elapsed time. These results provide a further step in understanding methods of incorporating many VACNT structures into polymeric matrices to achieve large scale effective polymer VACNT composite materials.

# Contents