Plasma Functionalization of Nanotubes and Carbon Fibres for Application in Composites

by

Zhiqiang Chen
(M. Eng)

Submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Deakin University
December, 2012
I am the author of the thesis entitled

Plasma Functionalization of Nanotubes and Carbon Fibres for Application in Composites

submitted for the degree of Doctor of Philosophy

This thesis may be made available for consultation, loan and limited copying in accordance with the Copyright Act 1968.

'I certify that I am the student named below and that the information provided in the form is correct'

Full Name: ..................................Zhiqiang Chen..............................................................

Signed: .......................................................... ..............................................................

Date: ........................................................ 13/05/2013 ..............................................................
DEAKIN UNIVERSITY

CANDIDATE DECLARATION

I certify that the thesis entitled *Plasma Functionalization of Nanotubes and Carbon Fibres for Application in Composites*

submitted for the degree of *Doctor of Philosophy*

is the result of my own work and that where reference is made to the work of others, due acknowledgment is given.

I also certify that any material in the thesis which has been accepted for a degree or diploma by any university or institution is identified in the text.

Full Name: ...................... Zhiqiang Chen .................................

Signed: ...................... .................................

Date: .................................
Acknowledgments

I would like to take this opportunity to express my sincerest gratitude to my supervisors, Professor Xungai Wang and Dr. Xiujuan J Dai. I am grateful to Professor Wang for offering me the opportunity to pursue my PhD degree in Deakin University and for his endless support and guidance throughout the course of this work. I wish specially to thank Dr. Dai for her valuable guidance, encouragement and caring throughout these years. Her extensive knowledge in the field of plasmas has given me a valuable insight into plasma treatment, for which I am extremely thankful. I have greatly benefited from the research training and methodology for approaching research challenges which Dr. Dai imparted to me. I also thank her for providing an excellent research team-work environment. Her lofty character has set a good example for me to follow in scientific research.

I would particularly like to thank to Dr. Peter Lamb for his valuable advice and discussions as well as for helping with my written English. I also have benefited from his strong logical thinking. I would also like to thank to Dr. Kevin Magniez and Associate Professor Bronwyn Fox for their expert guidance on composites and valuable discussions.

I express thanks to Dr. Luhua Li for kindly providing boron nitrogen nanotubes for this work as well as assisting on some of the AFM measurements. I wish to thank Dr. Abdullah Kafi for kindly providing carbon fibres for this project and helping to perform the analysis of surface wettability. Thanks also to Dr. Jenny Bungur for advice on nanocomposites and to Dr. Bin Tang for providing the chemical polyvinylpyrrolidone.
I would like to thank the plasma group at Deakin University for their support and care. Special thanks to David Rubin de Celis Leal for assisting me on some of the AFM measurements.

I wish to thank Marion Wright, Dr. Andrew Sullivan, Rob Pow, August Deveth and Patrick Brisbane for their great technical support. A huge thank you to Robert Lovett and Ladge Kviz (from CSIRO Material Science and Engineering, Geelong) for the enthusiastic help they have given me.

I would like to acknowledge assistance for XPS measurement and analysis from Dr. Dai and Associate Professor Johan du Plessis (from RMIT University). I would also thank Dr. Matthew Field and Dr. Peng from RMIT University for conducting TEM, and RMIT University for access to their XPS and TEM facilities. I would also like to thank to Deakin University International Research Scholarships for financial support.

During these years, the support of my friends has been extremely valuable. I express my wholehearted special thanks to Jinfeng Wang, Qingtao Liu, Yaqiong Zhou, Zhenyu Li, Hali Li and Ailan Wan for their kindness, understanding and support, and for the delicious food they have cooked for me. I would like to express my deep gratitude to Kindness groups from Geelong Chinese Church for their great support and caring. Special thanks to my old friends in China, Botong Si, Qiang Lu, Jingjing Nie and Puyang Wang for their comfort and support.

Last but not least, I would like to extend special appreciation to my parents and my sisters for their endless support and love. Without them none of this would have been possible.

Thanks to God.
Publications

Journals


Conferences


List of Figures

Figure 2.1 The bicyclic step growth polymerization mechanism .........................10
Figure 2.2 Schematic showing the typical constituents present in a pulsed plasma. ..........................................................12
Figure 2.3 The CW + P plasma polymerization .................................................13
Figure 2.4 Covalent Functionalization of SWCNTs. (a) Direct covalent
functionalization; (b) covalent chemistry at defects or open ends .................16
Figure 2.5 Direct covalent functionalization of CNTs through nucleophilic
substitution reactions in fluorinated nanotubes ..............................................17
Figure 2.6 Defect functionalization of CNTs ....................................................18
Figure 2.7 Covalent primary amine-functionalized SWCNTs: via Hofmann
rearrangement of carboxylic acid amide (Pathway A); via Curtius reaction of
carboxylic acid chloride with sodium azide (Pathway B). ..............................20
Figure 2.8 Different types of non-covalent functionalization of CNTs: (a)
molecular surfactant adsorbed around nanotube; (b) polymer wrapping around
nanotube, (c) endohedral functionalization with, for example, C60 ...............22
Figure 2.9 Plasma approaches used to create amine groups on CNT surfaces. ....28
Figure 2.10 Functionalization MWCNTs by plasma-induced grafting
polymerization for preparation of epoxy composites ......................................32
Figure 2.11 The reaction between primary amine functionalized CNTs and an
epoxy resin ........................................................................................................34

Figure 3.1 Chemical structure of Epon 862 Epoxy resin ....................................48
Figure 3.2 Schematic diagram of the plasma polymerization system ..................49
Figure 3.3 Schematic diagram of the stirring plasma system ...............................50
Figure 3.4 Schematic diagram of chemical derivatization by TFBA of primary amine groups. .................................................................54

Figure 3.5 A Cypher AFM. .................................................................57

Figure 3.6 Demonstration of the masking technique for measuring the thickness of the plasma polymer using AFM. ..................................................58

Figure 3.7 Three-point bending test geometry (load P, thickness h, span length L). ...........................................................................60

Figure 3.8 A schematic of the load-displacement curve. ......................61

Figure 3.9 A magazine loaded with CFs. .............................................62

Figure 4.1 XPS high resolution C1s and survey spectra of MWCNTs: (a, b) untreated; (c, d) N2/H2 CW + P plasma modification. ...................67

Figure 4.2 XPS survey spectrum of N2/H2 CW + P-MWCNTs..................68

Figure 4.3 (a) The NH2/C and N/C ratios and (b) the NH2 /N ratios at the surface of N2 /H2 plasma treated MWCNTs using three plasma modes. ...............68

Figure 4.4 The proposed reaction mechanism of N2/H2 plasma treatment for MWCNTs. .............................................................................69

Figure 4.5 TEM and SEM images of MWCNTs before (a) and after (b) N2/H2 CW plasma treatment. The insets show electron diffraction patterns from MWCNT clusters in a nearby region. .....................................................74

Figure 4.6 AFM images of MWCNTs observed in a same spot before (a) and after (b) N2/H2 CW plasma treatment. ........................................75

Figure 4.7 (a) XRD profiles of MWCNTs before and after the plasma treatments, (b) TGA (weight loss vs. temperature) and (c) DSC profiles of untreated MWCNTs and N2/H2 plasma treated MWCNTs........................................76
Figure 4.8 XPS high resolution C1s (a) and survey spectra (b) of MWCNTs after HA CW + P plasma polymerization. ................................................................. 79
Figure 4.9 (a) XPS survey spectra after derivatization with TFBA for MWCNTs after HA CW + P plasma polymerization; (b) the NH_2/C and N/C ratios and (c) the NH_2/N ratios at the surface of HA plasma polymerized MWCNTs using three plasma modes. ......................................................................................... 80
Figure 4.10 SEM (a) and TEM (b) images of MWCNTs after HA CW + P plasma polymerization, (c) XRD profiles of MWCNTs. .............................................. 82
Figure 4.11 The ratios of N/C and O/C from XPS of MWCNTs under different plasma conditions. ......................................................................................... 84
Figure 4.12 XPS high resolution C1s spectra for MWCNT samples: (a) HAPP1-750 MWCNTs; (b) HAPP2-750 MWCNTs ....................................................... 84
Figure 4.13 FTIR spectra for HAPP2-750 MWCNTs and HA. ............................ 85
Figure 4.14 (a) TGA and (b) DSC profiles of u-MWCNTs and HAPMWCNTs. ............................................................................................................. 86
Figure 4.15 SEM image of MWCNTs: (a) HAPP1-750 MWCNTs; (b) HAPP2-750 MWCNTs. .......................................................................................................... 87
Figure 4.16 XPS spectra for the untreated BNNTs: (a) B1s and (b) N1s. .......... 89
Figure 4.17 XPS spectra (a) B1s, (b) N1s, (c) C1s of BNNTs after N_2/H_2 CW plasma treatment ................................................................. 90
Figure 4.18 XPS spectra (a) B1s, (b) N1s, (c) C1s of BNNTs after CW + P N_2/H_2 plasma treatment ................................................................. 91
Figure 4.19 HRTEM images (scale bar, 10 nm) of (a) untreated BNNT; (b) close-up of the wall; (c) N_2/H_2 CW plasma treated BNNT ;(d) close-up of the wall. .... 92
Figure 5.1 Scheme of the preparation of the f-MWCNT/epoxy nanocomposites.

Figure 5.2 Dispersion of MWCNTs (0.2 g/L in ethanol) before (A) and after (B) N\textsubscript{2}/H\textsubscript{2} CW + P plasma treatment; left (0 hour) and right (2 weeks later).

Figure 5.3 DSC curing curves of different Epon 862/Epikure W systems.

Figure 5.4 (a) stress-strain curves of the composites; (b) summary of mechanical properties.

Figure 5.5 SEM images of fractured surfaces of composite samples: (a) neat epoxy, (b) 0.1 wt% u-MWCNT/epoxy and (c) 0.1 wt% f-MWCNT/epoxy; (d) and (e) are enlargements of the regions indicated with white rectangles from (b) and (c) respectively, insets are close-ups of the boxed region.

Figure 5.6 DMA results for neat epoxy and MWCNT reinforced nanocomposites.

Figure 5.7 Representative load–displacement curves of nanoindentations for the epoxy, unmodified MWCNT/epoxy and the plasma modified MWCNT/epoxy composites at maximum loads of (a) 2 mN and (b) 3 mN. Insets are SPM images of the indentation impressions.

Figure 5.8 Typical DSC curves of the epoxy curing reaction: (a) Epon862/Epikure W/u-MWCNTs; (b) Epon862/Epikure W/HAPP-MWCNTs.

Figure 5.9 SEM images of fractured surfaces of u-MWCNT/epoxy nanocomposites: (a) 0.3 wt% u-MWCNT/epoxy, (c) 0.5 wt% u-MWCNT/epoxy; (b) and (d) are enlargements of the regions indicated with red rectangles from (a) and (c) respectively, insets are close-ups of the boxed region.

Figure 5.10 SEM images of fractured surfaces of HAPP-MWCNT/epoxy nanocomposites: (a) 0.1 wt% HAPP-MWCNT/epoxy, (e) 0.5 wt% HAPP-MWCNT/epoxy; (b), (d) and (f) are
enlargements of the regions indicated with red rectangles from (a), (c) and (e), and the insets are close-ups of the boxed region. ................................................ 113

Figure 5.11 DMA results of neat epoxy and their MWCNT reinforced nanocomposites: (a) storage modulus vs. temperature; (b) loss factor vs. temperature. .......................................................... 115

Figure 6.1 The sample holder.............................................................. 119

Figure 6.2 XPS C1s spectra of CFs: (a) u-CFs; (b) Ar-CFs; (c) O2-Ar-CFs; (d) HASS-O2-Ar-CFs. ............................................................................................... 122

Figure 6.3 FTIR spectra for (a) HASS-O2-Ar-CF and (b) HA.................. 124

Figure 6.4 SEM images of CFs: (a) u-CF; (b) Ar-CF; (c) O2-Ar-CF; (d) HASS-O2-Ar-CF; (e) the enlargement of the region indicated by the red rectangle in (d). ............................................................................................................................. 125

Figure 6.5 AFM images of the CF surface: (a) u-CF; (b) Ar-CF; (c) O2-Ar-CF; (d) HASS-O2-Ar-CF. ................................................................................................ 127

Figure 6.6 AFM image of a HA plasma polymer deposited on a Si wafer using CW + P plasma polymerization, the inset is a close-up of the boxed region..... 127

Figure 6.7 (a) AFM image of a HASS step on a Si wafer; (b) an individual scan line. The inset is the three-dimensional AFM image of the HASS step on the Si wafer. ............................................................................................................... 129

Figure 6.8 Weibull plots and linear fits for carbon fibres: (a) u-CF; (b) Ar-CF; (c) O2-Ar-CF; (d) HASS-O2-Ar-CF. .............................................................................. 131

Figure 6.9 SEM images of the fracture cross-section of CFs (a) u-CF; (b) Ar-CF; (c) O2-Ar-CF; (d) HASS-O2-Ar-CF. ................................................................. 134
Figure 6.10 Samples for interfacial tests: (a) micro-debond test, (b) fragmentation test and (c) single fibre pull-out test.
List of Tables

Table 2.1 Some of the processes producing excited species which may occur in plasmas. .......................................................................................................................... 6

Table 2.2 Plasma functionalization of CNTs with amine group. ....................... 24

Table 4.1 The plasma experimental conditions. .................................................. 65

Table 4.2 Contact angle and work of adhesion of CNT thin films measured using three probe liquids (diiodomethane is non-polar; glycerol and ethylene glycol are polar). ................................................................................................................ 71

Table 4.3 Surface energy components of untreated and plasma treated MWCNT thin films determined from a CQC model.................................................... 73

Table 4.4 The plasma conditions of HA plasma polymerization in System 2. ..... 78

Table 4.5 Plasma conditions for treating BNNTs. ............................................. 88

Table 5.1 The onset temperature, peak temperature and heat of curing for Epon 862/Epikure W with and without MWCNTs. .................................................... 97

Table 5.2 The storage modulus and $T_g$ of the neat epoxy with and without the ultrasonication. ................................................................................................. 103

Table 5.3 Summary of nano-mechanical properties........................................ 105

Table 5.4 The onset temperature ($T_o$), peak temperature ($T_p$) and the enthalpy ($\Delta H$) for Epon 862/Epikure W with and without MWCNTs. ....................... 108

Table 5.5 Flexural properties of epoxy nanocomposites.................................. 109

Table 5.6 A comparison between our results and some previous reported results on mechanical properties of chemically functionalized amine-CNT/epoxy nanocomposites. ..................................................................................... 110
Table 5.7 Average glass transition temperature of nanocomposites. ........................... 116

Table 6.1 The plasma parameters. ....................................................................................... 119

Table 6.2 Atomic concentrations of C, O and N on the surface of untreated and treated CFs. ................................................................................................................................. 121

Table 6.3 Binding energy of the C1s components and attribution of the components obtained from peak deconvolutions in Figure 6.2. ................................................................. 123

Table 6.4 Surface roughness of CFs before and after plasma treatment measured by AFM on flattened images of 3 μm × 3 μm. ..................................................................................... 128

Table 6.5 Summary of results from the Weibull model analysis of single fibre tensile tests. ............................................................................................................................................. 131
# Table of Contents

Acknowledgments........................................................................................................... I
Publications................................................................................................................... III
List of Figures ............................................................................................................... V
List of Tables ................................................................................................................ XI
Table of Contents .......................................................................................................... XIII
Abstract ...................................................................................................................... XVII

Chapter 1 Introduction ................................................................................................. 1
  1.1 Research Motivation and Objectives ................................................................. 1
  1.2 Thesis Structure ................................................................................................. 3

Chapter 2 Literature Review ......................................................................................... 5
  2.1 Non-thermal Plasma Technology ...................................................................... 5
  2.2 Plasma Treatment .............................................................................................. 7
    2.2.1 Gas Plasma Treatment ............................................................................... 7
    2.2.2 Plasma Polymerization .............................................................................. 9
  2.3 Surface Functionalization of Carbon Nanotubes and their Epoxy
    Nanocomposites ................................................................................................. 13
    2.3.1 Introduction ............................................................................................ 13
    2.3.2 Functionalization of Carbon Nanotubes ............................................... 15
    2.3.3 Amine-functionalized CNT/Epoxy Nanocomposites ........................... 33
  2.4 Plasma Functionalization of Boron Nitride Nanotubes (BNNTs)............... 37
  2.5 Plasma Surface Modification of Carbon Fibres ............................................. 38
    2.5.1 Introduction ............................................................................................ 38
    2.5.2 Gas plasma modification of CFs ........................................................... 39
Chapter 3 Materials and Methodology ............................................................. 47

3.1 Introduction.................................................................................................. 47
3.2 Materials and Chemicals.............................................................................. 47
3.3 Equipment.................................................................................................... 48
3.4 Processes for the Manufacture of Nanocomposites................................. 50
3.5 Characterization Techniques .................................................................... 51
  3.5.1 X-ray Photoelectron Spectroscopy....................................................... 51
  3.5.2 Fourier Transform Infrared Spectroscopy ............................................. 52
  3.5.3 Contact Angle Measurement................................................................. 52
  3.5.4 Chemical Derivatization ....................................................................... 54
  3.5.5 Scanning Electron Microscopy ............................................................. 55
  3.5.7 Atomic Force Microscopy ................................................................. 56
  3.5.8 X-ray Diffraction................................................................................... 58
  3.5.9 Differential Scanning Calorimetry........................................................ 58
  3.5.10 Thermogravimetric Analysis............................................................... 59
  3.5.11 Dynamic Mechanic Analysis .............................................................. 59
  3.5.12 Three-Point Bending Test ................................................................. 59
  3.5.13 Nanoindentation.................................................................................. 60
  3.5.14 Single Fibre Tensile Test .................................................................... 61

Chapter 4 Plasma Functionalization of Nanotubes ........................................... 63

4.1 N$_2$/H$_2$ Plasma Treatment of CNTs ....................................................... 64
  4.1.1 Experimental......................................................................................... 64
  4.1.2 Results and Discussion........................................................................ 65
4.2 Heptylamine Plasma Polymerization ........................................................... 76
  4.2.1 Experimental ......................................................................................... 76
  4.2.2 Results and discussion for HAPP in System 1 ................................. 78
  4.2.3 Results and discussion for HAPP in System 2 ................................. 82
4.3 Plasma Functionalization of BNNTs ......................................................... 87
  4.3.1 Experimental ......................................................................................... 87
  4.3.2 Results and Discussion ........................................................................ 88
4.4 Summary ...................................................................................................... 92

Chapter 5 Plasma Functionalized Nanotube Reinforced Epoxy Nanocomposites ................................................................................................... 94
  5.1 N₂/H₂ Plasma Treated MWCNT/Epoxy Nanocomposites ..................... 94
    5.1.1 Experimental ......................................................................................... 94
    5.1.2 Results and Discussion ........................................................................ 95
  5.2 HAPP MWCNT/Epoxy Nanocomposites ................................................. 105
    5.2.1 Experimental ....................................................................................... 105
    5.2.2 Results and Discussion ....................................................................... 106
  5.3 Summary .................................................................................................... 116

Chapter 6 Plasma Functionalization of Carbon Fibres ........................................ 118
  6.1 Experimental ............................................................................................ 118
  6.2 Results and Discussion ............................................................................ 120
    6.2.1 XPS Analysis ...................................................................................... 120
    6.2.2 FTIR Analysis .................................................................................... 123
    6.2.3 SEM Results ...................................................................................... 124
    6.2.4 AFM Results ...................................................................................... 125
    6.2.5 Single Fibre Tensile Strength .......................................................... 129
6.3 Summary ........................................................................................................... 135

Chapter 7 Conclusions and Future Work ......................................................... 137

7.1 Conclusions .................................................................................................. 137

7.2 Future work .................................................................................................. 139

References ........................................................................................................ 140
Abstract

Plasma functionalization of multi-walled carbon nanotubes (MWCNTs), boron nitride nanotubes (BNNTs) and carbon fibres (CFs) has been investigated. In order to maximize the strength of light weight nanocomposites a uniform distribution of nanotubes and good interfacial adhesion between nanotubes and matrix are crucial. These require functionalization of the surface of the nanotubes which has been difficult to achieve, particularly if damage to the nanotubes is to be avoided. More effective and practical plasma functionalization methods have been developed and shown to give improved mechanical properties of MWCNT/epoxy nanocomposites at both the nano and macro scale.

The surface of MWCNTs was functionalized with a higher density of primary amine (NH₂) groups by a combined continuous plus pulsed plasma method (CW + P) using: i) a mixture of N₂ and H₂ (N₂/H₂, 85/15) and ii) the monomer heptylamine (HA). In the first mode, toxic ammonia was replaced by N₂/H₂ and in the second mode, HA replaced the toxic and unstable allylamine. The combined method captures the advantages of both continuous wave (CW) and pulsed (P) plasmas and a higher density of NH₂ than previously reported for any nitrogen-containing plasma treatment was achieved. Additionally, the integrity of the MWCNT structure was maintained by the plasma treatments. Finally, a stirring plasma system was developed for larger scale uniform surface treatment of MWCNTs.

The NH₂ on the MWCNT surface is essential for achieving covalent bonding to the epoxy. Both treatments improved the dispersion of the MWCNTs and their interfacial bonding with epoxy. The incorporation of only 0.1 wt% of N₂/H₂...
plasma functionalized MWCNTs led to marked increases in both nano- and macro-mechanical properties compared to neat epoxy. The addition of only 0.5% of HA functionalized MWCNTs increased the toughness by about 70%.

Controlled surface modification of BNNTs was also achieved by N₂/H₂ CW + P plasma treatment. An amorphous surface layer was removed without damaging the nanotube structure.

Improved surface preparation of carbon fibres for use in composites was also demonstrated. A three-step plasma method: activation, functionalization and polymerization, was developed to functionalize CFs. The first two steps: surface activation by Ar plasma followed by O₂ plasma functionalization, helped remove small flaws, increase the surface roughness and introduce the required functional groups for improved interfacial bonding of plasma polymerized HA. The single fibre tenacity was unchanged by the treatment.

The work introduces more practical and effective methods for capturing the extraordinary mechanical properties of light weight polymeric composites, especially nanocomposites, for applications in aerospace, automobiles and sporting goods.
Chapter 1 Introduction

1.1 Research Motivation and Objectives

Carbon nanotubes (CNTs) are unique nano-materials with a combination of excellent mechanical, electrical, and thermal properties. Therefore, CNTs have been recognized as ideal filler materials for producing polymer nanocomposites with high mechanical, electrical and thermal properties [1-3]. However, the agglomeration of CNTs into bundles, owing to van der Waals interactions, makes it extremely difficult to uniformly disperse them into a polymer matrix. As a result, the mechanical and electrical properties of the CNT/polymer nanocomposites are often found to be poor [4]. Moreover, CNTs have inert surfaces, which results in poor interfacial adhesion with the polymer matrix. This limits the efficiency of load transfer [5]. On the other hand, boron nitride nanotubes (BNNTs) like CNTs possess superb mechanical, thermal and electrical properties to be nanofillers, but their inert surface also hinders applications in nanocomposites. It has been reported that surface functionalization of carbon nanotubes can effectively improve their interfacial adhesion to a polymer matrix and their dispersion [4]. The favoured methods to functionalize nanotubes use wet chemical functionalization. These approaches require multi-step reactions to achieved the desired functionality and in most cases involve chemical functionalization conducted in solvents like strong acids, which can damage the nanotube structure and affect the unique advantages of nanotubes [6]. Carbon fibres (CFs) have also been widely used for reinforcing polymer materials for automotive, aerospace and sport applications [7-9], due to their unique advantages such as low weight, high mechanical properties, high fatigue
endurance, high damping and resistance to elevated temperatures [7, 10, 11]. However, their smooth surface and poor wettability makes it impossible to form strong mechanical interlocking and interfacial adhesion with polymeric matrices. Therefore, the CF surface needs to be modified before they are used to reinforce polymers. To avoid decreasing the CF strength as well as multi-step chemical reactions, there has been extensive work on plasma modification of CFs [12]. A common approach has been plasma polymerization to functionalize the CF surface using a thin polymer. The functional groups on the film can increase the interfacial adhesion between CF and epoxy matrix. However, most such treatments have used continuous wave (CW) plasma polymerization, which makes it difficult to retain the functionality of the monomer. This could compromise the adhesion to a polymer and hence degrade the properties of the resulting CF reinforced polymers. Additionally, to some extent, plasma polymerization belongs to the non-covalent approach, so it has a similar drawback to non-covalent functionalization, which is weak bonding between the CF and the deposited film. This is not beneficial for the load transfer between the CFs and polymer.

For a nanocomposite, the desired high mechanical performance relies on a uniform dispersion of the nanotubes and good interfacial adhesion between the nanotube and the matrix. For a (macro-) fibre reinforced composite, the interfacial adhesion between the fibres and matrix is also a crucial factor in determining the mechanical properties. Surface functionalization is a crucial step to tune the interfacial adhesion between nanofillers or fibres and a polymer matrix as well as improve the dispersibility of nanofillers.
Therefore, this research focuses on the surface functionalization of different one-dimensional fillers, namely, carbon nanotubes (CNTs), boron nitride nanotubes (BNNTs) and carbon fibres (CFs), for application in composites. An epoxy resin is chosen as the matrix due to its wide application in polymer composites.

The overall objective of this study was to establish a more effective and practical method of interfacing nanotubes and CFs to other materials. More specifically, more effective and practical plasma functionalization methods were sought, developed and tested. The detailed objectives were as follows:

1) To further develop a combined continuous wave and pulsed (CW + P) plasma treatment to achieve a higher level of primary amines firmly attached to an undamaged CNT surface, as well as BNNTs. Moreover, to develop and test a plasma system as a means for uniform treatment of nanotubes at a larger scale.

2) To investigate the performance of gas and monomer plasma amine-functionalized CNTs in a reinforced epoxy resin and study the nano and macro-mechanical properties of these nanocomposites.

3) To establish a more effective plasma approach to obtain a plasma polymer film with strong bonding to the CF surface.

1.2 Thesis Structure

A descriptive review based on the literature is presented in Chapter 2, focusing on functionalization of CNTs, BNNTs and CFs as well as the mechanical properties of their composites. The issues associated with current functionalization approaches are discussed.

Details of the materials, chemicals and plasma equipment used throughout this study are presented in Chapter 3. Sample preparation and characterization techniques are described.
The novel combined continuous wave and pulsed (CW + P) plasma method used to functionalize the CNT surface with amine groups is described in Chapter 4. The combined method is used in two different plasma treatments using (1) N$_2$/H$_2$ and (2) heptylamine (HA) as the precursors for the formation of amine groups. The density of primary amines incorporated onto the CNT surface is quantified using chemical derivatization with 4-trifluoromethylbenzaldehyde (TFBA) followed by XPS. The detailed mechanism of this approach in N$_2$/H$_2$ is presented. The effectiveness of the combined method is compared with only using CW or P plasma mode alone. Plasma surface functionalization of BNNTs in N$_2$/H$_2$ is then examined and the flexural mechanical properties of these treated BNNT/epoxy nanocomposites are presented.

Investigations into the effect of plasma amine-functionalization of CNTs on their dispersion in, and interfacial bonding with, an epoxy resin are set out in Chapter 5. N$_2$/H$_2$ plasma treated CNTs and HA plasma polymerized CNTs are both used to reinforce an epoxy resin. The mechanical properties of their nanocomposites are investigated.

Details of the three-step plasma polymerization for CFs are presented in Chapter 6. The effect of each treatment step on the tensile strength and surface of the CFs is carefully examined.

The key results of this work are summarized in Chapter 7, together with suggestions and recommendations for future research directions.
Chapter 2 Literature Review

Plasma technology and the different kinds of plasma surface treatment are introduced. Then, plasma functionalization of carbon nanotubes with primary amines and the effect of these nanotubes on the mechanical properties of epoxy resins are reviewed. Finally, progress in plasma surface functionalization of boron nitrogen nanotubes and of carbon fibres is discussed.

2.1 Non-thermal Plasma Technology

The term plasma was first used by Tonks and Langmuir in 1929 to describe a gas discharge [1]. Plasma as the fourth state of matter is a fully or partially ionized gas, which is composed of free electrons, ions, neutral atoms and/or molecules, free radicals, and ultra-violet (UV) photons. Generally speaking, the numbers of negative and positive charges are equal, and thus the overall charge of the plasma is neutral.

Plasma states can be divided into hot plasmas and cold plasmas (non-equilibrium plasmas), according to the degree of ionization of the plasma. Hot plasmas are almost fully ionized. Non-thermal plasmas, also known as cold plasmas, have a low degree of ionization and consist of low temperature atoms, molecules, or ions and relatively high-temperature electrons [2]. The term plasma in the rest of this thesis means a cold plasma.

Non-thermal plasmas can be divided into: atmospheric pressure plasmas and low pressure plasmas. There are three common forms of atmospheric pressure plasmas: corona discharge, dielectric barrier discharge and glow discharge [3]. In this work, low pressure plasma is the main tool used to functionalize different materials. Compared to atmospheric pressure plasmas, a low pressure plasma allows more controllable and reproducible introduction of functional groups [4]. A low
A pressure plasma apparatus typically consists of a reaction chamber (including electrodes), a power supply, a pumping unit, and a gas-feeding system with gas controllers and pressure gauges.

A plasma is a collection of positive, negative and neutral species as well as UV photons. These species play critical roles in plasma surface modification. Electrons play the most important role in the plasma. They are the main contributor to the production of active species. Since they are the lightest species in the plasma, electrons absorb the largest amount of energy from the electric field. This energy can be transferred via collisions with the gas atoms or molecules resulting in excitation, ionization and dissociation [5, 6], as shown in Table 2.1.

Table 2.1 Some of the processes producing excited species which may occur in plasmas.

<table>
<thead>
<tr>
<th>Name</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electron impact</strong></td>
<td></td>
</tr>
<tr>
<td>Excitation</td>
<td>$A + e \rightarrow A^* + e$</td>
</tr>
<tr>
<td>Ionization</td>
<td>$A + e \rightarrow A^+ + 2e$</td>
</tr>
<tr>
<td>Dissociation</td>
<td>$A + e \rightarrow A^* + \cdot A +$</td>
</tr>
<tr>
<td>De-excitation</td>
<td>$A^* \rightarrow A + hv$</td>
</tr>
<tr>
<td>Recombination</td>
<td>$A^+ + e \rightarrow A^* + hv$</td>
</tr>
</tbody>
</table>

Where $e$, $hv$ represent an electron and optical emission, respectively, $A$: atom or molecule, $A^*$: excited species, $A^\cdot$, $\cdot A$: free radicals, $A^+$: ion.

Ions can break bonds on the surface during the interactions of plasma species with a substrate, which is significant for the surface chemistry [7, 8]. Free-radicals can form cross-linked polymeric layers or graft onto the surface [7, 9]. UV photons emitted by the plasma also have some effects on the surface of substrates [10, 11].
There are many different categories of plasma reaction with the surface of inorganic and organic materials [7-10, 12-15], but, plasmas can be broadly classified into gas plasma treatment and plasma polymerization. Gas plasma treatment, which leads to etching reactions, activation and the production of surface functional groups, is generally conducted using non-polymerizing gases, while plasma polymerization is carried out using polymerizing gases and monomers to form a thin plasma polymeric film.

2.2 Plasma Treatment

Non-thermal plasmas are a highly developed technology for surface functionalization. They have become a convenient and versatile tool for the surface modification of various materials used in a wide range of fields including biomaterial and biomedicine [16-20], nanotechnology [2, 21, 22], energy conversion [23] and environmental control [24-27]. This is due to the many advantages of the plasma technique which include [4, 9, 13]:

1) all kinds of materials (different sizes, shapes, and types) can be modified, without altering the bulk properties; typically, the depth of modification is at the nano-scale.

2) various functional groups can be introduced, which can be selected and controlled by choosing different gases and plasma conditions (treatment time, pressure, power, flow rate);

3) a room temperature, environmentally benign and dry process.

2.2.1 Gas Plasma Treatment

Inert gas plasmas such as helium and argon are often used for pre-treatment to clean and activate the substrate surface before reactive gases are employed. Due
to its low cost, argon has been used in the inert gas plasma pre-treatments in this thesis. Ar plasmas initially create active sites on the surface which provides a good foundation for introducing functional groups produced by the reactive gases. In an inert gas plasma, the excited and energetic plasma species (ions, UV photons) bombard the substrate surface, leading to chain scission which results in surface etching, cleaning and activation [9, 12]. Inert gases also can be used as the carrier gas for polymerizing plasmas [28-30]. In plasma-induced grafting, inert gas plasmas are used to create free radicals on the substrate surface, and then the activated substrate is exposed to a monomer to form a grafted polymer [9, 19]. Plasma-induced grafting is different from plasma polymerization in which the gas itself is a monomer [19].

Generally speaking, NH₃ [31, 32], or NH₃ with H₂ or Ar [33-36], or a mixture of N₂ and H₂ or ethylene (C₂H₄) [37-39] or N₂ [40, 41] are used to generate nitrogen containing functional groups to improve wettability, printability, bondability, and biocompatibility of material surfaces [9, 10, 13, 42]. Among nitrogen containing functional groups, primary amines are the most important for biomaterials [9, 14, 39, 42, 43] and polymer composites [44-46]. They have been introduced on the carbon nanotube surface to promote covalent bonding between carbon nanotubes and epoxy resins [47], which are cured by amine crosslinking.

Commonly, O₂ [48, 49], air [3], H₂O [50, 51], CO₂ or CO [52, 53] are used to produce oxygen containing plasmas and introduce oxygen containing functional groups such as C-O, C=O, O-C=O, C-O-O, and CO₃ [10, 13], onto material surfaces. Normally, when the substrates are polymers, two processes can take place concurrently in oxygen or oxygen-containing plasmas: etching and formation of the oxygen functional groups. In oxygen-containing plasmas, ion
bombardment and UV radiations can etch the polymer surface. Moreover, the atomic oxygen reacts with the carbon atoms on the polymer surface to create volatile reaction products [10]. The reactive species produced in the oxygen containing plasmas react with the atoms on the polymer surface to form oxygen functional groups [13]. The balance of these two competing processes depends on the plasma parameters. The oxygen containing functional groups can improve wettability, printability, and biocompatibility of the polymer surface. The carboxyl (COOH), hydroxyl (OH) groups can be used for biomolecule immobilization and cell colonization [9, 19].

In contrast to nitrogen and oxygen-containing plasmas, fluorine-containing plasmas are used to produce inert and hydrophobic surfaces [19]. In fluorine-containing plasmas, surface reactions, etching, and plasma polymerization can occur simultaneously, depending on the operating parameters [13].

2.2.2 Plasma Polymerization

Plasma polymerization is a special technique for functionalizing material surfaces by depositing a thin polymer film [54]. In plasma polymerization, a monomer vapour is converted into reactive fragments which subsequently recombine to form a polymer [43]. It is quite different from conventional polymerization. Conventional polymerization requires several steps such as synthesis of the polymer, preparation of a solution, cleaning of the substrate surface, then deposition, drying and curing. Plasma polymerization is a one-step polymerization beginning with a monomer [54]. According to the form of the input power, plasma polymerization can be divided into: continuous wave (CW) plasma polymerization and pulsed (P) plasma polymerization. Recently, Dai et al.
[55] proposed a combined CW and pulsed (CW + P) plasma polymerization, which combines the advantages of both plasma modes.

**Continuous Wave Plasma Polymerization**

In CW plasma polymerization, the excitation, ionization and dissociation processes happen throughout the whole treatment, since the plasma is “on” all the time. This leads to high fragmentation of monomers. These fragments recombine randomly in first-order processes, but are then rearranged and further activated and fragmented [54, 56, 57], which results in the formation of a highly branched and highly cross-linked plasma polymer [55]. The resulting plasma polymer has a composition and structure that is little related to that of the original monomer [57]. This kind of plasma polymer is characterized by ultra-thin, pinhole-free polymer-like layers with unique chemical and physical properties [57] and good adhesion to substrates [58].

Yasuda [54] regarded CW plasma polymerization as ‘atomic polymerization’ and proposed a bicyclic step-growth polymerization mechanism, as shown in Figure 2.1. The first cycle relies on mono-functional species, M₁•, to form large molecules with or without radicals while the second cycle depends on bi-functional species, •M_k• [59].

![Figure 2.1 The bicyclic step growth polymerization mechanism [54].](image)
**Pulsed Plasma Polymerization**

Pulsed plasma polymerization was introduced in order to retain the chemical structure or functionality of the monomer in the plasma polymer. Modulation of the operational parameters can allow control of the chemical structure of the plasma polymer [60-62]. The key parameters for retaining the chemical structure of an original monomer for the plasma polymer are input power and the duty cycle (DC) [62]. The DC is determined by the plasma on-time ($t_{on}$) and the off-time ($t_{off}$):

$$
DC = \frac{t_{on}}{t_{on} + t_{off}} \quad (2.1)
$$

The average power ($P_{av}$) of a pulsed plasma is

$$
P_{av} = DC \times P_{peak} \quad (2.2)
$$

where $P_{peak}$ is the input power. It is significantly lower than that under typical CW conditions.

In a pulsed plasma, during the $t_{on}$ period, the plasma is generated as for a CW plasma, where the active species including charged particles, free radicals and UV radiations [14]. During the $t_{off}$ phase, the charged particles and UV radiations will disappear, which will remove ion bombardment and ablation [14, 60]. However, the radicals with relatively long lifetimes (about a few milliseconds or many seconds) will continue the radical polymerization reactions at the surface [14, 63]. This principle is shown in Figure 2.2 [14]. Therefore, the pulsed plasma process can be regarded as a succession of initiation ($t_{on}$) and chain propagation ($t_{off}$) reactions [14]. Meanwhile, careful control of the process conditions can retain the functionalities of a precursor without significant fragmentation of the monomer molecule, and also can balance the production and consumption of free radicals during the polymerization process [14, 26, 62, 63].
Figure 2.2 Schematic showing the typical constituents present in a pulsed plasma [14].

**Combined Continuous Wave plus Pulsed Plasma Polymerization**

Although, compared to the CW plasma polymers, the plasma polymer produced by pulsed plasma polymerization provides good retention of the chemical functionality, it has poor adhesion to substrates, especially for inert surface [55, 58]. The CW + P plasma polymerization was developed by Dai et al. [55, 64] to produce a plasma polymer which captures the advantages of both CW and pulsed plasma polymerization. Firstly, CW plasma polymerization produces a very thin cross-linked plasma polymer that strongly attaches to the substrate, which provides a good foundation for better bonding of a pulsed plasma polymer in the immediately following pulse plasma polymerization. This pulsed plasma polymer retains the chemical functional groups from the monomer (Figure 2.3). Therefore, the plasma polymer obtained by CW + P plasma polymerization characteristically has high retention of desired functional groups and good adhesion to substrates.
2.3 Surface Functionalization of Carbon Nanotubes and their Epoxy Nanocomposites

2.3.1 Introduction

Carbon nanotubes (CNTs) are unique one-dimensional materials with excellent mechanical, thermal and electronic properties. There are two main types of CNTs: single-walled (SWCNTs) and multi-walled (MWCNTs). SWCNTs are comprised of a single graphite sheet wrapped into a seamless and hollow cylinder, while MWCNTs consist of two or more concentric cylinders with interlayer spaces between each cylinder [65, 66]. Historically, MWCNTs were the first to be discovered in 1991 [67], followed by SWCNTs in 1993 [68]. A variety of ways have since been developed to synthesize CNTs including carbon-arc discharge [68], laser ablation [69], high pressure carbon monoxide (HiPCO) [70], chemical vapour deposition (CVD) (typically on catalytic particles) [71, 72] and plasma enhanced chemical vapour deposition (PECVD) [73].

CNTs have extraordinarily mechanical properties. Yu et al. [74] measured tensile strengths of individual MWCNTs inside an electron microscope. Their Young’s modulus was between 0.27 and 0.95 TPa, with strengths in the 11–63 GPa range and a toughness of 1240 J/g. For SWCNTs, their Young’s moduli were found to be in the range of 0.32 to 1.47 TPa with strengths between 10 and 52 GPa and a
toughness of 770 J/g [75]. These make CNTs stronger and stiffer than any other material. CNTs also show unique thermal and electrical properties. The measured room temperature thermal conductivity for an individual MWCNT is more than 3000 W/m•K and for an individual SWCNT more than 6000 W/m•K [66, 76]. The electric-current-carrying capacity of CNTs is 1000 times higher than copper wire [77, 78]. This collection of properties makes CNTs potentially ideal reinforcing nanofillers for conductive and ultra-high performance polymer composites [79-81]. The first ever CNT reinforced polymer nanocomposites were reported in 1994 by Ajayan [82]. Since then, there have been numerous reports of CNTs as nanofillers in polymer composites giving improved mechanical, electrical and thermal properties [83-95].

Epoxy resins are commonly used in composite materials for electronic, automotive and aerospace applications [45, 96]. As casting resins, they have a wide range of advantages, including good mechanical properties, resistance to environmental degradation, good adhesive properties, and low shrinkage during curing, good chemical resistance, high electrical insulation, good wear resistance, good stiffness, toughness and heat resistant properties [45]. However, epoxy matrices are relatively brittle and often display low fracture toughness which has hindered some of their applications [97, 98]. Moreover, local stress concentrations may initiate cracks which lead to spontaneous failure [96]. These hinder use in most structural, adhesive, or coating applications. To improve their mechanical properties, the addition of reinforcing nanofillers has become increasingly common [97].

As CNTs have distinctive electrical, thermal and mechanical properties and a high aspect ratio, they have been used for reinforcing nanofillers in conductive and
ultra-high performance polymer composites [66]. Research has shown CNTs to be excellent nanofillers for epoxy composites giving improved mechanical and electrical properties [45, 99-104].

**2.3.2 Functionalization of Carbon Nanotubes**

The mechanical properties of a nanocomposite are determined by the physical properties of the matrix material and of the additives, including stiffness, diameter, length, distribution, volume, and orientation [7, 13]. Effective reinforcement of the polymer matrix requires uniform dispersion of the nanofiller in the matrix. The interfacial adhesion between the matrix and nanofiller is also a key factor in determining nanocomposite performance. The interfacial adhesion is determined by the surface chemical and physical properties of the components [13, 79, 80]. Strong adhesion will help the effective transfer of stress from the matrix to the nanofiller during load, thus improving the mechanical properties of the nanocomposite [45, 80, 98].

However, because CNTs tend to agglomerate into bundles owing to strong van der Waals interactions, it is very difficult to achieve their homogeneous dispersion into the polymer matrix. As a result, the mechanical and electrical properties of the CNT/polymer composites are often found to be poor [76]. Moreover, their naturally inert surface results in poor interfacial adhesion with the polymer matrix which limits the effective transfer of stress during load [97]. Therefore, achieving uniform dispersion of the CNTs and optimum adhesion with the matrix have been a focus of research and many methods have been reported, such as mechanical dispersion [76, 105] (ultrasonication, calendering, ball milling) and chemical functionalization. The most commonly used approach is wet chemical functionalization, which can be divided into two categories: covalent
and non-covalent functionalization [78, 106-109]. Besides the wet chemical methods, there are also some dry modification approaches: plasma treatment [36, 41, 64, 84, 110-117], and proton [118], electron [119] or gamma [120] irradiation treatment.

Amongst a range of chemical functionalities, amine groups (especially primary amines –NH₂) are the most useful for curing epoxy resins. The amine groups on the CNT surface improve the dispersion in the epoxy matrix but also allow direct covalent bonding to the epoxide groups [104, 121, 122]. Many studies have shown that the incorporation of low amounts of primary amine-functionalized CNTs into the epoxy matrix can greatly enhance mechanical properties [101, 120, 123-126].

**Covalent and non-covalent functionalization**

The covalent functionalization of CNTs directly introduces functional groups to the sidewalls of the nanotubes or on the defects of nanotubes [76, 78, 80, 127]. The former normally is referred to as direct covalent functionalization, while the latter as defect functionalization [76, 128], as illustrated in Figure 2.4.

![Covalent Functionalization of SWCNTs](image)

**Figure 2.4 Covalent Functionalization of SWCNTs.** (a) Direct covalent functionalization; (b) covalent chemistry at defects or open ends [128].
Direct covalent functionalization of CNTs with functional groups can be made by reaction with some molecules of high chemical reactivity, such as fluorine [76]. It has been shown that the fluorinated CNTs have weak C-F bonds and thus the fluorine atoms can be replaced through nucleophilic substitution reactions by primary amine, alkyl and hydroxyl groups [76, 107, 108], as shown in Figure 2.5. Similar methods to sidewall fluorination, including hydrogenation [129, 130], cycloaddition reactions [131] and radical additions [132] have also been successfully employed.

![Figure 2.5 Direct covalent functionalization of CNTs through nucleophilic substitution reactions in fluorinated nanotubes [108].](image)

However, the most common of method for surface functionalization of CNTs is defect functionalization. In defect functionalization, CNTs are treated with strong acids like nitric acid (HNO₃) [133], oleum (H₂SO₄) or a mixture of them [134], H₂SO₄ with SO₃ [135], or with other strong oxidizing agents, such as KMnO₄ [136], KMnO₄/H₂SO₄ [137], ozone [138], H₂SO₄/H₂O₂ [139] to open the tubes and introduce oxygen functional groups such as carboxyl (–COOH) or hydroxyl (–OH) groups. These functional groups can serve as precursors for chemical
Covalent functionalization can improve the interaction between CNTs and polymer molecules, leading to improved mechanical properties of composites [78-80]. However, covalent functionalization inevitably influences the electrical, mechanical, and transport properties of CNTs, especially SWCNTs, by disturbing the intrinsic nanotube sp² structure when forming the chemical bonds [80, 107, 140, 141]. With increasing degree of functionalization, the tubes can totally lose their conductivity and become insulators [106], and in some cases, CNTs are fragmented [139]. Bergeret et al. [142] reported that SWCNTs lost their metallic character after nitric acid purification and functionalization. Pumera et al. [133] found nitric acid treatment had significant effects on the physico-chemical
properties of different types of MWCNTs. Brozena et al. [143] used a combination of oleum and nitric acid to oxidize the outer walls of double-walled carbon nanotubes (DWCNTs) in order to retained their electrical conductivity. Compared to the functionalized SWCNTs, the conductivity of functionalized DWCNTs was better, but was reduced by 40% compared to untreated DWCNTs. In addition, the mechanical properties of CNTs may be degraded by these severe chemical treatments. Grag et al. [144] reported chemical covalent functionalization may reduce the mechanical strength of CNTs by 15%, according to molecular dynamics simulations. Moreover, the covalent approach to incorporation of primary amines often requires time consuming and costly multistep reactions. Gromov et al. [145] reported on the direct attachment of primary amine groups to SWCNTs. Two covalent approaches were employed for the synthesis of primary amine-derived SWCNTs via two different reactions: Hofmann rearrangement of the corresponding amides and Curtius reactions of carboxylic acid azide, followed by hydrolysis, as shown in Figure 2.7. Each pathway needs multiple steps and more than a hundred hours to functionalize SWCNTs with primary amines, but only a small amount of N (1.05%) was detected on the functionalized SWCNT surface by XPS. Furthermore, as strong acids or oxidants are normally required by the
covalent approach, environmental concerns have been raised.

Figure 2.7 Covalent primary amine-functionalized SWCNTs: via Hofmann rearrangement of carboxylic acid amide (Pathway A); via Curtius reaction of carboxylic acid chloride with sodium azide (Pathway B) [145].

Non-covalent functionalization of CNTs mainly involves surfactants, biomolecules or polymers, where the nanotubes are modified via van der Waals forces and \(\pi-\pi\) interactions, by adsorption or wrapping of surfactants, biomolecules or polymers [78, 80, 106, 146, 147], as shown in Figure 2.8 (a) and (b). Beside adsorption or wrapping of polymer molecules, another non-covalent method, called the endohedral method, has been used for CNT functionalization [128, 147], as shown in Figure 2.8(c). In this method, different constituents, such as biomolecules, fullerene derivatives and inorganic species, and liquids, are introduced into the inner cavities of CNTs through the capillary effect [146]. This endohedral method integrates the properties of the two components in hybrid materials which are particularly useful for catalysis, energy storage, nanotechnology and molecular scale devices [76].
Unlike covalent functionalization, non-covalent functionalization does not change the structure of the nanotubes. Therefore, the properties of CNTs should also not be affected [106]. However, the weak bonding between the adsorbing or wrapping molecules and the CNT surface will reduce the efficiency of the load transfer. Recently, Liu et al. [148] compared the influence of covalently and non-covalently functionalized MWCNTs on the electrical and mechanical properties of epoxy composites. MWCNTs were functionalized by chemically bonding or physically adsorbing polyethylenimine (PEI) molecules. Both forms of functionalization improved the dispersion of the MWCNTs. They found that the conductivity of the non-covalent MWCNT/epoxy nanocomposite was higher than that of the covalent MWCNT/epoxy sample, which they suggested was due to the structure of the nanotube being maintained by non-covalent functionalization. However, the storage modulus was lower than for the covalent MWCNT/epoxy sample, which was attributed to the weak bonding between the MWCNT and the adsorbed PEI molecules.

It is also possible that the surfactant used in the non-covalent approach could compromise the thermal and mechanical properties of CNT reinforced polymer composites. Liao et al. [149] reported that when a surfactant was used to disperse SWCNTs into an epoxy resin, the glass transition temperature, $T_g$, of the nanocomposite dramatically decreased. Similar results were reported by Cui et al. [150]. They used a non-ionic surfactant in the process of MWCNT dispersion to make MWCNT/epoxy nanocomposites and also found $T_g$, density and electrical conductivity of the nanocomposites decreased with the amount of surfactant added.
Figure 2.8 Different types of non-covalent functionalization of CNTs: (a) molecular surfactant adsorbed around nanotube; (b) polymer wrapping around nanotube, (c) endohedral functionalization with, for example, C60 [128, 147].

Plasma surface functionalization of carbon nanotubes with amine groups

Compared to wet chemical functionalization, plasma treatment of CNTs is a one-step functionalization and hence avoids the complex procedures of filtration, washing and drying. It is more environmentally benign because it also avoids using solvents such as strong acids. Moreover, plasma treatment generally does not alter the bulk properties, and the functionality and its level can be controlled by choice of gases or monomer and plasma parameters. For example, oxygen containing gases plasmas such as O\textsubscript{2} [84, 151, 152], Ar/O\textsubscript{2} [49, 153] or Ar/CO\textsubscript{2} [154] or Ar/H\textsubscript{2}O [50], have been used to introduce oxygen-containing functional groups such as C-O, C=O, O-C=O to improve the dispersion of CNTs for applications in nanocomposites, biomaterials and sensors. Plasma etching has been used to purify aligned carbon nanotubes and open their tips or change their topography [155, 156]. However, the focus here is on plasma functionalization of CNTs with amine groups, especially primary amines.
There have been many approaches to the functionalization of CNTs with amine groups using plasma methods. These are listed in Table 2.2, and it can be seen that the approaches can be divided into three groups, as summarized in Figure 2.9. In most cases, the treatment was using continuous wave plasma.
Table 2.2 Plasma functionalization of CNTs with amine group.

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>Precursor</th>
<th>Sample type</th>
<th>Sample handling</th>
<th>Functional groups</th>
<th>NH\textsubscript{2}/C \textsuperscript{b}</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF</td>
<td>NH\textsubscript{3}/Ar</td>
<td>MWCNTs</td>
<td>Deposited on the grounded electrode.</td>
<td>Amine, amide, imine and nitrile groups detected by XPS.</td>
<td>---</td>
<td>[157]</td>
</tr>
<tr>
<td>Atmos. pressure</td>
<td>N\textsubscript{2}/NH\textsubscript{3} (35%)</td>
<td>Acid treated MWCNTs</td>
<td>Deposited onto an Au coated Si substrate.</td>
<td>Amines and amides detected by near edge x-ray absorption fine structure.</td>
<td>---</td>
<td>[158]</td>
</tr>
<tr>
<td>MW</td>
<td>NH\textsubscript{3}</td>
<td>SWCNT film</td>
<td>---</td>
<td>Amine, amide, imine and nitrile groups detected by XPS, FTIR, and Raman spectroscopy.</td>
<td>---</td>
<td>[159]</td>
</tr>
<tr>
<td>RF</td>
<td>NH\textsubscript{3}</td>
<td>MWCNTs</td>
<td>Attached to a Scotch tape.</td>
<td>Amine, amide, imine, nitrile and imide groups detected by XPS.</td>
<td>---</td>
<td>[152]</td>
</tr>
<tr>
<td>Process</td>
<td>Atmosphere</td>
<td>MWCNTs</td>
<td>Comments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
<td>--------</td>
<td>----------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>MWCNT film</td>
<td>Primary amines were confirmed by a chemical derivatization with pentafluoro-benzaldehyde (PFB). ~1%. [160]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>NH&lt;sub&gt;3&lt;/sub&gt;/Ar</td>
<td>MWCNTs</td>
<td>Placed in a glass beaker. Primary amines were confirmed by a chemical derivatization with 4-trifluoromethyl-benzaldehyde (TFB). ~1.7%. [36]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>SWCNTs</td>
<td>Deposited on a CaF&lt;sub&gt;2&lt;/sub&gt; disk. Amine, amide, and nitrile groups detected by XPS, FTIR and Raman spectroscopy. — [41]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td>N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>MWCNT film</td>
<td>Amine, amide, and nitrile groups detected by XPS, and Raman spectroscopy. — [161]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>Gas</td>
<td>Material</td>
<td>Post-treatment</td>
<td>Detected by</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>--------------</td>
<td>-------------------</td>
<td>---------------------------</td>
<td>----------------------------------------</td>
<td>----------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td>Pulsed dc</td>
<td>N\textsubscript{2}</td>
<td>Aligned MWCNT film</td>
<td>–</td>
<td>Amine and imine groups detected by XPS.</td>
<td>[162]</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>N\textsubscript{2}/Ar</td>
<td>MWCNTs</td>
<td>–</td>
<td>Amine, nitrile, amides and oxime groups detected by XPS.</td>
<td>[163]</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>N\textsubscript{2}/Ar</td>
<td>MWCNTs</td>
<td>Deposited on different supports (a conductive adhesive tape or a copper grid).</td>
<td>Amine, nitrile, amides and oxime groups detected by XPS.</td>
<td>[164, 165]</td>
<td></td>
</tr>
<tr>
<td>RF</td>
<td>N\textsubscript{2}/H\textsubscript{2} (1:1 ratio)</td>
<td>SWCNTs</td>
<td>Placed on a silicon wafer.</td>
<td>Amine, amide, oxime groups detected by XPS.</td>
<td>[39, 114, 166]</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>N\textsubscript{2}/H\textsubscript{2} (2:3 ratio)</td>
<td>Aligned CNT film</td>
<td>–</td>
<td>Amine and amide groups detected by XPS.</td>
<td>[167]</td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>Ar plasma assisted UV</td>
<td>SWNT film</td>
<td>–</td>
<td>The imidazole ring detected by XPS, and N/C was about 7.8%.</td>
<td>[168]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>grafting of 1-vinylimidazole</td>
<td>Pre-treatment Ar, graft polyacrylicnitrile (PAN)</td>
<td>Deposed on the grounded electrode.</td>
<td>Amine groups detected by XPS.</td>
<td></td>
<td>[169]</td>
</tr>
<tr>
<td>---</td>
<td>-----------------------------</td>
<td>-----------------------------------------------</td>
<td>----------------------------------</td>
<td>-------------------------------</td>
<td>---</td>
<td>------</td>
</tr>
<tr>
<td>RF</td>
<td>MWCNTs</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MW</td>
<td>N₂ plasma induced chitosan (CS)</td>
<td>MWCNTs</td>
<td>Put in a stirring reactor</td>
<td>Amine and amide groups detected by FTIR.</td>
<td></td>
<td>[170]</td>
</tr>
<tr>
<td>RF</td>
<td>Allyamine</td>
<td>MWCNTs</td>
<td>Put in a rotating reactor</td>
<td>Amine, amide, imine and nitrile groups detected by FTIR, XPS.</td>
<td></td>
<td>[171]</td>
</tr>
</tbody>
</table>

* indicates how nanotube powder was handled in the plasma treatment;

* indicates the percentage of primary amines if the quantification was performed.
Amine-containing surfaces for CNTs have been prepared using ammonia (NH$_3$). Delpeux et al. [157] reported the residual oxygen in the reactor could impede the reactivity of MWCNTs with NH$_3$ plasma. They suggested this was due to a competition between nitrogen and oxygen reactive species. They also found that NH$_3$ plasma treatment was less efficient when pristine MWCNTs were annealed to remove oxygen contamination. The reason for this was not given. However, recently, Roy et al. [158] reported using a dielectric barrier discharge plasma in a NH$_3$ atmosphere to modify acid treated carbon nanotubes. They found that oxygen groups introduced on the CNT surface by acid treatment could act as activation sites that attracted N atoms. The acid treated CNTs, after NH$_3$ treatment, attracted higher nitrogen concentration (about 5.5%) than non-activated CNTs. The nitrogen containing functional groups were identified by near edge x-ray absorption fine structure (NEXAFS) spectroscopy. Khare et al. [159] confirmed amine functional groups on SWCNTs functionalized by a microwave discharge of
NH$_3$ through Fourier transform infrared (FTIR) spectroscopy with band assignment aided by computational modelling which was further supported by XPS and Raman spectroscopy results. Felten and his co-workers [152] further found that ammonia plasma could introduce various nitrogen-containing groups (amine, amide, nitrile) on the MWCNT surface and the concentration and type of functional groups were chiefly related to the plasma conditions such as input power, treatment time, pressure and position of the sample inside the chamber. Although those approaches have shown that the primary amine groups can be introduced onto the surface of the CNTs using NH$_3$ plasmas, the density of primary amines and the effect of the plasma treatment on the structure of the nanotubes were not reported.

N$_2$ and N$_2$ with H$_2$ or Ar have also been utilized, instead of ammonia, to modify the CNT surface for the incorporation of amine groups. Khare et al.[41] studied the functionalization of SWCNTs with a microwave-generated N$_2$ plasma. The authors found the results strongly relied on the distance between the discharge source and the sample. At a relatively large distance, no functionalization was observed. They supposed this was because recombination of atomic nitrogen increased with increasing distance. At the shortest distance studied, cyanides were observed. They suggested that the formation of cyanides was due to highly reactive species, either directly forming the cyanide or indirectly by first causing a defect that subsequently reacts to form the cyanide products. They also observed $\cdot$NH and $\cdot$NH$_2$ radicals in N$_2$ plasma and that UV photons can de-functionalize the nanotubes.

Gohel et al. [161] examined field emission properties of N$_2$ plasma-treated MWCNT films. They found the field emission properties of modified MWCNT
films were significantly improved. They suggested that this was attributable not only to shortening of the nanotubes and reducing the nanotube density, but also to the nitrogen containing groups on the MWCNT surface introduced by plasma treatment. Jones et al. [162] studied the functionalization of vertically aligned MWCNT films using a pulsed dc N$_2$/Ar plasma treatment. Pulsed dc power was used because a stable glow discharge could only be observed under a pulsed mode. SEM images of treated MWCNT films showed ball-shaped structures at the ends of bundled tubes. XPS results showed nitrogen containing functional groups on the surface of the MWCNTs. Ruelle et al. [164, 165] modified MWCNTs in the post-discharge region of a N$_2$/Ar microwave plasma. XPS analysis showed the presence of amine, nitrile, amides and oxime grafted onto the MWCNT surface. To confirm the actual location of amine functional groups on the MWCNTs, they utilized amine initiation of the ring-opening polymerization of $\varepsilon$-caprolactone using triethylaluminium as activator. TEM observations of the MWCNT surface grafted with $\varepsilon$-caprolactone showed the amine groups were on the sidewall. TEM and SEM images revealed that the plasma treatment did not damage the surface of the MWCNTs, but the density of valence electronic states was altered according to ultra-violet photoelectron spectroscopy studies. Kalita et al. [163] functionalized MWCNTs with N$_2$/Ar plasma for the fabrication of photovoltaic devices. XPS results showed the surface modification of MWCNTs with imine, amine, nitrile and amide groups incorporated on the side walls, which resulted in a homogenous distribution of MWCNTs in solvent. The performance of the devices was improved using the functionalized MWCNTs. TEM results showed the inside wall of the functionalized MWCNTs was unaffected, but some defects were found on the outermost walls.
Recently, Yoon et al. [166] functionalized SWCNTs with primary amine groups with N$_2$/H$_2$ plasma in order to prepare nanofibre composites by electro-spinning with poly [(D, L-lactic)-co-(glycolic acid)] (PLGA). The primary amine groups on the SWCNT surface introduced by N$_2$/H$_2$ plasma treatment improved their dispersion and adhesion with PLGA. The influence of the plasma treatment on the structure of the SWCNTs was not discussed.

An alternative way to create amines on the surface of CNTs is plasma-induced grafting or plasma polymerization of amine-based polymers or monomers. Yan et al. [168] studied Ar plasma assisted UV grafting of 1-vinylimidazole. UV radical grafting of 1-vinylimidazole took place on the defect sites of the nanotubes created by Ar plasma. Chen and colleagues [169, 172] have studied primary amine-functionalization of MWCNTs by plasma induced grafting polymerization for preparation of covalently-integrated epoxy composites. First, the surface of MWCNTs was activated by Ar plasma treatment. Subsequently, two polymers were used for grafting onto the MWCNTs: maleic anhydride (MA) and polyacrylonitrile (PAN), as shown in Figure 2.10. After grafting MA onto the MWCNTs (MWCNTs-g-MA), they were mixed with the curing agent (diamine) in order to obtain primary amine groups which could covalently bond with the epoxy resin. For the PAN grafted MWCNTs (MWCNTs-g-AN), a further reaction of the MWCNTs with hydroxylamine was required to produce the aminated MWCNTs (MWCNTs-g-mAN). Both methods were effective at improving the dispersion of functionalized MWCNTs and the mechanical and electrical properties of functionalized MWCNT/epoxy nanocomposites.
Figure 2.10 Functionalization MWCNTs by plasma-induced grafting polymerization for preparation of epoxy composites [169, 172].

A similar method was used to graft chitosan (CS) onto the surface of MWCNTs (MWCNTs-g-CS) after N₂ plasma treatment [170]. The prepared MWCNT-g-CS was used to remove UO₂²⁺, Cu²⁺, and Pb²⁺ ions from aqueous solution. Compared to untreated MWCNTs, MWCNT-g-CS had higher adsorption capacity for the removal of heavy metal ions.

Chen et al. [173] immobilized two different dextran chains onto plasma-polymerized aligned CNTs. The aligned CNTs were first functionalized by plasma polymerization of acetaldehyde, then amine-dextran was grafted onto the CNT surface. The same approach was used to immobilize the periodate-oxidized dextran-FITC chains onto ethylenediamine plasma polymerized aligned CNTs. They found both polysaccharide-grafted carbon nanotubes were very hydrophilic.

Most recently, and after these studies were begun, Abou Rich et al. [171] have reported using CW plasma polymerization of allylamine to attach amine groups to the surface of MWCNTs. They evaluated the effect of the plasma conditions (RF power and time) on the nitrogen content. Amine, amide, imine and nitrile groups were detected on the MWCNTs by FTIR and XPS. The surface morphology of
the functionalized MWCNTs and the thickness of plasma polymer were not reported.

As can be seen from the above review, functionalization of CNTs with amine groups by plasma approaches have been performed by many researchers and the nitrogen incorporation has been confirmed. However, in most cases, NH$_3$ was used; the density of primary amines has not been quantified, and the level of primary amines was low (NH$_2$/C < 2%) if they were quantified [36, 160]. Moreover, CNTs are hard to deal with in plasma systems due to their aggregation and large surface area [174, 175]. Generally, they are deposited on a substrate for treatment in the plasma system (Table 2.2). In order to achieve uniform functionalization of the large scale of CNTs, a suitable plasma equipment becomes essential. Most recently, Shao et al. [170] and Abou Rich et al. [171] used stirring or rotating plasma reactors, in order to achieve a uniform treatment on CNTs, but the effects on uniformity of treatment were not clearly demonstrated.

2.3.3 Amine-functionalized CNT/Epoxy Nanocomposites

The presence of amine groups, especially primary amines, on the CNT surface should greatly improve their dispersion in, and interfacial bonding with an epoxy resin (Figure 2.11), thus increasing the strength of CNT/epoxy nanocomposites. The first experimental work on the MWCNT/epoxy interfacial strength was conducted by Cooper et al. [176]. They used a special pull-out test for individual MWCNTs from the epoxy matrix to quantify the interfacial shear strength. It ranged from 35 to 376 MPa. They suggested that covalent bonding between MWCNTs and epoxy could enhance the interfacial shear strength. Frankland et al. [177] used molecular simulations to predict the shear strength of the SWCNT-
polymer interface. They found that the interfacial interactions could be increased by the introduction of functional groups onto CNTs, and projected that a relatively low density (<1%) of chemical bonds between a nanotube and the polymer matrix would improve the interaction between SWCNTs and the polymer without decreasing their strength.

Figure 2.11 The reaction between primary amine functionalized CNTs and an epoxy resin [178].

Many researchers have shown that CNTs that have been primary amine functionalized by chemical treatments can improve the properties of epoxy resin. Gojny et al. [179] refluxed oxidized MWCNTs directly in the triethylenetetramine, and obtained primary amine grafted MWCNTs. The TEM images of the primary amine functionalized MWCNT/epoxy nanocomposites showed an improved interfacial interaction with the matrix. The investigation of the thermo-mechanical properties of the nanocomposites showed primary amine-functionalized MWCNTs had a bigger effect on $T_g$ than untreated MWCNTs [180]. The same group also used commercial primary amine functionalized double-wall carbon nanotubes (DWCNTs) to increase the Young’s modulus of epoxy by 6% by adding 0.1 wt% of functionalized DWCNTs [123] and a 43% increase in toughness of epoxy with 0.5 % functionalized DWCNTs [181].
Valentini et al. [182] functionalized SWCNTs with amine groups in diethylenetriamine and then used them as conductive fillers in an epoxy matrix. They found the functionalized SWCNTs could affect the crosslinking reaction of the epoxy resin. The amine groups on the SWCNTs surface provided a vehicle for the migration of charges during epoxy curing which further contributed to an increase in intrinsic conductivity of the nanocomposites. Wang et al. [122] obtained primary amine-functionalized MWCNTs by grafting triethylenetetramine (TETA) on the surfaces of MWCNTs through the acid-thionyl chloride route. The primary amine-functionalized MWCNTs showed more homogenous dispersion in an epoxy resin. They reported that adding the MWCNTs greatly increased the Charpy impact strength, glass transition temperature, and initial decomposition temperature of cured epoxy resin. Shen et al. [183, 184] functionalized MWCNTs using oxidation, acylation and amidation and then produced MWNCT/epoxy nanocomposites. The primary amine-functionalized MWCNTs greatly improved the thermal and mechanical properties of the epoxy resin [183]. Chen et al. [185] functionalized MWCNTs with primary amine groups by the addition of carboxyalkyl radicals after oxidation, and then acylation and amidation. With the incorporation of 1.5 wt% of primary amine-functionalized MWCNTs, the tensile strength and impact strength of the epoxy increased by 51% and 93%, respectively. They reported that the improvement in the properties of the primary amine-functionalized MWCNT/epoxy nanocomposite was larger than that of an oxidized-MWCNT/epoxy nanocomposite. They attributed the improvement to the formation of covalent bonds between the primary amine-functionalized MWCNTs and epoxy matrix, leading to more effective stress transfer. Hosur et al. [101] reported an increase of
11.63% in flexural modulus with the optimum loading (0.2 wt%) of commercial MWCNTs with primary amine-functionalization (< 0.5% of primary amines) into an epoxy matrix. Commercial aminated MWCNTs have also been employed by Lachman and Wagner [124] to reinforce an epoxy. Their results showed an increase in Young’s modulus of 23% with 0.34 wt% addition of aminated MWCNTs. Yang et al. [125] also showed that adding 0.6 wt% of MWCNTs, which were amine functionalized by a chemical method, increased the flexural modulus by 22%, compared with the neat epoxy.

Recently, Hu et al. [186] modified three different carbon materials (MWCNTs, expandable graphite oxide (EGO) and graphene (G)) with primary amine groups using 4,4’-dipriprimary aminediphenyl sulphone (DDS) and then fabricated their epoxy nanocomposites. The results showed the primary amine functionalization improved the interfacial heat transfer between the carbon materials and the epoxy resin. The $T_g$ of the functionalized MWCNTs/epoxy nanocomposites increased the most of the three carbon material reinforced epoxy matrices.

There have been two recent reports in which the CNTs have been physically treated to enhance surface functionality. Chen et al. [169] reported using an argon plasma as a pre-treatment to help graft polyacrylonitrile onto the CNT surface in order to introduce primary amine functionality. The electrical properties of the resulting CNT/epoxy nanocomposites were found to be enhanced. Most recently, Zhang et al. [120] introduced primary amine groups on the MWCNT surface using gamma ray irradiation and found that 1 wt% loading of the modified MWCNTs into the epoxy could lead to a 20% increase in tensile modulus. Although a lot of work on primary amine-functionalized CNT/epoxy nanocomposites has been reported, so far, the use in these nanocomposites of
CNTs which have primary amine groups directly attached to their surface by plasma functionalization has not been reported.

2.4 Plasma Functionalization of Boron Nitride Nanotubes (BNNTs)

Boron nitride nanotubes (BNNTs) are structurally similar to CNTs, which can be regarded as a carbon nanotube in which alternating B and N atoms substitute for C atoms [187, 188]. BNNTs have excellent mechanical and thermal properties which are similar to those of CNTs [189, 190], but BNNTs possess better thermal and oxidation stability than CNTs[191]. These properties make them promising nanofillers for the improvement of both mechanical and thermal properties while preserving the electrical insulation and optical transparency of a polymer [192]. In order to better capture the potential of BNNTs in composite applications, surface functionalization is also needed to improve the solubility and strength of the interactions between a polymer and BNNTs. However, experimental modification of BNNTs has been much less common than theoretical investigations due to their chemical inertness and poor wetting properties [193] as well as difficulties in controlling the modification processes.

Unlike the plasma functionalization of CNTs, functionalization of BNNTs is still in its early stage. So far, there have only been a few reports on plasma functionalization of BNNTs [194, 195]. Cao et al. [194] investigated the reaction behaviour of radicals such as NH$_2$ and H in NH$_3$ plasma on the surface of BNNTs by density functional theory calculations. They found that, in the NH$_3$ plasma functionalization of BNNTs, it was more favourable for NH$_2$ radicals to form covalent bonds with B atoms than with N atoms while H radicals would prefer to combine with the N atoms neighbouring NH$_2$-functionalized B atoms. Ikuno et al. [195] reported on amine-functionalized BNNTs using a NH$_3$ plasma treatment in
a microwave plasma system. They suggested the positive ions with high energies in the NH₃ plasma such as N₂⁺, NH⁺, NH₂⁺ and NH₃⁺ could create defects on BNNTs and the amine groups were formed in the following termination of vacancies by radicals. However, the TEM images showed the surface of BNNTs was damaged after plasma treatment. Effective surface functionalization without damage to BNNTs is needed.

2.5 Plasma Surface Modification of Carbon Fibres

2.5.1 Introduction

Carbon fibres (CFs) have been widely used for reinforcing materials in automotive, aerospace and sporting applications [196-198]. This is due to their unique advantages such as low weight, high strength, high fatigue resistance, high damping and resistance to elevated temperatures [196, 199, 200]. In fibre-polymer composites, their mechanical properties rely on not only the properties of fibres and matrices, but also on the interfacial bonding between the fibres and matrices [201]. The interface is significant for transferring the load from the fibres to the matrices [44]. However, since the CF surface is non-polar and consists of highly crystallized graphitic basal planes [202], the fibres have very poor wettability and adhesion with most polymers. Moreover, CFs also have smooth surfaces, which prevents mechanical interlocking with polymer matrices, and the relatively large diameter of CFs reduces a specific contact area with a matrix, leading to lower surface energy [201]. Consequently, it is hard to form a strong interfacial bond between CFs and polymer matrices, which compromises the mechanical properties of the composites [197]. Nevertheless, surface modification of CFs can improve their interfacial adhesion to polymers, resulting
in improved mechanical properties. As a result, a variety of surface treatments, such as chemical or electrochemical modification [203-206], radiation treatment [207-209], gas-phase and liquid-phase oxidation [210-213], plasma treatment [48, 198, 201, 214-223], have been used to functionalize the CF surface in order to increase the reactivity with the matrix, or enhance surface roughness to produce better mechanical interlocking [202]. However, challenges that still remain include high energy consumption, long treatment time, environmental pollution, and high maintenance cost, and, in most cases, the treatment is accompanied by a decrease in fibre strength [44, 198, 201, 224]. Plasma treatment is simpler, more environmentally friendly, and can be done without altering the fibre bulk properties. Plasma treatment can also provide a method for tailoring the surface functionalization by simply choosing different precursors as well as experimental conditions. Therefore, plasma surface functionalization of CFs has been investigated. Generally, two kinds of plasma treatments have been used: gas plasma and plasma polymerization.

2.5.2 Gas plasma modification of CFs

Among gas plasma treatments, oxygen-containing plasmas have mostly been used to modify the CF surface. Jang and Kim [225] modified CFs using O₂ plasma treatments for CF/polyetheretherketone (PEEK) composites. They observed an increase in CF surface roughness using a relatively short treatment time (3 min), while longer treatments (>5 min) could lead to overall smoothing and did not increase the oxygen functionality of the CF surface. This was due to the continuous plasma etching resulting in a smoothing of the overall surface and removing of the active sites on the CF surface. The flexural strength and inter-laminar shear strength (ILSS) of CF/PEEK composites were improved after the 3
min plasma treatment. In this case, the adhesion between the CFs and PEEK was mainly affected by mechanical interlocking. Fukunaga et al. [226] treated pitch-based ultra-high modulus CFs using O2 or Ar plasmas and compared them with anodized CFs. After plasma treatment, the double layer capacity of the CF surface, which was related to the surface area, significantly increased, and the surface crystal size was reduced. They proposed the surface layer was peeled off and aromatic bonds in the basal plane were broken by O2 or Ar plasma. The increase in active sites on treated CFs gave them much higher adhesion to an epoxy matrix than the anodized samples. Montes-Morán et al. [227] examined the effects of O2 plasma treatment on the physical and chemical properties of CFs. They observed that the oxygen content on the CF surface increased and the carbonaceous impurities on the original surfaces were removed by plasma treatment. As a consequence, the single filament tests on single-fibre epoxy composites showed an improvement in CF/epoxy adhesion. Bubert et al. [228] found that oxygen plasma treatment changed the surface of vapour grown CFs by forming a layer with a thickness of the order of one nanometre mainly consisting of oxygen functionalities, such as hydroxyl, carbonyl and carboxyl.

Brandl and Marginean [229] observed that oxygen plasma treatment not only introduced oxygen containing functional groups (hydroxylic, carboxylic and carboxylic) onto the carbon nanofibre surface, but also increased the surface porosity and the surface energy, without damaging the fibre structure. Boudou et al. [48] found that very gentle O2 plasma treatment could introduce a large amount of oxygen functional groups, while more intense treatments had an adverse effect. There was no significant change in the structure of the fibre after plasma treatment. Tang et al. [230] also utilized O2 plasma to modify the surface
of activated carbon fibres and examined the effect of parameters such as plasma treatment time and power on the surface structure and chemistry of CFs. After plasma treatment, the specific surface area and micropore volume increased and oxygen containing groups were incorporated onto the CF surface. Oxygen plasma treated CFs have been used to reinforce ultra-high molecular weight polyethylene by Fu et al. [199]. They reported the O$_2$ plasma treatment introduced oxygen functionalities on the CF surface and increased the surface roughness of CFs, which improved the adhesion, leading to higher inter-laminar shear strength.

Besides low pressure plasmas, atmospheric pressure plasmas have also been used to modify the CF surface. Table 2.3 summarizes recent work on atmospheric plasma surface functionalization of CFs. It shows that an atmospheric plasma is also capable of functionalizing the CF surface to improve the adhesion with a polymer.

Table 2.3 Atmospheric plasma functionalization of CNTs

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Sample type</th>
<th>Main results</th>
</tr>
</thead>
<tbody>
<tr>
<td>He, Ar, O$_2$</td>
<td>Poly(acrylonitrile) (PAN) based unsized electrochemically-treated CF</td>
<td>XPS measurements indicated that oxygen functional groups, mainly C=O, were introduced onto the CF surfaces by He, He/O$_2$ and Ar plasma treatments. [220]</td>
</tr>
<tr>
<td>Air</td>
<td>Industrially oxidised PAN-based CF</td>
<td>The treatment did not affect the surface properties of CF and increased the surface energy of CF. The interfacial shear strength of single CF/Polyamide 12 composites evaluated by single fibre fragmentation tests had a great increase after plasma treatment. [231]</td>
</tr>
<tr>
<td>He/O$_2$</td>
<td>AS4 PAN-based CFs</td>
<td>The concentration of the carboxyl groups was shown to continuously increase after a few plasma passes. [221, 232]</td>
</tr>
</tbody>
</table>
Treated CFs in both inert and air environments exhibited similar decay profiles. The adhesive bond strength of treated CF/epoxy samples was increased by 50% relative to untreated samples. The crack delamination resistance analysis showed the plasma-treated composites were two times as resistant to fracture as conventionally prepared CF/epoxy specimens.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>He/O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>AS4 PAN-based CFs</td>
<td>The plasma treated and rinsed samples had better adhesion than only plasma treated samples. This was because the isopropanol rinse could help remove a thin layer of ash from the plasma-treated surface. [233]</td>
</tr>
<tr>
<td>He/O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PAN-based CFs</td>
<td>No obvious changes in the single fibre tensile strength of at short gauge lengths after plasma treatment while the fibre strength tends to decreased at larger gauge lengths. The interfacial shear strength of plasma treated CF/polyimide sample was greatly improved due to the increase of oxygen containing functional groups and changing of the surface topology after plasma treatment. [198]</td>
</tr>
<tr>
<td>Ar</td>
<td>CFs</td>
<td>XPS analysis revealed the oxygen functionalities on the CF surface after plasma treatment, and filament fragmentation tests showed the treated CF samples had better interfacial properties, compared to the untreated CF samples. [200]</td>
</tr>
</tbody>
</table>

2.5.3 Plasma polymerization of CFs

Plasma polymerization has been used to deposit a thin film on CFs to improve the adhesion to a polymer. This enhanced adhesion can be mainly attributed to the
introduction of oxygen- and nitrogen-containing functionalities [44]. Dagli and Sung [234] deposited plasma polymers on CFs in an acrylonitrile and styrene CW plasma at low pressure. The plasma polymers contained many oxygen functional groups. Compared to the untreated CFs, the tensile strength of the plasma treated CFs was increased by about 7%. They argued that this increase was not due to an additive contribution from the plasma polymer coatings, since its tensile strength was far lower than the CF. Therefore, they suggested that it was because the plasma coating healed surface flaws of the CFs. Similar results were also observed by Dilsiz et al. [216]. They found that the tensile strength of both dioxane and xylene plasma polymerized CFs was increased by about 21%. They also suggested that it was because some surface flaws on the CFs were filled during plasma polymerization, thus being healed. Weisweiler and Schlitter [235] studied the effect of CW plasma polymerization of acetylene/air and found improved mechanical properties of epoxy resin composites due to the oxygen functional groups on the plasma polymer. Kettle et al. [236] conducted CW plasma polymerization of HMDSO/O₂ for functionalization of the CFs. They found both the fracture toughness and strength of CF/epoxy composites were improved after plasma polymerization. Feih and Schwartz [237] deposited CW plasma polymers on PAN-based CFs using a mixture of acetylene and oxygen to improve the adhesion of CF and an epoxy resin in composites. They found that the treatment with a high acetylene/oxygen ratio (6.5:1), where polymerization was the major process of plasma treatment, did not give an improvement in the interfacial shear strength between the CF and the epoxy, which was due to weak bonding between CF and the deposited plasma polymer and no mechanical interlocking with the epoxy. But when using low acetylene/oxygen ratios (1:1 and
2:1), they found that the plasma polymerization and formation of oxygen free radicals happened simultaneously in the plasma treatment, which gave an increase in the interfacial shear strength between CFs and the epoxy. This increase was attributed to the reaction between the epoxy groups and functional groups on the CF surface as well as to long-living free radicals entrapped within the plasma polymer.

So far, most investigations have used CW plasma polymerization. As described in Section 2.2.2, the plasma polymers produced by CW plasma polymerization generally retain little functionality from the monomer, which could compromise any improvement in the adhesion to a polymer. Moreover, to some extent, plasma polymerization belongs to non-covalent methods [238], in which the interfacial bonding between the plasma polymer and the CF could be relatively weak. A new plasma approach which produces a plasma polymer with high levels of the desired functionality and having good adhesion to the fibre is highly desirable.

2.6 Summary

This chapter has provided an overview of research on plasma surface functionalization of CNTs with amine groups as well as the mechanical properties of CNT reinforced epoxy resins. The plasma functionalization of BNNTs and CFs also has been reviewed.

To address the inert surface and agglomeration of CNTs, wet chemical approaches, such as covalent and non-covalent functionalization, have been widely used. However, these methods have unfavourable traits. In most cases, covalent functionalization has involved chemical functionalization conducted in solvents like strong acids, which can damage the CNT structure and affect the unique advantages of CNTs, such as their exceptional physical and chemical
properties. Non-covalent bonding, by van der Waals forces and π-π interactions, is weak attachment which is not robust enough to provide effective load transfer in CNT/epoxy nanocomposites. Compared to chemical functionalization, plasma treatment avoids the complex procedures of filtration, washing, and drying and is more environmentally benign. The functional group and its level can be controlled by choice of gases or monomer and plasma parameters.

Amongst the range of chemical functionalities that can be achieved on CNTs, amine groups, especially primary amines, are very important for application in composites. Although many methods of functionalization of CNTs with amine groups using plasma treatments have been reported, the density of primary amines has been moderate (or not quantified). Additionally, the use in these nanocomposites of CNTs which have primary amine groups directly attached to their surface by plasma functionalization has not been reported. Moreover, to achieve large scale, uniform plasma treatment of CNTs is a challenging task. The study of large scale treatment methods is still in its early stages.

Like CNTs, BNNTs have high chemical inertness and poor wetting properties, which limit their application. The surface modification of BNNTs is still in its early stages and effective surface functionalization without damage to the nanotubes is a challenging task.

Plasma polymerization is an alternative way to modify the surface of the CFs to improve their adhesion in composites. So far, most such treatments have used CW plasma polymerization, which makes it difficult to retain the functionality of the monomer. Moreover, to some extent, plasma polymerization belongs to the class of non-covalent attachment, it has similar drawbacks to non-covalent
functionalization. Therefore, studies on improving the interfacial strength between the deposited plasma polymer and the CF surface are very important. The key challenges in functionalization of CNTs and CFs have been addressed in the studies reported in this thesis. The combined method (CW + P) plasma in a mixture of N₂ and H₂ (N₂/H₂) is examined as a way of achieving a higher level of primary amines firmly attached to the MWCNT surface, without damaging its structure and avoiding using toxic ammonia gas. The alternative of replacing polymer wrapping using less toxic monomer heptylamine (HA) under the CW + P mode to covalently bind the polymer to the surface of MWCNTs while also achieving a high level of primary amine groups is also studied. Both methods are tested in terms of the improvement in the mechanical properties of epoxy composites. The use of a home-built stirring plasma system to improve the uniformity of treatment of MWCNTs at a larger scale of production is also examined. The surface functionalization of BNNTs using a N₂/H₂ plasma is also examined. Finally, the production of a plasma polymer with strong interfacial adhesion to the CFs using a three-step plasma treatment: activation, functionalization and polymerization, is examined as a potential method of improving their interfacial properties.
Chapter 3 Materials and Methodology

3.1 Introduction
In this chapter, the materials, chemicals, equipment, manufacturing procedures and characterization methods used in these studies are described. Firstly, the materials and chemicals are given in Section 3.2. The two low pressure plasma systems used in this thesis, which were developed in the Plasma laboratory of Deakin University, are presented in Section 3.3. Then, the procedures used in the manufacture of nanocomposites are given in Section 3.4. Finally, the surface analysis methods as well as the nanocomposite mechanical characterization techniques are set out in Section 3.5.

3.2 Materials and Chemicals
In these studies, multiwalled carbon nanotubes (MWCNTs), boron nitrogen nanotubes (BNNTs) and carbon fibres (CFs) were functionalized by plasma treatment and then the nanotubes were used as nanofillers to reinforce an epoxy resin. The MWCNTs were purchased from Sigma-Aldrich Co. LLC. They were produced by a CoMoCAT® catalytic Chemical Vapor Deposition (CVD) process with a purity of more than 95% carbon. The diameter of the MWCNTs was 15-20 nm and their length was about 5 μm. The density of the MWCNTs was about 0.22 g/cm³. BNNTs were supplied by the Nanotechnology Laboratory of Deakin University. They were synthesized on stainless steel substrates using a boron ink brushed on the surface and heating in a horizontal tube furnace at 1100 °C for 3 h in nitrogen plus hydrogen gas (N₂/H₂) [239, 240]. Commercially available PAN based un-oxidised CFs were purchased from Zoltek. The average diameter of the CFs is about 7.2 μm, and the density was about 1.81 g/cm³ [241].
Epon 862 epoxy resin (Bisphenol F) and Epikure W aromatic amine curing agent were purchased from Hexion Specialty Chemicals Inc. The chemical structure of Epon 862 epoxy resin is shown in Figure 3.1.

![Chemical structure of Epon 862 Epoxy resin.](image)

The density of Epon 862 epoxy was about 1.17 g/cm³. The viscosity of Epon 862 epoxy was about 25-45 P and the curing agent was about 1-3 P at 25 °C. The mixing ratio of Epon 862 epoxy to Epikure W curing agent was 100:26.4 by weight.

During plasma treatment, several gases are used as precursors. They were argon (purity 99.9%), oxygen (purity 99.9%) and nitrogen plus hydrogen gas (N₂/H₂, volume ratio of 85:15). All gases were purchased from Australian BOC Company. Heptylamine (CH₃(CH₂)₆NH₂, 99% purity, Sigma Aldrich) was used as the monomer for plasma polymerization. The chemical, 4-trifluoromethybenzaldehyde (TFBA, 95% purity, Sigma Aldrich), was used to identify and quantify the primary amine groups [55].

### 3.3 Equipment

Two purpose-built low pressure plasma systems were used in the project. The first system (System 1) is referred to as the plasma polymerization system (Figure 3.2), which can be used for both gas plasma treatment and plasma polymerization. The plasma reactor of System 1 consists of a glass cylinder (15 cm in diameter and 30 cm in length), mounted in a Faraday cage. The antenna has two loops, made from
copper wire (3.74 mm in diameter), diametrically opposed and held on the outside of the glass cylinder. A RF generator (Kurt J. Lesker Company, USA) can be operated in a continuous wave (CW) mode and in a pulsed (P) mode. The maximum output power of the generator is 300 W. The RF power generates the plasma via the antenna around the inlet side of the chamber (the plasma source area), leaving the rest of the chamber as the afterglow region. The antenna with an automatic matching network (EJAT6, Kurt J. Lesker Company, USA) can transfer 100% of the RF power into the plasma. Samples were located in the plasma source on a stainless steel platform. The gases or monomers are introduced via a gas inlet. The chamber pressure, monitored by a pressure gauge, can be reduced to below $10^{-3}$ mbar using a rotary pump.

Figure 3.2 Schematic diagram of the plasma polymerization system.

The second system (System 2) is a stirring plasma system, (Figure 3.3), which has been developed to functionalize nanomaterials. The vacuum chamber of the plasma reactor consists of a Pyrex glass tube about 40 cm high and 4 cm in internal diameter connected to a round flask. The connection between the glass tube and the round flask is well sealed using vacuum grease and a clamp. This setup makes sample collection easy. The round flask is located on a magnetic stirrer which allows control of the stirring speed as well as temperature. A magnetic bar is used to stir the powders. The antenna is made of copper wire,
coiled around the outside of the glass tube and sealed by a copper mesh to prevent radiation. The power is supplied by the same RF generator as used in System 1.

Figure 3.3 Schematic diagram of the stirring plasma system.

3.4 Processes for the Manufacture of Nanocomposites

In this thesis, neat epoxy, untreated nanotube/epoxy as well as functionalized nanotube/epoxy nanocomposites were fabricated. Neat epoxy samples were prepared by manually mixing Epon 862 epoxy resin and Epikure W curing agent. The mixing ratio of the epoxy and curing agent was 100:26.4 as recommended by the manufacturer. The mixture was degassed with stirring at 500 rpm under vacuum for 30 minutes at room temperature before curing.

The epoxy was reinforced with both untreated nanotubes and functionalized nanotubes. Firstly, the carefully weighed nanotubes and Epon 862 epoxy resin were manually mixed in a 250 ml beaker. Then the mixture was blended by a probe sonication (UIP100hd, 1000W, 20 kHz) at 30% amplitude for 30 minutes with a pulsing rate of 2:1 (4 seconds on, 2 seconds off). The pulsing rate can be varied to help in keeping the temperature stable. Additionally, in order to avoid
overheating of the nanotube/epoxy mixture during sonication, the mixing beaker was immersed in ice water to keep the mixture at about 25 °C. After the sonication, the curing agent was added to the nanotube/epoxy mixture and then the mixture underwent stirring at 500 rpm for 30 minutes under vacuum at room temperature to degas in order to remove entrapped air and voids. All resin systems were injected into an aluminium mould and cured in an oven at 177 °C for 2.5 hours.

3.5 Characterization Techniques

3.5.1 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a widely used technique for the quantitative analysis of elements and the identification of functional groups [242]. The atoms in a sample absorb X-rays, which leads to ejection of photoelectrons. These photoelectrons can be used to directly determine a binding energy of an element. The energies are unique to each element and sensitive to the chemical state of the element, allowing identification of each element on the surface of the sample [243]. XPS has been used extensively for the chemical analysis of the plasma surface modification [219, 244-248].

XPS analysis in this work was carried out on a K-Alpha X-ray photoelectron spectrometer from Thermo Fisher Scientific. The base pressure of the analysis chamber was about 5×10⁻⁹ mbar. A spot size of 400 μm was used to scan in the region of the C1s binding energy as well as provide a broad survey spectrum to detect additional elements. Excessive charging of the samples was minimized using a flood gun. The C1s binding energies of all the samples were accurately established by charge shift correcting the lowest binding energy peak of the C1s
to 284.6 eV. The survey spectra were obtained at a pass energy of 100 eV while high resolution peak scans were performed at a 20 eV pass energy. The peak scans were used to obtain the elemental composition of C, N, O, and F for CNTs, and C, N, O, and B for BNNTs, C, O and N for CFs. The XPS data was fitted using a Gaussian-Lorentzian (G/L) product where the relative parameters were varied to obtain the best fit. Triplicate samples were analysed with atom percent uncertainties being of the order of 2%.

3.5.2 Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy (FTIR) is widely used for investigations of the near surface chemical composition and structure [249]. FTIR in these studies was mainly used to study the surface chemistry of heptylamine (HA) plasma polymerized MWCNTs and CFs. For the plasma polymerized MWCNT measurements, a small amount of MWCNTs was mixed with about 100 mg KBr and compressed to make pellets. In order to examine the composition of the polymer deposited on the plasma polymerized CFs, the HA plasma polymer was also deposited on KBr tablets and transferred to the spectrometer for analysis. FTIR spectra were carried out on a Bruker VERTEX 70 instrument using the transmission mode with a resolution of 4 cm$^{-1}$ and accumulating 32 scans in the spectral region of 4000–400 cm$^{-1}$. Since the analysis depth of FTIR (about a few microns) is generally larger than the thickness of the plasma polymerized film, a background spectra that was collected without the sample was subtracted from the sample spectra.

3.5.3 Contact Angle Measurement

Contact angle measurement is generally used to estimate the wettability of a localized area on a solid surface. In this study, static contact angles of untreated
and plasma treated MWCNT thin films were determined using a CAM101 video camera based contact angle measurement system (KSV Instruments Ltd., Finland). The MWCNT films were prepared by ultrasonically dispersing the MWCNTs in ethanol, then placing several drops of the suspension on pieces of glass slides (2.5 cm × 6.0 cm) and finally, drying the samples at room temperature.

Before the contact angle measurement test, a 1 ml plastic syringe was cut at the very end of the tip using a precision cutter in a way that slowed down the motion of probe liquids. Diiodomethane (DM), glycerol (G), and ethylene glycol (EG) were employed as probe liquids, and the nonpolar and polar surface energy components used for calculation were 50.8 and 0 mJ/m² for DM, 34 and 30 mJ/m² for G, and 29 and 19 mJ/m² for EG [250]. The contact angle measurement was made by placing a droplet of probe liquid at various spots on the film’s surface and recording images at a speed of 220 frames/sec. It was observed that the volume of the droplets, for the probe liquids used, remained constant (2.52 ± 0.02 μl) over the duration of the measurement, indicating that capillary effects could be ignored. Contact angles were measured for at least five different places on each film for 0.46 sec.

To examine the change in wettability of the MWNCT thin films before and after plasma treatment, the Chang–Qin–Chen (CQC) model [251] has been used to understand the interfacial interactions. The work of adhesion is given by:

\[
W_a = \gamma_L (1 + \cos \theta) = P_{L}^{LW} P_{S}^{LW} - P_{L}^{a} P_{S}^{b} - P_{L}^{b} P_{S}^{a}
\]  

(3.1)

where three unknowns: \(P_{S}^{LW}\) (the Lifshitz-van der Waals, LW, components of the solid), \(P_{a}^{S}\) and \(P_{b}^{S}\) (principal acid and base values) in equation (3.1) were determined by multiple regression analysis using a semi-interactive spread sheet.
From the calculated parameters of the solid, i.e., $P_s^a$ and $P_s^b$, the acid-base components, the magnitude of interaction was calculated by the multiplication of $P_s^a$ and $P_s^b$ which provided a value for the acid-base component of surface energy, $\gamma_{s}^{AB}$ of the MWCNT thin film using equation (2):

$$\gamma_{s}^{AB} = -P_s^a P_s^b \quad (3.2)$$

The surface is referred to as acidic if both $P_s^a$ and $P_s^b$ are positive, and basic when both are negative, and amphoteric if they are opposite in sign.

### 3.5.4 Chemical Derivatization

XPS can be used to determine the surface N/C ratio that is a measure of the amount of nitrogen, but this parameter alone is not sufficient to quantify the relative proportions of the different N-containing surface groups. Therefore, chemical derivatization with TFBA was used to determine and quantify the primary amine groups (-NH$_2$) on the surface of plasma treated samples. The TFBA exclusively reacted with primary amines so that the amount of primary amine can be determined from the amount of fluorine detected by XPS [62]. The reaction is shown in Figure 3.4. The samples were exposed to vapours from a drop of TFBA put into a sealed vessel for 2 hours at room temperature before XPS analysis.

![Figure 3.4 Schematic diagram of chemical derivatization by TFBA of primary amine groups.](image-url)
The TFBA molecule has a labelling reaction with the NH₂ groups. Therefore, the NH₂/C and NH₂/N ratios, as percentages, can be calculated from the detected amount of F[62], as shown in equations (3.3) and (3.4). NH₂/C (%) is the primary amine percentage relative to carbon concentration and NH₂/N indicates the selectivity for primary amines.

\[
[NH₂/C]\% = \left(\frac{[F]}{3} \times \frac{1}{[C] - \frac{8[F]}{3}}\right) \times 100 
\]

\[
[NH₂/N]\% = \frac{[NH₂/C]}{[N/C]} \times 100 
\]

Where \([F]\), \([C]\) are the fluorine and carbon concentrations determined by XPS after the reaction with TFBA, \([N/C]\) is calculated from the concentrations detected by XPS before derivatization. To avoid the effect of the possible physical absorption of TFBA, the samples were placed in a fume hood for overnight before XPS analysis.

3.5.5 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is commonly employed for imaging the surface morphology and fine structure of materials [252]. The use of SEM requires sample preparation. For nanotube sample preparation, the nanotubes were added to ethanol and mixed by sonication and the solution was dripped onto a Si wafer. The Si wafers were ultrasonically cleaned in acetone, ethanol and deionized water, each for 15 min, then dried by nitrogen gas flow before use. The nanotube sample was then dried at room temperature. For CF sample preparation, several CFs were laid on double-sided conductive tape then stuck on an aluminium stub. For composite sample preparation, the surface of the composite
was coated with a 5 nm layer of gold prior to observation. The investigation of the surface morphology and structure of samples was performed on a Zeiss Supra 55VP4 scanning electron microscope. Images were taken at 5-10 kV accelerating voltage and 3-10 mm working distance with an aperture of 30 μm.

### 3.5.6 Transmission Electron Microscopy

Transmission electron microscopy (TEM) is normally applied to determine the interior structure of nanomaterials. In this research, TEM was used to observe whether the structure of the nanotubes (MWCNTs and BNNTs) was damaged by plasma treatment. TEM was carried out using a JEOL 2100F electron microscope. This microscope had an accelerating voltage from 80 to 200 kV and magnification from 1000 to 80000 times. Very thin samples mounted on fine-meshed grids are required. To prepare the samples for TEM, a very small amount of each nanotube powder was ultrasonically dispersed in deionized water and one drop of the suspension was placed on a copper grid. The sample was observed using a microscope operating voltage of 200 kV and a Gatan Tridium imaging filter.

### 3.5.7 Atomic Force Microscopy

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy (SPM). It measures surfaces in three dimensions and provides the roughness over a scanned surface area. The AFM used in these studies was the Cypher atomic force microscope produced by Asylum Research. The Cypher AFM (Figure 3.5) is regarded as the world’s fastest and highest resolution AFM [253]. A 4-sided silicon tip was used in this work. Imaging was performed using a tapping mode in air with silicon cantilevers. The drive frequency of the cantilever was 310–345 kHz. The AFM was used to observe the indentation impressions on
the nanocomposites after nanoindentation tests, to examine the changes in CF surface roughness after plasma treatment, and to measure the thickness of the plasma deposited polymer.

Figure 3.5 A Cypher AFM.

A surface masking technique [254] was used to measure the thickness of the plasma desposited polymer. The whole process is shown in Figure 3.6. Firstly, a solution of polyvinylpyrrolidone (PVP) in deionized water (volume ratio 1:1) was prepared. Then, about 2-3 μl of the solution, taken by a 20 μl automatic pipette, was dropped on a cleaned Si wafer (2 × 2 cm) and dried in an oven at 60 °C for 1 hour. This resulted in a film of PVP about 0.2 mm thick and 0.5 mm in diameter on the Si wafer surface. The Si wafer was then subjected to the normal plasma polymerization. After plasma polymerization, the Si wafer was immersed in deionized water for 1 hour to swell the mask. Finally, the mask was lifted off the substrate using a scalpel. Tapping mode AFM was employed to analyse the topography of the created polymer steps.
3.5.8 X-ray Diffraction

X-ray diffraction (XRD) is a non-destructive analytical technique for collecting information about crystal structure, chemical composition, and physical properties of materials and thin films [255]. This technique is based on observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength [214].

In these studies, XRD patterns of as-received MWCNTs and plasma treated MWCNTs were recorded on a Phillips PW-1729 Diffractometer (Amsterdam, the Netherlands) with a Cu Kα source (λ=0.154 nm) from 5° to 80° at a scanning rate of 0.05° sec⁻¹. The accelerating voltage and applied current were 45 kV and 40 mA.

3.5.9 Differential Scanning Calorimetry

In this research, the curing behaviour of the Epon 862/Epikure W system with or without MWCNTs was analysed using a TA Q200 Differential Scanning Calorimeter (DSC). The sample (8-10 mg) was heated from 30 °C to 300 °C at a
constant heating rate of 10 °C/min under nitrogen (20 ml/min). The onset temperature ($T_o$), the peak temperature ($T_p$) as well as the enthalpy ($\Delta H$) were calculated using TA Universal Analysis 2000 software.

**3.5.10 Thermogravimetric Analysis**

Thermogravimetric analysis (TGA) was used to investigate the sample composition, the thermal stability under a specific atmosphere, and the decomposition temperature. The analysis was conducted on a Netzsch STA 409 PC/PG simultaneous TGA-DSC analyser. About 5–10 mg of nanotubes was placed in a ceramic pan and placed in the instrument’s furnace. The temperature of the sample was increased from room temperature to 800 °C at 20 °C/min under air flow (30 ml/min).

**3.5.11 Dynamic Mechanic Analysis**

Dynamic mechanic analysis (DMA) was used to characterize the thermal properties of the nanocomposites and was performed on a TA Instruments Q800 controlled by TA Instrument Explorer software. All the nanocomposite samples were cut to 60 mm (length) × 10 mm (width) × 3 mm (thickness). Measurements were carried out in the cantilever bending mode at a frequency of 1 Hz and a strain of 0.05%. The temperature range analysed was from 30 °C to 180 °C at a heating rate of 2 °C/min.

**3.5.12 Three-Point Bending Test**

Three-point bending tests were used to examine the flexural properties of the nanocomposites and were conducted according to ASTM D790-03 using a Lloyd tensile tester. ASTM D790-03 is the standard for testing flexural properties of high-modulus composites and electrical insulating materials in the form of rectangular bars [256]. In the three point bending test, a sample rested on two
supports and then was loaded by means of a loading head midway between the supports, as shown in Figure 3.7. According to the test standard [256], the support span \( L \) shall be \( 16 \pm 1 \) times the thickness of the sample, and the sample width shall not be over one fourth of the support span. In this study, specimens 70 mm long, 10 mm wide and 3.3 mm thick were tested. The tests were performed with a 10 kN load cell at a cross-head speed of 2 mm/min under room temperature to failure. Five samples of each were tested.

![Figure 3.7 Three-point bending test geometry (load P, thickness h, span length L).](image)

3.5.13 Nanoindentation

Nanoindentation tests were used to determine the nano-mechanical properties of the nanocomposites. The composite samples were tested using a UMIS-2002 system (CSIRO, Australia). The load and the indenter displacement were recorded during the indentation process, to determine the elasticity \( E \) and hardness \( H \) of the sample. A schematic of a typical load-displacement curve is shown in Figure 3.8. The analysis was performed using the Oliver-Pharr method [257] which uses measurements of the load, at a constant rate of loading up to a set peak load, as a function of depth to calculate the mechanical properties. In Figure 3.8, the indentation depths \( h_r, h_c, h_{\text{max}} \) stand for residual impression depth, contact indentation depth, and depth at the maximum load, respectively. The elasticity and hardness were calculated using:
where $E^*$ is the elastic modulus of the indenter and sample; $H$ is the hardness of the sample; $P_{\text{max}}$ is the peak load; $h$ and $A$ are the depth and area of the indentation mark.

Figure 3.8 A schematic of the load-displacement curve.

The Berkovich pyramid indenter was used. The contact area of a perfect Berkovich indenter can be calculated as a function of the contact indentation depth $h_c$ using [91]:

$$A = 24.5h_c^2$$  \hspace{1cm} (3.7)

The indentation impressions after testing were observed with the Cypher AFM. An array (5×5) of indentations was made for each composite using a maximum load of 2 or 3 mN. When the load reaches the peak value, it is held for 5 s. This step can avoid increasing or decreasing the slope of an unloading curve and hence minimize the possibility of over or under estimating the modulus [258]. The gap between indents was set at 20 μm.

3.5.14 Single Fibre Tensile Test
Single fibre tensile tests were carried out using a FAVIMAT+ automatic linear density, crimp and tensile tester (Textechno H.Stein GmbH &Co. KG, Germany). The fibres were firstly fixed on a magazine (Figure 3.9), then the magazine was loaded onto the machine for testing. With a robot, the fibres can automatically be fed to the tester. At least 50 fibres were tested. The tensile strength of the CFs was measured at a gauge length of 20 mm and the fibre was extended to failure at a downward speed of 1 mm/min.

Figure 3.9 A magazine loaded with CFs.
Chapter 4 Plasma Functionalization of Nanotubes

The challenges in fully exploiting the properties of carbon nanotubes (CNTs) are that CNTs have intrinsically inert surface and agglomeration readily. As discussed in Chapter 2, functionalization of the CNT surface is the key to overcoming these problems and plasma methods have the advantages of environmentally benign processing, time saving and allowing various, selectable and controllable functional groups depending on plasma parameters [64]. Moreover, plasma processing has the potential to produce less damage than chemical functionalization. The most suitable functional groups for polymer composites are amines, especially primary amines, which can also act as anchoring points for other species [185, 259]. Plasma methods, such as using nitrogen-containing gases plasma, plasma induced grafting or plasma polymerization, have been used to introduce amine groups onto the CNT surface such as, but the density of primary amines has only been moderate (NH2/C < 2%) or even not quantified [64]. Another challenge has been the difficulty of obtaining an even treatment of the large scale CNTs.

The aim has therefore been to investigate improved plasma methods for functionalizing CNTs that addressed the challenges. The strategy has been to test a method that has already had success with titanium and stainless steel [55]. This is to combine continuous wave and pulsed (CW + P) plasma modes. The desired outcome was to achieve a higher level of primary amines directly and firmly attached to an undamaged multi-walled carbon nanotube (MWCNT) surface. Two approaches were tested. The first used a N2/H2 plasma and the second plasma polymerization of an amine-containing monomer. The combined method was compared with using continuous wave or pulsed plasma modes alone for both
Two different plasma systems were used. In System 1, the MWNCTs were prepared in a thin film on a glass slide, which has been a common method for powder samples in plasma treatment, in order to get reasonably uniform treatment [39]. A stirring plasma apparatus (System 2) was assembled to address the problem of homogenous treatment of MWCNTs at a larger scale. This was then used (in addition to System 1) for the heptylamine (HA) plasma polymerization. The plasma functionalization of BNNTs was also investigated using a N₂/H₂ plasma and System 1.

4.1 N₂/H₂ Plasma Treatment of CNTs

4.1.1 Experimental

Commercially available MWCNTs, as described in Section 3.2, were used in the experiments without purification. Before being placed in the plasma chamber, the MWCNT powder was ultrasonically dispersed in ethanol. Representative samples for XPS analysis were prepared by placing three drops of the suspension on a cleaned Si wafer (1 cm × 1 cm). The sample was then dried at room temperature. The MWCNT thin films on glass slides were prepared for contact angle measurement to examine the wettability change before and after plasma treatment. Three different liquids were used in the tests: diiodomethane (DM), glycerol (G), and ethylene glycol (EG). The details of the tests have been described in Section 3.5.3. The plasma treatment was conducted in the plasma polymerization system, System 1, as described in Section 3.3. Samples were located in the plasma source area. The samples were first treated by argon plasma (CW 75 W, 5×10⁻² mbar) for 1 minute to activate and clean the surfaces before N₂/H₂ (85 % : 15 % volume ratio) plasma treatment.
The three plasma modes (CW, P and CW + P) were used with N$_2$/H$_2$. The total input energy [$E = P$ (peak RF power) $\times t$ (total treatment time) $\times D$ (duty cycle, $t_{on}/(t_{on}+t_{off})$)] was kept the same (100 W min) for all experiments. The input power for N$_2$/H$_2$ plasma was maintained at 75W, but the plasma exposure time was varied. The chamber pressure was maintained at 8.0$\times$10$^{-2}$ mbar. The detailed experimental conditions are listed in Table 4.1.

Table 4.1 The plasma experimental conditions.

<table>
<thead>
<tr>
<th>Plasma types</th>
<th>Plasma conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$/H$_2$ - CW</td>
<td>CW Ar plasma, 75 W, 80 s</td>
</tr>
<tr>
<td>N$_2$/H$_2$ - P</td>
<td>Pretreatment, 75 W (Peak power), 5% (duty cycle, $t_{on} = 1$ ms, $t_{off} = 19$ ms), 1600 s</td>
</tr>
<tr>
<td>N$_2$/H$_2$ - CW + P</td>
<td>CW: 75W, t = 40 s, P: 75W, 5%, t = 800 s</td>
</tr>
</tbody>
</table>

4.1.2 Results and Discussion

**Surface chemistry**

The surface atomic composition of the MWCNTs before and after plasma treatment was determined from the XPS spectra. Figure 4.1 shows typical XPS C1s and survey binding energy spectra obtained for the untreated and N$_2$/H$_2$ CW + P plasma treated MWCNTs. The as received MWCNTs have 97.4% C and 2.6% O. The small amount of oxygen could be from air contamination during the production process. No evidence of nitrogen content was observed in the survey spectrum (Figure 4.1b). The C1s peak of untreated MWCNTs in Figure 4.1a is
composed of peaks at 284.6 eV and 285.2 eV, which correspond to a graphite signal (C=C) and sp$^3$ carbon bonds (C-C), respectively.

After plasma treatment, nitrogen atoms are detected in the survey spectrum (Figure 4.1d). The C1s spectrum, after the N$_2$/H$_2$ plasma treatment (Figure 4.1c), can be deconvoluted into four peaks. Besides the graphite signal, three new peaks are observed at 285.8 eV, 286.7 eV and 288.1 eV, which correspond to amine (C-NH$_2$ or C-NH-C), imine (C=N) and amide (CO-NH) groups, respectively [152].

The N1s peak for plasma treated MWCNTs is relatively wide and featureless. It should be composed of a mixture of components including amine, imine and amide groups but it is not possible to reliably resolve the components by fitting [36].

In Figure 4.1d the oxygen content after N$_2$/H$_2$ CW + P plasma treatment is observed to increase slightly compared to that of the untreated MWCNTs. The oxygen might come from the substrate surface during plasma treatment as well as post-plasma reactions on exposure to air, since the XPS was done ex situ [41, 160].
Figure 4.1 XPS high resolution C1s and survey spectra of MWCNTs: (a, b) untreated; (c, d) N2/H2 CW + P plasma modification.

A typical XPS survey for the treated MWCNTs after derivatization with TFBA (as described in Section 3.5.4) is presented in Figure 4.2. The F atom is clearly detected on the modified MWCNT surface due to the labelling reaction with the NH2 groups. The NH2/C and NH2/N ratios were calculated from the detected amount of F atoms, according to equations 3.3 and 3.4 (in Section 3.5.4). The NH2/C ratio gives the primary amine percentage relative to carbon concentration and the NH2/N ratio indicates the primary amine selectivity.
Figure 4. 2 XPS survey spectrum of N₂/H₂ CW + P-MWCNTs.

The NH₂/C and N/C ratios for the MWCNTs functionalized by N₂/H₂ plasma are presented in Figure 4.3a. For the samples treated by N₂/H₂ plasma, the highest recorded density of NH₂ is about 2.3% for CW + P, while the lowest is for CW (about 0.6%), even though the N/C ratios for both samples are very similar. It can also be seen that although the pulsed plasma modified sample has the highest level of nitrogen (nearly 12%), its NH₂ density (1.4%) is relatively low compared to that for CW + P.

The formation of primary amine groups on the surface of substrates when using ammonia (NH₃) plasma treatment has been attributed to •NH or •NH₂ radicals in the plasma [36, 160]. In N₂/H₂ plasma, the gas phase reactions become much
more complex [40] due to some additional mechanisms for both production and destruction of atomic species of nitrogen. Basically, production of •NH radicals can be from the following channels [40, 260]:

\[
\begin{align*}
N (^2 D) + H_2 & \rightarrow \cdot H + \cdot NH \quad (4.1) \\
\cdot N + H_2 (v) & \rightarrow \cdot H + \cdot NH \quad (4.2) \\
H N_2^+ + e & \rightarrow \cdot NH + N^{(4) S} \quad (4.3) \\
H_2 + \cdot N & \rightarrow \cdot NH + \cdot H \quad (4.4)
\end{align*}
\]

Where \( N (^2 D) \) is electronically excited states of atomic nitrogen and \( N^{(4) S} \) is ground state atomic nitrogen, the \( H N_2^+ \) in channel 4.3 was mainly from (1) \( H_2^+ + N_2 \) and (2) \( N_2^+ + H_2 \) [260]. A detail about molecular dissociation in \( N_2/H_2 \) plasma is available elsewhere [41, 260].

According to the XPS results and the above dissociation in \( N_2/H_2 \) plasma, an interpretation of the results is presented in Figure 4.4. In the CW plasma, the production of the •NH radicals was accompanied by their destruction due to the continuous ion bombardment. This will reduce the formation of amine groups on the surface of MWCNTs [31].

![Figure 4.4 The proposed reaction mechanism of \( N_2/H_2 \) plasma treatment for MWCNTs.](image)

69
For the N₂/H₂ pulsed plasma, the •NH radicals are produced during the ‘on’ time. The ‘off’ period then provides sufficient time for them to form amine groups on the surface with minimum destruction by charged particles and UV photons. In addition, compared to the CW plasma, the pulsed mode can optimize the balance between N₂/H₂ fragmentation and the fresh N₂/H₂ feed. It can help to minimize the recombination reactions and hence increase •NH radical formation, allowing more NH₂ to form on the MWCNT surface. For the N₂/H₂ CW + P plasma treatment, the active sites on the MWCNT surface created by the CW plasma made it easier to graft the •NH radicals to form primary amine groups in the following pulsed plasma treatment. Moreover, •H radicals created in the pulsed plasma can reduce other nitrogen-containing groups, introduced onto the surface of the MWCNTs during the CW plasma treatment, to amine groups [31, 37]. Therefore, the highest density of primary amine groups is obtained by the N₂/H₂ CW + P plasma, and this significantly improves the ease of MWCNT dispersion. Selectivity for primary amines (NH₂/N) for N₂/H₂ CW + P plasma (about 30%) is also higher than any other treatment (Figure 4.3b). In fact, the density of primary amine groups is even higher than that reported using CW NH₃ plasma treatments [36, 160]. To confirm this result, another sample was treated using 50 W N₂/H₂ CW + P. The TFBA derivatization results showed a NH₂ /C ratio of about 3% was achieved, which is higher than that obtained by 75 W N₂/H₂ CW + P plasma treatment. This is because the low input power can reduce the continuous ion bombardment during CW treatment to help retain more NH₂.

**Surface Wettability**

The contact angles and work of adhesion of the MWCNT thin film before and after plasma treatment using three liquids are presented in Table 4.2. The work of
adhesion was calculated according to equation 3.1, as described in Section 3.5.3. As can been from Table 4.2, the mean contact angles for the polar probe liquids (glycerol and ethylene glycol) decreased by about 30° to 40° after plasma treatment, while the work of adhesion increased. This indicates that the surface energy of the MWCNT film after plasma treatment increased for the polar liquids, which is directly related to the presence of hydrophilic nitrogen-containing polar groups on the MWCNT surface. On the other hand, the changes in mean contact angle and work of adhesion for diiodomethane were the opposite to that for glycerol and ethylene glycol. This is perhaps because the increased polarity of the plasma treated surface reduced the availability of the non-polar solvent, diiodomethane, for non-polar interactions.

Table 4.2 Contact angle and work of adhesion of CNT thin films measured using three probe liquids (diiodomethane is non-polar; glycerol and ethylene glycol are polar).
Surface energy components of the MWCNT thin film before and after plasma treatment calculated using the CQC model (described in Section 3.5.3) are shown in Table 4.3. After plasma treatment, the total surface energy ($\gamma_{S}^{\text{tot}}$) of the MWCNT film increased, while the Lifshitz-van der Waals, LW, surface energy component ($\gamma_{S}^{\text{LW}}$) of solids was unchanged. The acid-base component of surface energy ($\gamma_{S}^{\text{AB}}$) increased significantly. The increase in value (of $\gamma_{S}^{\text{AB}}$) was mainly due to the increase in the principal acid parameter, $P_{s}^{a}$ and decrease in base parameter, $P_{s}^{b}$ (see equation 3.2). This indicates that the surface is converted from basic to amphoteric by the plasma treatment. The untreated MWCNTs are metallic (or semi-metallic) and contain electron-donating sites and so present a basic surface (both $P_{s}^{a}$ and $P_{s}^{b}$ are negative), but after plasma treatment, primary amines introduced onto the MWCNT surface contain electron-accepting sites, which helps the basic surface (untreated) be converted to an amphoteric surface ($P_{s}^{a}$ and $P_{s}^{b}$ are opposite in sign). The decreased contact angle between the MWCNT thin film and polar probe liquids and the change to an amphoteric surface chemistry is in good agreement with the XPS results. These indicate that the wettability changes in the thin film of carbon nanotubes by the plasma treatment were due to the changes in surface chemistry.
Table 4.3 Surface energy components of untreated and plasma treated MWCNT thin films determined from a CQC model.

<table>
<thead>
<tr>
<th>MWCNTs</th>
<th>$\gamma_{S_{\text{tot}}}^\text{(mJ/m}^2\text{)}$</th>
<th>$\gamma_{S_{LW}}^\text{(mJ/m}^2\text{)}$</th>
<th>$\gamma_{S_{AB}}^\text{(mJ/m}^2\text{)}$</th>
<th>$P_{S_{a}}^{1/2}$</th>
<th>$P_{S_{b}}^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>42.33</td>
<td>45.26</td>
<td>-2.93</td>
<td>-1.38</td>
<td>-2.11</td>
</tr>
<tr>
<td>Plasma treated</td>
<td>49.62</td>
<td>45.21</td>
<td>4.40</td>
<td>0.47</td>
<td>-4.52</td>
</tr>
</tbody>
</table>

**Surface morphology**

The morphologies of the untreated and treated MWCNTs observed by SEM and HRTEM are shown in Figure 4.5. In the SEM images, the MWCNTs are more clearly seen after N$_2$/H$_2$ plasma treatment because some contamination was removed. From the TEM images it can be seen that the surface of the N$_2$/H$_2$ plasma treated MWCNTs appears rougher than the untreated. However, the electron diffraction patterns of MWCNT clusters before and after N$_2$/H$_2$ plasma treatment (see insets of Figure 4.5a and b) appear similar. This indicates that the integrity of the MWCNT structure is maintained.
Figure 4.5 TEM and SEM images of MWCNTs before (a) and after (b) N$_2$/H$_2$ CW plasma treatment. The insets show electron diffraction patterns from MWCNT clusters in a nearby region.

In order to examine the effect of plasma treatment on the MWCNT surface, the same spot on a sample before and after plasma treatment was recorded using AFM, as shown in Figure 4. 6. Comparison of Figure 4. 6a and b shows the MWCNTs are more clearly seen after N$_2$/H$_2$ plasma treatment. This is because some contamination and amorphous carbon layers were removed during the N$_2$/H$_2$ plasma treatment.
In Figure 4.7a, the XRD patterns show no obvious difference between the untreated and treated MWCNTs. The main peak ($2\Theta = 25^\circ$) of both samples is assigned to the structure of graphite [261]. This indicates that the structure of the MWCNTs before and after plasma treatment is similar, and so was not altered by the plasma treatment. The TGA trace of treated MWCNTs (Figure 4.7b) shows about a 10% loss below 600 °C, which may be due to oxidation or decomposition of the added nitrogen functional groups [262], whereas the mass of the untreated MWCNT sample is stable. In Figure 4.7c, the greatest rate of carbon decomposition occurs at 584 °C for both samples. This indicates that the N$_2$/H$_2$ plasma did not significantly damage the MWNCTs. The XRD and the TGA results further confirm that the integrity of the untreated MWCNT structure was maintained. This is important for applications of MWCNTs, for which the required surface functionality must be achieved without damage to the tube structure.
4.2 Heptylamine Plasma Polymerization

4.2.1 Experimental

Heptylamine plasma polymerization (HAPP) for functionalization of the CNT surface was performed using both System 1 and System 2. For System 1, the samples were prepared in the form of thin films and then located under the plasma source. Samples were firstly activated and cleaned by argon plasma (CW 75 W, \(5\times10^{-2}\) mbar) for 30 s. For comparison with N\(_2\)/H\(_2\) plasma treatment, the total input energy was kept the same (100 W·min) for all experiments. The plasma...
conditions of the HA plasma polymerizations for this work were: (i) CW: continuous wave alone (50 W, 2 min); (ii) P: pulsed alone (peak RF power 50 W, duty cycle 1/20, 40 min); (iii) CW + P: continuous wave plus pulsed (CW 50 W, 1 min; P 50 W, duty cycle 1/20, 20 min). During CW + P operation, the mode was quickly shifted from CW to P mode in 1 to 2 s without closing the monomer inlet valve. The exiting gas was passed through a cold trap and the chamber pressure (1×10^{-1} mbar) was maintained constant for all experiments. After deposition, the monomer inlet valve was immediately closed and the reactor chamber was pumped down to base pressure (< 1×10^{-3} mbar) to keep the samples in vacuum for 30 min, before taking them out from the chamber to be stored in a desiccator.

In order to achieve a uniform treatment, the stirring plasma system, System 2, was adopted. About 200 mg of MWCNT powder was placed in the bottom of the round flask (as described in Section 3.3), where the nanotubes were vigorously stirred using a magnetic bar and thus the surface of nanotubes exposed to the plasma for thin film deposition can be continuously renewed during the plasma polymerization process. Argon plasma (CW 75 W, 5×10^{-2} mbar, 30 sec) was used to first activate and clean the surface before the polymerization followed by CW + P plasma polymerization of HA. In order to examine the effect of the stirring speed on the plasma treatment, three different stirring speeds were tested: 250 rpm, 500 rpm and 750 rpm, under the same plasma parameters. Moreover, plasma polymerization was evaluated by using different parameters under a same stirring speed. The input power was 50 W for the CW plasma, while a peak power of 50 W or 100 W was used for the pulsed plasma. The duty cycles were 1/20, and 1/10, with t_{on} of 1 ms for the pulsed plasma. The system pressure was maintained at
5×10^{-2} \text{ mbar} \text{ for all the treatments. The detailed plasma conditions are listed in Table 4.4.}

Table 4.4 The plasma conditions of HA plasma polymerization in System 2.

<table>
<thead>
<tr>
<th>Plasma conditions</th>
<th>Stirring Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>HAPP1-250</strong></td>
<td>CW: 50 W, 0.05 mbar, 1 min; 250 rpm</td>
</tr>
<tr>
<td>Argon plasma: CW, 75 W, 5×10^{-2} \text{ mbar, 30 sec}</td>
<td></td>
</tr>
<tr>
<td><strong>HAPP1-500</strong></td>
<td>P:50 W, duty cycle 1/20, 500 rpm</td>
</tr>
<tr>
<td>5×10^{-2} \text{ mbar, 30 sec}</td>
<td></td>
</tr>
<tr>
<td><strong>HAPP1-750</strong></td>
<td>0.05 mbar, 20 min; 750 rpm</td>
</tr>
<tr>
<td>Argon plasma: CW,75 W, 5×10^{-2} \text{ mbar, 30 sec}</td>
<td></td>
</tr>
<tr>
<td><strong>HAPP2-750</strong></td>
<td>CW: 50W, 0.05 mbar, 1 min; 750 rpm</td>
</tr>
<tr>
<td>Argon plasma: CW,75 W, 5×10^{-2} \text{ mbar, 30 sec}</td>
<td>P:100W, duty cycle 1/10, 0.05 mbar, 10 min</td>
</tr>
</tbody>
</table>

4.2.2 Results and discussion for HAP in System 1

**Surface chemistry**

The chemical nature of the MWCNT surface after HA plasma polymerization was investigated by XPS. As shown in the analysis in Section 4.1.2, the C1s spectrum of untreated MWCNTs (Figure 4.1a) is composed of a graphite signal and sp³ carbon bonds. After plasma polymerization, the C1s peak in Figure 4.8a is composed of two peaks, at 284.6 eV and 285.8 eV. In the analysis of components, the chemical shifts for C-N and C-O species are very similar [152], but in the case of HA plasma polymerization, MWCNTs after plasma polymerization have been covered by a plasma polymerized HA film (as can be seen in Figure 4.10a), so the small amount of oxygen (about 0.8 %) detected is from post-plasma reactions after exposure to air. Therefore, the peak at 285.8 eV can be fully attributed to amine (C-N) groups. Compared to the N₂/H₂ plasma treatment, where several
different nitrogen containing functional groups were introduced onto the MWCNT surface as previously discussed, HA plasma polymerization, to a large extent, retains the amine functional groups from the monomer.

Figure 4.8 XPS high resolution C1s (a) and survey spectra (b) of MWCNTs after HA CW + P plasma polymerization.

After plasma polymerization, samples were tested using chemical derivatization with TFBA (in Figure 4.9a). Then the N/C, NH₂/C and NH₂/N ratios were calculated according to the amount of F atoms detected by XPS. The results are shown in Figure 4.9 (b and c). A similar N/C ratio is found for P and CW + P (about 7.5%). The highest N/C ratio was found in the CW plasma polymerized sample. This higher N/C ratio comes from a reduction in the amount of carbon on the surface, due to fragmentation of the monomer and etching of the forming polymer during CW treatment [55]. The density of NH₂ groups for CW is about 1.7% which is slightly lower than that for the pulsed plasma modified sample (about 1.9%). This is because some of these groups have been transformed into imine or nitrile groups [263]. The NH₂/C ratio for HAPF CW + P is the highest (about 4%) of the three modes, because the combined method possesses the advantages of CW and pulsed modes. In the CW plasma polymerization, the
precursor undergoes a high level of fragmentation leading to a highly cross-linked plasma polymer film which provides a good foundation for better bonding of a pulsed HAPP layer with a higher level of retention of amino groups due to the reduction of the fragmentation of the monomer during the pulsed plasma polymerization. Selectivity for primary amines (NH$_2$/N) for HAPP CW + P (about 42%) is higher than any other treatment (Figure 4.9c), which demonstrates that the combined method can provide a relatively high selectivity for primary amines.

Figure 4.9 (a) XPS survey spectra after derivatization with TFBA for MWCNTs after HA CW + P plasma polymerization; (b) the NH$_2$/C and N/C ratios and (c) the NH$_2$/N ratios at the surface of HA plasma polymerized MWCNTs using three plasma modes.
For both gas and monomer plasma treatments with the three different modes, the density of primary amines was found in the following order CW + P > P > CW. It has been reported that the amount of primary amine groups achieved by plasma polymerization is usually higher than by using NH\textsubscript{3} or N\textsubscript{2}/H\textsubscript{2} plasma treatments [9]. However, by employing the combined (CW + P) plasma mode, the density of primary amine groups achieved using N\textsubscript{2}/H\textsubscript{2} plasma was higher than that using HA with CW or P plasma polymerization alone, although it was lower than that for HAPP CW + P. It was in the order of HA-CW + P > N\textsubscript{2}/H\textsubscript{2}-CW + P > HA-P > HA-CW. This enables a higher density of the desired functional group to be achieved by the mixed gas plasma than by CW or P plasma polymerization under the same plasma energy input.

**SEM, TEM and XRD results**

The SEM image for the MWCNTs after HA plasma polymerization in Figure 4.10a clearly shows a polymer film deposited on the MWCNT surface, with individual MWCNTs coated with a film about 3 nm thick (Figure 4.10b). There is no obvious difference between the XRD profiles of the untreated and HA plasma polymerized MWCNTs (Figure 4.10c). This indicates that the structure of the MWCNTs has not been altered.
4.2.3 Results and discussion for HAP in System 2

**Surface chemistry**

The chemical nature of the MWCNT surface before and after HA plasma polymerization was investigated by XPS. The N/C and O/C ratios on the surface of MWCNTs after HA plasma polymerization with different plasma conditions in System 2 are shown in Figure 4.11. Typical XPS C1s spectra obtained for MWCNTs after plasma polymerization are shown in Figure 4.12. From Figure 4.11, it can be seen that there is no difference in the N/C ratios (about 5.4%) on the surface of MWCNTs between the plasma treatments, HAP1-250, HAP1-500 and HAP1-750, which had the same plasma conditions but different stirring conditions.
speeds. This indicates that the stirring speed has little effect on the incorporation of functionality during the plasma polymerization. A change in the O/C was observed between the three treatments. The presence of oxygen in HA plasma polymers is due to post-plasma reactions with oxygen from air [62], so the exposure to air and moisture may have been different for the three samples. The C1s peaks for both HAPP1-750 MWCNTs and HAPP1-750 MWCNTs are composed of two peaks, at 284.6 eV and 285.8 eV, which are attributed to C= C and C-N signals. However, the relative intensity distribution of amine groups (C-N) in the C1s spectra for HAPP1-750 MWCNTs is much larger than that for HAPP2-750 MWCNTs. This suggests that the level of amine functional groups on the HAPP1-750 MWCNTs is higher. From Table 4.5, the N/C ratio is highest for the HAPP2-750 MWCNTs. It is about 8.8%, but higher nitrogen content does not mean higher amine functionality. This higher N/C comes from less carbon on the surface, due to fragmentation of the monomer and etching of the forming polymer [55]. Compared to the plasma condition HAPP1-750, the HAPP2-750 treatment had double the input power and duty cycle but half the treatment time for the pulsed plasma polymerization (Table 4.4). Such increases in input power or duty cycle generally result in a decrease in the level of functional groups achieved by pulsed plasma polymerization [6], due to the increase in fragmentation of the monomer (during $t_{on}$) and the decrease in the reaction time for radicals (during $t_{off}$).
Figure 4.11 The ratios of N/C and O/C from XPS of MWCNTs under different plasma conditions.

Figure 4.12 XPS high resolution C1s spectra for MWCNT samples: (a) HAPP1-750 MWCNTs; (b) HAPP2-750 MWCNTs.

A typical FTIR spectrum of MWCNTs after plasma polymerization of HA is presented in Figure 4.13. For comparison, the FTIR spectrum of the monomer HA was also obtained as shown in Figure 4.13. The peaks in the range 3300-3400 cm⁻¹ observed in Figure 4.13 correspond to the N-H stretching vibration of primary amines [264]. In Figure 4.13, both spectra show similar peaks around 2900 cm⁻¹, which are assigned to the aliphatic C-H stretching bands [171, 265, 266]. This indicates some similarities in structure between the HAPP films on the MWCNT
surface and HA. The peaks at 1671 and 1097 cm\(^{-1}\) in the spectra of HAPP2-750 MWCNTs are C-N stretching in primary amines [145, 171].

![FTIR spectra for HAPP2-750 MWCNTs and HA.](image)

Figure 4.13 FTIR spectra for HAPP2-750 MWCNTs and HA.

**TGA-DSC analysis**

The TGA profile gives a function of temperature with mass loss, while the DSC profile provides a function of temperature with heat flux. In Figure 4.14a, there is no significant weight loss before 550 °C in the untreated MWCNTs (u-MWCNTs), while the TGA profiles for HAPP1-750 MWCNTs and HAPP2-750 MWCNTs show a weight loss of about 50% and 20%, respectively, at 550 °C. In both cases most of the weight loss came from the plasma polymer on the MWCNTs. This suggests that more polymer was deposited by HAPP1-750 than HAPP-750. This is because the lower input energy helped retain relatively long fragmented molecules of the monomer and the longer deposition time allowed more plasma polymer to be formed. Meanwhile, the onset of decomposition for both plasma polymerized MWCNTs was significantly lowered, as shown in Figure 4.14.

Unlike u-MWCNTs, the DSC traces of both HAPP coated MWCNTs in Figure 4.14b show a degradation peak at 350 °C before the greatest rate of carbon decomposition occurs at 584 °C. This is because the added organic functional
groups are decomposed before the onset of combustion of the MWCNTs [218], which provides further evidence for a HA plasma polymer on the MWCNTs.

Figure 4.14 (a) TGA and (b) DSC profiles of u-MWCNTs and HAP MWCNTs.

**Surface morphology**

The SEM images of the HAP1-750 MWCNTs and HAP2-750 MWCNTs are shown in Figure 4.15. From the SEM image in Figure 4.15a the MWCNTs for HAP1-750 are covered by the HA plasma polymeric film, while most MWCNTs in HAP2-750 treatment are coated by the HA plasma polymer. This is in good agreement with the TGA observations. The diameter of the HAP2-750 MWCNTs is obviously increased compared with that of u-MWCNTs (Figure 4.5a). It is likely that the HAP1-750 MWCNTs would be unsuitable for use in a nanocomposite due to too much deposited plasma polymer.
Figure 4.15 SEM image of MWCNTs: (a) HAPP1-750 MWCNTs; (b) HAPP2-750 MWCNTs.

4.3 Plasma Functionalization of BNNTs

In this section, plasma functionalization of BNNTs with nitrogen functional groups is presented.

4.3.1 Experimental

BNNTs used in this study were synthesized on stainless steel substrates, as described in Section 3.2. The plasma modification was carried out in System 1. Argon plasma was used to clean and to activate the surface before nitrogen functionalization. N\textsubscript{2}/H\textsubscript{2} was chosen for introducing nitrogen-functional groups, by bonding a N or H to the nanotube surface. The addition of H\textsubscript{2} was to try to remove oxygen contamination and also to possibly allow formation of amine (NH or NH\textsubscript{2}) groups.

Since a thin amorphous layer was found on the received BNNTs (Figure 4.19a and b), CW plasma treatment was first chosen for removing the amorphous layer. Then, the CW + P approach was applied to functionalize the BNNTs with amine groups. The input power was kept at 100 W for all the treatments. This power is low enough to minimize damage to the tube surface by energetic electrons/ions.
and UV photons in the plasma while the level of modification can be altered by changing the treatment time. The pressure of the N₂/H₂ plasma was chosen at 1 × 10⁻¹ mbar. This pressure was the optimum pressure for obtaining a maximum atomic nitrogen, which was proofed in our previous work [267]. After each experiment, the gas flow was stopped and the samples were left in the chamber under vacuum for 30 min to allow the surface to stabilize before exposure to air. The experimental conditions are listed in Table 4.5.

Table 4.5 Plasma conditions for treating BNNTs.

<table>
<thead>
<tr>
<th>N₂/H₂ plasma</th>
<th>1 min Ar plasma</th>
<th>CW: 5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-treatment</td>
<td>CW: 5 min</td>
<td>P: 10 min, DC = 10%</td>
</tr>
</tbody>
</table>

XPS was employed to study changes in surface chemistry. SEM and TEM were used to investigate the surface morphology of the BNNTs before and after the plasma treatment.

4.3.2 Results and Discussion

Surface chemistry

The XPS B1s and N1s spectra of the untreated BNNTs (u-BNNTs) are shown in Figure 4.16. The B1s spectrum (Figure 4.16a) has only one peak, at 190.7 eV. This B1s binding energy is slightly higher than that of hexagonal BN (h-BN) (190.3 eV), which could be due to the presence of boron atoms simultaneously bonded to oxygen and nitrogen [268]. There is also only one peak in the N1s spectrum at 398.3 eV, which has been identified as a turbostratic structure (t-BN) [269], attributed to the presence of N-O and N-OH bonds [270]. Rivière et al.
[270] reported that a Rutherford back-scattering study indicated that amorphous BN (a-BN) containing a significant amount of oxygen, exhibited similar behaviour to t-BN, and its behaviour during exposure to air was analogous. Additionally, as XPS used in this work only detects the surface layer to a depth of about 1-3 nm, the elements detected on the u-BNNTs were in the a-BN layer, if this covers most of the surface. This is confirmed by TEM images of the u-BNNTs in Figure 4.19a and b, where an a-BN layer (about 5-10 nm thick) was observed on the BNNT surface.

![Figure 4.16 XPS spectra for the untreated BNNTs: (a) B1s and (b) N1s.](image)

The XPS B1s spectrum of the BNNTs after treatment by N2/H2 CW plasma (Figure 4.17a) shows the emergence of a h-BN peak (at 190.4 eV), which indicates that the a-BN has been removed allowing the h-BN to be observed, which is further conformed by TEM observation. The B1s spectrum also shows another peak at 191.6 eV, (higher than the binding energy of h-BN), labelled “non-h-BN”. It corresponds to boron atoms bonded to oxygen atoms. From the deconvolution of the N1s peak (Figure 4.17b), it can be seen that amide groups (400.2 eV, CO-NH) were introduced into the BNNTs. The obvious shoulder in the C1s peak (Figure 4.17c) is further evidence for the presence of amide groups.
(288.1 eV). The carbon content was come from contamination during producing the BNNTs.

Figure 4. 17 XPS spectra (a) B1s, (b) N1s, (c) C1s of BNNTs after N2/H2 CW plasma treatment.

The B1s spectrum of BNNTs (Figure 4.18a) after N2/H2 CW + P plasma treatment also shows h-BN and non-h-BN peaks. Compared to the N1s of BNNTs after CW plasma treatment, a new peak at 399.0 eV were found in the N1s spectrum (Figure 4.18b), which indicates the amine groups (C-NH2 or C-NH-C) were introduced onto the BNNT surface by N2/H2 CW + P plasma. Consistent with the N1s spectra, the C1s spectrum (Figure 4.18c) also shows that the CW + P method grafts amine groups (285.8 eV) on the surface of BNNTs, where the other two components at 286.7 eV (imine, C=N) and 288.1 eV (amide, CO-NH) were
also observed. Compared to N$_2$/H$_2$ CW plasma treatment, more nitrogen functional groups were introduced onto the BNNT surface by the combined method. This is because in the combined method, the CW plasma effectively removed the amorphous layer as well as created the active sites on the nanotube surface, which makes it easy to graft the radicals generated by the following pulsed plasma.

Figure 4.18 XPS spectra (a) B1s, (b) N1s, (c) C1s of BNNTs after CW + P N$_2$/H$_2$ plasma treatment.

**Surface morphology**

TEM was further used to observe possible changes in the BNNT surface induced by plasma treatment. The surface structure of the BNNTs before and after plasma treatment is shown in Figure 4.19. TEM images (Figure 4.19a and b) show there
was a-BN layer about 5-10 nm thick on the u-BNNT surface. After plasma treatment, the a-BN layer was basically removed (Figure 4.19c). Its thickness dropped to less than 1 nm, which is in good agreement with the XPS analysis. Figure 4.19d shows that the treated BNNT surface became rough, but the structure of the nanotubes was not damaged.

Figure 4.19 HRTEM images (scale bar, 10 nm) of (a) untreated BNNT; (b) close-up of the wall; (c) N₂/H₂ CW plasma treated BNNT ;(d) close-up of the wall.

4.4 Summary

The use of a combination of continuous wave and pulsed plasma treatment has been shown to be very effective at functionalizing the surface of MWCNTs with amines in one step. The CW + P plasma mode for both the gas and the monomer
gives a more selectable and higher level of functional groups. The interpretation of the gas CW + P method was given. It is shown that a level of primary amines of 3%, higher than previously reported for any nitrogen-containing gas plasma treatment, can be achieved using a mixture of N₂ and H₂, which is preferable to using NH₃. Even higher levels (about 4%) of primary amines can be achieved by coating the MWCNTs with a thin layer of plasma polymerized heptylamine. In both cases, the highest levels were achieved using the combined continuous plus pulsed plasma mode. The TEM, XRD and TGA-DSC results show that the integrity of the MWCNT structure was maintained by the plasma treatments. Therefore, the combine plasma is a non-destructive, more effective and practical method for covalent functionalization of nanotubes with high levels of primary amines. In the next chapter, the effectiveness of these functionalized MWCNT on their dispersion in, and adhesion to, an epoxy resin was studied. The effect of the CW + P plasma on the mechanical properties of the functionalized MWCNTs/epoxy nanocomposites was also studied.

The CW + P HA plasma polymerization was also investigated in plasma System 2. HA plasma polymers with amine functional groups were uniformly deposited on the MWCNT surface. It is believed that the System 2 could well address the problem for plasma treatment for powders or nano materials. The amorphous surface layer found on the outside of the BNNTs can be removed without damaging the nanotubes after CW plasma treatment, allowing their h-BN structure to be seen. More nitrogen functional groups were introduced onto the surface of BNNTs using N₂/H₂ CW + P plasma.
Chapter 5 Plasma Functionalized Nanotube Reinforced Epoxy Nanocomposites

In chapter 4, it was shown that the surface of the MWCNTs was functionalized with primary amines using plasma in a N\textsubscript{2}/H\textsubscript{2} gas mixture and by HA plasma polymerization. The highest densities of primary amines were achieved using the combined (CW + P) plasma mode. Neither plasma treatment damaged the MWCNT structure.

In this chapter, the influence of the primary amines, on the surface of the MWCNTs, on the dispersion of the MWCNTs and their interfacial adhesion to an epoxy resin is examined. N\textsubscript{2}/H\textsubscript{2} plasma treated MWCNTs in plasma System 1 and HAPP treated MWCNTs in plasma System 2 were used to reinforce the epoxy resin. The mechanical properties of the amine functionalized MWCNT/epoxy nanocomposites were determined by DMA and three-point bending tests. Nanoindentation tests were used to investigate the mechanical properties at the nano scale. The curing behaviour of the Epon 862/Epikure W system, with and without MWCNTs, was studied by DSC. The fracture surfaces of the nanocomposites after the three-point bending tests were investigated by SEM in order to evaluate the dispersion of the MWCNTs and their adhesion to the epoxy resin.

5.1 N\textsubscript{2}/H\textsubscript{2} Plasma Treated MWCNT/Epoxy Nanocomposites

5.1.1 Experimental

Prior to N\textsubscript{2}/H\textsubscript{2} plasma treatment, the MWCNT powder (50 mg) was ultrasonically dispersed in ethanol. Droplets of the suspension were placed on four pieces of glass (25 cm ×15 cm) and then dried at room temperature. The samples were then
treated using N\textsubscript{2}/H\textsubscript{2} CW + P plasma, as described in Section 4.1.1. The N\textsubscript{2}/H\textsubscript{2} plasma conditions were: (i) CW: continuous wave alone (50 W, 1 min); followed by (ii) P: pulsed alone (peak RF power 50 W, duty cycle 1/20, 20 min). The chamber pressure was maintained at 0.08 mbar. The density of primary amines (NH\textsubscript{2}/C) on the plasma treated nanotubes was quantified by derivatization with TFBA. The density was calculated from the amount of F atoms using equation 3.3 (Section 3.5.4). The relatively high density of approximately 3\% was achieved.

Figure 5.1 Scheme of the preparation of the f-MWCNT/epoxy nanocomposites. Untreated MWCNT (u-MWCNT)/epoxy and functionalized MWCNT (f-MWCNT)/epoxy nanocomposites were prepared, plus neat epoxy. The preparation procedure for the f-MWCNT/epoxy nanocomposites is illustrated in Figure 5.1. The details of the procedure can be found in Section 3.4. A low loading (0.1 wt\%) of MWCNTs were used to reinforce the epoxy resins. The mechanical properties of the nanocomposites were investigated at both nano and macro scale.

5.1.2 Results and Discussion

Dispersion test

The dispersion of the u-MWCNTs and f-MWCNTs in ethanol was investigated. Figure 5.2 presents a visual comparison. It was found that the f-MWCNTs dispersed well and the solution was stable as no sedimentation was visible even
after two weeks. On the other hand, the u-MWCNTs formed a sediment at the bottom of the bottle (Figure 5.2).

![Figure 5.2 Dispersion of MWCNTs (0.2 g/L in ethanol) before (A) and after (B) N₂/H₂ CW + P plasma treatment; left (0 hour) and right (2 weeks later).](image)

DSC analysis

The curing behaviour of the Epon 862/Epikure W system with u-MWCNTs, f-MWCNTs and without MWCNTs was studied by DSC. The DSC curves are presented in Figure 5.3 and the detailed results which calculated from the DSC curves are listed in Table 5.1. Only one exothermic reaction peak is seen in all the curves. The peak temperature ($T_p$) for the curing reaction decreased slightly with the addition of the MWCNTs (Table 5.1), compared to the system without MWCNTs. This indicates that MWCNTs can accelerate the curing reaction [271]. This is because MWCNTs contributes to the higher thermal conductivity into the epoxy [272]. The $T_p$ (196.5 °C) of the epoxy resin system with f-MWCNTs is lower than that with u- MWCNTs (197.7°C), which could be due to the interfacial reaction between the amine groups on the f-MWCNT surface and epoxy groups. This reaction improved the dispersibility of f-MWCNTs in the epoxy resin, which also results in the resin system with f-MWCNTs having the lowest cure onset temperature ($T_o$) and the highest enthalpy ($\Delta H$) [272, 273].
Figure 5.3 DSC curing curves of different Epon 862/Epikure W systems.

Table 5.1 The onset temperature, peak temperature and heat of curing for Epon 862/Epikure W with and without MWCNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T_o (°C)</th>
<th>T_p (°C)</th>
<th>ΔH(J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon 862/Epikure W</td>
<td>121.2</td>
<td>199.9</td>
<td>126.6</td>
</tr>
<tr>
<td>Epon 862/Epikure W/u-MWCNTs</td>
<td>105.6</td>
<td>197.7</td>
<td>165.1</td>
</tr>
<tr>
<td>Epon 862/Epikure W/f-MWCNTs</td>
<td>100.7</td>
<td>196.5</td>
<td>167.1</td>
</tr>
</tbody>
</table>

**Flexural analysis**

The flexural properties of composite samples were determined by three-point bending tests. Flexural modulus is used as an indication of the stiffness of a sample when flexed. Flexural strength is defined as an ability of a sample to resist deformation under stress and it represents the maximum stress during the bending test. Toughness is an ability of a sample to absorb energy in the testing before fracture. It has been reported that with addition of CNTs, the flexural modulus, flexural strength and toughness of the epoxy resin can be improved, due to the extraordinary mechanical properties of CNTs [274]. The surface functionalized CNTs can further give a better improvement in these properties of the epoxy due
to improved dispersion and adhesion [125, 180, 275]. The typical stress-strain curves of the three point bending tests are shown in Figures 5.4a, where the slopes of stress-strain curves are the flexural modulus of samples. The flexural properties are summarized in Figure 5.4b. Each result is the average of at least three tests, and the error bars show the mean deviation of each set of measurements. It can be seen (Figure 5.4a) that the addition of u-MWCNTs to the epoxy enhances the flexural strength due to the incorporation of rigid components into the relatively soft epoxy matrix. The flexural strength of the epoxy increases by 13% after introduction of the f-MWCNTs (Figure 5.4a). Although the u-MWCNTs slightly increase the flexural modulus and toughness as shown in Figure 5.4b, the f-MWCNTs provide significant increases of about 15% and 38%, respectively, in comparison to neat epoxy. Part of this could be attributed to the better dispersion of MWCNTs in the epoxy matrix after plasma treatment. Additionally, the reaction between the primary amines on the f-MWCNTs and the epoxy (Figure 5.1) results in improved interfacial adhesion [122], which leads to more effective load transfer between the epoxy and MWCNTs. Recently, Hosur et al. [101] have reported increases of about 12% in flexural modulus and about 14% in flexural strength with 0.2 wt% loading of commercial MWCNTs with primary amine-functionalization (< 0.5%) in an epoxy matrix. Gojny et al. [123] have shown that with 0.1 wt% of commercial primary amine-DWCNTs, the toughness of epoxy increased by about 20%.
The fractured surfaces of the samples were examined by SEM. The unfilled epoxy has cleavage planes showing a relatively flat and smooth fracture which is typical of brittle materials (Figure 5.5a). The fracture surfaces of the epoxy filled with 0.1 wt% u-MWCNTs and 0.1 wt% f-MWCNTs (Figure 5.5b and c) appear very rough compared to that of the neat epoxy. This is because the crack propagation was forced to change direction by the presence of MWCNTs [98]. It indicates that the fracture of MWCNT reinforced samples results from a ductile deformation [125], which is in agreement with their flexural properties. Some agglomeration of the u-MWCNTs in the resin can be seen in Figure 5.5d. Many MWCNTs were visibly pulled out of the epoxy matrix suggesting poor adhesion. The dispersion of the f-MWCNTs (Figure 5.5e) appears to be improved as most of the visible nanotubes were well separated (shown by red circles in the inset of Figure 5.5e). The magnified image (Figure 5.5e) shows the MWCNTs, which appear as bright dots on the fracture surface, were not pulled out but broken during the three-point bending test. This suggests good interfacial bonding between the modified MWCNTs and epoxy resin. From the above results, it can be concluded that the amine groups on the surface of the MWCNTs introduced by the N$_2$/H$_2$ plasma
treatment improved both the dispersion of the MWCNTs and their interfacial bonding with the epoxy matrix, which led to the marked improvement in the flexural properties of the f-MWCNT nanocomposites.

Figure 5.5 SEM images of fractured surfaces of composite samples: (a) neat epoxy, (b) 0.1 wt% u-MWCNT/epoxy and (c) 0.1 wt% f-MWCNT/epoxy; (d) and
Figure 5.6 shows the loss factor (tan delta) and storage modulus of the neat epoxy and MWCNT reinforced nanocomposites. The loss factor (tan delta) is the ratio of loss modulus to storage modulus and is a measure of the energy lost, expressed in terms of the recoverable energy [276]. From Figure 5.6a, it can be seen that the addition of the MWCNTs increases the storage modulus of the epoxy in the glassy region, owing to their high elastic modulus [275]. The increase is higher for the f-MWCNT samples. This is again attributed to the improved adhesion between the plasma treated MWCNTs and epoxy. As the storage modulus reflects the elastic modulus of the composite [277], it suggests that the f-MWCNTs are more effective at increasing the modulus, which is in agreement with the nanoindentation results below. It is also worth noting that the storage modulus for the f-MWCNT samples is greater at higher temperature (in the rubbery region). At 140 °C the storage modulus of the composite with f-MWCNTs is about 4 times that of both the epoxy and u-MWCNT reinforced samples. However, a slight decrease in the storage modulus of the u-MWCNT/epoxy was observed around the rubbery region, which is consistent with poor interfacial bonding and dispersion of the MWCNTs [278].
Figure 5.6 DMA results for neat epoxy and MWCNT reinforced nanocomposites. The glass transition temperature, $T_g$, defined as the temperature at which maximum loss factor is reached, is slightly lower after adding either u-MWCNTs or f-MWCNTs, as shown in Figure 5.6b. The slight drop in $T_g$ for u-MWCNT/epoxy samples might be due to partial absorption of the curing agent by agglomeration of u-MWCNTs in epoxy resin (see Figure 5.5d) [122, 278]. This leads to change in curing stoichiometric ratio, thus decreasing the $T_g$ [278]. A small decrease in $T_g$ for epoxy was also observed with the f-MWCNTs. This can be because f-MWCNTs are covalently attached to the epoxy matrix which may also result in an increase in free volume bringing out a slight drop in $T_g$ [279].

It was worth noting that the dispersion procedures such as hot stirring and ultrasonication might have an effect on the thermal properties of nanocomposites. Recently, González-Domínguez et al. [276] reported that storage modulus at room temperature of neat epoxy dropped by about 18% and the $T_g$ decreased by about 10°C when the epoxy resin was processed using hot stirring (at 60°C, for 45 min) and tip ultrasonication (200 W, continuously for 15 min) steps. They suggested it was because such dispersion procedures caused some chain scission of the epoxy, which in turn would reduce both the degree of crosslinking of the cured epoxy resin. In this work, the neat epoxy which were subjected to the same preparation
procedure as the nanocomposite samples (tip ultrasonication, 300 W, a pulsed mode, 2 seconds on, 4 seconds off, for 30 min, see Section 3.4) were also prepared and tested. It can be seen from Table 5.2 that storage modulus and $T_g$ of the neat epoxy after ultrasonication had a very slight drop. This suggests that the ultrasonication procedure in this work do not cause a serious damage to the epoxy matrix, which can be attributed to the chosen pulsed mode during the ultrasonication.

Table 5.2 The storage modulus and $T_g$ of the neat epoxy with and without the ultrasonication.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Storage modulus (MPa) (at 30 °C)</th>
<th>$T_g$ (°C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy</td>
<td>2051 ± 19</td>
<td>155.3 ± 0.3</td>
</tr>
<tr>
<td>Epoxy-ultrasonication</td>
<td>2033 ± 15</td>
<td>154.2 ± 0.6</td>
</tr>
</tbody>
</table>

**Nanoindentation results**

Nanoindentation has been used as an accurate method for evaluating the deformation behaviour, hardness and elastic modulus of CNT reinforced polymer composites [258]. The method was used here to obtain the typical load-displacement curves of the neat epoxy and of epoxy reinforced with MWCNTs (with and without plasma treatment) using maximum loads of 2 mN and 3 mN. According to equations 3.5 and 3.6 of the Oliver-Pharr method, as described in Section 3.5.13, the area of the indentation is inversely proportional to the hardness of the composite, while the slope of the unloading curve is directly proportional to the elastic modulus. Typical load-displacement curves and SPM images of indentations made using a peak load of 3 mN are shown in Figure 5.7, and the
calculated nano-mechanical properties for peak loads of 2 mN and 3 mN are presented in Table 5.3.

![Graphs showing load–displacement curves](image)

Figure 5.7 Representative load–displacement curves of nanoindentations for the epoxy, unmodified MWCNT/epoxy and the plasma modified MWCNT/epoxy composites at maximum loads of (a) 2 mN and (b) 3 mN. Insets are SPM images of the indentation impressions.

For both loads, it can be seen from Figure 5.7 that the depth and area of the indentations in the f-MWCNT reinforced sample are smaller than those in the neat epoxy and u-MWCNTs samples. However, the unloading slope is the highest of all the samples. Thus the f-MWCNT/epoxy nanocomposites have better nano-mechanical properties. Compared to the neat epoxy, the elastic modulus and hardness of the f-MWCNT/epoxy samples have increased by 10% and 6% at 2 mN. Larger improvements are seen at a load of 3 mN. The hardness and elastic modulus have increased by about 40% and 19%. For the u-MWCNT/epoxy nanocomposites, the improvements in the elastic modulus and hardness are more modest than those of f-MWCNTs at either the 2 mN or 3 mN load.
Table 5.3 Summary of nano-mechanical properties.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Load (mN)</th>
<th>$E^*$ (GPa)</th>
<th>$H$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>2</td>
<td>4.617 ± 0.009</td>
<td>0.364 ± 0.001</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.227 ± 0.007</td>
<td>0.325 ± 0.001</td>
</tr>
<tr>
<td>u-MWCNT/epoxy</td>
<td>2</td>
<td>5.066 ± 0.018</td>
<td>0.506 ± 0.007</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>4.702 ± 0.028</td>
<td>0.388 ± 0.012</td>
</tr>
<tr>
<td>f-MWCNT/epoxy</td>
<td>2</td>
<td>5.099 ± 0.011</td>
<td>0.556 ± 0.008</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5.051 ± 0.032</td>
<td>0.456 ± 0.006</td>
</tr>
</tbody>
</table>

The results shown in Table 5.3 indicate that the measured values of both the elastic modulus and hardness of neat epoxy and nanocomposite samples are dependent on the peak load. The elastic modulus and hardness decrease with the increase of the peak load from 2 mN to 3 mN. However, the f-MWCNT/epoxy nanocomposites have the smallest decrease among the tested samples. The improvement in interfacial bonding after plasma treatment which gives better load transfer between the epoxy and MWCNTs is the most likely explanation for the increases. The increase in elastic modulus of the f-MWCNT/epoxy nanocomposite is also consistent with the results of the dynamic mechanical analysis.

5.2 HAPP MWCNT/Epoxy Nanocomposites

5.2.1 Experimental

The performance of nanocomposites using MWCNTs coated with a uniform thin polymer layer produced by HA plasma polymerization was also examined. About 200 mg of MWCNTs was placed inside the reactor and stirred by a magnetic bar.
(750 rpm). A fresh batch of the monomer liquid was placed in a round bottom flask and connected to the reactor chamber by a stainless steel line and a manual flow control valve. The system pressure was maintained at 0.05 mbar by a rotary pump which was protected by a liquid nitrogen trap. The CW + P plasma mode was used (CW: 50 W, 0.05 mbar, 1 min; P: 100 W, duty cycle 1/10, 0.05 mbar, 10 min). The surface chemistry and topography were examined by XPS, FTIR, TGA-DSC and SEM. The technical details can be found in Section 4.2.3. Neat epoxy and epoxy nanocomposites containing 0.1 wt%, 0.3 wt% and 0.5 wt% of u-MWCNTs or HAPP-MWCNTs were prepared. The details of their manufacture can be found in Section 3.4.

5.2.2. Results and Discussion

DSC analysis

The curing behaviour of both u-MWCNT and f-MWCNT reinforced epoxy were examined by DSC. Typical DSC curves are presented in Figure 5.8. Only one exothermic reaction peak is seen in all the curves. The onset temperature ($T_o$) of the exothermic peak, the temperature of the peak ($T_p$) and the enthalpy ($\Delta H$) are listed in Table 5.4.

![DSC curves](image)

Figure 5.8 Typical DSC curves of the epoxy curing reaction: (a) Epon862/Epikure W/u-MWCNTs; (b) Epon862/Epikure W/HAPP-MWCNTs.
In Figure 5.8, the peaks of all the curves shift to lower temperature with the addition of either u-MWCNTs or HAPP-MWCNTs. This indicates the MWCNTs accelerate the curing reaction. Both $T_o$ and $T_p$ decrease with increased loading of MWCNTs (Table 5.4). This is because MWCNTs contribute to the higher thermal conductivity into the epoxy [272]. Additionally, at each of the loadings, both the $T_o$ and $T_p$ for the epoxy resin with f-MWCNTs are lower than with u-MWCNTs. The $T_o$ and $T_p$ for the epoxy with 0.5 wt% HAPP-MWCNTs both dropped about 5 °C, relative to the neat epoxy. The larger decreases in $T_o$ and $T_p$ for the epoxy with HAPP-MWCNTs result from the interfacial reaction between amine groups on HAPP-MWCNTs and the epoxy. The peak area indicates the enthalpy change due to the chemical reaction [280]. The $\Delta H$ with either u-MWCNTs or HAPP-MWCNTs increased, compared to that for the neat epoxy. However, the $\Delta H$ with HAPP-MWCNTs is higher than with u-MWCNTs. With the addition of 0.5 wt% HAPP-MWCNTs, the enthalpy of the curing reaction increased by about 33% from 289.7 J/g (for the neat epoxy) to 386.8 J/g. The increase in $\Delta H$ of the epoxy with HAPP is due to the reaction between the amines on the HAPP-MWCNT surface and the epoxy groups [280].
Table 5.4 The onset temperature ($T_o$), peak temperature ($T_p$) and the enthalpy ($\Delta H$) for Epon 862/Epikure W with and without MWCNTs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content (wt%)</th>
<th>$T_o$ (°C)</th>
<th>$T_p$ (°C)</th>
<th>$\Delta H$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epon 862/Epikure W</td>
<td>0</td>
<td>144.5</td>
<td>199.9</td>
<td>289.7</td>
</tr>
<tr>
<td>Epon 862/Epikure W/u-MWCNTs</td>
<td>0.1</td>
<td>143.1</td>
<td>197.7</td>
<td>349.4</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>142.5</td>
<td>196.4</td>
<td>360.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>140.5</td>
<td>195.8</td>
<td>376.5</td>
</tr>
<tr>
<td>Epon 862/Epikure W/HAPP-MWCNTs</td>
<td>0.1</td>
<td>142.5</td>
<td>197.2</td>
<td>355.5</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>141.8</td>
<td>195.4</td>
<td>367.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>139.6</td>
<td>194.5</td>
<td>386.8</td>
</tr>
</tbody>
</table>

**Flexural analysis**

Three-point bending tests were performed to determine the flexural properties of the neat epoxy and the nanocomposites in order to evaluate the effectiveness of the plasma treatment. The key flexural properties are listed in Table 5.5. The errors shown in Table 5.5 are the mean deviation of each set of measurements. They were mostly improved by the incorporation of u-MWCNTs. More specifically, among the u-MWCNT/epoxy nanocomposites, the greatest increase in flexural properties was found for the epoxy with 0.3% u-MWCNTs. The flexural modulus increased by 8%, the flexural strength by 14% and the toughness by 66%. However, the addition of 0.5% u-MWCNTs decreased the flexural modulus by about 3%. Although its flexural strength grew by 3% and toughness by 30%, these increases are far lower than those for the 0.3% u-MWCNT/epoxy.
This could be because the dispersion of u-MWCNTs in the epoxy matrix becomes poor at the higher loading.

Table 5.5 Flexural properties of epoxy nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (GPa)</th>
<th>Increase (%)</th>
<th>Flexural strength (MPa)</th>
<th>Increase (%)</th>
<th>Toughness (MPa)</th>
<th>Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>2.86 ± 0.01</td>
<td>—</td>
<td>109.4 ± 2.7</td>
<td>—</td>
<td>0.47 ± 0.08</td>
<td>—</td>
</tr>
<tr>
<td>0.1% u-MWCNT/epoxy</td>
<td>2.91 ± 0.11</td>
<td>1</td>
<td>118.7 ± 5.9</td>
<td>8</td>
<td>0.51 ± 0.10</td>
<td>9</td>
</tr>
<tr>
<td>0.3% u-MWCNT/epoxy</td>
<td>3.10 ± 0.21</td>
<td>8</td>
<td>124.8 ± 3.8</td>
<td>14</td>
<td>0.78 ± 0.04</td>
<td>66</td>
</tr>
<tr>
<td>0.5% u-MWCNT/epoxy</td>
<td>2.77 ± 0.06</td>
<td>-3</td>
<td>112.9 ± 5.9</td>
<td>3</td>
<td>0.61 ± 0.14</td>
<td>30</td>
</tr>
<tr>
<td>0.1% HAPPMWCNT/epoxy</td>
<td>3.08 ± 0.14</td>
<td>7</td>
<td>122.3 ± 4.9</td>
<td>12</td>
<td>0.72 ± 0.06</td>
<td>53</td>
</tr>
<tr>
<td>0.3% HAPPMWCNT/epoxy</td>
<td>3.23 ± 0.24</td>
<td>13</td>
<td>125.1 ± 5.4</td>
<td>14</td>
<td>0.77 ± 0.05</td>
<td>64</td>
</tr>
<tr>
<td>0.5% f-MWCNT/epoxy</td>
<td>3.48 ± 0.18</td>
<td>22</td>
<td>126.8 ± 4.5</td>
<td>17</td>
<td>0.80 ± 0.13</td>
<td>70</td>
</tr>
</tbody>
</table>

The flexural properties of the HAPPMWCNT reinforced epoxy nanocomposites appear to increase steadily with the increasing loading of HAPPMWCNTs. Under the same loading, the increases in the flexural properties for the HAPPMWCNT/epoxy are consistently higher than those for u-MWCNTs. This is due to
the amine groups on the HAPP-MWCNT improving the dispersibility of MWCNT as well as their interfacial binding. Incorporation of 0.5 wt% of HAPP-MWCNTs gave the largest increases in flexural modulus (22%), flexural strength (17%) and toughness (70%). Both u-MWCNTs and f-MWCNTs gave improvements in toughness, the nearly 70% improvement in toughness given by f-MWCNTs is a clear step forward for epoxy resin composites. In order to further present the advantage of HAPP-MWCNTs on the improvement of mechanical properties of epoxy composites, a comparison between our results and some previous reported results using the same loading of CNTs is provided, as shown in Table 5.6. It can be seen that HAPP-MWCNT/epoxy nanocomposites possess comparable mechanical properties compared to chemically functionalized amine-CNT/epoxy nanocomposites.

Table 5.6 A comparison between our results and some previous reported results on mechanical properties of chemically functionalized amine-CNT/epoxy nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flexural modulus (%)</th>
<th>Flexural strength (%)</th>
<th>Toughness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>amine-MWCNT(0.5 wt%)/epoxy</td>
<td>19%</td>
<td>19%</td>
<td>—</td>
</tr>
<tr>
<td>amine-MWCNT(0.5 wt%)/epoxy</td>
<td>—</td>
<td>7%</td>
<td>—</td>
</tr>
<tr>
<td>amine-DWCNT(0.5 wt%)/epoxy</td>
<td>—</td>
<td>—</td>
<td>45%</td>
</tr>
<tr>
<td>HAPP-MWCNTs(0.5 wt%)/epoxy</td>
<td>22%</td>
<td>17%</td>
<td>70%</td>
</tr>
</tbody>
</table>

*ref. [103];  *b ref. [281];  *c ref. [181].
It is worth noting that HAPPP-MWCNTs (0.1 wt%) and N₂/H₂ plasma functionalized MWCNTs (0.1 wt%) give similar results for the flexural properties. This might suggest that the strength of the interfacial bonding is similar. So the CW + P plasma deposited polymer does not provide a weak link, it is at least of similar strength to the epoxy.

SEM was used to analyse the dispersion of the u-MWCNTs and HAPPP-MWCNTs in the epoxy matrix. Figure 5.9 and 5.10 show SEM images of the fracture surfaces of u-MWCNT/epoxy and HAPPP-MWCNT/epoxy nanocomposites after the three-point bending tests. The SEM images of fracture surfaces of the neat epoxy and 0.1 wt% u-MWCNT/epoxy have been presented in Figure 5.5a and b, and the analysis has also been given (5.1.1.3 Flexural analysis). As the loading increased, the fracture surface of the u-MWCNT/epoxy became rougher (Figure 5.5b, Figure 5.9a and c) and appeared like snake-scales, and the average size of the scales reduced with increased loading. A similar appearance of the fracture surface of the HAPPP-MWCNT/epoxy nanocomposites is also observed (Figure 5.10a, c and e). This is because the direction of crack propagation is changed due to the presence of MWCNTs [282]. From Figure 5.9b and d, the agglomeration of u-MWCNTs can be seen and it becomes larger as the loading increases (0.5 wt%), which is in good agreement with their flexural properties. From the insets in Figure 5.9b and d, many u-MWCNTs were pulled out of the epoxy resin, which indicates the interfacial adhesion between the u-MWCNTs and epoxy matrix is weak [278]. From Figure 5.10b, d and f, it can be seen that HAPPP-MWCNT have an improved dispersion, and even with the increased loading, the HAPPP-MWCNTs are still well dispersed. It can also be seen that most of the HAPPP-MWCNTs were not pulled out but broken during the flexural testing, which
demonstrates the interfacial bonding between the HAPP-MWCNTs and the epoxy is strong.

Figure 5.9 SEM images of fractured surfaces of u-MWCNT/epoxy nanocomposites: (a) 0.3 wt% u-MWCNT/epoxy, (c) 0.5 wt% u-MWCNT/epoxy; (b) and (d) are enlargements of the regions indicated with red rectangles from (a) and (c) respectively, insets are close-ups of the boxed region.
Figure 5.10 SEM images of fractured surfaces of HAP-MWCNT/epoxy nanocomposites: (a) 0.1 wt% HAP-MWCNT/epoxy, (c) 0.3 wt% HAP-MWCNT/epoxy, (e) 0.5 wt% HAP-MWCNT/epoxy; (b), (d) and (f) are enlargements of the regions indicated with red rectangles from (a), (c) and (e), and the insets are close-ups of the boxed region.
**DMA analysis**

The thermo-mechanical properties of the different nanocomposites were studied using DMA. The DMA results are presented in Figure 5.11 and the average $T_g$ values are given in Table 5.7. Three samples of each composite were tested. The storage modulus of the epoxy steadily increases with the loading of either u-MWCNTs or HAPPMWCNTs. The improvement in the storage modulus of the epoxy with the HAPPMWCNTs is greater than with the u-MWCNTs at each loading, especially at temperatures above $T_g$. At temperatures above $T_g$, the rubbery region, the addition of u-MWCNTs has little effect on the storage modulus. This is possibly due to the poor dispersion of u-MWCNTs and poor interfacial bonding with epoxy [278], which is consistent with the SEM analysis of their fracture surfaces. The storage modulus in the rubbery region is increased for all the HAPPMWCNT/epoxy nanocomposites. This is because the functionality on HAPPMWCNTs improves their dispersion and adhesion with epoxy, as confirmed by SEM images of their fracture surfaces. The good interfacial interaction reduces the mobility of the epoxy resin around the nanotubes which increases the thermal stability. This effect shows up in the rubbery region and in the vicinity of $T_g$ [180].
Figure 5.11 DMA results of neat epoxy and their MWCNT reinforced nanocomposites: (a) storage modulus vs. temperature; (b) loss factor vs. temperature.

It can be seen from Table 5.7 that the HAPP-MWCNT/epoxy nanocomposites showed higher $T_g$ than the u-MWCNT/epoxy nanocomposites. The $T_g$ for the neat epoxy is about 155.3 °C, but after adding the u-MWCNTs, it reduces by about 3 to 5 °C (Table 5.7). The u-MWCNTs have poor dispersion in the epoxy, as seen from the SEM images of fracture surfaces, which might result in an alteration of curing reaction ratio by partially absorbing the curing agent [278, 279]. This can bring about a drop in $T_g$. Additionally, the agglomeration of u-MWCNTs may lead to some holes in the epoxy matrix which makes the macromolecules to moving [7]. This can lead to a drop of $T_g$ of nanocomposites.

For the HAPP-MWCNT/epoxy, the $T_g$ for epoxy with 0.1 wt% and 0.3 wt% of HAPP-MWCNTs increases by about 10 °C and 2 °C, while with 0.5 wt% of HAPP-MWCNTs it drops by about 2 °C. This is consistent with the amine groups on the MWCNT surface reacting with the epoxy resin to form covalent bonds. This strong interfacial bonding greatly limits the mobility of the epoxy and thus increases the $T_g$ [180]. It is noted that the $T_g$ for epoxy with HAPP-MWCNTs
decreases with loading. The similar phenomena were found by other researchers [122, 183, 280]. They reported with increasing loading of amine-functionalized CNTs, the $T_g$ of epoxy decreased. This is mainly because with increasing addition of HAPP-MWCNTs, the amine groups on the CNTs lead to a change in the curing ratio between the epoxy groups and the curing agent, thus decreasing the conversion of curing reaction [183, 280]. Moreover, with increasing loading, some small aggregates could possibly occur [7, 23], which can result in a decrease of $T_g$.

Table 5.7 Average glass transition temperature of nanocomposites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat epoxy</td>
<td>155.3 ± 0.3</td>
</tr>
<tr>
<td>0.1 wt% u-MWCNT/epoxy</td>
<td>152.7 ± 0.6</td>
</tr>
<tr>
<td>0.3 wt% u-MWCNT/epoxy</td>
<td>150.8 ± 1.4</td>
</tr>
<tr>
<td>0.5 wt% u-MWCNT/epoxy</td>
<td>151.2 ± 1.1</td>
</tr>
<tr>
<td>0.1 wt% HAPP-MWCNT/epoxy</td>
<td>164.5 ± 0.6</td>
</tr>
<tr>
<td>0.3 wt% HAPP-MWCNT/epoxy</td>
<td>158.2 ± 0.2</td>
</tr>
<tr>
<td>0.5 wt% HAPP-MWCNT/epoxy</td>
<td>153.9 ± 0.8</td>
</tr>
</tbody>
</table>

It is worth noting that 0.1 wt% of HAPP-MWCNTs increased $T_g$ more than 0.1 wt% of N$_2$/H$_2$ plasma functionalized MWCNTs. This is probably due to a higher level of amine groups on the HAPP-MWCNTs (4% vs. 3%) which can create the higher crosslinkings in the nanocomposites, thus increasing $T_g$.

5.3 Summary

For both the N$_2$/H$_2$ plasma treatment and HA plasma polymerization, the functionalization of the MWCNT surface by the CW + P plasma method has been
shown to be effective in improving dispersion and interfacial adhesion in an epoxy matrix. Both functionalized MWCNTs had good adhesion with, and were dispersed uniformly in, the epoxy resin, which was confirmed by the SEM analysis of fracture surfaces. The DSC results confirmed the interfacial reaction between the amine groups on the treated MWCNT surface and the epoxy. The mechanical properties of the epoxy were greatly increased by both amino functionalized MWCNTs.

For the N$_2$/H$_2$ plasma treatment, the incorporation of only 0.1wt% of functionalized MWCNTs led to marked increases in both nano- and macro-mechanical properties compared to neat epoxy. Nanoindentation tests showed that the hardness and elastic modulus increased by 40% and 19%, respectively, using the functionalized nanotubes. Macro-mechanical properties from thermo-mechanical and flexural analysis were also enhanced, with a nearly 40% improvement in toughness.

SEM analysis indicates that HAPP-MWCNTs have good dispersion and interfacial bonding with epoxy at loadings of 0.1, 0.3 and 0.5 wt%. The flexural and thermal mechanical properties also have increased with the increased loading of HAPP-MWCNTs, while the untreated MWCNT/epoxy nanocomposites have shown an opposite trend. The epoxy with 0.5 wt% HAPPMWCNTs had the greatest increase in flexural properties, with the flexural modulus, flexural strength and toughness of epoxy increasing by about 22%, 17% and 70%, respectively.
Chapter 6 Plasma Functionalization of Carbon Fibres

The current methods of continuous wave (CW) plasma polymerization are difficult to retain the functional groups from the monomer. This could compromise chemical bonding to a polymer matrix and hence degrade the properties of the resulting carbon fibre (CF) reinforced polymers. A three-step plasma treatment was therefore developed to strongly attach a plasma polymer to the CF surface. The three steps are an Ar plasma pre-treatment, then followed by an O₂ plasma functionalization and finally the combined continuous wave and pulsed (CW + P) plasma polymerization of heptylamine (HA). The mechanism of this method is presented. Changes in the surface chemistry and morphology of the functionalized CFs have been used to demonstrate the effectiveness of the approach and single fibre tensile tests showed the fibres were not damaged. The treatment was expected to give an improvement in the mechanical properties of CF/epoxy composites but a reliable test method proved difficult to develop.

6.1 Experimental

Commercially available un-oxidized PAN based carbon fibres, as described in Section 3.2, were used in this work. The plasma treatments were carried out in plasma System 1, as described in Section 3.3. A bunch of CFs were well separated and then fixed on a sample holder, as shown in Figure 6.1, to allow plasma species to reach each fibre. The sample holder was under the plasma source. A three-step process of plasma functionalization of CFs was designed. Firstly, the CFs were treated by Ar plasma (Step I) for activating and cleaning the CF surface. This was followed by O₂ plasma treatment (Step II) for incorporation of oxygen-containing functional groups. Finally, a HA film was deposited on the CF surface by CW + P plasma polymerization (Step III). An O₂ plasma was
chosen because it can simultaneously provide etching and formation of oxygen functional groups. The etching process can help to remove carbonaceous impurities on the CFs by producing atomic oxygen which reacts with the carbon atoms to create volatile reaction products [13]. The oxygen functional groups can provide binding sites on the CFs to improve the attachment of the plasma polymerised layer. To evaluate the effect of each step on the CF surface, experiments using just Step I and just Steps I and II were also conducted. The CFs after Step I, Step I and II and all three steps are denoted as Ar-CFs, O$_2$-Ar-CFs and HAPPO$_2$-Ar-CFs, respectively. The detailed plasma conditions are listed in Table 6.1.

Figure 6.1 The sample holder.

Table 6.1 The plasma parameters.

<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Step I</th>
<th>Step II</th>
<th>Step III</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar : CW 75 W 0.05 mbar, 30 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ar : CW 75 W 0.05 mbar, 30 sec</td>
<td>O$_2$: P 100 W, DC 1/5, 0.05 mbar, 1 min</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Ar : CW 75 W 0.05 mbar, 30 sec</td>
<td>O$_2$: P 100 W, DC 1/5, 0.05 mbar, 1 min</td>
<td>HA: CW 50 W, 0.1 mbar, 10 min, DC=5%</td>
</tr>
</tbody>
</table>
After the plasma treatments, the chemical composition of the CFs was studied by XPS and FTIR. The surface topology of untreated carbon fibres (u-CFs) and treated CFs was analysed using SEM and AFM. The thickness of the deposited plasma polymer was measured using AFM (see Section 3.5.7). Single fibre tensile tests were conducted on a FAVIMAT+ automatic linear density, crimp and tensile tester. The gauge length for single fibre tensile tests was 20 mm. At least 50 fibres were tested for each sample. Details of the tests have been presented in Section 3.5.14. The Weibull distribution function was adapted to examine the tensile properties of the CFs.

6.2 Results and Discussion

6.2.1 XPS Analysis

The surface chemical compositions of the CFs before and after plasma treatment were determined from the XPS spectra. The content of C, O and N on the CF surface, as detected by XPS, is presented in Table 6.2. The XPS C1s spectra for untreated and plasma treated CFs are shown in Figure 6.2, where the insets are their XPS survey spectra. Table 6.3 lists the relative intensity distributions of component peaks obtained from the deconvolution of C1s peaks for all samples. The u-CFs had about 95% C and 5% O. The oxygen might come from air contamination during the production process. No nitrogen atoms were detected on the u-CF surface as shown in Table 6.2. At the Step I, Ar plasma treatment increased slightly the O content on the CF surface. This is because the oxygen from air incorporated onto the activated surface of CFs by Ar plasma treatment. The O concentration on the O2-Ar-CF surface (Step II) was increased by about
170% in comparison to the u-CFs. This is because the activated surface of CFs after Ar plasma treatment can easily react with oxygen species during the oxygen pulsed plasma to form oxygen functional groups [283].

Table 6.2 Atomic concentrations of C, O and N on the surface of untreated and treated CFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C  at.%</th>
<th>O  at.%</th>
<th>N  at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>u-CF</td>
<td>95.3</td>
<td>4.7</td>
<td>—</td>
</tr>
<tr>
<td>Step I</td>
<td>Ar-CF</td>
<td>94.8</td>
<td>5.2</td>
</tr>
<tr>
<td>Step II</td>
<td>O₂-Ar-CF</td>
<td>87.5</td>
<td>12.5</td>
</tr>
<tr>
<td>Step III</td>
<td>HAPP-O₂-Ar-CF</td>
<td>88.6</td>
<td>3.2</td>
</tr>
</tbody>
</table>

The C1s spectra of the u-CFs can be decomposed into two components at 284.6 eV, 286.2 eV, and 288.9 eV (Figure 6.2a), which correspond to graphite (C=C), hydroxyl (C-O/C-O-C) and carboxyl groups (O-C=C) (Table 6.3), respectively [152]. The relative intensities of these three peaks were found to be 94%, 3%, and 3% (Table 6.3). The same components were found in the C1s peaks of Ar-CFs and O₂-Ar-CFs (Figure 6.2b and c). After O₂ plasma treatment, the hydroxyl groups in Table 6.3 account for the largest part of the oxygen functionality (about 7% of the carbon bonds). The oxygen-containing functional groups could act as anchoring sites for binding with the HA plasma polymer formed in the CW + P plasma polymerization process, thus leading to good adhesion between the CF and the plasma polymer.
After the plasma polymerization of HA (Step III), N atoms were introduced on the CF surface. They constitute about 8% of the atoms (Table 6.2). The O content decreased from nearly 13% before, to 3.2% after, the plasma polymerization. This is because the CF is covered by a polymeric film after HA plasma polymerization, which is confirmed by SEM observations (Figure 6.4d). The C1s peak for the HAPPO2-Ar-CFs has components at 284.6 eV and 285.8 eV (Figure 6.2d). The peak at 285.8 eV corresponds to amine groups (C-NH2 or C-NH-C). Its relative intensity is about 6.5% (Table 6.3).

Figure 6.2 XPS C1s spectra of CFs: (a) u-CFs; (b) Ar-CFs; (c) O2-Ar-CFs; (d) HAPPO2-Ar-CFs.
Table 6.3 Binding energy of the C1s components and attribution of the components obtained from peak deconvolutions in Figure 6.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carbon binding energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>284.6</td>
</tr>
<tr>
<td></td>
<td>C=C</td>
</tr>
<tr>
<td>u-CF</td>
<td>94.0%</td>
</tr>
<tr>
<td>Ar-CF</td>
<td>93.3%</td>
</tr>
<tr>
<td>O2-Ar-CF</td>
<td>91.0%</td>
</tr>
<tr>
<td>HAPP-O2-</td>
<td>93.5%</td>
</tr>
<tr>
<td>Ar-CF</td>
<td></td>
</tr>
</tbody>
</table>

6.2.2 FTIR Analysis

FTIR spectroscopy was used to study the CFs after the three-step treatment. Figure 6.3 shows typical FTIR spectra of HAPP-O2-Ar-CFs and HA. Both spectra show similar peaks around 2900 cm\(^{-1}\) which are attributed to aliphatic C-H stretching bands [111, 171]. This indicates the structure of the HAPP film on the CF surface is similar to HA. The peak at 1675 cm\(^{-1}\) in the spectra of HAPP-CFs is assigned to amide (CO-NH) or imine (C=N) stretching [171], while the peaks at 1250 and 1097 cm\(^{-1}\) correspond to C-N vibrations [171, 284], which is in good agreement with the XPS analysis.
Figure 6.3 FTIR spectra for (a) HAPPO2-Ar-CF and (b) HA.

6.2.3 SEM Results

The surface morphology of the CFs before and after the different plasma treatments is shown in Figure 6.4. The surface of the u-CF seems to be relatively smooth. After the gaseous plasma treatments (Figures 6.4b and c), there is no significant visible change in the surface. Both samples of the Ar-CF and O2-Ar-CF show a smooth surface. This is because, under the gentle gaseous plasma treatment, the effect of surface etching is relatively weak and the changes on the surfaces are at the nanometre scale, which is hard to observe by SEM. Boudou et al. [48] also found that there was no significant change in the structure of the CF after very gentle O2 plasma treatment. However, using scanning tunnelling microscopy, they observed the surface of the treated CF was rougher compared to the u-CF surface. Figure 6.4d shows a SEM image of the CF after HA plasma polymerization. It can be seen that the CF is coated with the HA plasma polymer. From the enlarged image in Figure 6.4(e), the CF surface is fairly uniformly and tightly covered by the HA film.
Figure 6.4 SEM images of CFs: (a) u-CF; (b) Ar-CF; (c) O$_2$-Ar-CF; (d) HAPP-O$_2$-Ar-CF; (e) the enlargement of the region indicated by the red rectangle in (d).

6.2.4 AFM Results

The topography of the CFs before and after plasma treatment was examined by AFM (Figure 6.5). For comparison, the topography of a HA plasma polymer deposited on a Si wafer, a flat surface, by CW + P plasma polymerization is
shown in Figure 6.6. The surface roughness values, obtained from the AFM images, are given in Table 6.4. Root mean square (Rms) roughness is the root mean square average of the roughness profile ordinates, while roughness average (Ra) is the arithmetic average of the absolute values of the roughness profile ordinates [285]. The surface of u-CFs is smooth with a number of grooves along the fibre (Figure 6.5a). The grooves on the surface of both Ar-CFs (Figure 6.5b) and O2-Ar-CFs (Figure 6.5c) are slightly deeper, which may be due to plasma etching. The Rms and Ra of both Ar-CFs and O2-Ar-CFs were higher than those of the u-CFs. The increased roughness after the gaseous plasma treatments could provide better attachment between the CF and the HA plasma polymer, formed in the subsequent CW + P plasma polymerization. It can enhance the interfacial bonding between the HA plasma polymer and the CF. After the HA plasma polymerization, the grooves on the HAPP-O2-Ar-CF surface are nearly invisible (Figure 6.5d), and the surface roughness of the HAPP-O2-Ar-CF decreased in comparison with that of the O2-Ar-CF (Table 6.4). This is because the surface of the CFs is covered by a thin polymeric film, which is in good agreement with the SEM observations. From Figure 6.6, some conical structures on the plasma polymer were observed. Such conical structures have also been observed by other researchers [286, 287]. The surface of HAPP-O2-Ar-CFs with conical structures can give better mechanical interlocking between CFs and a polymeric matrix, and the amine groups on the plasma polymer detected by XPS and FTIR can also provide chemical bonding with the matrix, thus improving the interfacial adhesion.
Figure 6.5 AFM images of the CF surface: (a) u-CF; (b) Ar-CF; (c) O₂-Ar-CF; (d) HAPP-O₂-Ar-CF.

Figure 6.6 AFM image of a HA plasma polymer deposited on a Si wafer using CW + P plasma polymerization, the inset is a close-up of the boxed region.
Table 6.4 Surface roughness of CFs before and after plasma treatment measured by AFM on flattened images of 3 μm × 3 μm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rms (nm)</th>
<th>Ra (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>u-CF</td>
<td>22.1</td>
<td>18.1</td>
</tr>
<tr>
<td>Ar-CF</td>
<td>25.2</td>
<td>20.4</td>
</tr>
<tr>
<td>O₂-Ar-CF</td>
<td>30.6</td>
<td>25.3</td>
</tr>
<tr>
<td>HAPPO₂-Ar-CF</td>
<td>26.0</td>
<td>20.6</td>
</tr>
</tbody>
</table>

The thickness of HA plasma polymer on the CF surface was measured by AFM using the surface masking technique described in Section 3.5.7. A representative AFM image of the HA plasma polymer step on a Si wafer, with a section analysis on an individual scan line in the image is presented in Figure 6.7. An apparent boundary between the deposited and un-deposited areas on the surface is observed in Figure 6.7a. The plasma polymer step is also clearly shown in a three-dimensional AFM image in the inset of Figure 6.7b. From Figure 6.7b, the thickness of the HA film can be calculated by subtracting the lower peak value from the upper, which is about 40 nm.
Figure 6.7 (a) AFM image of a HAPP step on a Si wafer; (b) an individual scan line. The inset is the three-dimensional AFM image of the HAPP step on the Si wafer.

6.2.5 Single Fibre Tensile Strength

Weibull distribution which is a continuous probability distribution has been widely used in the analysis of single fibre tensile properties [288-290]. The basic equation of a two parameter Weibull distribution is [291]:

\[ F(\sigma_i) = 1 - \exp\left(-L\left(\frac{\sigma_i}{\sigma_o}\right)^m\right) \]  

(6.1)

where \( F \) is the probability of fibre failure under stress \( \sigma_i \); \( L \) is the gauge length, \( \sigma_o \) and \( m \) are the respective scale and shape parameters, which are determined from the single fibre tensile tests. Equation 6.1 can be changed to:

\[ \ln\ln\left(\frac{1}{1-F(\sigma_i)}\right) = m \ln \sigma_i + \ln L - m \ln \sigma_o \]  

(6.2)

where the \( F(\sigma) \) can be obtained by the following equation:

\[ F(\sigma_i) = \frac{i}{n+1} \]  

(6.3)

where \( n \) is the total number of fibres tested and \( i \) is the sequence number of the fibres under the tensile stress. The tensile strength of tested fibres is ranked in
ascending order. The Weibull parameters can be obtained from the plot of 

\[ \ln \ln \left( \frac{1}{1 - F(\sigma_i)} \right) \text{ vs. } \ln(\sigma_i) \]

using the linear regression equation:

\[ y = Ax + B \]  \hspace{1cm} (6.4)\]  

Comparing equation 6.2 and 6.4, the Weibull parameters can be calculated from:

\[ A = m \]  \hspace{1cm} (6.5)\]  

\[ \sigma_0 = \exp \left( \frac{\ln L - A}{m} \right) \]  \hspace{1cm} (6.6)\]  

The effective strength \( \bar{\sigma} \) can be obtained by the equation:

\[ \bar{\sigma} = \frac{\sigma_0}{L^{1/m}} \Gamma(1 + \frac{1}{m}) \]  \hspace{1cm} (6.7)\]  

where \( \Gamma() \) is the Gamma factorial function.

The Weibull plots and linear fits for the single fibre tensile tests are shown in Figure 6.8, where the Weibull parameters can be calculated. The results of the Weibull analysis for all the samples are presented in Table 6.5, where \( R^2 \) is the correlation coefficient for the corresponding fits. It can be seen that the Weibull plots are approximately linear, and all the \( R^2 \) values (Table 6.5) for the regression fits are over 90\%, which suggests the tensile strength of single CFs follows a Weibull distribution. The calculated shape parameters \( m \), scale parameters \( \sigma_0 \) and effective strengths \( \bar{\sigma} \) are given in Table 6.5. The use of a Weibull distribution for the analysis of single fibre tensile strength is based on the weakest link theory [290, 291]. This is consistent with the fracture of carbon fibres being due to defects, where the fracture is mainly because of the mis-orientation of the graphite crystal layers around some inclusions and voids [196, 292].
Figure 6.8 Weibull plots and linear fits for carbon fibres: (a) u-CF; (b) Ar-CF; (c) O$_2$-Ar-CF; (d) HAPPO$_2$-Ar-CF.

Table 6.5 Summary of results from the Weibull model analysis of single fibre tensile tests.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$B$</th>
<th>$A$ or $m$</th>
<th>$\sigma_0$ (GPa)</th>
<th>$\bar{\sigma}$ (GPa)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>u-CF</td>
<td>-5.80 ± 0.92</td>
<td>4.05 ± 0.62</td>
<td>4.19</td>
<td>3.80</td>
<td>0.99</td>
</tr>
<tr>
<td>Ar-CF</td>
<td>-8.56 ± 1.98</td>
<td>6.05 ± 1.53</td>
<td>4.12</td>
<td>3.82</td>
<td>0.92</td>
</tr>
<tr>
<td>O$_2$-Ar-CF</td>
<td>-8.90 ± 1.89</td>
<td>6.23 ± 1.40</td>
<td>4.17</td>
<td>3.87</td>
<td>0.94</td>
</tr>
<tr>
<td>HAPPO$_2$-Ar-CF</td>
<td>-9.67 ± 1.66</td>
<td>6.60 ± 1.20</td>
<td>4.33</td>
<td>4.03</td>
<td>0.97</td>
</tr>
</tbody>
</table>
The Weibull shape parameter $m$ denotes the variation of tensile strength due to defects distributed along the length of the fibre [198]. Generally, a higher $m$ means fewer flaws in the CFs [196]. From Table 6.5, the value of the $m$ slightly increased after plasma treatments, which may suggest plasma treatment reduces some defects on the CF surface. For the Ar plasma treatment, the main role of the Ar plasma treatment is to activate and clean the surface of the CFs, which does involve some surface etching. According to Own et al. [293] and Xie et al. [198], plasma surface etching generally does not create new flaws in CFs, but it may further weaken the large defects in the CF with prolonged treatment time. Therefore, the short time (30 sec) of Ar plasma treatment could just etch away small surface flaws but without aggravating the large defects, hence leading to the increase in the shape parameter [293, 294]. For O$_2$-Ar-CFs, after Ar plasma treatment, the following short duration and gentle (pulsed) O$_2$ plasma treatment may further help to etch the small flaws as well as remove carbonaceous impurities on the CFs [227], which results in the increase of $m$. The thin film deposited by the final step plasma polymerization may fill some flaws in the CFs, leading to an increased $m$. After the gaseous plasma treatments, the effective tensile strength $\bar{\sigma}$ of the CFs was marginally, but not significantly, improved (Table 6.5), which suggests the structure of the CFs was not damaged by the Ar and O$_2$ plasmas. A slight increase in the effective tensile strength $\bar{\sigma}$ was found for the HAPP-O$_2$-Ar-CFs. Similar results were also observed by Dagli et al. [234] and Dilsiz et al. [216]. They suggested that the plasma polymer could heal surface flaws of CFs, leading to the apparent increase in tensile strength. The healing mechanism was not provided.
The thin polymer layer with amines deposited on the CFs surface using this three-step plasma method could improve the adhesion of the CFs to the matrix resin. This plasma approach has two roles: 1) to deposit a thin plasma polymer layer that strongly bonds to the CF surface, like sizing and 2) to provide amine groups on the surface of the thin plasma polymer layer which can then chemically bond to a polymer matrix such as an epoxy resin.

In order to further examine the effect of the plasma treatments on the single fibre tensile strength, the fracture cross-sections of the samples were obtained by SEM after the tensile tests. No significant difference was observed between the fracture cross-sections for the u-CF and gaseous treated CFs (Figures 6.9a, b and c), where the cross-sections are quite regular. In Figure 6.9d, the cross-section image shows a layer of HAP still attached to the edge of its fractured cross-section. This layer was presumably extended along the broken part of the fibre before the tensile breakage. It suggests that there is good adhesion between the fibre and the plasma polymer, which is consistent with the XPS and AFM analysis.
Sample preparation for the evaluation of the interfacial bonding between a single carbon fibre and the epoxy resin proved difficult. Three sample preparation methods (Figure 6.10) were tried for three different interfacial tests: a micro-debond test [196], a fragmentation test [198] and a single fibre pull-out test [295]. Some of the issues encountered are set out below.

An ideal sample for the micro-debond test is a single fibre with a micro-sized cured epoxy resin droplet as shown in Figure 6.10a. The epoxy resin in this work had a high curing temperature (177 °C) and it was found that the epoxy droplet ran off the fibre during the curing process. The fragmentation test required a single fibre embedded along the geometric centreline of a dog-bone shaped matrix (Figure 6.10b). It was difficult to align the single fibre along the geometric centre.
Even when the fibre was given a pre-tension and fixed along the centreline by adhesive it would lose its pre-tension and become loose during the temperature curing. Additionally, during the tensile test, the epoxy matrix was often broken before the embedded CF. Adjustment of the thickness of the sample and, possibly, the use of an epoxy with higher tensile strength need to be examined. For the pull-out tests, it was hard to control the embedded length while keeping the CF vertically embedded in the epoxy (Figure 6.10c). At this stage, a satisfactory test procedure to confirm an improvement in the interfacial bonding of a treated CF has not been established.

(a)                                             (b)

Figure 6.10 Samples for interfacial tests: (a) micro-debond test, (b) fragmentation test and (c) single fibre pull-out test.

6.3 Summary

A three-step plasma treatment -- activation, functionalization and polymerization -- was used to deposit a thin plasma polymer containing amine groups on the carbon fibre surface. In Step I, the CF surface was activated and cleaned by Ar
plasma, which provides a good foundation for the formation of oxygen-containing functional groups on the CF surface by the Step II of O₂ plasma functionalization. These two steps have also resulted in the increase in surface roughness of the CFs. The increased roughness and the oxygen-containing functional groups on the CF surface after the first two steps could provide stronger attachment as well as chemical bonding between the CF and the plasma polymer formed in the CW + P plasma polymerization (Step III). In Step III, a thin plasma polymeric film with some conical structures and amine groups was uniformly coated onto the CF surface. Weibull analysis showed that the single carbon fibre tensile strength was not changed by plasma treatment. SEM images of the fracture cross-section of HAPP-O₂-Ar-CFs showed strong adhesion between the plasma polymer and the CF. This plasma polymer with amine functional groups will provide good mechanical interlocking and interfacial adhesion between the modified CFs and a polymeric matrix, which will improve the load transfer between a matrix and the CFs.
Chapter 7 Conclusions and Future Work

7.1 Conclusions

The objectives set out in Chapter 1.1 have been achieved as follows:

1. A gaseous (N$_2$/H$_2$) CW + P plasma functionalization method has been established to functionalize the surface of MWCNTs. Compared to using continuous wave plasma mode or pulsed plasma mode alone under the same energy input, the combined plasma mode gives a more selectable and higher level of primary amines groups, without damaging the nanotube structure. The level of primary amines of about 3% achieved by the N$_2$/H$_2$ CW+ P plasma is higher than previously reported for any nitrogen-containing gas plasma treatment. Even higher levels (about 4%) of primary amines can be achieved by coating the MWCNTs with a thin layer by plasma polymerization using a less toxic monomer, heptylamine , in the combined method. The higher levels of primary amine groups on the MWCNTs can improve adhesion between the nanotube and an epoxy via bonding to the epoxy groups to form covalent bonds, as well as can enhance the wettability of the nanotubes, thus improving their dispersion. This combined plasma mode provides a non destructive and one-step covalent functionalization of nanotubes. A stirring plasma system was developed for uniform treatment of hard to handle nanotubes. It has been shown that the MWCNTs can be uniformly covered with a thin polymeric film with a high level of amines by the CW + P plasma polymerization of HA. This method provides a practical approach for uniformly functionalizing larger amount of nanomaterial in a low-pressure plasma system.

Amine functionalization of BNNTs by N$_2$/H$_2$ CW + P plasma has been achieved. The amorphous surface layer found on the outside of the tubes can be removed
without damaging the nanotubes by the treatment. The undamaged and functionalized BNNTs could be beneficial of their applications in nanocomposites.

2. The effect of primary amine-functionalized MWCNTs on the mechanical properties of their reinforced epoxy nanocomposites has been studied. The MWCNTs were functionalized using the combined mode with both a gas (N$_2$/H$_2$) and monomer (heptylamine). The MWCNTs have shown an improved dispersion in, and good interfacial adhesion to, an epoxy matrix, in comparison to untreated MWCNTs. This led to an improvement in the thermal and flexural mechanical properties of their epoxy nanocomposites. In particular, both functionalized MWCNTs gave a marked increase in toughness of the epoxy, about 40% for adding 0.1 wt% of gas plasma functionalized MWCNTs, and 70% for adding 0.5% plasma polymerized MWCNTs. Such an improvement in toughness is a clear step forward for epoxy resin composites. The incorporation of only 0.1 wt% of gas plasma functionalized MWCNTs resulted in marked increases in both nano- and macro-mechanical properties compared to neat epoxy. The increase in mechanical properties given by both functionalized MWCNTs was competitive with, or even better than, the corresponding results obtained by other researchers using different chemical amine-functionalized CNTs. The CW + P plasma method gives a more environmentally friendly, less costly and less time consuming approach for the functionalization of nanomaterials for use in composites.

3. A three-step plasma method: activation, functionalization and polymerization, has been established to functionalize CFs with a thin plasma polymer film containing amine groups. The first two steps: surface activation by Ar plasma followed by O$_2$ plasma functionalization, helped increase the surface roughness, and introduce the oxygen functional groups, which provided better attachment as
well as chemical bonding between the CF and the plasma polymer formed in the last step of plasma polymerization. Such treatments did not damage the fibre strength. The three-step plasma treatment presents a potential way for replacing sizing of carbon fibres or reducing the amount of sizing agent needed.

7.2 Future work

A promising direction of future work would be to focus on functionalization of CFs and their application in composites. Firstly, a reliable method needs to be established for the evaluation of the interfacial strength between the deposited plasma polymer and the CFs. One possible method could be to use the nano-indentation technique to measure such interfacial strength. Secondly, a more practical approach needs to be sought to evaluate the interfacial shear strength of carbon fibre/epoxy composites. A possible method to is to make cruciform samples for tensile testing, since the process of preparing samples could not be affected by the properties of CFs and the epoxy [296]. Lastly, further possibilities of the three-step plasma treatment for sizing CFs should be explored.
References


[37] Sarra-Bournet C, Ayotte G, Turgeon S, Massines F, Laroche G. Effects of chemical composition and the addition of H$_2$ in a N$_2$ atmospheric pressure


[142] Bergeret Cl, Cousseau J, Fernandez V, Mevellec JY, Lefrant S. Spectroscopic evidence of carbon nanotubes’ metallic character loss Induced by


[214] Xie Y. Carbon fiber surface modification by microwave plasma and electrochemical techniques and characterization by XPS, XRD and SEM methods. United States -- Kansas: Kansas State University; 1990.


[218] Luo X. Chemical characterization of PAN based carbon fibers produced by microwave assisted plasma (MAP) technology and effect of plasma treatment on carbon fiber surface and interphase with polymer matrix [3220758]. United States -- Tennessee: The University of Tennessee; 2006.


