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

Acknowledgements 5

Publications 7

Abstract 9

Contents 11

List of Figures 15

List of Tables 22

1 Introduction, Motivation, and Outline 23
- 1.1 Introduction 23
- 1.2 Key Historical Events and Motivation 25
- 1.3 Thesis Outline 27

2 Introduction to Carbon Nanotube Science, Carbon Nanotube Composites and Polymer Composite Additive Manufacture Processes 31
- 2.1 Introduction 31
- 2.2 Carbon Nanotube Science 31
  - 2.2.1 Introduction. 31
  - 2.2.2 Carbon Nanotube Science 32
  - 2.2.3 Mechanical Properties 34
  - 2.2.4 Thermal Properties 36
  - 2.2.5 Electrical Properties 36
  - 2.2.6 Characterisation of CNT 38
  - 2.2.7 Functionalisation of CNT 39
- 2.3 Synthesis of CNTs 40
  - 2.3.1 Background 40
  - 2.3.2 Arc Discharge CNT Synthesis 40
  - 2.3.3 Laser Ablation CNT Synthesis 42
  - 2.3.4 Chemical Vapour Deposition CNT Synthesis 43
  - 2.3.5 Solar Energy CNT Synthesis 47
  - 2.3.6 Electrolysis CNT Synthesis 48
  - 2.3.7 Flame CNT Synthesis 48
  - 2.3.8 Bulk Polymer CNT Synthesis 48
- 2.4 CNT Composites 49
  - 2.4.1 Background 49
  - 2.4.2 Dispersion of CNTs in a Matrix. 49
  - 2.4.3 Polymer-CNT Composites. 51
  - 2.4.4 Polymer Matrix-CNT Interactions 56
  - 2.4.5 Mechanical Testing of CNT-Polymer Composites 57
- 2.5 Additive Manufacturing of Polymer Composite Materials 58
  - 2.5.1 Introduction to Additive Manufacturing 58
  - 2.5.2 Selective Laser Sintering 59
  - 2.5.3 Laser Engineered Net Shaping 60
  - 2.5.4 Three Dimensional Printing 60

2.5.5 Stereo Lithography 61
2.5.6 Laminated Object Manufacture 62
2.5.7 Fused Deposition Modelling 62
2.5.8 Nanocomposites 63
2.5.9 Conclusions 64
2.6 Strategies to Assemble Carbon Nanotube Composite Structures with Controlled Morphology through Additive Manufacture Methodologies 65
2.6.1 Introduction 65
2.6.2 CNT composite Additive Manufacture Approaches 68
2.6.2.1 Filled Polymer Sintering Approach. 69
2.6.2.2 In-Situ CNT Introduction Approach 71
2.6.2.2.1 In-Situ CNT Growth 71
2.6.2.2.2 Detached Ex-Situ CNT Growth 73
2.6.3 VACNT Forest Patterning and Net Shape 82
2.6.4 Summary 83

3 Synthesis of Vertically Aligned Carbon Nanotubes using the Sabretube Chemical Vapour Deposition System 85
3.1 Introduction 85
3.2 Production of Catalysts for use in 'Sabretube' CVD Processes 86
3.3 CVD Growth of VACNT Structures using the Sabretube System 89
3.3.1 The Sabretube Chemical Vapour Deposition System 90
3.3.1.1 The Pre-Heater System 90
3.3.1.2 CVD Chamber and Suspended Silicon Heating Platform. 91
3.3.1.3 Mass Flow Controllers and LabView Software 93
3.3.2 Typical VACNT Synthesis Process using the Sabretube 94
3.3.3 Growth Mechanics of VACNT produced using CVD 97
3.3.4 Examples of VACNT Forests Produced using the Sabretube System 101

4 Fabrication, Modelling and Mechanical Analysis of a Vertically Aligned Carbon Nanotube Composite Structure 113
4.1 Introduction 113
4.2 Fabrication of Large Millimetre Scale VACNT Composite Structures for Mechanical Analysis. 114
4.2.1 Fabrication Materials 114
4.2.2 Resin Infiltration of VACNT Forests 116
4.2.3 Curing of VACNT Composite Samples 118
4.2.4 Machining of VACNT Composite Samples 119
4.3 Mechanical Analysis of Large Millimetre Scale VACNT Composite Structures 122
4.3.1 Dynamic Mechanical Thermal Analysis: Experimental Techniques 122
4.3.2 Dynamic Mechanical Thermal Analysis: Results. 123
4.3.3 Micro Tensile Testing: Experimental Techniques 125
4.3.4 Micro Tensile Testing: Results 126
4.3.5 Thermo Gravimetric Analysis: Experimental Techniques 127
4.3.6 Thermo Gravimetric Analysis: Results 128
4.4 Modelling of a VACNT Composite Material 131
4.4.1 Modelling a VACNT Composite Material using Uniaxially Aligned Fibre Models 131
4.4.2 Modelling a VACNT Composite Material with Wavy Fibre Models 134
4.5 Discussions and Conclusions 139

5 Investigations into the wetting mechanisms of vertically aligned CNT structures **143**
5.1 Introduction 143
5.2 Static Capillary Rise in VACNT Forest Structures 144
5.3 Simple Dynamic Capillary Rise in Capillary Tubes 154
5.4 Application of Simple Dynamic Capillary Rise to VACNT Structures 156
5.5 Experimental Investigations into VACNT Forest Wetting Mechanisms 158
5.6 Experimental investigations into VACNT forest wetting mechanisms with EVA 40wt% 163
5.7 Experimental confirmation of early stage capillary rise in VACNT structures during capillary driven wetting using μ-CT analysis. 171
5.8 Conclusions. 174

6 Experimental Investigations and Modelling of Dynamic Capillary Driven Wetting in VACNT Forest Structures **175**
6.1 Introduction 175
6.2 Experimental Investigations into Dynamic Capillary flows in VACNT Forest Structures 176
6.2.1 Materials 176
6.2.2 Measurement of the Fluid Surface Tension of the LY3505/XB3403 Resin system 177
6.2.3 Details of the PHOTRON Fastcam XLR Hi-speed Camera System 179
6.2.4 Monitoring of Dynamic Capillary Rise using the PHOTRON Fastcam XLR Hi-speed Camera System. 180
6.3 Modelling of Dynamic Capillary Rise in VACNT Forest Structures 184
6.3.1 Simple Capillary Rise Phenomenon in VACNT Forest Structures 185
6.3.2 Modelling of Dynamic Capillary Rise in Porous Media and Structures. 185
6.4 Analysis of Experimental Video Data 187
6.5 Fitting Experimental Data to the Porous Lucas-Washburn Model 190
6.6 Conclusions 193

7 Conclusions **197**
7.1 Conclusions 197
7.2 Key Questions and Further Work 201
7.3 Feasibility of an industrial approach to multi layer VACNT composites through ALM 202

References 205