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Mechanics of Carbon Nanotube Based Composites

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Abstract

The aim of this work is to exploit the remarkable mechanical properties of CNTs for advanced composites, through comprehensive studies on the interfacial characteristics between the CNTs and the matrix materials, the tensile stiffness and strength, the long-term fatigue behaviors and mechanisms, as well as time-dependent fracture predictions of CNTs and their composites.

The interfacial adhesion of CNT-reinforced composites was studied by simulating CNT pullout from the embedding polymer matrices, using molecular mechanics. Interfacial shear stresses were deduced by relating pullout energies to micromechanics formulation. Results suggested that the interfacial shear stresses between CNTs and polymers are significantly higher than most micro fiber-reinforced polymer composites. Two kinds of simulation procedures, a single optimization simulation (SOS) and a multiple optimization simulation (MOS), produced essentially the same result for pullout energies, suggesting that pullout energy is not sensitive to polymer deformation during CNT pullout. Pullout simulations were also carried out at 100, 200, and 300 K, the temperature dependence of the selected composite systems is believed related to the “annealing process” at those temperatures.

Direct tensile tests of SWNT bundles were carried out through a self-devised tester. The tensile strength of SWNT obtained was in the range of 6.6 to 35 GPa (mean value of 14.72 GPa). The tensile strengths of the SWNT sub-bundles were fitted to a two-parameter Weibull distribution with Weibull modulus of 1.71 and characteristic

strength 17.8 GPa. Based on local load shearing mechanism in the SWNT bundles supported by results of molecular mechanics simulations and transmission electron microscopy (TEM) images, it is inferred that the strength distribution of the SWNT sub-bundles is close to that of individual SWNTs.

The long-term behavior of SWNT rope reinforced epoxy composite under tension-tension load was studied. The flat S-N diagram of SWNT/epoxy obtained is very similar to that of the carbodepoxy, although they were loaded at much higher cyclic stresses. The fatigue strength of SWNT in epoxy is at least 1.5 times that of carbon fibers. Morphology of the fatigue fracture surface of SWNT reinforced epoxy involves matrix plastic deformation and SWNT-bridged matrix cracks. Evidence of good wetting and adhesion between SWNTs and epoxy was demonstrated. Results suggested that SWNT can be used for fatigue resistant, high fracture toughness composites. Observed damage and failure modes include: 1) splitting of SWNT bundles; 2) kink formation and subsequent failure in SWNT; and 3) fracture of SWNT bundles. Patterns of crack propagation under tension in SWNTs were studied by molecular mechanics simulations, where defect-free SWNTs and SWNTs with two different modes of Stone-Wales (SW) defects were studied. It is demonstrated by the results of molecular mechanics simulations that the observed fracture surfaces of SWNT can be reproduced reasonably well.

A model is proposed for predicting time-dependent fracture of CNTs, based on the classical kinetic concept of solid fracture and a concept of strain energy concentration. The time-dependent fracture behaviors of a zigzag, armchair and chiral tube with and without SW defects subjected to axial tension were studied by molecular mechanics simulations and a numerical scheme using crack front strain energy concentration. The

Abstract

crack initiation and propagation was found to be closely related to the local strain energy concentration on the crack-front bond being ruptured rather than the average strain energy in a whole CNT. While the defect has a significant influence on the site of crack initiation, the path of crack propagation is closely related to the chirality. Effects at different level on the fatigue strength and lifetime of the CNTs induced by SW defects depend on both the modes of defect and the types of CNTs. CNTs with SW defects were generally found to have a longer lifetime at low strain level. Comparisons were made with the available fatigue experimental data of SWNT bundles embedded in epoxy composite. The experimental data fall within the range of predication of the proposed model reasonably well.

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Table of Contents	
Abstract	i
Acknowledgement	iv
Table of Contents	v
List of Figures	viii
List of Tables	xiv
Nomenclature	xv
List of Publications.....	xvii
Chapter 1 Introduction	1
1.1 Background	1
1.2 Objective and scope	4
1.3 Organization.....	6
Chapter 2 Literature Review	7
2.1 Structure of CNT	7
2.2 Elastic behaviors of CNT	10
2.2.1 Young’s modulus	10
2.2.2 Instability, deformability and nonlinearity of CNT	16
2.2.2.1 Structural instability	16
2.2.2.2 Radial deformability of CNT	19
2.2.2.3 Nonlinearity	22
2.3 Strength and fracture mechanisms of CNT	23
2.3.1 Experimental results	23
2.3.2 Theoretical studies	26
2.4 CNT-based polymer composites	32
2.4.1 Performances of CNT reinforced composites	32
2.4.2 Some critical issues	36
2.4.2.1 Interfacial characteristics	36

Table of Contents

2.4.2.2 Alignment and dispersion of CNTs	41
2.4.2.3 Intratube/interlayer sliding.....	42
2.5 Load transfer and long-term behavior of advanced composites	45
2.6 Summary	48
 Chapter 3 Interfacial Characteristics of CNT/Polymers Using Molecular Simulations	50
3.1 Introduction	50
3.2 Basic knowledge of molecular simulation methods	51
3.2.1 Molecular mechanics simulation	51
3.2.2 Energy minimization methods	54
3.2.3 Molecular dynamics simulation	55
3.3 Modeling and simulations of graphene/polymers.....	56
3.4 Modeling and simulations of CNT/polymers	59
3.5 Comparison of two optimization procedures	68
3.6 Temperature dependence of CNT pullout	72
3.7 Conclusions	76
 Chapter 4 Tensile Test of SWNT Bundles	79
4.1 Experimental	79
4.2 Results and discussion	82
4.2.1 Elastic modulus and tensile strength.....	82
4.2.2 Strength distribution of SWNT bundles	86
4.2.3 Molecular mechanics simulations.....	90
4.2.4 Morphologies of fracturedSWNT bundles	93
4.3 Conclusion	96
 Chapter 5 Fatigue of SWNT Embedded in Epoxy Composites	98
5.1 Materials	98
5.2 Experimental procedures	102
5.2.1 Quasi-static tensile test	102
5.2.2 Fatigue test	102
5.2.3 Fracture surface analysis	103
5.3 Results and discussion	104

Table of Contents

5.3.1 S-N data of SWNT embedded in epoxy	104
5.3.2 S-N curves of SWNT/epoxy and neat epoxy samples	106
5.3.3 Stiffness degradation.....	107
5.4 Morphology of fatigue fracture surface	109
5.4.1 Morphology of SWNT/epoxy	109
5.4.2 Comparison of SWNT/epoxy and carbodepoxy	116
5.5 Fatigue mechanisms of SWNT	118
5.5.1 TEM examination	118
5.5.2 Molecular simulations of fracture patterns	126
5.6 Summary.....	130
 Chapter 6 A Kinetic Model for Time-Dependent Fracture of Carbon Nanotubes	132
6.1 Introduction.....	132
6.2 Kinetic concept of fracture mechanism	133
6.3 Proposed kinetic model of CNT fracture	135
6.4 Life prediction of CNT: cases studies.....	139
6.4.1 Life prediction for CNTs with no defects	141
6.4.2 Life prediction of CNTs with SW defects	148
6.4.2.1 CNTs with SW defect of A-mode	149
6.4.2.2 CNTs with SW defect of B-mode	157
6.5 Comparison with experimental data	167
6.6 Conclusions.....	168
 Chapter 7 Conclusions and Recommendations	170
7.1 Conclusions.....	170
7.2 Recommendations.....	174
 Reference	176

List of Figures

Fig. 2.1 Schematic honeycomb structure showing how a hexagonal graphene sheet is rolled to form a CNT.	8
Fig. 2.2 Illustrations of the atomic structure of (a) an armchair, (b) a zigzag, and (c) a chiral nanotube.	8
Fig. 2.3 (a) A HRTEM image of a bent tube. (b) A computer-generated image of a bent tube. Adapted from Ref. [47]	18
Fig. 2.4 The four snapshots show the various stages of the 5/7/7/5 defect kinetic formation from an ab initio quantum mechanical MD simulation for the (5,5) tube at 1800 K. Adapted from Ref. [71].	27
Fig. 2.5 The evolution of the 5/7/7/5 dislocation in an armchair tube under tensile load. Adapted from Ref. [73].	29
Fig. 2.6 (a) An arc-discharge grown nanotube cap, with at least five crystalline polymer growths; (b) a catalytically grown nanotube high in defects. Adapted from Ref. [101].	38
Fig. 2.7 Strain-life diagrams used for clarifying fatigue damage mechanisms. Adapted from Ref. [127].	47
Fig. 3.1 A molecular model of a PS/graphene system; (a) the view front X axis and (b) from Z axis.	57
Fig. 3.2 Comparison of system energies among the three kinds of graphene/polymer systems for the same contact area.	58
Fig. 3.3 The front view (a) and side view (b) of an armchair MWNT with outer diameter of 13.4 Å and length of 20 Å involved in this study.	60
Fig. 3.4 The side view (a) and top view (b) of a molecular model of MWNT/polymer system with the CNT pullout from the polymer matrix.	62
Fig. 3.5 Energies of MWNT vs displacements for MWNT/polymer systems.	64
Fig. 3.6 Comparison of the CNT energies calculated from SOS and MOS procedures for MWNT/PE system.	69

List of Figures

Fig. 3.7 Comparison of the CNT energies calculated from SOS and MOS procedures for MWNT/PP system.	70
Fig. 3.8 Comparison of the CNT energies calculated from the SOS and MOS procedures for MWNT/PS system.	70
Fig. 3.9 Comparison of the CNT energies calculated from SOS and MOS procedures for MWNT/poly(iso-butyl-ethylene) system.	71
Fig. 3.10 The total and potential energies of MWNT/PS system versus time in MD simulations when the system was heated to 200 K.	73
Fig. 3.11 The side view (a) and top view (b) of a molecular model of MWNT/PE system after MD simulation with the CNT fully embedded in PE.	75
Fig. 3.12 Pullout energies of MWNT/polymers versus temperature. Connecting dotted lines are guide to eye.	76
Fig. 4.1 A photo of multi-purpose nano-mechanical testing device.	80
Fig. 4.2 A mounted SWNT bundle, in which one end is attached to the lead rod and the other end is fixed on the surface, is subjected to tensile loading: (a) before breaking, (b) just broken into two parts.	81
Fig. 4.3 Stress-strain curves of four SWNT bundle specimens tested.	83
Fig. 4.4 Force-displacement curves of lead rod under tension. No kinks were observed upon loading to full-scale range.	84
Fig. 4.5 A simple graphical method is used to determine the two parameters of Weibull distribution.	88
Fig. 4.6 Accumulative failure probability verse strength of SWNT ropes.	89
Fig. 4.7 Probability density function (Weibull distribution) of SWNT sub-bundle strength using $m=1.71$ and $\sigma_0=17.8$ GPa.	90
Fig. 4.8 Molecular mechanics simulation of single SWNT pullout from 7-SWNT array.	91
Fig. 4.9 Molecular mechanics simulations of a 7-SWNT rope pullout from 19-SWNT array.	93
Fig. 4.10 A TEM image of the fracture surface of a SWNT bundle after tension test.	94
Fig. 4.11 A close-up image of the region around the arrow A (in Fig. 4.9).	95
Fig. 4.12 Very tips of fractured SWNT bundles with brittle-like flat surfaces.	95

List of Figures

Fig. 4.13 Curling, spiral-like fracture morphology is seen which implies plastic deformations of SWNT bundles.	96
Fig. 5.1 TEM images of bared SWNT bundle samples used in fabricating SWNT composite samples.	99
Fig. 5.2 Typical SWNT/epoxy sample (a), carbon fiber/epoxy sample (b), and neat epoxy sample (c) failed under cyclic load.	101
Fig. 5.3 An Instron™ 8800 Microforce Tester for fatigue experiments. Inset is the close-up.	103
Fig. 5.4 S-N diagrams of SWNT-reinforced epoxy composites.	105
Fig. 5.5 S-N curves of SWNT/epoxy and neat epoxy specimens.	107
Fig. 5.6 Typical normalized stiffness change of two SWNT/epoxy specimens.	108
Fig. 5.7 Fatigue fracture surface of a SWNT/epoxy sample showing ductile-like failure with plastic deformation of epoxy and pullout of SWNT ropes on the right hand portion and featureless fracture surface on the left hand portion where the epoxy matrix contains no CNT reinforcement.	111
Fig. 5.8 Fatigue fracture surface of a SWNT/epoxy sample showing ductile-like failure with plastic deformation of epoxy and pullout of SWNT ropes.	111
Fig. 5.9 Fatigue fracture surface of a SWNT/epoxy sample showing bridging of matrix crack by SWNT rope.	112
Fig. 5.10 A FESEM image of SWNT ropes bridging across the crazing on the fracture surface.	112
Fig. 5.11 Close up of the fatigue fracture surface of a SWNT/epoxy sample showing pullout of SWNT ropes from the epoxy matrix is obvious, however, complete debonding is not seen.	113
Fig. 5.12 Epoxy matrix protruding from the CNT showing strong interfacial adhesion exists between epoxy and SWNT ropes.	113
Fig. 5.13 SEM image used to estimate pullout length of SWNT ropes from the epoxy matrix.	114
Fig. 5.14 SEM image used to estimate diameters of SWNT ropes pulled out from the epoxy matrix.	114
Fig. 5.15 A high magnification FESEM image shows a SWNT bundle fracture in the matrix crack on the fracture surface.	115
Fig. 5.16 A high magnification FESEM image shows some SWNT bundles fracture in the matrix crack on the fracture surface showing rather flat surface.	115

List of Figures

Fig. 5.17 A longitudinal surface of a survived SWNT/epoxy sample after 10^6 cycles showing a SWNT bundle with fragment and micro cracks on the epoxy matrix.	116
Fig. 5.18 Fatigue fracture surface of a carbodepoxy sample with substantial fiber/matrix debonding and short fiber pullout.	117
Fig. 5.19 Longitudinal surface of a carbon fiber/epoxy sample with fiber/matrix splitting and matrix micro-cracks.	118
Fig. 5.20 Dendritic morphology is seen with numerous fractures and splitting at the tip of SWNT ropes.	119
Fig. 5.21 Splitting of SWNT within ropes away from the fracture tips	119
Fig. 5.22 Several kink on the SWNT ropes that are being pulled out from the matrix are illustrated as white circle in this TEM image, possibly produced by repeated loading of split SWNT.	121
Fig. 5.23 Kink formation induced to a substantial fracture failure was obviously seen.	121
Fig. 5.24 TEM image of fractures of SWNT bundles with flat fracture surfaces. Some splitting of SWNT bundles are also seen.	122
Fig. 5.25 A TEM image of fractures of SWNT bundles with flat fracture surfaces.	23
Fig. 5.26 A TEM image of SWNT fracture under tearing mode. Some splitting of SWNT bundles are also seen.	23
Fig. 5.27 A TEM image of SWNT fracture under tearing mode.	24
Fig. 5.28 The broken SWNT bundles with abrupt changes in diameter is seen, indicating that SWNTs within a rope may not be broken at the same time or at the same location.	124
Fig. 5.29 A TEM image of SWNT/epoxy specimen reveals good wetting morphology between SWNT and epoxy thin sheet.	125
Fig. 5.30 The crack pattern of zigzag tube (a), armchair tube (b) and chiral tube without defect under a 10% constant applied strain.	127
Fig. 5.31 A zigzag tube with a preexisted SW defects of two modes, referred to as A mode (a) and B mode (b).	128
Fig. 5.32 The crack pattern of zigzag tube (a) with a SW defect of A mode (b) with a SW defect of B mode under a 10% constant applied strain.	129
Fig. 5.33 The crack pattern of armchair tube (a) with a SW defect of mode A (b) with a SW defect of mode B under a 10% constant applied strain.	129

List of Figures

Fig. 5.34 The crack pattern of chiral tube (a) with a SW defect of A mode (b) with a SW defect of B mode under a 10% constant applied strain.	130
Fig. 6.1 Schematics of the fracture modes of an intact zigzag tube (18,0).	141
Fig. 6.2 Schematics of the fracture modes of an intact armchair tube (10, 10).	142
Fig. 6.3 Schematics of the fracture modes of an intact chiral tube (10, 5).	142
Fig. 6.4 (a) Total energy change per atom, E_i , of a zigzag tube (18, 0) versus axial tensile strain. (b) Energy change, u_i , of a crack front C-C bond in the same tube versus axial tensile strain.	145
Fig. 6.5 Time-to-failure of a zigzag tube (18, 0) without defect versus applied stress.	146
Fig. 6.6 Time-to-failure of an armchair tube (10, 10) without defect versus applied stress.	147
Fig. 6.7 Time-to-failure of a chiral tube (10, 5) without defect versus applied stress.	147
Fig. 6.8 Comparison of time-to-failure of a zigzag, armchair and chiral tube without defect versus applied stress.	148
Fig. 6.9 Schematics of cracking modes of a zigzag tube (18, 0) with a SW defect of A-mode.	151
Fig. 6.10 Schematics of fracture modes of an armchair tube (10, 10) with SW defect of A-mode.	152
Fig. 6.11 Schematics of fracture modes of a chiral tube (10, 5) with SW defect of A-mode.	152
Fig. 6.12 (a) Total energy change per atom, E_i , of armchair tube (10, 10) with SW defect of A mode versus axial tensile strain. (b) Energy change, u_i , of the strained bond at the crack front of armchair tube (10, 10) with SW defect of A-mode versus axial tensile strain.	154
Fig. 6.13 Time-to-failure of a zigzag tube (18,0) with SW defect of A-mode versus applied stress.	155
Fig. 6.14 Time-to-failure of an armchair tube (10,10) with SW defect of A-mode versus applied stress.	155
Fig. 6.15 Time-to-failure of a chiral tube (10,5) with SW defect of A mode versus applied stress.	156
Fig. 6.16 Time-to-failure comparison of a zigzag, armchair and chiral tube with a defect of A-mode versus applied stress.	157

List of Figures

Fig. 6.17 Schematics of fracture modes of a zigzag tube (18,0) with SW defect of B-mode.	159
Fig. 6.18 Schematics of fracture modes of armchair tube (10, 10) with the SW defect of B-mode.	160
Fig. 6.19 Chiral tube (10, 5) with the SW defect of B-mode.	160
Fig. 6.20 (a) Total energy change per atom, E_i , of a chiral tube (10, 5) with defect of B-mode versus axial tensile strain. (b) Energy change, u_i , of a crack front C-C bond in a chiral tube (10, 5) versus axial tensile strain.	162
Fig. 6.21 Time-to-failure of zigzag tube (18, 0) with SW defect of B-mode versus applied stress.	163
Fig. 6.22 Time-to-failure of an armchair tube (10,10) with SW defect of B-mode versus applied stress.	163
Fig. 6.23 Time-to-failure of a chiral tube (10,5) with SW defect of B-mode versus applied stress.	164
Fig. 6.24 Time-to-failure comparison of a zigzag, armchair and chiral tube with a defect of B-mode versus applied stress.	165
Fig. 6.25 Comparison of time-to-failure curves versus applied stress of the three types of CNTs with and without SW defects of A- and B- mode.	166

List of Tables	
Table 2.1 Some of the key parameters of CNTs [17].	9
Table 2.2 Theoretic and experimental values of Young's modulus (E) for CNTs in the literatures.	15
Table 2.3 Tensile strength of SWNT and MWNT from experimental measurements.	26
Table 3.1 Structure, name and composition of the polymers used in this study.	61
Table 3.2 Pullout energies and the corresponding interfacial shear stresses of CNT/polymer systems.	63
Table 3.3 Calculated thermal residual stress and parameters used for calculations.	67
Table 4.1 Experimental results of tensile test for SWNT bundles tested.	85
Table 5.1 Properties of CNT and carbon fiber.	99
Table 6.1 Values of parameter $\gamma_i (\times 10^{-39})$, a_i (eV/atom) and b_i (eV) for the zigzag, armchair and chiral tube without and with defect of A-mode (AM) and B-mode (BM).	140
Table 6.2 Energies of the bonds around a SW defect of A-mode at the strain of about 5%.	150
Table 6.3 Energies and lengths of the bonds around a SW defect of B-mode at the strain of about 5%.	158

Nomenclature

Symbol	Description
α_r	CTEs of CNT in the radial direction
α_z	CTEs of CNT in longitudinal direction
E_r	Transverse Young's modulus
E_z	Longitudinal Young's modulus
γ	Poisson's ratio
W	Pullout energy of CNT
τ_i	Interfacial shear stresses of the CNT/polymer systems
P_f	Probability of failure of a sub-bundle
m	Weibull modulus
σ_0	Weibull characteristic strength
σ	Applied stress
R ratio	Ratio of minimum to maximum cyclic stress
N	Number of cycles to failure
m	Slope of the normalized S-N curve
k	Boltzmann constant
τ_0	Reciprocal of the natural oscillation frequency of atoms in a solid
U_0	Atomic binding energy
γ	Disorientation of the molecular structure of a solid
E_i	Strain energy of CNT tube
u_0	Strain energy associated with the C-C bond of an intact tube,
u_i	Strain energy associated with the i th mode crack front C-C bond oriented parallel to the tube axis
γ_i	Coefficient of strain energy concentration
i	Denotes the C-C bonds to be broken
t	Lifetime of CNT tube

Nomenclature

t_i	Lifetime of each individual C-C bond around its circumference.
AFM	Atomic force microscopy
CNT	Carbon nanotubes
CTE	Coefficients of thermal expansion
DFT	Density functionaltheory
FESEM	Field emission scanning electronic microscopy
FIB	Focused ion beam
MWNT	Muti-walled carbon nanotube
MOS	Multiple optimisation simulation
NMTD	Nano-mechanical testing device
SEM	Scanning electronic microscopy
SWNT	Single-walled carbon nanotube
SOS	Single optimisation simulation
SW defect	Stone-Wales defect
TEM	Transmission electron microscopy

List of Publications

1. Y. Ren, Y.Q. Fu, K. Liao F. Li, H. M. Cheng, "Fatigue failure mechanisms of single-walled carbon nanotube ropes embedded in epoxy" *Applied Physics Letters* **84**(15), 2811-2813,2004.
2. T. Xiao, Y. Ren, K. Liao, "A kinetic model for time-dependent fracture of carbon nanotubes" *Nano Letters* **4**(6), 1139-1142,2004.
3. Y. Ren, F. Li, H. M. Cheng, K. Liao, "Tension-tension fatigue behavior of unidirectional single-walled carbon nanotubes reinforced epoxy composite" *Carbon* **41**,2159-2179,2003.
4. Y. Ren, F. Li, H. M. Cheng, K. Liao, "Fatigue behavior of unidirectional single-walled carbon nanotube reinforced epoxy composite under tensile load" *Advanced Composites Letters* **12**(1), 19-24,2003.
5. M. Wong, M. Paramsothy, X. J. Xu, Y. Ren, S. Li, K. Liao, "Physical interactions at carbon nanotube-polymer interface", *Polymer* **44**(25), 7757-7764,2003.
6. Y. Ren, H. Zhang, G. Ma, W. Pan, F. Li, H. Cheng, and K. Liao, "Tensile strength distribution of single-walled carbon nanotube bundles", Submitted.
7. Y. Ren, Y.Q. Fu, K. Liao F. Li, H. M. Cheng, "Fatigue behavior and morphologies of unidirectional single-walled carbon nanotube reinforced epoxy matrix composite", Submitted.
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9. X. J. Xu, Y. Ren, M. M. Thwe, S. Li and K. Liao, "Mechanical properties and interfacial characteristics of carbon nanotube reinforced epoxy thin film",

- Proceedings of the tenth U.S.-Japan Conference on Composite Materials, 16-18 September 2002, Stanford, California, U. S. A.
10. Y. Ren, K. Liao, F. Li and H. M. Cheng, "Tension-tension fatigue behavior of unidirectional carbon nanotube reinforced epoxy composite", The 9th International Conference on the Mechanical Behaviour of Materials (ICM9), 25-29 May 2003, Geneva, Switzerland.
11. Y. Ren, F. Li, H. M. Cheng, Kin Liao, "Fatigue behavior of unidirectional carbon nanotube reinforced epoxy composite", Tenth International Conference on Composites/Nano Engineering (ICCE-10), 20-26, July 2003, New Orleans, U. S. A.
12. Y. Ren, F. Li, H. M. Cheng and K. Liao, "Fatigue behavior of carbon nanotube reinforced epoxy composite under tensile load" International Conference on Materials and Advanced Technology (ICMAT 2003), 7-12, December 2003, Singapore.
13. K. Liao, and Y. Ren, "Mechanics of Carbon Nanotube Pullout" International Conference on Materials and Advanced Technology (ICMAT 2003), 7-12, December 2003, Singapore.
14. Y. Ren, Y.Q. Fu, K. Liao, F. Li, H. M. Cheng, "Fatigue mechanisms of single-walled carbon nanotube bundles", The international conference of Thin film and Nanotech, 12-16, July 2004, Singapore.
15. Y. Ren and K. Liao, Design of Carbon Nanotube-Based Polymeric Composites Using Molecular Dynamics Simulation, 1st International Conference on Materials Processing for Properties and Performance (MP3), 1-3 August, 2002, Singapore.

Chapter 1 Introduction

1.1 Background

Since their discovery in 1991 [1], carbon nanotubes (CNTs) have been the focus of tremendous research efforts. CNTs exist as either single- or multi-walled structures. The structure of a single-walled nanotube (SWNT) is basically a rolled up sheet of graphene, finished off at the end with a piece of fullerene. A multi-walled nanotube (MWNT) consists of several concentric cylinders, each cylinder being a SWNT with the spacing between the adjacent layers of around 0.34 nm, close to the interlayer spacing of graphite, 0.335 nm. SWNTs are usually found in bundles/ropes of nearly parallel tubules but individual SWNTs are sometimes found as well. Van der Waals forces dominate the interlayer and intertubular interactions between CNTs.

It has been shown from both theoretical and experimental studies that CNTs possess exceptionally high stiffness and strength with excellent flexibility and resilience. Comprehensive reviews of the mechanical properties of CNTs have been given, for instance, by Qian et al. [2], Yu [3], Lau et al. [4] and Ruoff et al. [5]. The exceptional mechanical properties of CNTs suggest that they offer considerable promises as reinforcing components in high performance composites [6]. In order better to unlock the potential applications of CNTs for advanced composites, issues such as the interfacial characteristics between the CNTs and the matrix materials, and the mechanics-related properties of CNTs including the accurate estimation of the tensile

stiffness and strength, the fracture mechanisms (how CNTs respond to external mechanical load, formation of possible defects, etc.) and long-term behavior, to mention a few, should be well understood.

The interfacial characteristics, such as wetting, adhesion and stress transfer, between the CNTs and the matrix materials, play central roles in the performance of nanocomposites. While some reinforcement effect of the nanocomposites has been simulated and observed [7, 8], an in-depth understanding of the CNT/matrix interface remains fundamental to the optimization of their performances. In fact, mechanisms by which load is transferred between polymer phases and the CNTs is still an open problem. Presently, however, devising experiments to determine CNT/polymer interfacial behaviors is still difficult, although some progresses have been made [9, 10]. Molecular modeling, as a powerful tool in studying chemical and physical phenomenon at the nanometer scale, can be used to elucidate the interfacial characteristics between a nano particle and its surrounding, and thus can also be employed to actively design an interface. Particularly, molecular simulations allow us to impose conditions experimentally impossible at the present time.

On the other hand, owing to the recent rapid development of synthesis methods for CNTs, high quality, long and aligned CNTs and CNT ropes/bundles, ribbons and CNT composite fibers are now available. Aligned MWNTs with a length of 2 mm [11], long SWNT ropes/ bundles with rope diameter of 100 μ m and length up to 3 cm [12, 13], macroscopic SWNT fibers and ribbons made by postprocessing techniques [14], and long SWNT strands up to 20 cm in length and about 0.3 mm in diameter [15], have been reported. The breakthrough in synthesis methods has enabled the mechanical properties of CNT to be more easily assessed, and the potential applications of CNT as

an ideal class of superstrong reinforcement for high-performance composite materials to be a step closer to reality. Through more than a decade of theoretical and experimental investigations, a better understanding on the intrinsic mechanical properties, such as stiffness and strength, of individual CNT, has been greatly improved. Despite the high stiffness and strength of individual CNT, the CNT ropes/bundles, as a typical macroscopic form of CNT, have somewhat different stiffness and strength from those of individual CNT. Furthermore, due to the difficulties in producing defect-free CNTs, CNT tensile strength is not a single-valued quantity. Such scatter in macroscale materials/structures is commonly described by statistical distribution. However, public report on the distribution of CNT tensile strength is still absent to date. It is imperative to perform tensile tests to address these issues.

An understanding of long-term fatigue behavior and fatigue mechanisms of CNTs and their composites will promote their potential applications as reinforcements for high-performance composite materials. Notwithstanding numerous research endeavors have been devoted to study the mechanical behaviors of CNTs and their composites, at present, addressing the long-term performance of CNTs and their composites is still absent. It has been well established, from composites reinforced with micro-sized fiber, that the long-term behavior relies critically on the reinforcement, the matrix material and the interfacial characteristics between them [16]. This motivates pondering that the CNT, the matrix material and the interfacial characteristics between them will also play key roles in the long-term performance of CNT-reinforced composites.

1.2 Objective and scope

The objective of this work is to exploit the remarkable mechanical properties of CNTs toward the development of high-performance composite materials through comprehensive studies on the interfacial characteristics between the CNTs and the matrix materials, the tensile stiffness and strength, the long-term fatigue behaviors and mechanisms, as well as lifetime predictions of CNTs and their composites.

It is necessary and useful that the following fundamental works be carried out:

- 1) Investigations of interfacial characteristics between the CNTs and the matrix materials, using molecular mechanics and molecular dynamics simulations.*

The interfacial characteristics of CNT-reinforced composites were studied by simulating CNT pullout from embedding polymer matrices, using molecular mechanics approach. A group of thermoplastic polymers, including polyethylene (PE), polypropylene (PP), polystyrene (PS), poly(ethyl-ethane), poly(iso butyl-ethylene) and polyvinyl chloride (PVC), were used as matrices to achieve a better understanding of the influencing factors on the interfacial adhesion between the CNTs and polymer phases. The interfacial shear stresses of CNT/polymer composites were then derived from pullout energies using a micro-mechanics formulation. The influences of the conformational changes on the pullout energies and hence the interfacial shear stresses were evaluated while CNT was being pulled out from the embedding polymers. Temperature dependent CNT pullout was also performed through molecular dynamics simulations.

2) *Tensile test of SWNT bundles.*

The tensile strength and elastic modulus, as the intrinsic mechanical properties of CNTs, were characterized for SWNT bundles through experimental method. In addition to obtaining the values of tensile strength and Young's modulus through tensile tests, analyzing the failure loads of the sub-bundles statistically not only will provide information on the tensile strength distribution of the SWNT sub-bundles, but also will shed light on the tensile strength distribution of individual SWNT and on the structural characteristics of SWNTs.

3) *Investigations of the fatigue behaviors and mechanisms of CNTs and their composites under tension.*

A study on the long-term fatigue behavior and fatigue mechanisms of CNT based epoxy composite was carried out through experimental method and molecular mechanics simulations. The fatigue behaviors and mechanisms of unidirectional, aligned SWNT ropes embedded in epoxy composite were investigated under tension-tension load. Fatigue damage and failure modes of SWNT/epoxy composite were examined by scanning electronic microscopy (SEM) and field emission scanning electronic microscopy (FESEM). To unravel SWNT fatigue failure mechanisms at the nanometer level, transmission electron microscopy (TEM) was also used extensively.

4) *A Kinetic model for predicting time-dependent fracture behaviors of CNTs.*

A model is proposed for predicting time-dependent fracture of CNTs, based on the classical kinetic concept of solid fracture and a concept of strain energy concentration. The time-dependent fracture behaviors of intact SWNT and SWNT with two different

modes of SW defects subject to axial tensions were studied by molecular mechanics simulations and a numerical scheme using crack front strain energy concentration. Comparisons were made with available fatigue experimental data of SWNT bundles embedded in epoxy composite.

1.3 Organization

This thesis is organized into seven chapters. The background, objective and scope of the present research are introduced in Chapter 1. Chapter 2 is devoted to a brief overview of the current status of research on the mechanics-related properties of CNTs and their composites, with the emphasis placed on the intrinsic mechanical properties of CNTs and their composites, as well as some critical issues that need to be well understood in order better to take full advantage of the exceptional mechanical properties of CNTs for advanced composites. The molecular simulations of the interfacial behaviors of CNT/polymer systems are covered in Chapter 3, in which various contributors to the interfacial behaviors of CNT/polymers are studied in some detail. Chapter 4 is concerned with direct tensile testing of SWNT bundles through a nano-mechanical testing device. A study on tension-tension fatigue of SWNT/epoxy composites is presented in Chapter 5, where the fatigue morphology and mechanisms are investigated from micro-scale to nano-level through extensive microscopic examination (SEM and TEM). Chapter 6 addresses modeling the time-dependent fracture behaviors of CNTs on the basis of the classical kinetic concept of solid fracture and a strain concentration concept. Finally, conclusions and future work are outlined in Chapter 7.

Chapter 2 Literature Review

A review is presented on the mechanical properties of CNTs and their composites, including both theoretical and experimental work. This review is not intended to be comprehensive, since our focus is on exploiting the remarkable mechanical properties of CNTs toward the development of high-performance composite materials. Particularly, emphasis is placed on reviewing the exceptionally stiff and strong mechanical properties of CNTs and their composites, as well as the critical issues associated with CNT-reinforced composites that need to be well understood before the unique properties of CNTs to be successfully realized.

2.1 Structure of CNT

CNTs are long and thin cylinder(s) of carbon, which can be visualized as a sheet of graphene that has been 'rolled' into a tube. Different types of CNTs including chiral, zigzag and armchair tubes can be described by the chiral vector, (m, n) , where m and n are integers of the vector equation $\vec{R} = n\vec{a}_1 + m\vec{a}_2$, in the graphene plane, as shown in Fig. 2.1, in which the two basic vectors $\vec{a}_1$ and $\vec{a}_2$ are shown. The vector $\vec{a}_1$ lies along the zigzag line. The wrapping angle, θ , is formed between $\vec{R}$ and the zigzag line. If $\vec{R}$ lies along the armchair line ($\theta = 30^\circ$), then it is called an "armchair" nanotube. If $\theta = 0^\circ$ then the tube is of the "zigzag" type. Otherwise, if $0^\circ < \theta < 30^\circ$ then it is a "chiral" tube. The difference of patterns in armchair, zigzag and chiral tubes are shown in Fig. 2.2 (a), (b) and (c), respectively.

Fig. 2.1 Schematic honeycomb structure showing how a hexagonal graphene sheet is rolled to form a CNT.

Fig. 2.2 Illustrations of the atomic structure of (a) an armchair, (b) a zigzag, and (c) a chiral nanotube.

The mechanical properties of CNTs are strongly dependent on atomic arrangement (how the sheets of graphite are rolled), the diameter and length of the tubes, and the morphology, or nano-structure. Some of the typical parameters of a SWNT are listed in Table 2.1 [17].

Table 2.1 Some of the key parameters of CNTs [17].

Symbol	Name	Formula	Value
a_{C-C}	Carbon-carbon distance		1.42 Å
a	Length of unit vector	$\sqrt{3}a_{C-C}$	2.46 Å
$\vec{a}_1, \vec{a}_2$	Unit vectors	$\left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a, \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$	in (x,y) coordinates
$\vec{R}$	Chiral vector	$\vec{R} = n\vec{a}_1 + m\vec{a}_2 = (n, m)$	n, m: integer
L	Circumference of tube	$L = \vec{R} = a\sqrt{n^2 + m^2 + nm}$	$0 \leq m \leq n$
d	Diameter of tube	$d = \frac{L}{\pi} = \frac{a\sqrt{n^2 + m^2 + nm}}{\pi}$	
θ	Chiral angle	$\sin \theta = \frac{\sqrt{3}m}{2\sqrt{n^2 + m^2 + nm}}$ $\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$ $\tan \theta = \frac{\sqrt{3}m}{2n + m}$	$0 \leq \theta \leq 30^\circ$

It is worth noting that CNTs were first thought of as perfect nanostructures without defects. However, as more experimental observations and theoretical studies became available, CNTs were found to be not as perfect as they seem. The possible defective structures can be classified into four general groups [18]: *topological* (introduction of ring types other than hexagons), *rehybridization* (ability of carbon atom to hybridize between sp^2 and sp^3), *incomplete bonding defects* (vacancies, dislocations, etc.) and *doping* with other elements (i.e. catalyst metal).

Of these possible defects, pentagon-heptagon pair (topological defect) is one of the most important defective structures in CNTs, which is formed by rotating a C-C bond

in the hexagonal network by 90° (the so-called Stone-Wales (SW) transformation), resulting in the creation of a dipole of a 5/7 ring pair. The pentagon-heptagon topological defect (SW defect) was early found through HRTEM images in the open-ended growth of CNTs produced by arc-discharge method [19]. The SW defective structure and its formation mechanism strongly influence the mechanical properties of CNTs, such as the ductility, the fracture modes and the ultimate strength [20]. More recently, efforts have also been paid to study vacancy and its derivative point defects [21]. Here, a detailed review of all these defects in CNTs is not sought. Influences of the defects on the mechanical performances will be addressed in some detail in Section 2.3.

2.2 Elastic behaviors of CNT

Elastic behaviors under tension, compression, bending and torsion, as well as radial deformability of CNTs, are briefly reviewed in this section.

2.2.1 Young's modulus

Knowledge of the Young's modulus of a material is fundamental towards its use as a structural element for various applications. Many analytical and experimental studies have been carried out to date to estimate the elastic modulus of CNTs.

Robertson et al. [22] found that the elastic energy of a SWNT scales as $1/R^2$, where R is the radius of the tube, using both Tersoff and Tersoff-Brenner potentials. They concluded that CNTs behave softly in small radius and chiral angle, i.e., for a given radius, the zigzag and armchair tube yield the lower and upper limits of the stiffness

along the tube's axis, respectively. A similar relation was found by Gao et al. [23], where the Young's modulus for SWNTs was calculated ranging from 640.30 GPa to 673.94 GPa by computing the second derivative of the potential energy.

Yakobson et al. [24] obtained a Young's modulus for CNT, as high as 5.5 TPa, using the classic continuum shell model in combination with the results of MD simulations. This value of Young's modulus is probably overestimated according to recent experiments, possibly due to the assignment of a very small wall thickness of 0.066 nm. Lu [25] investigated the elastic properties of SWNTs and MWNTs through an empirical force-constant model. A Young's modulus of 1 TPa and the shear modulus of 0.5 TPa were calculated from the second derivative of the strain energy density with respect to various strains. These simulation results also show that such factors as chirality, radius and the number of walls have little effect on the Young's modulus.

Zhou et al. [26] investigated the morphology and mechanical properties of SWNTs using a first-principles cluster method within the framework of local density approximation. The Young's modulus was calculated to be 0.764 TPa. Using a local density approximation model combined with a classical elastic shell theory, Tu et al. [27] obtained a Young's modulus of 4.70 TPa for SWNTs. The Young's modulus for MWNTs was found to be an apparent function of the number of layers, N , varying from 4.70 TPa to 1.04 TPa for $N = 1$ to ∞ . Zhou et al. [28] proposed a method for the computation of the strain energy of CNTs directly from the electronic band structure without introducing any empirical potential. A nearest-neighbor tight-binding model was used for calculating the electronic energy bands of a SWNT. They obtained a Young's modulus of 5.1 TPa for a SWNT having an effective wall thickness of 0.71 Å.

Li et al. [29] obtained a Young's modulus of 1.05 ± 0.05 TPa for MWNTs, using the molecular structural mechanics method where a linkage was established between structural mechanics and molecular mechanics. The individual tube layer was simulated as a frame-like structure, whereas the interlayer van der Waals forces were represented by Lennard-Jones potential and simulated by a nonlinear truss rod model.

Hernandez et al. [30] obtained a Young's modulus of approximately 1.2 TPa for SWNTs, using a non-orthogonal tight-binding method. These simulation results also show that the Young's modulus is quite insensitive to the chirality but slightly dependent on the tube size, especially for small diameter CNTs ($D < 1.2$ nm). Sanchez-Portal et al. [31] found that the stiffness of SWNTs is close to that of the in-plane stiffness of graphite, using the ab initial density functional theory (DFT). The Young's moduli of SWNT rope and MWNTs were obtained to be 0.8 TPa and 0.95 TPa, respectively. Yao and Lordi [32] reported that the Young's modulus of various CNTs is approximately 1 TPa through MD simulations. The authors found that Young's modulus of CNTs was affected by tubes geometry structure (for example, chirality and diameter).

Owing to the nanometer scale in dimension, direct experimental measurement of Young's modulus of individual CNTs is not trivial. Atomic force microscopy (AFM) and high-resolution transmission electron microscopy (HRTEM) have been used for gaining very useful insights into the experimental determination of mechanical properties of CNTs.

The first measurement of the Young's modulus of MWNTs came from Treacy et al. [33]. A TEM was used to measure the mean-square vibration amplitudes of arc-grown

MWNTs produced over a temperature range from room temperature to 800°C. The Young's modulus ranging from 0.4 TPa to 4.15 TPa with an average value of 1.8 TPa and uncertainty of ± 1.4 TPa, was derived from the analysis of the temperature dependent vibration amplitude, by assuming the validity of the classic beam model for MWNTs. The authors suggested a trend for higher moduli with smaller tube diameters. This method was extended to measure the Young's modulus of SWNTs at room temperature [34]. The average of 27 tubes yielded a Young's modulus of 1.3 TPa.

Wong et al. [35] reported an AFM measurement of cantilevered MWNT. The bending force was measured as a function of displacement along the unpinned lengths. The bending modulus of MWNTs was then calculated as 1.28 TPa from the curve of bending force versus displacement. Salvetat et al. [36] measured the elastic properties of SWNT ropes deposited onto a special ultra-filtration membrane and bridged over a pore. A silicon nitride AFM tip was used to apply a force and to measure the resulting deflection of the CNT. The bending modulus of 1 TPa was deduced for small long ropes, similar to that of individual SWNTs, and the elastic modulus of SWNT ropes was estimated about 600 GPa.

Raman spectroscopy is known to be a sensitive mechanical sensor and can also be used to measure the elastic properties of CNTs. Lourie and Wagner [37] used micro-Raman spectroscopy to monitor the cooling-induced compressive deformation of CNTs embedded in an epoxy matrix. Through the observation of shift peaks on the Raman spectra, the Young's modulus was estimated to be 2.8-3.6 TPa and 1.7-2.4 TPa for SWNTs and MWNTs, respectively.

Electromechanical resonances of CNTs were applied by Poncharal et al. [38] to measure the elastic bending modulus of MWNTs as a function of the diameter (note that the authors have cautioned the readers by calling it elastic bending modulus). The elastic bending modulus as a function of diameter was found to decrease sharply from about 1 TPa to 0.1 TPa with increasing diameter from 8 nm to 40 nm. For a small diameter of CNT ($D < 10$ nm), the bending modulus can be identified as the Young's modulus with the value of 1 TPa.

Yu et al. [39] measured the stress-strain response and stress-at failure of individual arc-grown MWNTs under a tensile loading. The MWNT was mounted between two opposing AFM tips. The top AFM tip was a rigid cantilever that was driven upward to apply tensile load to the MWNT. The whole tensile loading device was operated inside a SEM and the tensile-loading situation of each CNT can be observed with the SEM. The broken MWNT fragments attached by AFM were examined by a TEM to determine the inner and outer diameters. The obtained Young's modulus values for MWNTs were in the range of 270 to 950 GPa, by assigning an effective thickness of 0.34 nm for the MWNT layer and assuming that the applied force is sustained only by the outermost layer. Yu et al. [40] applied a similar method for the tensile loading test on SWNT bundles. The obtained Young's modulus ranged from 320 GPa to 1470 GPa (mean 1TPa).

By pulling 2-mm long aligned CNT ropes, Pan et al. [41] measured the Young's modulus of MWNTs. The Young's modulus was 0.45 TPa, lower than those calculated and previously measured. Demczyk et al. [42] carried out a pulling and bending test on MWNTs in-situ in a TEM. From the corresponding bending studies on nanotubes, the Young's modulus was estimated to be 0.9 TPa.

Table 2.2 Theoretic and experimental values of Young's modulus (E) for CNTs in the literatures.

CNT	E (TPa)	Method	Author & Year	Ref.
SWNT	0.64-0.67	MD	Gao et al. (1998)	[23]
	5.5	MD & continuum shell model	Yakobson et al. (1996)	[24]
	1	MD	Lu et al. (1997)	[25]
	0.764	LDA (First principle cluster method)	Zhou et al. (2001)	[26]
	4.7	LDA & continuum shell theory	Tu et al. (2002)	[27]
	5.1	Tight binding and elastic theory	Zhou et al. (2000)	[28]
	1.2	Non-orthogonal tight binding	Hernandez et al. (1998)	[30]
	1	MD	Yao et al. (1998)	[32]
	1.3	Experimental	Krishnan et al. (1998)	[34]
	1	Experimental	Salvetat et al. (1999)	[36]
MWNT	2.8~3.6	Experimental	Lourie et al. (1998)	[37]
	0.32~1.47	Experimental	Yu et al. (2000)	[40]
	1.04~4.7	LDA & continuum shell theory	Tu et al. (2002)	[27]
	1.05 ± 0.05	Molecular structural mechanics	Li et al. (2003)	[29]
	0.95	Ab initial DFT	Sanchez-Portal et al. (1999)	[31]
	1.8	Experimental	Treacy et al. (1996)	[33]
	1.28	Experimental	Wong et al. (1997)	[35]
	1.7~2.4	Experimental	Lourie et al. (1998)	[37]
	0.1~1	Experimental	Poncharal et al. (1999)	[38]
	0.27~0.95	Experimental	Yu et al. (2000)	[39]
	0.45	Experimental	Pan et al. (1999)	[41]
	0.9	Experimental	Demczyk et al. (2002)	[42]

Although the Young's modulus of the order of 1 TPa for SWNT has been publicly accepted, the SWNT ropes as a typical macroscopic form of CNT have somewhat

different elastic modulus from that of individual SWNT, which has deduced to be around 600 GPa [25, 36], almost one-half that of diamond.

In short, theory and experiments have shown that CNTs possess high stiffness. There is a dispersion of theoretical and experimental values in the literatures for the elastic modulus of CNTs. The scatterings of theoretical predictions are probably due to the adoption of different empirical potentials or different relations in the continuum elasticity theory, particularly the different values of the effective wall thickness of the CNTs. The values of Young's modulus of CNTs from previous studies are tabulated in Table 2.2, for comparison.

2.2.2 Instability, deformability and nonlinearity of CNT

The structural instability of CNTs under compression, bending or torsion have been addressed by both theoretical and experimental studies. Furthermore, CNTs are much more compliant in the radial direction, as compared to their high stiffness and strength in the axial direction.

2.2.2.1 Structural instability

Two theoretical approaches, that is, MD simulations and continuum mechanics, are widely used to understand and predict the buckling behaviors of CNTs. Using both MD simulations and elastic continuum shell model, buckling due to axial compression, bending and torsion was demonstrated by Yakobson et al. [24] and Bernholc et al. [43]. Their simulations showed that an armchair (7, 7) tube of 6 nm in length and 1 nm in diameter was remarkably resilient and the first buckling pattern started at a compressive strain of 5%. In the case of bending, only one side of a tube was

compressed and thus can buckle, and the pattern was characterized by the collapse of the cross-section in the middle of the tube. When the tube was under torsion, flattening/collapse can occur due to the torsional load. These authors compared their results of atomistic modeling with continuum shell model and found that all changes of buckling patterns displayed by their MD simulations can be predicted satisfactorily by the continuum model.

Ru [44] treated double-walled CNTs as coaxial shells with van der Waals forces between the shells and studied their buckling under axial compression. The author concluded that the van der Waals forces do not increase the critical axial strain for buckling of the double-walled CNT as compared to a SWNT with otherwise identical nanotube. Buehler et al. [45] reported a shell-rod-wire transition of the mechanical behavior of SWNTs under compressive loading, as the aspect ratios (length-to-diameter) increase. For nanotubes with very small aspect ratios, the deformation mechanism is characterized by buckling of the cylindrical shell structure. Beyond a critical aspect ratio (~ 12.5), the shell buckling behavior of CNTs changes to rod-buckling described by the Euler theory of continuum mechanics. For even larger aspect ratios, the tube is extremely flexible and behaves as a bio-molecule. Ozaki et al. [46] simulated large axial deformations of SWNTs using an $O(N)$ tight-binding method, and found that the strain and shape of buckling under compression are closely related to temperature. These simulation results also show that in compression the armchair tube is greatly stiffer than the zigzag tube, while in tension the zigzag tube is slightly stiffer than the armchair tube.

Fig. 2.3 (a) A HRTEM image of a bent tube. (b) A computer-generated image of a bent tube. The network of hexagons is not disturbed; consequently, the tube can unbend without any damage. Adapted from Ref. [47]

Iijima et al. [47] reported experimental observations of bent SWNTs and MWNTs in a HRTEM. Shown in Figs. 2.3a and 2.3b are the images of bent SWNTs from HRTEM and atomistic simulations, respectively. Their results showed that the bending was fully reversible up to very large bending angles, with the occurrence of kinks and highly strained tube regions. Atomistic simulation results agreed with the experimental observations. Wong et al. [35] reported the elastic buckling behavior of MWNTs using AFM, in which buckling and rippling on the outmost layer under dynamic resonant bending was observed and could be responsible for the apparent softening of MWNTs of larger diameters. Falvo et al. [48] used a nano-manipulator and AFM to study the bending and buckling behaviors of MWNTs. They showed that MWNTs could be bent repeatedly through large angles without causing any apparent fracture in the tube. The observed reversible, periodic buckling of MWNTs indicated that CNTs are extraordinary flexible under large strain (up to 16%) and resist failure under repeated bending. Lourie et al. [49] captured the buckling behaviors of SWNTs under compression and bending by embedding them into a polymeric film. The buckling pattern under bending was characterized by a set of local rippling modes. Another pattern for the compressed tubes, i.e., the tubes remained straight, but the structure

collapsed locally, was also observed in the same experiment. Bower et al. [50] investigated the mechanical behaviors of MWNT-reinforced composites under bending, indicating that multiple buckles were ubiquitously found on the compressed sides of thick-walled CNTs, while thin-walled CNTs typically formed single buckles. The onset buckling strain was estimated to be about 4.7% and the fracture strain to be greater than 18%.

Waters et al. [51] reported the experimental observations of shell buckling instabilities in freestanding, vertically aligned MWNTs subjected to uniaxial compression. Albeit the experimental data did not provide insight into the critical buckling strain of MWNTs, the buckling load was found to be on the order of 2 μN for nanotubes with 25 nm outer radius, 13 nm inner radius, and heights of 50 and 100 nm.

2.2.2.2 Radial deformability of CNT

Knowledge of the radial elastic properties of CNTs is instrumental in understanding the failure mechanisms of CNTs and their composites. One of the major contributing factors to the buckling mode is the radial deformability of CNTs. CNTs are normally thought of as having a right cylinder type configuration. However, both experimental observations and theoretical studies have discovered that large diameter CNTs have an additional stable flattened structure.

Ruoff et al. [52] studied the radial deformations of MWNTs caused by van der Waals forces between adjacent nanotubes. Local flattening or collapse of tubes was observed in TEM, demonstrating, for the first time, that CNTs are not necessarily perfectly cylindrical. Chopra et al. [53] observed fully collapsed, flattened MWNTs in TEM, and

theoretical modeling demonstrated that, for a given range of tube parameters (radius and wall thickness, for instance), the collapsed state is energetically favorable. Tersoff and Ruoff [54] reported the deformation pattern of SWNTs, indicating that the tubes with diameters around or less 1~1.4 nm behave as rigid cylinders and less affected by the van der Waals force. For diameters over 2.5 nm, the tubes flatten against each other, forming a honeycomb structure. Elliott et al. [55] investigated the collapse of SWNT bundles under hydrostatic pressure using classical MD simulations, indicating that the collapse pressure is independent of the nanotube chirality, and a lower limit on the largest SWNT that remains inflated at atmospheric pressure is established ($d > 4.16$ nm). Tang et al. [56] revealed that SWNT was linearly elastic up to a hydrostatic pressure of 1.5 GPa at room temperature, using synchrotron x-ray diffraction. Structural instability occurred at ~4 GPa and became destroyed at 5 GPa. Using MD simulations, Liu et al. [57] demonstrated that, for small diameter nanotubes ($d < 20\text{\AA}$) the round right cylinder configuration was found to be energetically favorable, and for large enough nanotubes ($d > 20\text{\AA}$) the van der Waals forces provided a great enough energy contribution to allow the flattened dumbbell-like structure to be more energetically favorable.

Another way to investigate the radial deformation is to study the van der Waals interaction between CNTs and a surface. Hertel et al. [58] investigated the effect of surface van der Waals forces on the shape of MWNTs and SWNTs, indicating that CNTs on a substrate may experience radial and axial deformations, which significantly modify the idealized geometry of free nanotubes. The simulation results and experimental observations also show that the van der Waals interaction between CNTs

and a substrate results in high binding energy, depending on the tube diameter and number of shells.

Ru [59] reported a study of the elastic buckling of SWNT ropes under pressure, using a modified elastic honeycomb model (hexagonal network of elastic rods or plates). The author predicted that the critical pressure was about 1.8 GPa for SWNTs of diameters around 1.3 nm, and suggested that the elastic buckling would be responsible for the pressure-induced abnormalities observed for vibration modes and electric resistivity of SWNT ropes.

Nanoindentation test has also been used to characterize the radial deformability of CNTs. Shen et al. [60] investigated the radial properties of CNTs using a contact mode AFM, indicating that the radial compressive elastic modulus increase with compression, e.g., the modulus increased from 9.7 to 80 GPa when a 10 nm diameter tube was compressed from 26% to 46% in diameter. The radial compressive strength was estimated to be higher than 5.3 GPa. Yu et al. [61] studied the radial deformability of a MWNT using a tapping-mode AFM, demonstrating a remarkable reversible radial deformability (up to ~40%) of MWNTs. The radial compressive elastic modulus was obtained ranged from 0.3 to 4 GPa.

Briefly, to take full advantage of the reinforcing effect of CNTs on nanocomposite materials, an understanding of their radial properties is also important. Due to the anisotropic nature of the CNT structure, it is expected that the mechanical properties of CNT are also anisotropic. CNTs are much more compliant in the radial direction, as compared to their high stiffness and strength in the axial direction.

2.2.2.3 Nonlinearity

The aforementioned review has demonstrated that nonlinear elastic behaviors are obvious in CNTs under large deformations. There are few research endeavors devoted to the nonlinear analysis that takes into account the relatively large deformation.

Here, it is worth mentioning again the work carried out by Poncharal et al. [38], in which the elastic bending modulus as a function of diameter was found to decrease sharply from about 1 TPa to 0.1 TPa with increasing diameter from 8 nm to 40 nm. These authors attributed the decrease to the emergence of a mode of deformation in which a wavelike distortion or ripple forms on the inner arc of the bent MWNT since there was no evidence of nonlinearity, such as frequency shift with varying applied load (one of the typical indicatives of nonlinearity). Surprisingly, Liu et al. [62] used nonlinear vibration analysis that captures the rippling mode, and demonstrated that nonlinearity can cause a large reduction in the elastic effective bending modulus with increasing diameter. Using a generalized local quasi-continuum method, Arroyo et al. [63] also found that the nonlinear rippling mode deformations of MWNTs under bending were responsible for the measured drop of the effective bending stiffness with increasing diameter. Pantano et al. [64] reported a nonlinear structural mechanics based approach to investigate the mechanics of geometrically nonlinear deformations, including the onset and evolution of buckling in MWNTs under bending and compression. They found that the bent MWNT could develop characteristic wavelike distortions or wrinkles on the compressive side.

Xiao and Liao [65, 66] investigated nonlinear properties of SWNTs subjected to large-scale tensile and compressive deformation, using the Tersoff-Brenner potential. They

concluded that the in-plane stiffness of SWNTs under large-scale tensile deformation is linearly dependent on tensile strain, rather than a constant usually reported in the literatures. The nonlinear elastic response of the nanotubes should be taken into account in the case of large deformation when applied strain exceeds 2%. They found that the critical strains of the compressed CNTs on the condition that local buckling occurs are inversely proportional to their diameters. These simulation results also show that CNTs harden with compression but soften with tension.

2.3 Strength and fracture mechanisms of CNT

There are two kinds of behaviors corresponding to two types of stress-strain curves. The first one is typical of brittle conditions with plasticity absent, i.e., the rupture occurs in the elastic region, in which the strength is measured by the fracture stress. The second behavior is typical of ductile conditions, where the strength is associated with the *yield* stress, when the material ceases to behave elastically. Both brittle and ductile behaviors have been observed in CNTs. Another strength-related problem is the sliding of intra-layer within MWNTs or intrabundles within SWNT bundles.

2.3.1 Experimental results

To date, there are some experimental reports on testing the tensile strength of CNTs. As stated in section 2.2.1, Yu et al. [39] measured the stress-strain response and stress-at failure of individual arc-grown MWNTs under a tensile loading. The measured tensile strength of the outermost layer of each MWNT ranged from 11 GPa to 63 GPa. The applied load of the outer layer cannot be effectively transferred to the inner layer due to the weak van der Waals interactions between the MWNT layers, and the shear strength

between layers is possibly small. The inner layer in some practical cases was pulled out. Thus, the measured values were virtually the strength of the outermost layer of MWNTs. The MWNTs were found to fracture by a “swords-in-sheath” mechanism. Demczyk et al. [42] carried out a pulling and bending test on MWNTs in situ in a TEM. Based on the observation of the force required to break the tube, a tensile strength was estimated of 150 GPa.

To date, challenges still exist in directly determining CNTs’ tensile strength and other mechanical properties at macroscopic scale due to the very small dimension of CNTs. With the rapid advancement of synthesis and fabrication methods of CNTs, the high quality CNTs bundles with longer ropes aligned up to several tens centimeters have been obtained and characterized. Yu et al. [40] performed a tensile loading test on SWNT bundles. The strength of SWNTs was in the range of 13 GPa to 52 GPa (mean 30 GPa), and the Young’s modulus ranged from 320 GPa to 1470 GPa (mean 1 TPa). The maximum tensile strain they obtained was 5.3%.

Walters et al. [67] used AFM to directly apply and measure tensile strain in SWNT ropes. Freely suspended ropes were observed to deform as elastic string with tension proportional to elongation. The tensile strength of SWNT ropes was measured to be 45 ± 7 GPa using a Young’s modulus of 1.25 TPa for SWNT and the maximum elastic strain was evaluated about 5.8% using elastic string model.

By pulling 2-mm long aligned CNT ropes, Pan et al. [41] directly measured the tensile strength of MWNTs and found that the tensile strength of MWNTs was 1.72 GPa. The influencing factors to the much lower values, as stated in the report, may include (i) the MWNTs produced by chemical vapor deposition which may lead to more defects in

CNTs than those produced by arc-discharge method, and (ii) the weak interactions in MWNTs and hence some relative slippage may exist during pulling.

Another way of applying load is to use the load transferred by embedding the CNTs in a matrix material. Li et al. [68] estimated the tensile strength of the SWNT ropes with 10-mm gage length produced by catalytic decomposition through directly tensile test. Aligned SWNT ropes were impregnated with polyvinyl chloride (PVC) resin to form mini-composite samples. The samples were adhered to a hard paper with a rectangle hole in the center, which was very similar to conventional carbon fiber tensile test method. The well-known rule of mixtures was assumed to be valid to derive the strength of SWNT ropes from the uniaxially aligned fiber reinforced composite. The estimated SWNTs bundle strength ranged from 2.3 ± 0.2 GPa to 14.2 ± 1.4 GPa. Considering the SWNT volume fraction of 65% in a SWNT bundle, the strength of SWNT was estimated to be as high as 22.2 GPa with the average value of 11.5 GPa. Wagner et al. [7] examined stress-induced fragmentation of MWNTs in thin polymeric films, and obtained a tensile strength of 55 GPa. Lourie et al. [42] performed a compression test of the CNT embedded in polymeric film. The compressive strength and strain were estimated to be approximately 100~150 GPa and 0.5%, respectively. For comparison, the tensile strength reported in the open literatures to date are tabulated in Table 2.3.

Table 2.3 Tensile strength of SWNT and MWNT from experimental measurements.

CNT	Tensile strength (GPa)	Author & Year	Ref.
MWNT	1.72	Pan et al. (1999)	[41]
	11~63	Yu et al. (2000)	[39]
	150	Demczyk et al. (2002)	[42]
	55	Wagner et al. (1998)	[7]
SWNT (ropes)	45±7	Walters et al. (1999)	[67]
	22.2	Li et al. (2000)	[68]
	13~52	Yu et al. (2000)	[40]

2.3.2 Theoretical studies

Theoretical predictions of CNT strengths and fracture mechanisms have been carried out with the emphasis placed on the roles of defects, strain rate, and temperature. Yakobson et al. [69, 70] carried out atomistic studies of fractures of a zigzag (13,0) SWNT and reported that the fracture process is similar to the “unraveling of a sweater”. Before the strain reached a critical level, deformation in the CNT remained uniform. At this critical strain level, termed as the *breaking strain*, a few carbon bonds broke almost simultaneously, and the resulting “hole” in the CNT wall became a precursor of fracture. The atomic disorder propagated rapidly along the circumference of the CNT, and a largely distorted and unstable neck formed. The breaking strain, which represented the critical strain for a CNT to undergo nonuniform deformation, depended strongly on the temperature (decreased with increasing temperature). It was approximately 50% at 100 K, 34% at 600 K, and 25% at 1200 K. At later stages of fracture, the CNT fragments were connected by one (or few) unraveling monoatomic chain, which grew up to hundreds of atoms in length before its breakage.

Fig. 2.4 The four snapshots show the various stages of the 5/7/7/5 defect kinetic formation from an ab initio quantum mechanical MD simulation for the (5,5) tube at 1800 K. The atoms that take part in the SW transformation are highlighted in black. (a) System in ideal configuration ($t=0$ ps); (b) Breaking of the first bond ($t=0.10$ ps); (c) Breaking of the second bond ($t=0.15$ ps); (d) The defect is formed ($t=0.20$ ps). Adapted from Ref. [71].

Nardelli et al. [71, 72] reported the mechanism of strain release under tensile loading using both *ab initio* and classical molecular dynamics simulations. They found that in the case of tension, topological defects such as the “5/7/7/5” defect tend to form when strain is greater than 5% in order to achieve the relaxation of the structure. A single C-C bond rotation generates a double pentagon-heptagon defect, as shown in Fig. 2.4. At high temperature (2000 K), the 5/7/7/5 defect can, for a subset of the SWNT types, separate into two 5/7 pairs that can glide with respect to each other. They observed the ductile-to-brittle failure transition as a function of both temperature and strain. In general, high strain (15%) and low temperature (1300 K) lead to brittle behavior (crack extension or separation), while low strain (3%) and high temperature (3000 K) make CNTs more ductile (dislocation motion without cracking). These simulation results also show that the fracture behavior of zigzag tubes is more brittle than that of armchair tubes.

Yakobson et al. [73] proposed a dislocation theory to describe the route of mechanical relaxation in CNT under tensile load, indicating that the 5/7/7/5 dislocation can either evolve into a crack to result in a brittle fracture, or separate into two 5/7 pairs gliding away along the helical path to result in a ductile transformation for the CNT under high stress, as shown in Fig. 2.5. After several SW defects have migrated together fracture can be initiated via a mechanism whereby a bond connecting two pentagon rings is severed, resulting in the formation of larger rings, which ultimately leads to CNT yielding. These studies also show that the formation of SW defects is dependent on the chirality; defect nucleation is less favored in a zigzag tube compared to an armchair tube.

Fig. 2.5 The evolution of the “5/7/7/5” dislocation in an armchair tube under tensile load. Either a brittle fracture (b) or a plastic yielding (c) in which the dislocations glide away from each other can occur, resulting in a stepwise change of the diameter and the chirality of the tensile loaded CNT. Adapted from Ref. [73].

Zhang et al. [74] examined the plastic deformations of SWNTs induced by the SW dislocations under tensile strain, and found that the SW defects can release the strain energy. These simulation results also show that SW defects form more favorably in armchair tube than in zigzag tube because the rotation of the C-C bond can compensate for more tensile strain along the axis in the former case.

Zhao et al. [75] investigated the effects of the formation of strain-induced topological defects on the ultimate limits of the elastic response of strained CNTs by large-scale

quantum calculations. They found that, although the topological defects become energetically stable at strains of the order of 5%-6%, which agrees with the results of Nardelli et al. [71], the activation barriers for their formation are extremely high, implying that ideal, structurally perfect SWNT should be kinetically stable and resist strains well beyond the experimentally observed value of 5% [40,67].

Belytschko et al. [76] examined the fracture behaviors of three types of CNTs using MD simulations. The fracture behavior was found to be dependent primarily on the inflection point in the interatomic potential, rather than the separation (dissociation) energy. Their results also showed a moderate dependence of fracture strength on the chirality. The fracture strength of a zigzag tube (20,0) was in the range of 65-93 GPa with fracture strain ranging from 10% to 15%. The strength of an armchair tube (12,12) was 112 GPa, stronger than that of the zigzag tube. The strength of a chiral tube (16,8) was 106 GPa, and lay in between the two. The fracture of CNTs was predicted to be brittle. They also studied the effects of missing atoms and 5/7/7/5 defects, and found the latter have small effects on strength but changes the failure pattern, that is, the band of broken bonds occurs at an angle to the circumference of the CNTs.

Troya et al. [77] investigated CNT fracture behaviors under uniaxial tension, and found that the fracture mechanism discovered by Yakobson et al. [69] in a CNT with SW defect were not reproduced; instead, the bonds connecting two pentagon rings were especially strong. The tensile strength ranging from 103 to 163 GPa and strain of 23%-28% were obtained in their studies.

Samsonidze et al. [78] proposed a kinetic approach to study the effect of the rate of defect formation on the strength of CNT. The real-time strength was determined by the

rate of defect formation, defined in turn by the activation barrier for the bond flip. The simulation results of the kinetic barriers for a variety of strain-lattice orientations led to yield strain near 17% and tensile strength of 150–180 GPa, by assuming the Young's modulus of 1 TPa for CNTs.

Mielk et al. [79] investigated the effect of vacancy defects on the fracture behaviors of CNT under axial tension, using quantum mechanical simulations. One and two-vacancy defects were found to reduce tensile strength by as much as 26% and markedly reduce failure strains, which result in greater weakening of tube than SW defects. Marques et al. [80] studied the effects of temperature and the defects including SW defects and vacancies on the fracture behaviors of SWNTs. Two failure mechanisms: brittle failure and plastic yielding were identified.

Srivastave et al. [81] demonstrated that a defect of sp^3 bond formation could occur at the location of the collapse of CNTs under compressive load. Wei et al. [82] showed that, with thermal activation, CNTs under compressive strain could form both diamond-like (sp^3) bonds and SW defects. Wei et al. [83] developed a transition state theory based predictive model for examining the strain rate and temperature dependence of the yielding strain, indicating that the yield strain decreases at higher temperatures and at slower strain rates. These simulation results also show that a defect-free micrometer long SWNT at 300 K, stretched with a strain rate of 1%/h yields at about 961% tensile strain for small diameter CNT's, and about 2-3% higher for larger diameter CNT's.

Zhou et al. [84] carried out MD simulations to study the mechanical properties of an armchair (10,10) and a zigzag (17,0) SWNTs under tensile load with and without the presence of hydrogen, indicating that the hydrogen molecules reduce the fracture

strength of CNTs, which is attributed to the competition between the C-H and C-C bond formation.

Zhang et al. [85] proposed a continuum theory of fracture nucleation in SWNTs by incorporating interatomic potentials between carbon atoms into a continuum constitutive model for the nanotube wall. The fracture nucleation was viewed as bifurcation instability of a homogeneously deformed nanotube at a critical strain. The onset of the bifurcation was estimated to be at a tensile strain of 55%.

Briefly, previous studies have confirmed the high strength of CNTs. Compared with the theoretical predictions, experimental results suggested much lower yield strains and strengths, possibly due to the tube defects and much higher strain rates in MD simulations.

2.4 CNT-based polymer composites

Although attempts have been made to develop metal- and ceramic-matrix composites with CNTs as reinforcement [86], most research efforts have focused on the development of CNT based polymer composites. The present review is confined to CNT-based polymer composites, with the emphasis directed to CNTs as reinforcement in these new composites.

2.4.1 Performances of CNT reinforced composites

An efficient stress transfer from matrix to the CNT is necessary to take full advantage of the extraordinary mechanical properties of CNT in future composites. Considerable

research endeavors have been devoted to this field with both encouraging and discouraging results.

Wagner et al. [7] examined stress-induced fragmentation of MWNTs in thin polymeric films and concluded that the CNT/polymer interfacial shear stress is on the order of 500 MPa and higher. This value, if reliable, is an order of magnitude higher than the stress transfer efficiency of conventional fiber-based composites.

Lourie and Wagner [87] reported the formation of correlated damage doublets in adjacent CNTs embedded in a polymer matrix, comparable to those arising in fiber-reinforced composites as a result of the redistribution of stress from a failed fiber to its unfailed adjacent neighbors, which provided further evidence of stress transfer. Lourie and Wagner [88] observed the fractures of the aligned SWNT bundles under tensile stresses in a TEM. Qualitative evidence of good wetting and possibly adhesion between SWNTs and epoxy was presented.

Qian et al. [89] reported indications of significant load transfer in MWNT-reinforced polystyrene composites where good dispersion was achieved by an ultrasonic assisted solution-evaporation method. Just with the addition of only 1 weight percent (wt%) nanotubes (about 0.5 vol%) to the polystyrene matrix, elastic stiffness and strength was increased by 40 % and nearly by 25%, respectively, over those of pure matrix material. In situ TEM observations showed that the nanotubes tend to bridge a matrix crack, indicating the interfacial bonding between CNTs and matrix material. They also found that CNT breaking is a preferred process during film cracking. Contrastively, Watts et al. [90] reported that the embedded CNTs delay polymer film cracking via tube stretching and pulling out and no CNT breaking was observed.

Bower et al. [50] investigated the mechanical behaviors of MWNT-reinforced composites under bending. In addition to the buckling behaviors, which have been reviewed in section 2.2, they observed a high density of protruding CNTs having ball-like masses of polymer near the tip of the tubes, demonstrating the adherence of polymer to the CNTs. CNT pullout was also observed at the fracture surface. Xu et al. [91] studied microfabricated MWNT-reinforced epoxy composite thin films. The elastic modulus was evaluated from a shaft-loaded blister test using both linear and nonlinear elasticity models. With 0.1 wt % MWNTs added, the elastic modulus of MWNT-reinforced epoxy composite thin films increased remarkably by about 20%. Electron microscopic observations of the fracture surface suggested that strong interfacial shear stress exists between MWNTs and the epoxy matrix. The results showed good agreement with that obtained from molecular mechanic simulation and micromechanics calculations.

Mamedov et al. [92] investigated the freestanding multiplayered SWNT/polyelectrolyte membranes made by layer-by-layer assembly technique. This deposition technique prevents phase segregation of the polymer/SWNT binary system, and after subsequent crosslinking, the nanometer-scale uniform composite with SWNT loading as high as 50 wt% can be obtained. A tensile strength approaching that of hard ceramics were obtained. Cadek et al. [93] carried out tensile tests on free-standing composite films of poly(vinyl alcohol) and six different types of CNTs for different loading levels. Significant increases in Young's modulus by up to a factor of 2 were observed in all cases. They found that the reinforcement scaled inversely with the diameter of MWNT. The results also show that, in contrast to MWNTs, SWNTs displayed poorer reinforcement, probably due to bundle formation, suggesting that low-diameter MWNTs are the optimum material for polymer reinforcement.

Ye et al. [94] reported a SEM examination of CNT reinforced polyacrylonitrile composite fibers, where a two-stage rupture behavior of the composite fibers under tension, including crazing of polymer matrix and pullout of CNTs, has been observed. The results show that CNT reinforce the polymer fibers by hindering crazing extension, reducing stress concentration, and dissipating energy by pullout. They also demonstrated that the distribution of CNTs in the polymer matrix and the interfacial adhesion between CNTs and polymers are two major factors determining the reinforcement effect of CNTs in polymer fibers.

Despite the aforementioned encouraging results, negative results have also been reported. Schadler et al. [95] reported the mechanical behavior of MWNTs/epoxy composites under both tension and compression. A larger Raman peak shift was measured under compression as compared to that under tension, indicating the nanotubes carried more strain under compression than under tension. The difference in Raman response under tension and compression may be due to the poor load transfer behavior of nanotubes under tension. The authors proposed that only the outer layers were stressed in tension whereas all the layers responded in compression during load transfer. They concluded that there was poor interfacial load transfer in MWNTs/epoxy composites under tension compared with load transfer in compression. Lau and Hui [96, 97] evaluated experimental the hardness, the flexural strength of a CNT/epoxy. The hardness of the composites with less than 1 wt.% was less than that of a pure epoxy sample, and increased by about 20% for a sample with 2 wt.% nanotubes. The measured flexural strength was lower than that of pure epoxy. The long pulled-out nanotubes and local deformations of the matrix adjacent to stiff nanotubes suggested that the nanotubes had a poor interfacial bonding strength with the polymer matrices. The authors also presented two critical issues related to the use of nanotubes to form

advanced composites: (i) an in-depth investigation on the interfacial bonding characterization of the nanotubes to different types of polymer matrices and (ii) the use of SWNT is possibly more beneficial than the use of MWNT.

Thermomechanical or viscoelastic properties have also been investigated. Gong et al. [98] reported that, with the surfactant as the wetting agent, the addition of only 1 wt % CNTs in the composites could increase the glass transition temperature. Wei et al. [99] investigated the thermal expansion and diffusion characteristics of CNT-polyethylene composites, using classical molecular dynamics simulations, indicating that additions of CNTs to a polymer matrix increase the glass transition temperature and thermal expansion and diffusion coefficients in the composite above glass transition temperature.

2.4.2 Some critical issues

To take full advantage of the remarkable mechanical properties of CNTs, some issues, such as the ability to disperse the CNT homogeneously throughout the matrix without destroying the integrity of the CNT, the load transfer between concentric tubes within MWNTs and intra-bundles within SWNTs ropes, the alignment and quality of CNTs, as well as the CNT/polymer interfacial characteristics (wetting, stress transfer and adhesion), should be well understood before the unique properties of CNT to be successfully realized for CNT-reinforced composites.

2.4.2.1 Interfacial characteristics

The interfacial characteristics of CNT/matrix are critical to understand the mechanical behavior of CNT-based composites. Determining the mechanism and ways to enhance

it has been a central theme of recent studies. A number of researches have been devoted to the mechanism of interfacial stress transfer.

Previous studies on CNT-reinforced polymer composites showed that chemical bonding may or may not exist between CNT and polymer phase. Wagner et al. [7] suggested that the high interfacial shear stress determined from a CNT/polyurethane composite is attributed to a “2+2” cycloaddition reaction between the reinforcement and the polymer. Jia et al. [100] produced poly(methyl methacrylate) (PMMA)/CNT composites using an in situ process. The experiment suggested that CNTs might participate in PMMA polymerization and form a strong combining interface between CNTs and PMMA. McCarthy et al. [101] examined the MWNTs coated with poly(m-phenylenevinylene-co-2,5-dioctoxy-p-phenylenevinylene) (PmPV)), a electro-luminescent conjugated polymer, as shown in Fig. 2.6, through TEM. The evidence of the interaction between conjugated polymer and MWNTs was observed. The phenomenon of nucleation and crystalline growth of a semi-conjugated polymer from nanotubes defect sites demonstrated that chemical binding exist between the polymer chain and a pentagon defect on the nanotubes. More recently, Mylvaganam and Zhang [102] used DFT to investigate the possible chemical bonding formation between a polyethylene chain radical and a CNT. They demonstrated that (i) covalent bond formation between alkyl radicals and CNT is energetically favorable, (ii) the reaction may take place at multiple sites of CNTs, and (iii) the reaction is more favorable with tubes of a small diameter. However, using Raman scattering and x-ray diffraction, Chang et al. [103] showed that there is no chemical bonding between CNT and the polypyrrole matrix.

To study the interfacial characteristics, Liao and Li [8] reported CNT pullout from polystyrene (PS) composite system through molecular mechanics simulations. The results of CNT pullout energy suggested that the interfacial shear stress of the CNT/PS system is about 160 MPa. The authors concluded that the interfacial adhesion for a CNT/PS system, with no chemical bonding assumed, comes from (1) electrostatic and van der Waal's interaction, (2) mismatch in coefficients of thermal expansion (CTE), and (3) radial deformation induced by atomic interactions.

Fig. 2.6 (a) An arc-discharge grown nanotube cap, with at least five crystalline polymer growths; (b) a catalytically grown nanotube high in defects. Note correspondence between growths and defects. Adapted from Ref. [101].

Lord and Yao [104] investigated the adhesion mechanisms at the molecular level through MD simulations. Molecular mechanics calculations were used to determine the binding energy and sliding frictional stresses between pristine CNTs and a range of polymers in the absence of chemical bond between each other. The authors found that the binding energies and frictional forces played only a minor role in determining the strength of the interface, the helical conformation of polymer, however, was an

important factor to form a strong bond at the interface. The authors concluded that the interface strength was mainly due to the molecular-level entanglement of the two phases and forced long-range ordering of the polymer.

Frankland et al. [105] studied the effect of interfacial chemical crosslinks (low density $< 0.1\%$) on the interfacial shear strength between SWNTs and both amorphous and crystalline polyethylene matrix through MD simulations. In the non-bonded systems, both the amorphous and the crystalline polyethylene matrix models produced similar shear yield strengths. The shear strength of the corresponding cross-linked systems, however, was two times higher than that of the non-bonded composites. The results suggested that load transfer and hence the shear strength of CNT/polymer composites can be effectively increased by deliberately adding chemical cross-linking. It also suggested that inadvertent chemical bonding between CNT and polymer matrices during processing may be partly responsible for the enhanced stress transfer observed in some systems.

Wei et al. [106] investigated the structural properties of CNT polymer composite interface using MD simulations. Polymer (polyethylene) molecules were found to form discrete adsorption layers as a function of radial distance from the axis of the nanotube. The alignment of the molecules with the nanotube axis within the adsorption layers (structural ordering) was also found. The authors attributed the enhanced modulus and yielding behaviors of the CNT composites to such structural ordering.

In addition to molecular simulations, continuum models have also been used to study the load transfer mechanism between the CNTs and the polymer matrix. Wagner [107]

investigated the interfacial shear strength in SWNT based polymer composites using a classical Kelly-Tyson model, which can be expressed as a hollow tube model version:

$$\tau_{CNT}(\pi D_{CNT})dx = (\sigma_{CNT} + d\sigma_{CNT})\left(\frac{\pi D_{CNT}^2 - \pi d_{CNT}^2}{4}\right) - \sigma_{CNT}\left(\frac{\pi D_{CNT}^2 - \pi d_{CNT}^2}{4}\right) \quad (2.1)$$

where τ_{CNT} is the CNT/polymer interfacial shear strength, σ_{CNT} is the tensile strength of a CNT segment of length dx , and d_{CNT} and D_{CNT} are the inner and outer tube diameters, respectively. Integration of this equation provides an expression for the interfacial shear strength between a hollow tube and the surrounding polymer:

$$\tau_{CNT} = \sigma_{CNT} \left[\frac{1}{2} \left(\frac{l_c}{D_{CNT}} \right)^{-1} \left(1 - \frac{d_{CNT}^2}{D_{CNT}^2} \right) \right] \quad (2.2)$$

where l_c / D_{CNT} is the critical aspect ratio of the nanotube and d_{CNT} / D_{CNT} is its diameter ratio. The relationship among the shear strength, the critical aspect ratio and diameter ratio of CNT can be clearly seen from Eq. 2.2. Using tensile strength of 50 GPa for CNT, the interfacial shear strength was calculated in the range about 60 to 300 MPa for critical length values between 500 and 100 nm.

Odegard et al. [108] proposed an equivalent continuum modeling technique for CNT reinforced polymer composites, taking into account the discrete nature of the atomic interactions at the nanometer length scale and the interfacial characteristics of the nanotube and the surrounding polymer matrix. Gao et al. [109] proposed a shear-lag model for CNT reinforced polymer composites, suggesting that the nanotube aspect ratio was a critical controlling parameter for CNT reinforced composites.

In addition to the aforementioned theoretical studies, the first attempt to directly measure the interfacial adhesion in nanocomposites was reported by Cooper et al. [9]. In their study, the CNT/polymer interaction was quantified by detaching individual SWNT bundles and MWNTs from an epoxy matrix using the tip of a scanning probe microscope (SPM). A full force-displacement trace was recorded and correlated with TEM observations prior and subsequent to the tip action. The maximum interfacial shear strength of MWNT/polymer and SWNT/polymer were approximately calculated to be 376 ± 40 MPa and 366 ± 74 MPa, respectively. Further experimental work concerning measurement of CNT/polymer interfacial strength was reported by Barber et al. [10, 110]. Pullout experiments were performed at the nanoscale using AFM to assess the interfacial adhesion [10] and fracture energy [110] of CNT/polymers. These experimental results supported the predictions that the interfacial strength of CNT/polymers is significantly higher than that of fiber/polymers.

2.4.2.2 Alignment and dispersion of CNTs

Characterization of aligned CNTs is crucial to understanding the fundamental reinforcement mechanisms in nanocomposites. To date, attempts have also been made to align CNTs in order to better elucidate the reinforcement mechanisms. Jin et al. [111] showed that aligned CNT composites could be achieved by mechanical stretching of the composites, in which X-ray diffraction was used to evaluate the orientation and degree of alignment. Wood et al. [112] showed that CNTs could be aligned within a polymer by flowing the polymer prior to curing, or by stretching the specimen in simple tension. Raman spectroscopy was used as a tool to measure the degree of alignment of the tubes in a polymer. Haggenueller et al. [113] showed that melt spinning of SWNTs in fiber form could be used to create a well-aligned CNT

composite. More recently, Strobl et al. [114] reported an approach of using surface acoustic wave to align MWNTs to a sample surface.

Because of the extremely small size, CNTs tend to agglomerate when dispersed in a polymeric resin. In order to better achieve good reinforcement in a composite, it is critical to have uniform dispersion of CNTs within the polymer matrix. Agglomeration is significant in CVD-grown CNTs, since entanglement of the tubes occurs during CNT growth.

Sandler et al. [115] achieved a uniform distribution of CNTs within an epoxy matrix by repeated stirring at 2000 rpm both before and after adding the curing agent. Other investigators have utilized solution-evaporation methods with high-energy sonication [89], surfactant-assisted processing through formation of a colloidal intermediate [116]. Thostenson et al. [117] utilized a twin-screw extruder to obtain uniform dispersion of MWNTs with a polystyrene matrix, and extrusion and drawing was shown to create an aligned nanocomposite film. Gojny et al. [118] used a standard shear-mixing technique (calander) to disperse double-wall nanotubes in an epoxy resin, suggesting that using calanders was an appropriate and mild technique to exfoliate and disperse CNTs in epoxies. An increase was observed of strength, Young's modulus and strain to failure at a nanotube content of only 0.1 wt %.

2.4.2.3 Intratube/interlayer sliding

Other critical challenges lie in avoiding intratubular sliding within MWNTs and intrabundle sliding within SWNTs ropes/bundles. For a bundle of SWNT or for the

case of MWNT with nested, concentric shells, the degree of load transfer between adjacent tubes is a critical issue.

Yu et al. [39] indicated that there was little load transfer from the outer to the inner walls in MWNTs due to the weak van der Waals interaction, suggesting that the range of potential mechanical applications of MWNTs may be limited. The weak load transfer between the outer and the adjacent inner layer was estimated by Cumings et al. [119], using a manipulation stage inside TEM. The interlayer static and dynamic shear strength values were estimated to be around 0.66 and 0.43 MPa, respectively. Yu et al. [120] carried out a direct measurement of the dependence of the pulling force on the contact length between the layers. The shear strength between the outmost layer and the neighboring inner layer for two different MWNTs was found to be 0.08 and 0.3 MPa, respectively.

Lau et al. [96] indicated that the use of SWNT is possibly more beneficial than the use of MWNT to form advanced composites. Wei et al. [121] reported that for strain larger than 2%, the load transfer from the outmost layer to the adjacent inner layers begins to cease, suggesting that the van der Waals forces between the layers is not strong enough to sustain additional interfacial tensile stress. In contrast, the reinforcement effect between MWNTs and polymers was reported by Qian et al. [89], Xu et al. [91], Gojny et al. [118], to mention a few. Cadek et al. [93] demonstrated that, in contrast to MWNTs, SWNTs displayed poorer reinforcement, probably due to bundle formation, suggesting that low-diameter MWNTs are the optimum material for polymer reinforcement. In contrast, again, through analysis of SWNT bundle-PMMA thin films, Stephan et al. [122] found that PMMA was able to intercalate within the bundles, thus enhancing the interface between the SWNT bundles and polymer phases. Significant

wetting and interfacial adhesion for SWNT bundles embedded in an epoxy resin has also been reported by Lourie et al. [88].

Qian et al. [123] investigated the load transfer mechanism in SWNT bundles using both molecular mechanics and MD simulations, indicating that the necessary contact length to achieve a good load transfer must be around $1.3\ \mu\text{m}$. Compared with parallel bundles, twisting or larger diameter SWNTs that may naturally collapse into ribbons, can significantly enhance the load transfer between adjacent tubes. Using analytical potential molecular dynamics, Huhtala et al [124] calculated the critical shear stress (shear strength) between adjacent shells for double-walled CNTs with and without defects, suggesting that a small number of defects can give rise to a substantial increase (orders of magnitude) in the load transfer while the in-plane mechanical properties of individual defective nanotubes remain practically the same. Another mechanism is atomic registry between the shells, which may allow van der Waals forces to be strong enough to link them. Experiments have shown that a thin stripe of well registered atoms at the interface of a MWNT and a graphene sheet is sufficient to increase the force required for sliding by more than an order of magnitude [125,126].

It is evident that the structural behaviors of various forms of CNTs, such as MWNTs and SWNT bundles, particularly when they are embedded in polymer phases, still need to be further investigated in the future.

2.5 Load transfer and long-term behavior of advanced composites

Research on advanced composites started in the 1940s. Subsequently, from 1970s, it has been taking off with carbon, glass boron, and Kevlar fiber reinforced composites. Studies on load transfer and fatigue performance of micro fiber-reinforced polymer composites, in addition to providing basic understanding, also shed light on the behavior of CNT/polymer composites.

There are two load transfer mechanisms presented in fiber-polymer systems, one is global load sharing, another is local load sharing. Global load sharing is associated with a material where fiber breaks do not cause stress concentrations in the other intact fibers and stress along a broken fiber recovers to the applied stress linearly from the break. In contrast, local load sharing that renders fibers closest to the break experience stress concentration and other fibers further from the break are unaffected. The failure of composite can fall between the extremes of global load sharing on the one hand and nearest neighbor local load sharing on the other hand. To study load transfer mechanisms between fiber and matrix, shear lag model, as a stress transfer analysis method, was proposed by Cox [127]. Further works on shear lag theory based on Cox et al. can be found in [128, 129, 130, 131]. The basic assumptions of these shear lag models are that the fibers can be represented by one-dimensional axial springs and that the matrix transfers load between fibers via shear stress but does not carry any axial load itself. Landis et al. [131] used a finite element shear lag model to discuss the stress transfer in composite with cases of global versus local load sharing and the effects on composite failure. Although it is acceptable to analyze stress state in composite by

using shear-lag model, Narin [130] suggested that shear-lag analysis did not work at low fiber volume fractions.

Efforts devoted to understanding fatigue damage and failure mechanisms of fiber-reinforced polymer composites have been focused on tensile fatigue. Fatigue damage mechanisms of unidirectional composites have served as a basis for understanding the complex fatigue behavior of advanced composites. Konur and Matthews [16] presented a review of the effects of the material properties on the general fatigue performance of carbon, glass and Kevlar fiber composites. The following conclusions can be drawn from their review: the constituents of composites with improved properties, such as fibers with high strain, matrices with high strain and toughness, as well as interphases with strong fiber-matrix adhesion does not always result in improved fatigue performance, i.e., a longer fatigue life and a higher fatigue ratio. However, it should be expected that composites with improved fibers, improved matrices and an optimum degree of interfacial adhesion can lead to an improved fatigue resistance, depending on the interaction of the fiber, matrix and interphase damage for a specific composite.

Strain-life diagrams, as shown in Fig. 2.7, proposed by Talreja [132] can be used to clarify fatigue damage mechanisms. Damage mechanisms in the unidirectional composites depend greatly upon the relations between composites static failure strains and the matrix resin fatigue strain limits. At low cycles, catastrophic fiber damage is dominant, resulting in failures within the tensile static strength scatter band. For intermediate cycles, progressive damage mechanisms become dominant, corresponding to the sloping band. The horizontal line below the sloping band shows the fatigue strain limit of the matrix. Below the matrix limit, only matrix micro-crack nucleation is seen.

The strain-life diagram constitutes a conceptual framework for interpretation of fatigue test results and fatigue damage mechanisms.

Fig. 2.7 Strain-life diagrams used for clarifying fatigue damage mechanisms. Adapted from Ref. [132].

It has been acknowledged that carbon fiber composites have excellent fatigue behavior with nearly flat stress-life curves and low strength degradation. Harris et al. [133] investigated the fatigue behavior of several different types of carbon fiber reinforced plastic composites. To eliminate differences in fiber strength and composite volume fraction, the following simple linear functional relationship was used to represent the S-N curve,

$$\sigma / \sigma_{ult} = 1 - m \log N \quad (2.3)$$

where σ and σ_{ult} is the applied cyclic stress and ultimate stress, respectively, N the number of cycles to failure (life), and m the slope of the normalized S-N curve.

Statistical analysis of normalized data suggested the slope m for most unidirectional carbodepoxy composites ranging from 0.035 to 0.059.

An understanding of long-term fatigue behavior and fatigue mechanisms of CNTs and their composites will promote their potential applications as reinforcements for high-performance composite materials. While numerous research efforts have been made to study the mechanical behaviors of CNTs and their composites, at present, addressing the long-term performance of CNTs and their composites is still absent. It is expected that the research efforts that have been made to study the fatigue behavior and mechanisms of micro fiber-reinforced polymer composites, will also shed light on the fatigue behaviors of CNT/polymer composites.

2.6 Summary

A brief review has been presented of the previous researches on the mechanics-related properties of CNTs and their composites, with the emphasis placed on the intrinsic mechanical properties of CNTs and their composites, as well as some critical issues that need to be well understood in order better to take full advantage of the exceptional mechanical properties of CNTs for advanced composites.

In sum, CNTs do possess extraordinary mechanical properties, such as ultrahigh stiffness and strength, outstanding flexibility and resilience, suggesting that they hold considerable promises as reinforcing components in high performance composites. One of the major topics concerning CNT as reinforcement in polymer composites is the load transfer from the polymer matrix to the CNTs. While progress has been made, the load transfer mechanism is still need to be investigated. However, devising experiments to

determine CNT/polymer interfacial behaviors is still difficult, albeit some progresses have been achieved. On the other hand, the intrinsic mechanical properties of CNTs, such as Young's modulus and tensile strength, have been relatively well studied and understood. Other mechanics-related properties, such as the response of CNTs to mechanical load (for instance, defect formation, fracture mechanism, etc.), although investigations are still under way, knowledge of them begins to emerge. However, study on the long-term fatigue failure and fatigue mechanisms of CNTs and their composites is still absent to date. For the present study, it is necessary and useful that the following fundamental works be carried out: (i) interfacial behavior of CNT-reinforced composites; (ii) tensile testing of SWNT bundles; (iii) fatigue behavior and mechanisms of CNTs and their composites and (iv) kinetic model for predicting time-dependent fracture behavior of CNTs.

Chapter 3 Interfacial Characteristics of CNT/Polymers Using Molecular Simulations

Interfacial characteristics of CNT-reinforced composites were studied by CNT pullout simulation from the embedding polymers, using molecular mechanics. The interfacial shear stresses of CNT/polymer composites were then derived from pullout energies using a micro-mechanics formulation. The influences of the conformational changes on the pullout energies and hence the interfacial shear stresses were evaluated while CNT was being pulled out from the embedding polymers. Temperature dependent CNT pullout was also performed through molecular dynamics (MD) simulations.

3.1 Introduction

Interfacial shear stress is a critical parameter controlling the efficiency of stress transfer and hence some of the important mechanical properties, such as elastic modulus, tensile strength, fracture toughness, as well as long-term performance of a composite. Remarkable mechanical properties of CNTs render them an ideal class of reinforcement for composite and interfacial characteristics between CNTs and polymers have been studied experimentally and theoretically using computational methods. To date, devising experiments to determine CNT/polymer interfacial behavior is still difficult, despite some recent progresses [9, 10]. Fortunately, recent advances in molecular simulation have made it possible to study the microscopic details in many research fields, such as physics, chemistry, and biology. With the development of high-speed

computational techniques, the application of molecular simulation has been expanded from individual atoms to large-scale molecular systems [134]. Hence, molecular modeling, as a powerful tool in studying chemical and physical phenomenon at the nanometer scale, can be used to elucidate the interfacial characteristics between a nano particle and its surrounding, and thus can also be employed to actively design an interface. Molecular simulation method as a major approach to study the interface interactions of CNT/polymer systems have been reported, such as the study performed by Lordi and Yao [104], the simulation work done by Frankland [105], etc.

In this chapter, molecular mechanics and MD simulations are employed to study the interfaces of CNT/polymer systems. Pullout simulations of CNT from several embedding polymer systems were used to investigate the interfacial shear stresses of CNT/polymers (MWNT/polymers and SWNT/polymers). Moreover, the influences of polymer configuration, geometry optimization method and temperature on the shear stress values of the CNT/polymer systems, are investigated.

3.2 Basic knowledge of molecular simulation methods

3.2.1 Molecular mechanics simulation

Molecular mechanics is an empirical force field that can be employed to perform calculations on systems containing significant numbers of atoms. Unlike quantum mechanics that deals with the electrons in a system, molecular mechanics ignores the electronic motions and calculates the energy of a system as a function of the nuclear positions only. Thus, molecular mechanics cannot provide properties that depend on the electronic distribution in a molecule. Molecular mechanics works at all is due to the

validity of several assumptions [135]. The first of these is the Born-Oppenheimer approximation, without which it would be impossible to contemplate writing the energy as a function of the nuclear coordinates. Molecular mechanics is based upon a rather simple model of the interactions within a system with contributions from processes such as the stretching of bonds, the opening and closing of angles and the rotations about single bonds. Transferability is a key attribute of a force field, for it enables a set of parameters developed and tested on a relatively small number of cases to be applied to a much wider range of problems. Moreover, parameters developed from data on small molecules can be used to study much larger molecules such as polymers.

Molecular mechanics force fields describe the potential energy surfaces and physical properties of molecules by means of classical mechanics equations. The potential energy of a molecular system in a molecular mechanics force field is the sum of the individual energy components

$$E_{Total} = \sum E_{bond} + \sum E_{angle} + \sum E_{crossterm} + \sum E_{non-bonded} \quad (3.1)$$

where E_{bond} is the energy associated with bond stretching, E_{angle} the energy of angle variation and torsion, $E_{non-bonded}$ the energy of non-bonded interactions including van der Waals and electrostatic effects, and $E_{crossterm}$ the coupling energy associated with the interactions of bonding stretching and angle variation and torsion.

Various functional forms can be used for these energy terms depending on the particular material and loading conditions considered. In the following, a general representation of each term contributing to the total potential energy in Eq. 3.1 is given.

The energy associated with bond stretching, E_{bond} , can be written as [135]

$$E_{bond} = \sum K_1 (l - l_0)^2 \quad (3.2)$$

where K_1 is the stretching constant of the bond; $l - l_0$ refers to the stretching bond length.

The term E_{angle} , including the total energy of angle bending term and torsion term is given by [135]:

$$E_{angle} = \sum K_2 (\theta - \theta_0)^2 + \sum \frac{V_n}{2} [1 + \cos(n\omega - \gamma)] \quad (3.3)$$

where K_2 , V_n , ω and γ , are bending constant of the bond, the relative “barrier” to rotation, the torsion angle and the phase factor, respectively.

Cross terms consist of two internal coordinates such as stretch-bend, stretch-torsion terms, and more than two internal coordinates such as the bend-bend-torsion. Various functional forms for the cross term energy can be refereed to Ref. [136]. The non-bonded term $E_{non-bonded}$ are usually considered in two groups, electrostatic interactions, van der Waals interactions. The van der Waals interactions in the force field can be expressed by the well-known Lennard-Jones function as [137]

$$V_{VDR} = \sum_{i < j} \left[\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right] \quad (3.4)$$

where R_{ij} is the non-bonded distance, A_{ij} and B_{ij} van der Waals parameters, R^{-6} the attractive London dispersion interaction and R^{-12} the repulsive interaction, respectively, between two atoms. The electrostatic potential can be expressed as [137]

$$V_{EEL} = \sum_{i < j} \frac{q_i q_j}{\epsilon R_{ij}} \quad (3.5)$$

where q_i and q_j are point charges of the two atoms i and j , respectively, and ϵ is effective dielectric constant. From Eq. 3.5, one can see that the magnitude of the electrostatic energy (V_{EEL}) varies inversely with the distance, R_{ij} , between two atoms. Based on functional form expression of the each energy term, the total potential energy can be rewritten as:

$$E_{total} = \sum K_1(l-l_0)^2 + \sum K_2(\theta-\theta_0)^2 + \sum \frac{V_n}{2}[1+\cos(n\omega-\gamma)] + \sum E_{crossterm} + \sum \frac{q_i q_j}{\epsilon R_{ij}} + \sum \left(\frac{A_{ij}}{R_{ij}^{12}} - \frac{B_{ij}}{R_{ij}^6} \right) \quad (3.6)$$

In this study, the component potential terms consist of the bond stretching energy, the energy of angle variation and torsion and the energy of non-bonded interactions associated with van der Waals and electrostatic effects. In our practice, the potential energy in the empirical molecular mechanics force field is determined through the single point calculation. This calculation only determines the present molecular configuration, a single point on the energy surface for the molecular system.

3.2.2 Energy minimization methods

In molecular modeling, we are especially interested in minimum points on potential energy surface, corresponding to a stable state of a system. To identify the geometries of the system with locally minimum potential energy, some minimization algorithm called geometry optimization or minimization should be performed. There are three minimization methods that are widely used in geometry optimization, i.e. the steepest descents method, the conjugate gradient method and the Newton-Raphson method. For

conjugate gradient methods, there are two proposed methods frequently used: the Fletcher-Reeves algorithm and the Polak-Ribiere algorithm. It has been reported that the Plak-Ribiere method performed better than the original Fletcher-Reeves method [135]. The Newton-Raphson method may have some problems for structures that are far from the minimum and thus is appropriate for being used for smaller molecular or for a system that only needs a few steps of minimization [135].

3.2.3 Molecular dynamics simulation

MD simulation is employed to study the thermodynamic properties and possible conformations of a molecule based on Newton's law of motion. MD trajectories with continuous potential models are generated through finite difference techniques. There are many algorithms for integrating the equations of motion using finite difference methods. Here, the 'leap-frog' algorithm, as a modification to the basic Verlet algorithm, is employed to describe the corresponding position and velocity as

$$x(t + \Delta t) = x(t) + \Delta t x\left(t + \frac{1}{2} \Delta t\right) \quad (3.7)$$

$$v(t) = \frac{1}{2} \left[v\left(t + \frac{1}{2} \Delta t\right) + v\left(t - \frac{1}{2} \Delta t\right) \right] \quad (3.8)$$

In MD simulations, various factors need to be taken into account when considering the integration schemes. The first important consideration is energy conservation. The kinetic and potential energy components of a system would be expected to fluctuate in equal and opposite directions during MD simulation to ensure that the total energy be constant (In practice, the total energy fluctuates about a constant value). Energy conservation in MD can be expressed as

$$E(t) = K(t) + P(t) \quad (3.9)$$

$$\frac{dK}{dt} + \frac{dP}{dt} = \frac{dE}{dt} = 0 \quad (3.10)$$

where $E(t)$, $P(t)$, and $K(t)$ represent the total, potential and kinetic energy, respectively. Another important influencing factor is to choose an appropriate time step in MD simulation. If the time step is too small, the trajectory will cover only a limited proportion of the phase space or spend much longer time to perform the simulations; if the time step is too large, instabilities may arise in the integration due to high energy overlaps between atoms. The useful guideline to choose an appropriate time step is the value of time step should be approximately one-tenth the time of the shortest period of motion. In this study, MD simulations are carried out to investigate the temperature dependence of CNT pullout.

3.3 Modeling and simulations of graphene/polymers

Since CNT can be viewed as a graphene sheet rolled into a tube, the adhesion energies between graphene and several polymers, including PE, PP and PS were first studied using molecular mechanics models. Random coils of PE, PP, and PS molecules of 120 monomers were constructed in a planar configuration and placed near a layer of graphene sheet of much larger dimension (The length of graphene along X-axis is 70 Angstrom.). With the graphene sheet fixed, the constructed polymers were optimized to reach the state of minimal energy via a conjugated-gradient method, followed by calculation of the energy of the graphene/polymer system at each specified distance between the graphene sheet and the polymer while it was being pushed towards or pulled away from the graphene sheet. The adhesion energy was calculated as the

difference between the minimum energy and the energy at infinite separation for the PE/graphene, PP/graphene and PS/graphene systems, respectively. A molecular model of a PS/graphene system, in which the PS molecular is 120 monomers in length, is shown in Fig. 3.1.

Fig. 3.1 A molecular model of a PS/graphene system; (a) the view front X axis and (b) from Z axis.

Comparison of system energies among the three kinds of graphene/polymer systems are shown in Fig. 3.2, in which the energies are plotted against the distance between the polymer and the graphene sheet. Note that the energy was obtained from approximately the same contact area. With an aromatic ring, PS has the largest side group, followed by PP with CH₃ group, and PE is a linear polymer with no side group. The adhesion energy for PE/graphene, PP/graphene, and PS/graphene is calculated as 430 kcal/mole, 373 kcal/mole and 343 kcal/mole, respectively. It is clear that the size of side groups has considerable influence on the adhesion energy. The larger size of the side group, the much more restriction for the polymer chains to approach to the graphene sheet and thus less adhesion energy induced.

Fig. 3.2 Comparison of system energies among the three kinds of graphene/polymer systems for the same contact area.

3.4 Modeling and simulations of CNT/polymers

The interfacial characteristics of a CNT/PS composite system were studied recently through molecular mechanics simulations and elasticity calculations [8]. The authors concluded that, for a CNT/PS system with no chemical bonding, the CNT/matrix adhesion comes from (i) electrostatic and van der Waals' interaction, (ii) mechanical interlocking arising from the mismatch of coefficients of thermal expansion (CTE) between CNT and matrix, and (iii) radial deformation induced by atomic interaction.

To achieve a better understanding of the interfacial characteristics of CNTs to different types of polymer matrices, the interfacial characteristics of CNTs to a group of thermoplastic polymers were studied through molecular mechanics simulations and elasticity calculations. The molecular structure of the CNT and adjacent polymer chains were constructed by molecular modeling. Then, the simulations of pullout of CNT from the embedding polymers were carried out to investigate the interfacial behavior of CNT/polymer matrix. The CNT constructed here are an armchair MWNT with outer wall diameter of 13.4 Å, inner-wall diameter of 6.7 Å and length of 20 Å, as shown in Fig. 3.3, and an armchair SWNT with the same size as that of MWNT.

The matrices used here are a range of thermoplastic polymers, including PE, PP, PS, poly(ethyl-ethane), poly(iso butyl-ethylene) and polyvinyl chloride (PVC) with backbone structure of ethylene $[CH_2-CH_2]$, in which one of the hydrogens was replaced by side chains of different function groups. These polymers are chosen in this study due to their simplicity and generic representation feature for polymeric materials. The outer diameter of polymer block is approximately 56 Å and its thickness is about 20 Å. Each of the systems contains about 4500 atoms, and each polymer chain with 20

repeating units. The SWNT and MWNT contained in the composite systems have 320 and 490 atoms, respectively. No chemical bonding exists between the CNT and the polymers in the construct systems. Note that the polymer chain with 20 monomers is extremely short, and hence effect of the molecular weight on interfacial characteristics could not be exhibited for these short polymers. However, it is mostly acceptable to simulate polymer with small size in molecular simulations [104, 105] due to computational cost. Note that the small size of polymer molecules has little influence on the comparison of interfacial behaviors for the CNT/polymer systems. The structure, name and composition of the polymers used in this study are tabulated in Table 3.1.

Fig. 3.3 The front view (a) and side view (b) of an armchair MWNT with outer diameter of $13.4 \text{ \AA}$ and length of $20 \text{ \AA}$ involved in this study.

One of the constructed CNT/polymer composite systems, in which an armchair MWNT is fully embedded in a nearly cylindrical polymer block, is shown in Fig. 3.4. To evaluate the constructed model structure, the densities of PE and PP of the polymer systems, calculated directly by HyperChem software, are 0.705 g/cm^3 and 0.73 g/cm^3 , respectively. The calculated density is probably low due to the low

molecular weight. However, the density value of PE system agrees well with the value of 0.71 g/cm^3 of an amorphous PE constructed by Frankland et al. [105].

Structure	Name	Composition
polyethylene	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
polypropylene	$\left[\begin{array}{c} \text{H} \quad \text{CH}_3 \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
polystyrene	$\left[\begin{array}{c} \text{H} \quad \text{C}_6\text{H}_5 \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$
poly(ethyl-ethane)	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{CH}_2-\text{CH}_3 \end{array} \right]_n$
poly(iso butyl-ethylene)	$\left[\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{CH}_2 \\ \quad \quad \text{CH}-(\text{CH}_3)_2 \end{array} \right]_n$
poly vinyl chloride	$\left[\begin{array}{c} \text{H} \quad \text{Cl} \\ \quad \\ -\text{C} - \text{C}- \\ \quad \\ \text{H} \quad \text{H} \end{array} \right]_n$

Fig. 3.4 The side view (a) and top view (b) of a molecular model of MWNT/polymer system with the CNT pullout from the polymer matrix.

A force-field based molecular mechanics, known as molecular mechanics method, was employed to describe the potential energy surfaces and physical properties of molecules for all the system to explore local interaction and regions of short-range order of CNT/polymers. The Plak-Ribiere conjugate gradient algorithm as geometric optimization method was first performed on the constructed CNT/polymer systems to ensure the whole system to reach a stable state with minimal potential energy. Then, the CNT was pulled out when the polymer molecules were fixed. The single-point energies were calculated against different displacement between CNT and the polymer matrices while the CNT was being pulled out from the matrices.

Table 3.2 Pullout energies and the corresponding interfacial shear stresses of CNT/polymer systems.

CNT/polymer systems	Pullout energy (kcal/mole)		Interfacial shear stress (MPa)	
	MWNT	SWNT	MWNT	SWNT
CNT/PVC	221	201	202	198
CNT/poly (iso butyl-ethylene)	212	195	194	192
CNT/PS	209	189	190	186
CNT/poly (ethyl-ethane)	206	186	188	183
CNT/PE	195	173	178	170
CNT/PP	185	167	170	164

The energies of CNT from different polymer systems, plotted against the displacement of CNT from the polymer matrices, are shown in Fig. 3.5. Note that the pullout energy is the energy difference between the fully embedded tube and the complete pullout configuration. The pullout energies of CNT (including MWNT and SWNT) from all of the embedding polymers are summarized in Table 3.2.

Fig. 3.5 Energies of MWNT vs displacements for MWNT/polymer systems.

It can be seen from Table 3.2 that the pullout energies of CNT embedded in different polymer matrices are different even under the same physical conditions. Among the CNT/polymer systems studied so far in this work, the CNT/PVC system has the highest pullout energies, followed by the CNT/poly(iso-butyl-ethylene), CNT/PS, CNT/poly(ethyl-ethane), CNT/PE and CNT/PP system.

The energy difference (i.e., pullout energy) between the fully embedded tube and the complete pullout configuration is the work required for CNT pullout. The total work done, W , in pulling out the CNT from polymer matrix can be related to the shear stress between the CNT and the polymer by

$$W = \int_{x=0}^{x=L} 2\pi r(L-x)\tau dx \quad (3.11)$$

or

$$W = \pi r \tau L^2, \quad \tau = \frac{W}{\pi r L^2} \quad (3.12)$$

where r and L are the outer radius and length of the CNT, respectively, and x is the displacement along the longitudinal direction. It can be seen from Eq. 3.11 or 3.12 that pullout energy is directly related to the interfacial shear stress, τ . The interfacial shear stresses of all the CNT/polymer systems studied so far in this work are calculated, and the results are also tabulated in Table 3.2. The interfacial shear stresses estimated here are comparable to the experimental results of Cooper et al. [9]. It has been indicated that the interfacial shear stress is about an order of magnitude higher than most advanced microfiber reinforced composites [7, 8]. As shown in Table 3.2, it is obvious that the interfacial shear stresses between CNTs and polymers are significantly higher than most micro fiber-reinforced polymer composites [7].

Since pullout energy is directly related to interfacial shear stress, thereby the contributors to the pullout energy are also responsible for the interfacial strength between CNT and embedding polymer. Van der Waals and electrostatic forces are important contributors to the pullout energy and hence the strength of interfacial bonding between CNT and polymer. Here we have assumed that there is no chemical

bonding at the interface between CNT and polymer. The nature and magnitude of van der Waals adhesion rely on the choice of polymer matrix and also the conformation of the polymer. The polymer matrices constructed are a group of vinyl polymers. With simple vinyl monomers of the type $\text{CH}_2=\text{CHX}$, PP, PS, PE and PVC are of atactic configurations and poly(ethyl-ethane) and poly (iso butyl-ethylene) are of isotactic configurations.

The spatial hindrance induced by rigid benzene rings adversely affects the adhesion of CNT to the surrounding polymer. Nonetheless, the interfacial shear stress or pullout energy of CNT/PS is larger than that of CNT/PE or CNT/PP, which suggests that the strong interaction effect between the surfaces of phenyl-groups and CNT is much larger than the spatial hindrance effects induced by rigid benzene rings. It is believed that the strong interaction could be attributed to the correlation between the arrangement of the aromatic hexagons in nanotube's lattice structure and phenyl-groups of the surrounding polymer. The interaction between PS and CNT were also simulated as aromatic gear teeth formed by benzene molecules bonded onto the nanotube [138]. The larger pullout energy of CNT/PVC, as compared with CNT/PS, CNT/PE and CNT/PP, is attributed to the strong interaction between the CNT and PVC due to the polar group.

The isotactic conformation is known to form helix structure [139]. The strong adhesion between the CNTs and the polymers with helix configuration, such as poly(ethyl-ethane) and poly (iso butyl-ethylene), is because the forming trend of helix conformation in their structure allows the polymers to entangle around the CNTs to better extent, which agree with the results of Lordi and Yao [104].

The mechanical interlocking arising from mismatch in CTEs between CNT and polymer also contributes to the adhesion mechanism between them. Mismatch in CTE

between CNT and polymer results in thermal residual radial stress and deformation along the tube when the polymer is cooled from its melt. From a concentric cylinder model of elasticity [140], here, the thermal residual stresses induced by mismatch in CTEs between CNT and PP, PE and PS were calculated when the temperature changed from 75 to 25 °C. The results and the parameters used for calculations are tabulated in Table 3.3. In Table 3.3, α_r and α_z , accounting for the CTEs of CNT in the radial and longitudinal direction, respectively, are used as the CTEs of graphite crystal in the c axis and a axis, since CNT has a similar hexagonal arrangement of carbon atoms as the graphite crystal [8, 141].

Table 3.3 Calculated thermal residual stress and parameters used for calculations.

Items	CNT	PE	PP	PS
Elastic modulus (GPa) [142]	-	0.17	1.5	3.2
Poisson's ratio γ [143]	0.16	0.46	0.35	0.35
Transverse Young's modulus E_r (GPa)[25]	410	-	-	-
Longitudinal Young's modulus, E_z (GPa) [25]	1000	-	-	-
CTE ($10^{-6}/K$) [142]	-	210	86	70
α_r ($\times 10^{-6}/K$)	25	-	-	-
α_z ($\times 10^{-6}/K$)	-1.5	-	-	-
Thickness of matrix (μm)		5		
Outer diameter ($\oplus$)	13.34	-	-	-
Calculated thermal stress (MPa/K)		-185	-61	-45

It is noticed from Table 3.3 that PE has the largest thermal stress, followed by PP and PS, which does not agree with the order of CNT pullout energies from the corresponding polymer matrices, namely, the CNT/PS system has the largest pullout energy, followed by CNT/PP and CNT/PE system, as tabulated in Table 3.2. This is possibly because the mismatch in CTEs is not the major factors influencing the interfacial adhesion between CNT and polymer, as compared to the electrostatic and van der Waals interaction relying on the choice of polymer matrix and also the conformation of the polymer.

3.5 Comparison of two optimization procedures

In the preceding simulations, the pullout energies of CNT/polymer systems were obtained from single point calculations at a specified displacement of CNT from the embedding polymers. The geometry optimizations were only performed when CNT/polymer systems were constructed. No further optimization procedures were carried out while the CNT was being pulled out from the polymer matrices. That means no geometric optimization was performed except the fully embedded state. In this case, the polymer conformations were held constant and, thus the changes of polymer molecules or CNT Conformation were absent from the CNT pullout. This optimization procedure is referred to as ‘single optimization simulation (SOS)’, hereafter.

To consider the deformations of polymers and hence their influences on the simulated results of pullout energies, the geometry optimizations were performed on the polymers and the whole systems subsequently at each step when the CNT was displaced from the matrix in stepwise manner until complete pullout from the polymer matrices. Geometric optimization was carried out at least 15 times during CNT pullout (CNT is

displaced about 1.5 Å per step). This procedure is referred to as ‘multiple optimization simulation (MOS)’. It is not seen that the configurations of polymer significantly distort after MOS procedures. Comparisons of CNT energies versus displacements of the MWNT embedded in PE, PP, PS and poly (iso butyl-ethylene) systems, calculated from the two optimization procedures, are illustrated in Figs. 3.6-3.9.

Fig. 3.6 Comparison of CNT energies calculated from SOS and MOS procedures for MWNT/PE system.

Fig. 3.7 Comparison of CNT energies calculated from SOS and MOS procedures for MWNT/PP system.

Fig. 3.8 Comparison of CNT energies calculated from the SOS and MOS procedures for MWNT/PS system.

Fig. 3.9 Comparison of CNT energies calculated from SOS and MOS procedures for MWNT/poly(iso-butyl-ethylene) system.

From Figs. 3.6 - 3.9, it is seen that the pullout energies and the corresponding intermediate energy values calculated from the SOS and MOS are very close for the four selected systems. However, there are slight discrepancies in the results of the intermediate energies calculated from the SOS and MOS procedures for CNT/PS and CNT/poly(iso butyl-ethylene) (as shown in Figs. 3.8 and 3.9), since the interfacial adhesion of CNT/PS and CNT/poly (iso butyl-ethylene) are stronger than those of CNT/PE and CNT/PP systems. In this case, the slight configurationally changes of PS or poly (iso butyl-ethylene) did have some influence, though very small, on the intermediate energy values as CNT was being pulled out.

In summary, the pullout energies calculated from the two optimizations, SOS and MOS, show good agreement. It is therefore concluded that the configurationally changes while CNT was being pulled out from the polymers have no influences on the simulation results of the pullout energies, which is because the pullout energy is

dependent on the difference of energies between the fully embedded CNT and the complete pullout configuration.

3.6 Temperature dependence of CNT pullout

In the last two Sections, the pullout energies were calculated at the default temperature, 0 K. The temperature dependent contributions to the pullout energy are absent from the energy terms.

To investigate the thermodynamic properties of CNT/polymer systems, each of the systems including CNT/PE, CNT/PP, CNT/PS, CNT/poly (iso butyl-ethylene), CNT/poly(ethyl-ethane) and CNT/PVC systems were heated from 0 to 100, 200 and 300 K, respectively, through MD simulations. Geometric optimizations were then performed to obtain the optimized system structures at the elevated temperatures, followed by pullout simulations. In this study, the heating and running period are involved in the MD simulations. It took about 50 pico-seconds, including 20 pico-seconds heating and 30 pico-seconds running time, to reach an equilibratory state for all the systems. The time step size is 0.5 femto-seconds. Note that MD simulations must be long enough so that representative conformations are sampled. Thus, employing a very short time-step is very important for the system to be simulated. It took about one month or more to complete the MD simulations for each of the systems running on a PC with P4 processor.

Fig. 3.10 The total and potential energies of MWNT/PS system versus time in MD simulations when the system was heated to 200 K.

The trajectory of system energy, as a function of time, was recorded. The potential and total energies of CNT/PS versus time when the system was heated to 200 K, are shown in Fig. 3.10. The stability of the system can be evaluated according to the fluctuation of the total energy. The total energy of the systems should conserve and its fluctuation should be very small when the system reaches a stable state. It is noticed from Fig. 3.10 that the potential and total energies of the systems increase substantially during the heating period and thereafter reach a plateau at the specified temperature during the running period.

A molecular model of CNT/PE system with the CNTs fully embedded in PE after MD procedures is shown in Fig. 3.11. It can be seen from Fig. 3.11 that the conformation of the system due to the presence of the deformations of CNTs and polymer after MD procedures, differs from the starting axial-symmetric one. Thermal motion of polymer chains along the longitudinal surfaces of CNTs results in more even adsorption of polymer onto the CNT surfaces. On the other hand, slight deformation of CNTs is also

seen. The deformations of CNT and polymer are important contributors to the increase in pullout energy. After the completion of MD procedures, the polymer chains covering on the ends of CNTs as a result of thermal motion were removed, followed by geometric optimization to obtain new structures at 100, 200 and 300, respectively, for subsequent pullout simulations. The pullout energies for the six CNT/polymer systems at elevated temperatures are shown in Fig. 3.12.

It is noticed from Fig. 3.12 that the pullout energies of CNT/polymer systems increase at elevated temperatures. However, the increase in pullout energy, amounting to about 40 kcal/mole from 0 to 100 K, is nearly the same as those from 0 to 200 K or 300 K for all of the systems studied here. While the pullout energies of CNT/polymers increase substantially at elevated temperatures, their order almost remain the same, namely, CNT/PVC has the largest pullout energy, followed by CNT/poly (iso butyl-ethylene), CNT/CNT/PS, CNT/poly(ethyl-ethane), CNT/PE system, and CNT/PP system has the least

The MD procedures carried out can be interpreted as an annealing process where the conformation of the polymeric chains as well as the CNT/polymer interactions can be better optimized with the introduction of thermal energy. The plateaus formed from 100 to 300 K imply that further increase in annealing temperature may not influence the conformation of the composite system. It seems that 100 K is critical for all the six selected systems.

The result shown in Fig. 3.12 may not correlate with the glass transition temperatures of the polymers, simply because the time scale involved in this study is too small. The glass transition temperature, T_g , refers to the temperature at which long-range cooperative motion of the polymer chains occurs. The glass transition temperatures of PE,

PP and PS are 163 K, 255 K and 373 K, respectively [144]. For glass transition of polymer, 10^{-6} to 10^{-1} s relaxation time of the motion of chains is required. However, the time scale involved in the present MD simulation is too small to capture the motion of polymer chains for glass transition.

Fig. 3.11 The side view (a) and top view (b) of a molecular model of MWNT/PE system after MD simulation with the CNT fully embedded in PE.

Fig. 3.12 Pullout energies of MWNT/polymers versus temperature. Connecting dotted lines are guide to eye.

From the results of studies so far, it is believed that the temperature dependent contributions to the interfacial strength of CNT-reinforced polymer composite could be mainly attributed to (i) the increase in electrostatic and van der Waals interaction between CNT and polymer with the increase in temperature, and (ii) the increase in mechanical interlocking induced by mismatch in CTEs and the deformations of CNT and polymer.

3.7 Conclusions

Interfacial behavior of CNT-reinforced composite was studied by simulating CNT (including MWNT and SWNT) pullout from the embedding polymer, using molecular

mechanics. A group of thermoplastic polymers were used as matrices. Pullout energies were then related to the interfacial shear stress between the polymer and the embedded CNT, by means of continuum mechanics approach. Results suggest that the interfacial shear stresses between CNTs and the polymers are significantly higher than those of most micro fiber-reinforced polymer composites. It is believed that, the adhesion between the reinforcement and the matrix material with no chemical bonding is attributed to the larger extent to the electrostatic and van der Waals interaction. The nature and magnitude of electrostatic and van der Waals adhesion rely on the choice of polymer matrix and also the conformations of the polymers, which has been exemplified by the phenyl-groups and the helical conformations of the polymers.

The influences of the configurational changes on the pullout energies and hence the interfacial shear stresses were evaluated while CNT was being pulled out from the embedding polymers. Results suggested that the configurational changes have no influences on the simulation results of the pullout energies, which is because the pullout energy is dependent on the difference of energies between the fully embedded CNT and the complete pullout configuration.

Temperature dependent CNT pullout was also performed through MD simulations. The pullout energies of CNT/polymer systems increase at elevated temperatures. However, the increase in pullout energy from 0 to 100 K, is nearly the same as those from 0 to 200 K or 300 K for all of the systems. While the pullout energies of the six selected CNT/ polymers increase substantially at elevated temperatures, their order almost remain the same. The MD procedures carried out can be interpreted as an annealing process where the conformation of the polymeric chains as well as the CNT/polymer interactions can be better optimized with the introduction of thermal energy. The

plateaus formed from 100 to 300 K imply that further increase in annealing temperature may not influence the conformation of the composite system. The temperature dependent contributions to the interfacial strength of CNT-reinforced polymer composite could be attributed to (i) the increase in electrostatic and van der Waals interactions between CNT and polymer with the increase in temperature, and (ii) the increase in mechanical interlocking induced by mismatch in CTEs and the deformations of CNT and polymer.

Chapter 4 Tensile Test of SWNT Bundles

In this work, 3 mm-long SWNT bundles were subjected to tensile loading using a nano-mechanical testing device (NMTD). The tensile strength of SWNT obtained was in the range of 6.6 to 35 GPa (mean value of 14.72 GPa). Tensile failures of SWNT sub-bundles, suggested by the load drop on the stress-strain curves of all of the samples tested span from low to high load (1.92-35 GPa). The tensile strengths of the SWNT sub-bundles were fitted to a two-parameter Weibull distribution. Weibull modulus of 1.71 and characteristic strength of 17.8 GPa were obtained, the former indicates a large scattering. Based on local load sharing mechanism in the SWNT bundles supported by results of molecular mechanics simulations and TEM images, it is inferred that the strength distribution of the SWNT sub-bundles is close to those of individual SWNTs.

4.1 Experimental

A multi-purpose nano-mechanical testing device (NMTD) for the measurement of micro/nano structures has been developed. A photo of the device is shown in Fig. 4.1. The hardware consists of three major components: the motion control unit, the force acquisition and analysis unit, and the side-view image acquisition and analysis unit. Two achievable levels of motion, i.e., micro- and nano-level of motion, are controlled by a DC motor and a PZT actuator, respectively. The micro motion control unit offers a wide travel up to 10 mm with a resolution of around 0.1 μm and the nano motion control unit has a travel distance of 180 μm with a very high resolution up to 1 nm. A

force transducer with a resolution of $0.2\ \mu\text{N}$ is attached to the terminal end of a PZT actuator. The force signal is then filtered and amplified using a specified amplifier, and the amplified signal is transmitted and acquired through a data acquisition (DAQ) board. A computerized video enhanced side-view imaging system, which is composed of a long focal distance objective lens incorporated with a computer-linked CCD camera, is included to continuously record the gradual deformation of the sample under test. The acquired images can be analyzed, refined and stored via the cell workstation software, which is an interactive software system based on the LabVIEW platform. Equipped with a video enhanced side-view image monitoring system, the NMTD is able to continuously capture, display, and store images during testing. Due to the small size of SWNT bundle, the imaging system is necessary, for example, to ensure the loading of SWNT to be performed accurately, and to make sure that SWNT is straight under tension so that the start point of displacement is identified

Fig. 4.1 A photo of multi-purpose nano-mechanical testing device.

All SWNT bundle samples used in this study were synthesized by catalytic decomposition of hydrocarbon (the structure of these bundle can be referred to Fig.5.1). Long (several tens of centimeters), straight, aligned SWNT ropes with diameter of about 100 μm were obtained. These SWNT ropes were carefully separated manually into several thinner, 3 mm-long SWNT bundles for testing.

Fig. 4.2 A mounted SWNT bundle, in which one end is attached to the lead rod and the other end is fixed on the surface, is subjected to tensile loading: (a) before breaking, (b) just broken into two parts.

Each SWNT bundle was mounted vertically between a stage surface using epoxy and a replaceable lead rod that is firmly attached to the force transducer of the NMTD. Displacement, force, as well as images of a SWNT bundle under loading were recorded simultaneously. The strain rate was controlled at 0.1 s^{-1} during testing. No slipping of SWNT bundle from the mounting grip was observed from the video images recorded. All of the samples were broken in the region between the two mounting ends, typical images of a SWNT bundle before and after tensile testing are shown in Fig. 4.2. Total of 15 SWNT bundles were tested. Through electron microscopy, the apparent diameters

of the SWNT bundles were measured in the range of 15 to 25 μm . It should be noted that the final effective diameter (instead of the apparent diameter) of sub-bundle was used to calculate the effective load-sharing surface. The effective diameter of the final fracture surface of SWNT bundle was evaluated through SEM or TEM. The final load-bearing surface or the final effective surface, which only consists of the surfaces of several sub-bundles, are measured in the range of around several hundred to one thousand nanometers. The detailed results are shown in Table 4.1. Once the final effective fracture surface was determined, strength of sub-bundles corresponding to the final breakage was obtained. The stresses of those kinks corresponding to sub-bundle failures were then deduced by the obtained final strength and the associated load-drop at each kink in the force-displacement curve.

4.2 Results and discussion

4.2.1 Elastic modulus and tensile strength

Through analyzing the stored data, stress-strain curves were obtained. The stress-strain curves of four SWNT bundles tested are shown in Fig. 4.3. It is worth noticing that there are kinks on the stress-strain curves, which exist in all of the samples tested, appear at more or less regular load intervals, and span from low to high load (1.92-35 GPa). On the average, there are nine kinks on each stress-strain curve.

Fig. 4.3 Stress-strain curves of four SWNT bundle specimens tested. Several kinks on each curve are shown. Each kink implies that one or more ropes in the bundle broke, while the survived bundle bears the load until final rupture of the sample. The linear region between point A and B and non-linear region between point B and C on stress-strain curve of one specimen are also indicated.

In order to confirm the kinks on the stress-strain curve coming from CNT sub-bundle failure rather than CNT pullout, 6 CNT bundles of varying size from 20 to 40 μm were prepared and then tensile load up to the full range ($10000\mu\text{N}$) was applied. If the kinks on the stress-strain curve are caused by CNT pullout, more kinks will be seen with the increase in the size of CNT bundles, since the adhesive (epoxy) transfers the full load to the peripheral of the bundle, and thus resulting in more pullouts. However, the results showed that there was no correlation between kinks and bundle size. Hence, kinks were not caused by CNT pullout from the epoxy.

A pull test was also performed on the lead rod prior to testing of SWNT bundle to ensure that it is firmly attached to the transducer. The force-displacement curve under tensile loading on lead rod is shown in Fig. 4.4. No kink was observed upon loading to the full-scale range, suggesting that the kinks was not caused by the lead rod slippage.

Fig. 4.4 Force-displacement curves of lead rod under tension showed that no kinks were observed upon loading to full-scale force.

After confirming that the kinks on the stress-strain curve is caused by CNT sub-bundle failure, the strength of CNT sub-bundle can be calculated from the stress-strain curves, as shown in Fig. 4.3. The strength, Young’s modulus and strain for all the samples tested are tabulated in Table 4.1.

Table 4.1 Experimental results of tensile test for SWNT bundles tested.

No.	Final		Strength (GPa)	Strain (%)	Kink Number	E-value (GPa)
	Apparent Diameter (μm)	Effective Diameter (nm)				
1	25	800	18.11	5	8	1024
2	16	477	33.00	7.0	11	720
3	32	1020	8.71	12.0	14	290
4	25	950	11.07	10.0	16	295
5	17	550	12.82	5~9	9	300
6	17	569	10.80	5.8	11	385
7	26	825	6.61	7.5	11	360
8	26	894	15.13	5.2	11	972
9	24	748	11.6	7	13	300
10	17	506	11.6	3.3	8	725
11	15	467	30	6.80	10	870
12	27	823	8.5	4.50	7	-
13	17	533	7	4.80	10	600
14	15	473	9.05	6.30	7	380
15	25	605	~35	5	12	1020
Average			14.72			~600

It can be seen from Table 4.1 that the strength of SWNT bundles ranges from 6.6 to 35 GPa (mean value of 14.7 GPa), Young’s modulus ranges from 220 to 1200 GPa (mean value of ~600 GPa), and the strain ranges from 3.3% to 12%. These values obtained are much comparable with the results from other research groups (for instance, see Table 2.1 in Chapter 2).

It is noted from Fig. 4.4 that the SWNT bundles experienced elastic (a linear region) and plastic (a non-linear region) responses upon the applied uniaxial force till their final

fracture. The non-linearity in the high strain regime of the stress-strain curve with decreased slope could be related to plastic deformations of SWNTs and the succeeding sub-bundle fracture induced decrease of stress. The highest yielding strain measured is about 12%, much comparable with the results from other research groups [40, 72]. The large spanning range of strain, ranging from 3.3% to 12%, suggests the possible existence of both brittle and plastic failure in the SWNT bundles.

4.2.2 Strength distribution of SWNT bundles

It has been suggested that kinks on the stress-strain curves shown in Fig. 4.4 represent CNT sub-bundle failures, rather than the results from pullout of CNT or slip of lead rod. Analyzing the failure loads of the sub-bundles statistically will not only provide information on the tensile strength distribution of the SWNT sub-bundles, but also shed light on the tensile strength distribution of individual SWNT and on the structural characteristics (for instance, distribution and size of defects) of SWNT.

The as-prepared SWNT ropes consist primarily of many rope-like sub-bundles of SWNT with diameter of 10 to 40 nm [12], and it is estimated that each of the SWNT bundles prepared for the tensile test contain from a few hundred to about a thousand sub-bundles. We assume that there is no interaction among SWNT sub-bundles, thus each SWNT sub-bundle is equally stressed. The applied tensile load on a SWNT bundle is evenly redistributed among the remaining intact sub-bundles after failure of one or more sub-bundles at a specific load, until final failure of the entire SWNT bundle. Because only limited number of kinks is observed on a stress-strain curve, and there are at least a few hundred sub-bundles within a SWNT bundle, more than one SWNT sub-bundle could have failed at a kink point. Within a SWNT sub-bundle,

however, there could be local load sharing as a result of weak van der Waals interactions.

We assume that the tensile strength of SWNT sub-bundles follows a two-parameter Weibull distribution, a statistical model based on the weakest link concept that has been widely used for describing the strength of a broad spectrum of engineering materials [145]. The probability of failure of a sub-bundle, P_f , at an applied stress, σ , is

$$P_f = 1 - \exp \left[- \left(\frac{\sigma}{\sigma_0} \right)^m \right] \quad (4.1)$$

where m and σ_0 are the Weibull modulus and characteristic strength, respectively. Here, these two parameters are evaluated by analyzing collectively all of the stress-at-the-kink on the 15 stress-strain curves. Since the effective cross-sectional area or the amount of ruptured SWNT sub-bundle is difficult to measure at any instant during tensile loading, the stress at each kink point is simply deduced from the amount of load drop. The amount of load drop is proportional to the reduction in cross-sectional area, assuming that SWNT sub-bundles are carrying equal load prior to failure. In Eq. 4.1, the cumulative probability of failure, P_f , is estimated by the median rank method:

$$P_f = (i - 0.3) / (n + 0.4) \quad (4.2)$$

where i is the rank of tensile strength value in ascending order and n is the total number of samples. In our case, n is 114, the total number of kinks collected from stress-strain curves of 15 SWNT bundles tested. Median rank regression [145] is used to find the best-fit straight line to minimize the sum of the squared deviation (regressing X on Y). This regression is considered as the standard parameter estimation method because it

provides the most accurate results on the majority of data sets [145]. To calculate the two parameters, double logarithms were taken on both sides of Eq. 4.1, i.e.,

$$\ln[-\ln(1 - P_f)] = m \ln \sigma - m \ln \sigma_0 \tag{4.3}$$

where m and σ_0 can be obtained from linear regression of the collective strength data. As shown in Fig. 4.5, $m=1.71$ and $\sigma_0=17.8$ GPa are respectively related to the slope and intercept of the curve. As a common criterion for goodness-of-fit for regression model, the coefficient of correlation is 0.964, which indicates a reasonably good fit of data to model prediction.

Fig. 4.5 A simple graphical method is used to determine the two parameters of Weibull distribution.

The accumulative probability of failure of SWNT sub-bundles is shown in Fig. 4.6. Although the distribution of CNT tensile strength is still not available to date, analysis on those data from literatures [39, 40] and comparison with our results will certify the

reasonableness of strength distribution of CNT. Here, tensile strength data of individual MWNT from Yu [39] and SWNT ropes from Yu [40] are also plotted in Fig. 4.6.

Fig. 4.6 Accumulative failure probability verse strength of SWNT ropes. The circle curve represents the Weibull failure probability curve with fitted parameter $m=1.71$, $\sigma_0=17.8$ GPa. The curves with rectangles and triangles represent the tensile strength data of individual MWNTs from Yu [39] and SWNT ropes from Yu [40], respectively.

The Weibull modulus, m , is 2.6, and the characteristic strength, σ_0 , is 31.4 GPa, calculated from the 19 tensile strength data of individual MWNT; m is 2.5 and σ_0 is 34 GPa for the 15 tensile strength data of SWNT ropes. The low Weibull modulus from the present study and those of Refs. [39, 40] all indicate a wide scattering of tensile strength of CNT. As a comparison, the Weibull modulus for T300 carbon fiber is 8.26 ($\sigma_0=3.58$ GPa) [146], indicating a narrow distribution.

Note that the characteristic strength is considerably higher for data from Refs. [39, 40] because the length of the samples were substantially shorter (average length about 5

μm) than ours (3 mm). However, a direct comparison is not possible because sample length in ref. [39, 40] has a wide variation. The probability density function of the Weibull model for tensile strength using $m = 1.71$ and $\sigma_0 = 17.8$ are shown in Fig. 4.7.

Fig. 4.7 Probability density function (Weibull distribution) of SWNT sub-bundle strength using $m=1.71$ and $\sigma_0=17.8$ GPa.

4.2.3 Molecular mechanics simulations

It is found that fracture of a SWNT sub-bundle can happen at approximately the same location, suggesting a possible mechanism of local load sharing. SWNTs adjacent to a broken SWNT are carrying higher stress than those further away, and thus prone to failure. Otherwise the fracture surface of a failed sub-bundle would contain protruded individual SWNTs rather than exhibiting a flat surface.

To find out whether local load sharing is possible within a SWNT sub-bundle, we have constructed molecular models containing 7- (Fig. 4.8) and 19-SWNT bundles (Fig. 4.9) arranged in hexagonal array using molecular mechanics, in which each SWNT has a

diameter of 13.3 Å and a length of 40 Å. When the inter distance between SWNTs after optimization reaches 16.5 Å (center-to-center distance), pullout of the center tube(s) is performed, that is, a single SWNT is pulled out from the surrounding 7-SWNT array and 7 SWNTs are pulled out from the surrounding 19-SWNT array.

Fig. 4.8 Molecular mechanics simulation of single SWNT pullout from 7-SWNT array.

Shear stress between the pulled-out SWNT(s) and their host array is determined by correlating the energy difference between the embedded state and the pulled-out state to the work done by shear stress. From molecular simulations, the shear stress that originates from inter-tubular van der Waals' interaction between the central SWNT and the 6 adjacent SWNTs is 96 MPa, and that between the 7 central SWNTs and the 12 adjacent SWNTs is about 49 MPa, which implies that tensile stress could be transferred to the adjacent tubes near a broken SWNT over some distance.

A kink point on the stress-strain curve can reflect the following possible scenario: a) failure of individual SWNT that does not result in sub-bundle failure and b) sub-bundle failure induced by local load sharing after an individual SWNT has failed.

Many SWNT sub-bundles can have more or less the same strength, suggested by limited number of observable kinks. For sub-bundle failures caused by local load sharing, it can be inferred that the tensile strength of individual SWNT within the sub-bundle could be approximately the same at the failure site because of weak inter-tubular interactions. That is, if failure of a single SWNT starts from a defect, similar defect may be present on SWNTs adjacent to the failure site such that those SWNTs fail as a result of local load sharing. In either case, the estimated tensile strength at a kink point is close to the strength of individual SWNT.

The Weibull modulus calculated from the present study and those from Yu and co-workers [39, 40] all indicate substantial dispersion of CNT tensile strength, suggesting that CNT may contain defects of different size and form, and they are distributed along a tube. Moreover, these defects can interact when stressed, leading to low tensile strength. Subsequent works in elucidating the physics of such wide range of tensile strength scattering would be critical in controlling the distribution for structural applications.

Fig. 4.9 Molecular mechanics simulations of a 7-SWNT-rope pullout from 19-SWNT array.

4.2.4 Morphologies of fractured SWNT bundles

To investigate the morphology of the fracture, most SWNT bundle samples after the tensile test were examined by TEM. An image of the fracture surface of a SWNT bundle sample is shown in Fig. 4.10. It is obviously seen from the morphology of the fracture surface that several SWNT sub-bundles fracture subsequently rather than simultaneously with increasing tension load, and not all bundles sustained the ultimate tensile load when final failure occurred.

The marked region denoted by the arrow A is shown in Fig. 4.11 with a higher resolution. It is found from Fig. 4.11 that, along the longitudinal surface of the sample, a number of sub-bundles or ropes fracture and then pull out prior to the failure of those majority sub-bundles.

Image of the very tips of fractured SWNT bundles, as shown in Fig. 4.12, suggests brittle-like fracture. Within the sub-bundles, there is no individual SWNT split out,

which implies a local load shearing mechanism between the ropes within the SWNT bundles. While, compared with the brittle-like surface shown in Fig. 4.12, fracture morphology shown in Fig. 4.13 is seen curling, spiral-like surfaces, implying existence of possible plastic deformation of SWNT bundles under higher tensile strain.

Combined the evidences that shown in these figures, it is suggested that both brittle fracture and plastic deformation are possible to occur after a SWNT bundle is tensioned to failure.

Fig. 4.10 A TEM image of the fracture surface of a SWNT bundle after tension test.

Note that the marked region around the arrow A will be shown at a higher resolution in Fig. 4.10.

Fig. 4.11 A close-up image of the region around the arrow A (in Fig. 4.9). Along the longitudinal surface of the bundles sample, it is found a number of smaller ropes or bundles failure occurred away from the main fracture location and pulled out.

Fig. 4.12 Very tips of fractured SWNT bundles with brittle-like flat surfaces. Within the sub-bundles, there is no individual SWNT split out, which implies a local load shearing mechanism between the ropes within the SWNT bundles.

Fig. 4.13 Curling, spiral-like fracture morphology is seen which implies plastic deformations of SWNT bundles.

4.3 Conclusion

We have performed tensile tests on SWNT bundles using a nano-mechanical testing device. The strengths of SWNTs were estimated in the range of 6.6 GPa to 35 GPa (mean value of 14.72 GPa) and Young's modulus was estimated to be 600 GPa. The values of strength and elastic modulus obtained are comparable with those from published literatures. Tensile failures of SWNT sub-bundles, represented by load drop on the stress-strain curves of all of the samples tested span from low to high load (1.92 - 35 GPa). The tensile strengths of the SWNT sub-bundles were fitted to a two-parameter Weibull distribution with Weibull modulus of 1.71 and characteristic strength 17.8 GPa. The value of Weibull modulus indicates a large scattering of the distribution.

TEM images of SWNT bundles reveal that both brittle fracture and plastic deformation are believed to occur after the tension test. The morphologies of fracture surfaces of SWNT bundles suggest sub-bundle fracture succeeding rather than simultaneously. Based on local load shearing mechanism in the SWNT bundles supported by results of molecular mechanics simulations and TEM images, it is believed that the strength distribution of the SWNT sub-bundle is close to those of individual SWNTs.

Chapter 5 Fatigue of SWNT Embedded in Epoxy Composites

An understanding of fatigue behavior and fatigue mechanisms will enable the potential of CNT be better realized for long-term structural applications. In this chapter, the fatigue behavior of unidirectional, aligned SWNT ropes reinforced epoxy composite under tension-tension load is presented. Stress-life data, detailed fracture morphologies of SWNTs, that reveal the SWNT/epoxy damage and fracture modes, are shown. Extensive TEM examinations were also carried out for examining damage at the nanometer scale. Molecular simulations of crack propagation under constant strain were also performed to interpret experimental results.

5.1 Materials

Carbon fiber/epoxy composites, CNT/epoxy composites and epoxy samples were fabricated for fatigue study. The SWNT ropes used in this study were synthesized by the catalytic decomposition of hydrocarbon, with length ranged from 20 to 40 mm [12, 13] (courtesy of Prof. Cheng HM, Shenyang Institute of Metal Research). TEM images of the SWNT (ropes-like) bundles are shown in Fig. 5.1, in which the SWNTs are aligned with rope diameter in the range of 10 to 40 nm. The very high aspect ratio of SWNT ropes render them aligned uniaxial reinforcement. The density of the SWNT is 1.138 g/cm^3 and mass fraction 60% (or volume fraction 65%) in SWNT bundles [12,

68]. The matrix material used was Epicote 1006 epoxy resin, a room temperature curing system with specific ratio of 10:6 by weight for proper curing. The tensile strength of epoxy is about 36.58 MPa and the density 1.11 g/cm³. The basic properties of SWNT and carbon fiber used in this study are tabulated in Table 5.1.

Table 5.1 Properties of CNT and carbon fiber.

Item	Carbon fiber	Carbon nanotubes
Specification	PAN HTA 6000	SWNTs bundle
Specific gravity (g/cm ³)	1.78	1.138
Tensile strength (GPa)	4.31	3.6 ± 0.4-22.2 ± 2.2
Young's modulus (GPa)	230	800
Manufacturer	Ashi Nippon Fiber Co. Shenyang Institute of Metal Research

Fig. 5.1 TEM images of bared SWNT bundle samples used in fabricating SWNT composite samples.

To fabricate the composite sample, a thin layer of as-prepared epoxy resin was evenly brushed onto a hard surface pre-pasted with release tape to ensure the composite

sample can be easily detached from it after curing. 20 mm long, weighted SWNT ropes were picked up, separated carefully from a thicker bundle and then aligned by a slight tension using two sharp tweezers attached at two ends of the SWNT rope and subsequently laid onto the epoxy layer. More epoxy was then applied and the thickness of the small composite plate was controlled in the range of 0.4-0.6 mm using a roller. The SWNT/epoxy sample was cured completely after 72 h at room temperature.

Dog-bone SWNT/epoxy specimens with dimensions of about 40 mm in length (gauge length 15 mm) and 3.5 mm in width were cut from the cured thin composite plate in a mounting holder, and their edges were polished to reduce the possibility of edge-related failures during testing. The volume fraction of SWNT ropes in the composite was controlled in the range of 0.1-1.25 %. The variation of SWNT content in the SWNT composite is due to the difficulty of processing on SWNT such as weighting, separation and alignment of SWNT bundles in composite. Neat epoxy and carbon fiber/epoxy composite specimens with about 1% fiber volume fraction were also produced by the same procedures. SWNT/epoxy, carbon fiber/epoxy and neat epoxy specimens failed under cyclic load are shown in Fig. 5.2. It is seen from Fig. 5.2(a) that the SWNTs in SWNT/epoxy sample have a 'matted' appearance, indicating that the SWNTs are not 100% aligned in the composite. Alignment of SWNTs in epoxy composite resulting in unique stiffness change during fatigue testing, which will be discussed in Section 5.4.3. The carbon fiber/epoxy and neat epoxy samples were used for comparing the fatigue behavior and damage modes with that of SWNT/epoxy composite.

Fig. 5.2 Typical SWNT/epoxy sample (a), carbon fiber/epoxy sample (b), and neat epoxy sample (c) failed under cyclic load.

5.2 Experimental procedures

5.2.1 Quasi-static tensile test

The tensile strength of SWNT ropes was obtained previously and the estimated value ranging from 3.6 to 22.2 GPa [68]. It should be mentioned that the length of the SWNT ropes for tensile test was about 10 mm, which is less than those used in the present fatigue study (15 mm). The influence of the gauge length of specimen on experimental results can be described by Weibull distribution. The fiber failure model can be expressed as

$$F(\sigma_f) = 1 - \exp\left[-\left(\frac{\sigma_f}{\sigma_0}\right)^\beta\right] \quad (5.1)$$

where σ_f is the applied stress, $F(\sigma_f)$ the probability of failure, β , σ_0 the Weibull modulus and characteristic strength of the material specimen, respectively. For most engineering materials, failure distribution is related to the size of specimen. If CNTs also follow certain failure distribution, it is possible that longer CNTs fail at lower load.

5.2.2 Fatigue test

Constant-load-amplitude tension-tension fatigue tests were performed on an Instron™ 8800 Microforce Tester with a static load cell with capacity of 100 N, which is shown in Fig. 5.3. A sinusoidal waveform was employed at R ratio (ratio of minimum to maximum cyclic stress) of 0.1, and frequency was set at 5 Hz. A typical test span of 10^6

or 10^7 cycles takes about 55 to 555 h. A total of 31 SWNT/epoxy, 23 neat epoxy and 10 carbodepoxy samples were tested.

Fig. 5.3 An Instron™ 8800 Microforce Tester for fatigue experiments. Inset is the close-up.

5.2.3 Fracture surface analysis

The failed samples with the fracture surface upward were coated with Platinum using a JFC-1600 auto fine coater for 60 seconds before SEM examination. Fatigue morphology and failure modes were examined through a JSM-5600 LV (SEM) and JEM-2010 field-emission scanning electron microscopy (FESEM). To unravel SWNT fatigue failure mechanisms at the nanometer level, TEM was extensively used in this study. In order to examine the fracture surfaces for greater detail by TEM, samples were trimmed down to thickness of 200 nm by focused ion beam (FIB) trenching.

5.3 Results and discussion

5.3.1 S-N data of SWNT embedded in epoxy

Since the volume fraction of SWNT varied from sample to sample, the maximum cyclic stress of SWNT, instead of the stress of composite, is plotted against the number of cycles to failure of the composite. The stress of SWNT in the composite was estimated using a parallel model,

$$\sigma_{CNT} = (E_{CNT} / E_c) \sigma_c \quad (5.2)$$

where σ_{CNT} and σ_c are the stress of SWNT and of the composite, respectively, and E_{CNT} and E_c the Young's modulus of SWNT and of the composite, respectively. In order to compute the stress in CNT, E , was measured by tensile test prior to fatigue test. The values of E_c are in the range of 2.2-2.35 GPa due to the variation of volume content of CNT in epoxy composites.

The maximum cyclic stresses of SWNT were calculated to be between 5.7 - 24 GPa using a Young's modulus of 800 GPa [68]. From our tensile test for SWNT bundles (Chapter 4), the Young's modulus of SWNT bundle was measured of around 600 GPa, resulting in maximum cyclic stresses of 4.8-17 GPa.

The S-N data of the SWNT embedded in epoxy composite is shown in Fig. 5.4. The S-N data of unidirectional carbon fiber-reinforced epoxy, shown in the gray rectangular region of Fig. 5.4, are adapted from the results by Harris [133], which encompasses

most unidirectional carbodepoxy data. It is seen that the results of carbon fiber/epoxy samples involved in this experiment agree well with those from Harris [133]. Note that the maximum cyclic stress of the carbon fiber instead of the composite stress is used in Fig. 5.4, in order to compare with the data from the present study. A simple linear relation often used for S-N curve of unidirectional composite is

$$\sigma_a / \sigma_{ult} = 1 - m \log N \tag{5.3}$$

where σ_a and σ_{ult} are applied and ultimate stress, respectively, N the number of cycles to failure, and m the slope of the normalized S-N curve.

Fig. 5.4 S-N diagrams of SWNT-reinforced epoxy composites. Filled circles are data obtained from this study. Quasi-static tensile data (filled square with white circle) are adapted from Li [68], error bar represents standard deviation. The gray rectangular region covers most S-N data (filled triangle) for unidirectional carbon fiber-reinforced epoxy composite adapted from Harris [133].

In general, SWNTs embedded in epoxy specimens show a good linearity with less decreasing stresses in the range of 10^3 - 10^7 cycles. However, substantial decrease in the maximum stress is shown in the range of 10^0 - 10^3 cycles. At low stress level, especially during 10^6 - 10^7 cycles, most samples were survived, in which the stress experienced by SWNTs is around 6-7 GPa. The S-N curve obtained for the SWNT/epoxy composite is very flat, comparable to unidirectional carbodepoxy composites. Slope m for most unidirectional carbodepoxy composites ranged from 0.035 to 0.057 [133]. For SWNT/epoxy composites, m obtained from linear regression of quasi-static tensile strength and S-N data is calculated to be 0.042, which is very close to that of the unidirectional carbodepoxy composites. However, it should be mentioned that the maximum cyclic stress of SWNT estimated is about 1.5-2 times that of the carbon fiber in unidirectional composites. In other words, the fatigue strength of SWNT in epoxy is at least 1.5 times that of carbon fibers.

5.3.2 S-N curves of SWNT/epoxy and neat epoxy samples

Fatigue behaviors of SWNT/epoxy and neat epoxy specimens are shown in Fig. 5.5. It is found that the S-N curve of SWNT/epoxy composite with slope $m = 0.086$ is slightly flatter than that of neat epoxy ($m = 0.093$) and both of the materials exhibit a long linear range lifetime up to 10^6 - 10^7 cycles. Cyclic stress experienced by SWNT/epoxy is found higher than that of neat epoxy specimen. Fatigue strength of SWNT/epoxy at high cycles (10^6 - 10^7) is around 20 MPa, which is higher than the average value of 13-15 MPa for pure epoxy specimen at the same lifetime. Comparing the regression curves of SWNT/epoxy and epoxy matrix, the reinforcing effect by SWNT under lower stress and higher cycles is more prominent than those under lower cycles and higher stress condition. The non-distinct reinforcing effect by SWNT under lower cycles, as

compared to that under higher cycles may attribute to the realignment of SWNTs in composites. This evidence also suggests that SWNT could be fatigue resistant reinforcement with good long-term mechanical properties.

Fig. 5.5 S-N curves of SWNT/epoxy and neat epoxy specimens.

5.3.3 Stiffness degradation

In order to measure the elastic modulus of the fatigue sample, cyclic tests were interrupted and tensions loading were applied on the sample at intervals, up to 10% stress level, at a crosshead speed of 1 mm/min followed by load released. This procedure was repeated on fatigue samples for 5-6 times to measure average stiffness (elastic modulus) value.

A typical normalized stiffness change of two SWNT/epoxy specimens is shown in Fig. 5.6. The tensile modulus is shown a gradual increase during the stage of 0-10⁵ cycles and then become constant with a slight waviness until the catastrophic breaking during fatigue loading at low stress level. The plausible reason for the increase in tensile modulus is believed to be induced by the occurrence of realignment of SWNT ropes and macro-molecular chains of polymer matrix along the direction of applied stress. It takes a relatively long time for SWNTs to be re-aligned, possibly because the interactions in the SWNT bundles render a unidirectional alignment of individual SWNT along the direction of applied stress difficult. Overall, no obvious stiffness degradation of SWNT/epoxy implies that CNT have excellent fatigue resistant property.

Fig. 5.6 Typical normalized stiffness change of two SWNT/epoxy specimens.

5.4 Morphology of fatigue fracture surface

5.4.1 Morphology of SWNT/epoxy

All fatigue fracture of SWNT/epoxy samples occurred within the gauge region, a typical one is shown in Fig. 5.2(a). Selected SEM and FESEM images of the fatigue fracture surfaces of SWNT/epoxy specimens are shown in Figs. 5.7-5.16.

A typical fracture surface is shown in Fig. 5.7. On the left side of the figure, where the epoxy matrix contains no CNT reinforcement, a flat, featureless fracture surface is seen. However, local failure around the SWNT ropes showed ductile-like failure with plastic deformation of epoxy and pullout of SWNT ropes (as seen from Figs. 5.7 and 5.8.). Also shown in Figs. 5.7 and 5.8, no SWNT-bridged transverse matrix cracks were observed on the specimen surface, which could be attributed to the fact that the SWNT ropes were fully embedded in the matrix material.

Bridging of matrix crack by SWNT rope is clearly seen from Fig. 5.9. A similar image examined by FESEM, is shown in Fig. 5.10, where some aligned SWNT ropes were stretched, bridged cross the matrix crack. In Fig. 5.11, polymer debris is seen sticking onto the SWNT bundles, and pullout of SWNT ropes from the epoxy matrix is obvious. On the left hand portion of Fig. 5.12, indicated by the white circle, the epoxy matrix protruding from the pulled-out CNT suggests strong adhesion interaction between the SWNTs and the epoxy matrix, similar adhesion evidence also observed by TEM (will be shown in Fig. 5.29). In short, images shown in Figs. 5.9-5.12, such as small contact angle between the thin epoxy sheets and the embedded SWNT ropes and sticking polymer debris on the SWNT bundles suggest a good wetting of SWNT with epoxy.

From molecular simulations of CNT pullout from epoxy [91], the interfacial shear stress between CNT and epoxy is estimated to be 138 MPa, about an order of magnitude higher than that of carbon fiber and epoxy, which coincide with experimental evidence.

In Fig. 5.12, epoxy matrix protruding from the CNT suggests strong interfacial adhesion exists between epoxy and SWNT ropes. Pullout length of SWNT ropes from the epoxy matrix, examined from SEM image (Fig. 5.13), ranged from 30 to 40 μm . Diameters of the SWNT bundles pulled out from the epoxy matrix, estimated from SEM image (Fig. 5.14) can reach about 0.5 μm or more.

In Fig. 5.15, higher magnification images show alignment of SWNTs with one bundle broken in the epoxy crazing, similar image can also be seen from Fig. 5.10. The alignment of SWNTs in the crazing area hinders the crazing extension. In Fig. 5.16, failure of SWNT bundles with rather flat fracture surfaces are seen, a characteristic of brittle-like failure. It may suggest a local load sharing mechanism of SWNT (more will be said on this in section 5.6). A longitudinal surface image of a survived SWNT/epoxy specimen after 10^6 cycles is shown in Fig. 5.17. The microscopic examination revealed micro crack development on epoxy matrix and a SWNT bundle with subsequent breakage along the loading after high cycles.

Fig. 5.7 Fatigue fracture surface of a SWNT/epoxy sample showing ductile-like failure with plastic deformation of epoxy and pullout of SWNT ropes on the right hand portion and featureless fracture surface on the left hand portion where the epoxy matrix contains no CNT reinforcement.

Fig. 5.8 Fatigue fracture surface of a SWNT/epoxy sample showing ductile-like failure with plastic deformation of epoxy and pullout of SWNT ropes.

Fig. 5.9 Fatigue fracture surface of a SWNT/epoxy sample showing bridging of matrix crack by SWNT rope.

Fig. 5.10 A FESEM image of SWNT ropes bridging across the crazing on the fracture surface. Wetting of SWNT ropes by epoxy near the ends seems very good: thin sheets of epoxy containing SWNT ropes showed small contact angle.

Fig. 5.11 Close up of the fatigue fracture surface of a SWNT/epoxy sample showing pullout of SWNT ropes from the epoxy matrix is obvious, however, complete debonding is not seen.

Fig. 5.12 Epoxy matrix protruding from the CNT showing strong interfacial adhesion exists between epoxy and SWNT ropes.

Fig. 5.13 SEM image used to estimate pullout length of SWNT ropes from the epoxy matrix.

Fig. 5.14 SEM image used to estimate diameters of SWNT ropes pulled out from the epoxy matrix.

Fig. 5.15 A high magnification FESEM image shows a SWNT bundle fracture in the matrix crack on the fracture surface.

Fig. 5.16 A high magnification FESEM image shows some SWNT bundles fracture in the matrix crack on the fracture surface showing rather flat surface.

Fig. 5.17 A longitudinal surface of a survived SWNT/epoxy sample after 10^6 cycles showing a SWNT bundle with fragment and micro cracks on the epoxy matrix.

5.4.2 Comparison of SWNT/epoxy and carbon/epoxy

On the fracture surface of the carbon fiber/epoxy sample, as shown in Fig. 5.18, larger gaps are seen between epoxy matrix and carbon fibers. Most carbon fibers are subsequently debonded and pulled out from the epoxy matrix. On the longitudinal surface of carbon fiber/epoxy, as shown in Fig. 5.19, carbon fiber splitting from the epoxy matrix and matrix cracking are seen. From Figs. 5.18 and 5.19, it is concluded that interfacial adhesion between the carbon fiber and epoxy matrix is poor.

The fracture surface of SWNT/epoxy exhibited a brittle type fatigue failure with flat fracture surfaces, similar to the fracture surface of unidirectional carbodepoxy composites. However, local failure modes are obviously different, where the SWNT showed ductile-like failure, but carbon fiber exhibited brittle failure. The ductile-like

failure that is shown in SWNTs/epoxy image (Fig. 5.8) is believed induced by the local load-shearing mechanism between the intratubes in SWNTs ropes (More will be said on this topic in Section 5.6) and the strong interfacial adhesion between SWNTs and epoxy matrix. Clean debonding of SWNT/epoxy, polymer debris sticking onto the SWNT ropes, is not seen compared to carbon fiber/matrix. The 30-40 μm pullout length of SWNT ropes from epoxy matrix is longer than that of carbon fiber, which is approximately several micrometers in length. SWNT/matrix splitting are also observed through TEM (More will be said on this in the next section), as compared to fatigue damage of carbon fiber composites where fiber-matrix splitting is a common damage mode.

Fig. 5.18 Fatigue fracture surface of a carbon/epoxy sample with substantial fiber/matrix debonding and short fiber pullout.

Fig. 5.19 Longitudinal surface of a carbon fiber/epoxy sample with fiber/matrix splitting and matrix micro-cracks.

5.5 Fatigue mechanisms of SWNT

5.5.1 TEM examination

Detailed fatigue damage/failure mechanisms, such as splitting of SWNT bundles, kink formation in the SWNT bundle, and fracture of SWNT bundles, were revealed by TEM examinations.

(1) Splitting

Two kinds of SWNT splitting are seen: a) dendrite-like splitting at the very fracture tip (Fig. 5.20) and splitting within a rope away from the fractured tip (Figs. 5.21 and 5.22). Both kinds of splitting are observed extensively. The dendritic morphology of pulled-out SWNT ropes at the fractured tips is found to be a ubiquitous damage mode. From

the images of SWNT splitting within a rope away from the very tips, kinks of SWNT can be found, usually at the branching points.

Fig. 5.20 Dendritic morphology is seen with numerous fractures and splitting at the tip of SWNT ropes.

Fig. 5.21 Splitting of SWNT within ropes away from the fracture tips.

Splitting of SWNT rope is believed caused by difference in interactions between the SWNTs of the outer-layer of a bundle with the polymer matrix, and inter-tubular interactions within a bundle. Around the potential failure site where SWNT/polymer debonding and SWNT splitting have accumulated, the weak interactions between the split SWNTs ceased to exist. Once failure of the sample has occurred and the SWNT are pulled out from the matrix, the already split SWNTs give rise to the dendritic morphology. Briefly, the dendritic morphology formation of pulled-out SWNT is the results of debonding and splitting of SWNT inside the matrix during fatigue.

(2) Kink formation and failure of ropes

In Fig. 5.22, several kinks are seen on the SWNT ropes that are being pulled out from the matrix. These kinks are characterized by sharp angle on the convex side, with occasion failures, such as the one shown in Fig. 5.23. Repeated kinking could eventually lead to rupture of SWNT bundles, as shown in Figs. 5.22 and 5.23. Also seen in Fig. 5.22 are split SWNT ropes, which are likely the results of repeated loading of misaligned SWNTs, or SWNTs debonded from the matrix.

CNT have been known [48] to have excellent resilience, even larger bending deformations would not produce plastic deformation involving observed kink formation. This kind of kink is not seen in raw samples or samples failed under quasi-static tensile load. However, kink formation is observed extensively in some splitting SWNT ropes after fatigue test, as shown in Fig. 5.22. Thus, the kink formation and subsequent failure suggest possible fatigue damage (i.e., accumulated carbon bond dissociation over time) has occurred within the vicinity of the kink. However, this kind of kink-induced failure is not commonly seen in our samples. Since kinks are

associated with splitting, but a split SWNT rope not necessarily contains a kink, it can be deduced that kinks come after splitting.

Fig. 5.22 Several kink on the SWNT ropes that are being pulled out from the matrix are illustrated as white circle in this TEM image, possibly produced by repeated loading of split SWNT.

Fig. 5.23 Kink formation induced to a substantial fracture failure was obviously seen.

(3) Fracture surfaces

SWNT fractures are observed at the very tips of pulled-out SWNTs (Fig. 5.20), and within SWNT bundles away from the tips (Figs. 5.22-5.27). The fracture topography of SWNT contains both brittle-like flat surface and ductile-like spiral surface. In Fig. 5.20, dendritic morphology is seen with numerous fractures and splitting at the tip of SWNT ropes. However, it is difficult to obtain focused images with high resolution from the very tips because these SWNT ropes fluctuate as a result of TEM irradiation. In Fig. 5.24, a number of fractures are seen in SWNT bundles oriented more or less parallel to the loading direction. These SWNT failures are characterized by rather flat fracture surfaces, a characteristic of brittle-like failure. It should be mentioned that the fractured bundle shown in Fig. 5.24 may contain a number of SWNTs. At higher magnification (inset of Fig. 5.24) flat fracture surface is still obvious.

Fig. 5.24 TEM image of fractures of SWNT bundles with flat fracture surfaces. Some splitting of SWNT bundles are also seen.

Fig. 5.25 A TEM image of fractures of SWNT bundles with flat fracture surfaces.

Fig. 5.26 A TEM image of SWNT fracture under tearing mode. Some splitting of SWNT bundles are also seen.

Fig. 5.27 A TEM image of SWNT fracture under tearing mode.

Fig. 5.28 The broken SWNT bundles with abrupt changes in diameter is seen, indicating that SWNTs within a rope may not be broken at the same time or at the same location.

Fig. 5.29 A TEM image of SWNT/epoxy specimen reveals good wetting morphology between SWNT and epoxy thin sheet.

Fractures of SWNTs at approximately the same location in a bundle such as those shown in Figs. 5.24 and 5.25 suggest a mechanism of local load sharing. SWNTs adjacent to a failed SWNT are carrying higher stress than those further away, and thus prone to failure at that location. Otherwise the fracture surface of a failed bundle will contain protruded individual SWNTs, very much like the sword-in-sheath type failure mode in quasi-static tests. In order to certify that local load sharing is possible within a SWNT bundle, we have performed molecular mechanics simulations of pullout of a central SWNT and SWNT ropes from arrays of SWNT with inter-tubular van der Waals interactions (Discussed in chapter 4). The calculated shear stress is about several tens of MPa, which implies that tensile stress could be transferred to the adjacent tubes near a broken SWNT over some distance.

In Figs. 5.26 and 5.27, tearing fractures are seen, where SWNT ropes are torn apart, leaving a ductile-like fracture surface. Although it is possible that fractures shown in Fig. 5.26 could be a result of multi-axial stress state, it is believed that the SWNTs had been carrying repeated tensile load for the most part because most of them were more or less aligned with the applied load. More brittle-like fracture surfaces were observed compared to spiral-like surfaces. For some ropes, abrupt changes in diameter are seen, indicating that SWNTs within a rope may not be broken at the same time or at the same location, as shown in Fig. 5.28.

5.5.2 Molecular simulations of fracture patterns

Recent studies [18, 76] on CNT defects and fractures suggested that topological defects of CNTs could be explained by the SW mechanism, and fracture of CNTs can be attributed to the plastic deformation of CNTs as a result of the gliding and separation of 5-7-7-5 defects. In order to gain a better understanding of CNT fatigue fracture mechanisms, fracture patterns of 9 different SWNTs (defect-free armchair, zigzag and chiral SWNTs, and these three types of SWNTs with two different modes (A- and B-mode) of SW defects, shown in Figs. 5.30-5.34, are studied using molecular mechanics simulations.

In all of the simulations, molecular mechanics force field and a 10% constant strain was applied. An energy minimization procedure (or geometric optimization procedure) was carried out for the entire SWNT after a bond dissociation step while the strain of the tube was maintained at 10%, and the next bond with the highest strain energy was dissociated subsequently. The same procedures were carried out for SWNTs with SW defects. For defect-free SWNTs, the location of crack initiation was randomly selected

in the middle of the tube, and a crack was made to propagate by first dissociating a bond with the highest strain energy within the regular hexagonal array. Fracture modes of the simulated defect-free SWNTs are shown in Fig. 5.30.

Fig. 5.30 The crack pattern of zigzag tube (a), armchair tube (b) and chiral tube without defect under a 10% constant applied strain.

SW defects of A- and B-mode on a zigzag tube are shown in Fig. 5.31. In these cases a C-C bond around the defect with the highest strain energy was first identified and then dissociated. The first bonds to be dissociated in zigzag tubes with SW defects of A- and B-mode are indicated by arrows. The rationale of the simulation approach is based on the kinetic strength of solids: the effect of applied stress on an atomic bond is to lower the energy barrier and thus resulting in a higher probability of bond dissociation. The accumulation of broken bonds over time leads to a SWNT fracture. Here, we are

not concerned explicitly with the time-to-failure; it will be dealt with in the next Chapter.

Fig. 5.31 A zigzag tube with a preexisted SW defects of two modes, referred to as A-mode (a) and B-mode (b).

Fracture modes of the simulated SWNTs with SW defects are shown in Figs. 5.32-5.34. For a zigzag tube, it is the C-C bond oriented in the direction of the longitudinal tube axis, as shown in Fig. 5.30(a); for an armchair tube it is one of those 4 C-C bonds oriented 30° to the longitudinal tube axis (Fig. 5.30(b)); for a chiral tube, the fracture orientation depends on the chiral angle of the tube. Failures of defect-free zigzag tubes all resulted in brittle-like, flat fracture surface, so are the zigzag tubes with SW defect of both A- and B-mode. These simulated results do bear a resemblance to those observed fracture surfaces shown in Figs. 5.24 and 5.25. For an armchair tube, crack propagation from the SW defects occurs along the maximum shear direction ($\pm\pi/4$) of the tube, resulting in a spiral-like fracture surface, similar to those seen in Figs. 5.26 and 5.27. For a chiral tube, crack propagation from the SW defect occurs along a

direction relating to the chiral angle of the tube, resulting in a similar spiral-like fracture surface as that of an armchair tube.

Fig. 5.32 The crack pattern of zigzag tube (a) with a SW defect of A-mode (b) with a SW defect of B-mode under a 10% constant applied strain.

Fig. 5.33 The crack pattern of armchair tube (a) with a SW defect of A-mode (b) with a SW defect of B-mode under a 10% constant applied strain.

Fig. 5.34 The crack pattern of chiral tube (a) with a SW defect of A-mode (b) with a SW defect of B-mode under a 10% constant applied strain.

5.6 Summary

We have studied the tension-tension fatigue behavior of unidirectional, aligned SWNT rope reinforced epoxy composites. The flat S-N diagram of SWNT/epoxy is very similar to that of the carbodepoxy, although they were loaded at higher cyclic stresses. The fatigue strength of SWNT in epoxy is at least 1.5 times that of carbon fibers. Cyclic stresses experienced by SWNT/epoxy are found to be higher than that by pure epoxy specimens. Reinforcing effect by SWNTs is more prominent for composite at higher cycles (10^6 - 10^7). Morphology of the fatigue fracture surface of SWNT reinforced epoxy involves matrix plastic deformation and SWNT-bridged matrix cracks. Evidence of good adhesion between SWNT and epoxy, alignment of SWNTs in crazing

area hindering the crazing extension and pullout of SWNTs are seen, which suggest that SWNT can be used for fatigue resistant, high fracture toughness composites.

Fatigue failure mechanisms of SWNT bundles embedded in epoxy matrix were revealed through extensive TEM examinations. The major observed damage and failure modes of SWNT bundles include: 1) splitting of SWNT bundles, 2) kink formation and subsequent failure, and 3) fracture of SWNT bundles. Patterns of crack propagation under tension in SWNTs were studied by molecular mechanics simulations, where defect-free SWNTs and SWNTs with two different modes of SW defects were studied. It is demonstrated by the results of molecular simulations that the observed fracture surfaces of SWNTs can be reproduced reasonably well, suggesting possible fatigue failure mechanisms of SWNTs in the composite.

Chapter 6 A Kinetic Model for Time-Dependent Fracture of Carbon Nanotubes

Based on the classical kinetic concept of solid fracture and a strain concentration concept, a model is proposed for predicting time-dependent fractures of CNTs [147]. The time-dependent fracture behaviors of the three types of SWNTs with and without defects, including a zigzag tube (18,0), an armchair tube (10, 10) and a chiral tube (10, 5) under tensions, were studied by molecular mechanics simulations and a numerical scheme using strain energy concentration of crack front. Comparisons are made with available experimental measurements.

6.1 Introduction

As reviewed in Chapter 2, there has been increasing interest in studying the phenomenon of CNT fractures. To date, predictions of CNT failure, with defect-free atomic structure assumed at the beginning, are limited to yielding and fracture behaviors at relatively high strain levels ($>5\%$), and hypothesizing the onset and propagation of defects such as the 5/7/7/5 type [71, 74] or the diamond-like bonding transitions [81], and C-C bond breakage [69]. All these hypotheses apply to the transient behaviors of CNT under critical conditions, However, in actual applications, CNT will most likely be loaded at much lower strains and for longer terms.

Recently, kinetic approach was developed for predicting CNT yielding behavior [148, 149]. From the kinetic theory of strength, fracture is a kinetic process where time is an important parameter. This approach has also been proposed to represent the lifetime of receptor-ligand bonds in a model for specific cell-cell adhesion [150]. As presented in Chapter 5, the study on fatigue behaviors of SWNT bundles indicated that SWNT fractures did occur after sustaining sufficient number of load cycles, at low strain (stress) levels. These examples have manifested the potential validity of the kinetic concept for describing the time-dependent bond fracture of CNT, that is, life prediction for CNT.

In this chapter, a kinetic model combined with molecular simulations is described, and it is used to predict the time-dependent fracture of CNTs with and without defects under tensile load within the range of strains anticipated in structural applications (below 5%).

6.2 Kinetic concept of fracture mechanism

Zhurkov [151] examined experimentally the time-to-failure of a broad range of solid materials and proposed an empirical equation relating lifetime, τ , to applied stress, σ , and temperature, T , of the solids, on the basis of the kinetic concept of fracture [152],

$$\tau = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{kT}\right) \quad (6.1)$$

where k is the Boltzmann constant, τ_0 the reciprocal of the natural oscillation frequency of atoms in a solid, U_0 the atomic binding energy, and γ is related to the

disorientation of the molecular structure of a solid. Based on this concept, the fracture of a solid is considered as a time process whose rate is determined by mechanical stress and temperature.

To understand the physical sense of the kinetic equation, it is essential to interpret the physical meaning of each parameter in Eq. 6.1. The parameter, τ_0 , with the order of magnitude of 10^{-13} sec, has been found to be independent of different solids. The parameter U_0 can be interpreted as the magnitude of the initial energy barrier determining the probability of breakage of the bonds responsible for strength. The coefficient γ represents an important parameter determining the strength of a solid. The possibility of fracture of stressed solid is dependent strongly on the magnitude of tensile stress, which excites the bond being ruptured and reduces the activation barrier. The decrease of the energy barrier will be dependent on the parameter γ . It has been found that the more disoriented the structure in a metal, the smaller the coefficient γ , and hence the higher the metal strength [151]. On the other hand, in polymers, coefficient γ is most significantly influenced by the molecular orientation of polymer chains. However, it is still difficult to make precise formulations of the physical meaning due to its high sensitivity to various structure changes. Based upon the kinetic fracture concept that supposes nonuniform distribution of stress over the bonds being broken, the parameter γ can be interpreted as a coefficient taking into account the overstress on a bond as compared to the average stress in a specimen [151].

It is indicated by Eq. 6.1 “the existence of a direct connection between the kinetics of fracture of solids under the action of mechanical stress and the rupture of interatomic bonds” [151]. Based on the kinetic concept of strength, a fracture process can be

divided into three stages [151]: 1) excitation of the bonds to be broken by tensile stresses; 2) breakage of the excited bonds by thermal fluctuations; and 3) accumulation of rupture bonds that results in the loss of the stability in the body with its eventual breakdown.

6.3 Proposed kinetic model of CNT fracture

Based on the aforementioned kinetic concept, it is supposed that SWNTs will rupture along the direction where the C-C bond is having comparatively larger strain energy, as a result of the atomic thermal motion and the preference of bond dissociation under strain, although the stress it is experiencing may be smaller than the critical value for rupture. Each of the discrete crack geometries is identified with i , the number of broken C-C bonds within the crack, and u_0 and u_i represent the strain energy associated with the C-C bond of an intact tube, and the i th mode crack front C-C bond oriented parallel to the tube axis, respectively. In light of Zhurkov's model, it is postulated that the lifetime, t_i , of the strained i th mode crack front C-C bond in a CNT is predicted by

$$t_i = \tau_0 \exp\left(\frac{U_0 - u_i}{kT}\right) \quad (6.2)$$

where, U_0 is the bond dissociation energy, u_i represents the strain energy of the bond near absolute zero before dissociation, and thus $U_0 - u_i$ is the energy barrier. Belytschko et al. [76] suggested that the fracture behavior of CNTs is almost independent of the atomic binding energy like the U_0 in Eq. 6.1, but depends on the inflection point on the curve of C-C bond potential energy versus strain, which implies

that fracture of the tube starts once the applied tensile force reaches its peak value, so the U_0 in Eq. 6.2 is the corresponding bond dissociation energy at the inflection point.

Briefly, the interpretation of Eq. 6.2 is that, at certain temperature T , two bound atoms are in random motion due to the thermal energy described statistically by the Maxwell-Boltzmann distribution. It is possible that, at some instance, when the atoms acquire sufficient kinetic energy overcoming the energy barrier, bond dissociation will result. It is manifested in Eq. 6.2 that bond breakage of CNT depends on thermal motion of the atom (in terms of temperature T), and on tensile force (in terms of strain energy u_i), which lowers the energy barrier. Apparently, the bonds at the crack front have the highest u_i and thus the lowest energy barrier to be overcome by thermal fluctuations for dissociation to occur.

In order to predict time-dependent fracture of CNTs, u_i should be determined. At present, direct experimental determination of u_i is not possible due to the extremely small size of CNTs, although tensile experiments have been performed on individual MWNTs [39] and SWNT bundles (for instance, see Chapter 4). Alternatively, the strain energy can be estimated through molecular mechanics simulations. Due to the specific discrete structure of CNT and the possible absence of both the degree of heterogeneity and the variety of length scales on its molecular structure, molecular mechanics is a powerful tool for studying CNT fracture. The process of CNT fracture, as a series of molecular simulation results, is described in a statistical scheme where the probability of bond breakage is only determined by two parameters, the energy gap of the bonds before and after the dissociation, as well as temperature.

It is assumed that the crack initiation and propagation on CNT be induced by dissociation of each single bond at the front crack, step by step, under low strain (<5%) condition. Therefore “strain energy concentration” is proposed for CNT fracture analysis at each fracture mode. A parameter for characterizing the level of strain energy concentration at the crack front is derived as follows. The strain energies, E_i for CNT and u_i for C-C bond, which is the potential energy of the CNT molecular system and C-C bond, respectively, can be approximately fitted into quadratic functions at small strains (less than 5%) [65],

$$E_i = a_i \varepsilon^2 \quad (6.3a)$$

$$u_i = b_i \varepsilon^2 \quad (6.3b)$$

The tensile force per unit length (of the CNT circumference), T_i , applied at the ends of CNTs, is the first-order derivative of the strain energy

$$T_i = \frac{\partial E_i}{\partial \varepsilon} = 2a_i \varepsilon \quad (6.4)$$

where ε is strain of CNT, which can be specified in molecular simulations. a_i and b_i is corresponding regressive parameter in Eq. 6.3a and Eq. 6.3b. For SWNTs, different cross-sectional areas have been adopted in the literatures for calculations due to a lack of translation invariance in the radial direction [24, 25, 153]. Considering SWNT bundles as solid ensembles in a composite matrix, the cross-sectional area, A , of the tube is approximated by $A = \pi (r + h)^2$, in which r is the radius of the tube and $2h$ the gap between two adjacent CNTs. σ and ε is stress and strain on a tube, respectively. Using Eq. 6.4, the stress at the end of a tube is defined as

$$\sigma = \frac{2\pi r T_i}{A} = \frac{4a_i r}{(r+h)^2} \varepsilon \quad (6.5)$$

Substituting Eq. 6.5 into Eq. 6.3b yields the strain energy of the bond

$$u_i = \gamma_i \sigma^2 \quad (6.6)$$

where, γ_i is the coefficient of strain energy concentration which reads

$$\gamma_i = \frac{b_i (r+h)^4}{16a_i^2 r^2} \quad (6.7)$$

It is understood that γ_i characterizes the non-uniform local strain energy distribution as a result of a flaw in the CNT, and is related to the fracture mode, radial dimensions, and chirality of CNT. The lifetime, t_i , of a bond and time-to-fracture of CNT can be determined with γ_i . Thus, the time-to-failure of an intact tube can be expressed as,

$$t = \sum_{i=0}^n t_i = \sum_{i=0}^n \tau_0 \exp\left(\frac{U_0 - \gamma_i \sigma^2}{kT}\right) \quad (6.8)$$

where, i denotes the C-C bonds to be broken, t is the summation of the lifetime, t_i , of each individual C-C bond around its circumference. According to the simulation results by Belytschko et al. [76], the strain at the inflection point on the curve of the potential energy of a C-C bond, which is believed to be the critical point for bond dissociation, is 19%, and the corresponding bond dissociation energy, U_0 is 1.84×10^{-19} Joule. The reciprocal of the fluctuation frequency of atoms, τ_0 , is usually taken as 10^{-13} sec, the Boltzmann constant k is 1.38×10^{-23} Joule/K, the room temperature is assumed to be 300 K, and $2h$ of 0.34 nm is the representative distance between two adjacent graphite layers [141]. Using simulation results of a_i and b_i , combined with $r = 1.4$ nm and

$2h = 0.34 \text{ nm}$, γ_i are obtained for a range of crack sizes. The values of γ_i are then substituted into Eq. 6.8 for predicting the time-dependent fracture of CNT.

6.4 Life prediction of CNT: cases studies

To illustrate this idea, the time-dependent fractures of SWNTs including a zigzag tube, an armchair tube, and a chiral tube subject to axial tension, with and without defects, are investigated. As stated in Section 6.3, in order to obtaining the values of a_i and b_i , the strain energies, E_i , for the tube and u_i for the C-C bond at the crack front, can be approximately fitted into quadratic functions at small strains (less than 5%). Here, it is not intended to present all the curves used for determining the values of a_i and b_i ; instead, only the curves of E_i and u_i for the zigzag tube (18, 0) without defect, the armchair tube (10, 10) with SW defect of A-mode, and the chiral tube (10, 5) with defect of B-mode are presented (as will be shown later) for saving space. The values of a_i and b_i calculated from molecular simulations for the three types CNT with and without defects are directly tabulated in Table 6.1.

Once the values of a_i and b_i for tubes are determined, the coefficient of strain energy concentration γ_i , can be calculated based on Eq. 6.7, for a range of crack sizes and applied strains. The values of γ_i are tabulated in Table 6.1 for the purpose of facilitating analysis. Then, curves of time-dependent fractures of the three types of SWNTs with and without SW defect, obtained from Eq. 6.8, are plotted against the applied tensile loading.

Table 6.1 Values of parameter $\gamma_i (\times 10^{-39})$, a_i (eV/atom) and b_i (eV) for the zigzag, armchair and chiral tube without and with defect of A-mode (AM) and B-mode (BM) at strain up to 5%.

Types of CNT		$i=0$	$i=1$	$i=2$	$i=3$	$i=4$
zigzag	a_i	25.63	25.4	25.32	24.95	24.42
	b_i	66.38	91.19	115.34	137.94	156.15
	γ_i	0.0632	0.1154	0.1167	0.2593	0.3416
armchair	a_i	28.24	27.39	25.6	24.52	23.33
	b_i	60.07	115.43	154.5	170.6	178.12
	γ_i	0.0627	0.1281	0.1963	0.2363	0.2725
chiral	a_i	37.53	36.43	35.36	33.41	31.62
	b_i	106.27	173.90	165.22	347.6	410
	γ_i	0.0632	0.1154	0.1167	0.2593	0.3416
zigzag-AM	a_i	26.67	25.62	24.41	22.35	20.95
	b_i	195.5	86.15	235.53	152.4	211.0
	γ_i	0.2281	0.1092	0.3294	0.2534	0.4003
armchair-AM	a_i	34.63	32.3	30.58	29.42	28.21
	b_i	444.75	224.05	289.17	148.65	189.5
	γ_i	0.3088	0.1788	0.2573	0.1426	0.1978
chiral-AM	a_i	39.69	38.80	37.96	37.07	35.98
	b_i	708	233	404	169	267
	γ_i	0.3860	0.1304	0.2335	0.1024	0.1717
zigzag-BM	a_i	28.39	26.96	24.94	23.5	21.96
	b_i	180.04	316.43	99.25	105.8	127.12
	γ_i	0.1859	0.3625	0.1329	0.1595	0.2194
armchair-BM	a_i	26.55	24.83	23.7	22.95	21.8
	b_i	78.17	149.89	129.3	194.72	198.7
	γ_i	0.0923	0.1998	0.1912	0.3078	0.3482
chiral-BM	a_i	35.18	33.84	32.49	30.65	28.15
	b_i	136	240.1	239	285.8	337
	γ_i	0.0963	0.1733	0.1873	0.2516	0.3518

6.4.1 Life prediction for CNTs with no defects

Since the path of crack propagation and morphology of fracture are dependent on the chirality of the tube because of the isotropic nature of graphene from which the tube is formed, time dependent fractures are investigated of intact SWNTs including a zigzag tube (18, 0) of 13.76 Å in diameter, an armchair tube (10, 10) of 13.35 Å in diameter and a chiral tube (10, 5) of 13.80 Å in diameter, subject to axial tension. Schematics of the atomic-sized crack initiation and propagation (shaded regions) of the first five fracture modes ($i = 0-4$) of the intact zigzag, armchair and chiral tubes are illustrated in Figs. 6.1-6.3, respectively.

Fig. 6.1 Schematics of the fracture modes of an intact zigzag tube (18, 0). The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

Fig. 6.2 Schematics of the fracture modes of an intact armchair tube (10, 10). The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

Fig. 6.3 Schematics of the fracture modes of an intact chiral tube (10, 5). The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

As shown in Fig. 6.1, the intact zigzag tube is loaded along the direction parallel to C-C bonds, and the two C-C bonds at the crack front (highlighted in bold) oriented parallel to the tube axis are sustaining the greatest strain, and thus most likely to be broken, followed by the next two crack-front C-C bonds, step by step. Hence, the cracks induced by bond breakage are initiated and developed along the direction perpendicular to the loading direction. Molecular simulations revealed that cracks in the armchair tube (10, 10) oriented as an angle of 60° with respect to the loading direction (Fig. 6.2) whereas cracks in the chiral tube (10, 5) oriented 75° to the loading direction (Fig. 6.3).

Molecular simulation results of the total strain energies per atom, E_i , of the intact zigzag tube (18, 0), with discrete cracks for the first five fracture modes ($i = 0-4$) subject to tensile loads, are shown in Fig. 6.4(a). It should be noted that the energy unit of the parameter a_i is eV/atom, which must be converted to eV/m² in lifetime calculations. According to Refs. [141, 154], the specific area per atom can be deduced as 0.02624 nm² from the lattice constants of perfect graphite. The unit of energy per atom for graphite, 1eV/atom, corresponding to 6.1 J/m², should be considered for calculations. It is seen that the slopes of the curves ($a_i, i = 0-4$) decrease gradually with an increase of the number of broken C-C bonds, suggesting softening of the tube during the fracture process once crack is initiated. Similar relations are also found in the intact armchair and chiral tubes, as demonstrated in Table 6.1.

The front bond energies, u_i , of a single crack front C-C bond versus the strain of the zigzag tube, for the first five crack modes, are shown in Fig. 6.4(b). Note that on the abscissas, the strains of the CNTs rather than the strains of the C-C bonds are used, for the purpose of direct comparison with results shown in Fig. 6.4(a). It is seen from Fig. 6.4(b) that the strain energy of the crack front C-C bond (solid lines) is greater than that

of the intact CNTs (dashed line). Moreover, it increases from one mode to the next as more C-C bonds are being broken within the crack, and progressively approaches a limit, indicating a loss of sensitivity as the crack grows. In the cases of intact armchair and chiral tubes, similar tendency of b_i (increases from one mode to the next as more C-C bonds are being broken within the crack) are also found, as tabulated in Table 6.1.

The decrease of a_i and increase of b_i with an increase of the number of broken C-C bonds result in an increase of the corresponding values of γ_i for the three types of intact SWNTs, as demonstrated in Table 6.1.

Results of time-to-failures of the three types of intact tubes are shown in Figs. 6.5 to 6.7, respectively. Note that, unless otherwise specified in this Chapter, the dashed lines are lifetime curves of the bond at the crack front with i broken bonds within a crack ($i = 0-4$), and the solid lines are time-to-failure curves of CNTs with a crack of the i th mode including intact nanotube ($i=0$) and of nanotubes with preexisting flaws ($i > 0$). Only the results of the first five modes ($i=0-4$) are depicted.

It is obviously seen from each of these figures (Figs. 6.5-6.7) that the i -th solid curve (of the tube) is quite close to the dashed curve of t_i when the stress is relatively large, implying that the time-to-fracture of a CNT is dominated by the lifetimes of a few C-C bonds after initial bond dissociation. Thus, the time summation for the first five broken bonds ($i=0-4$) is adopted as the lifetime prediction for an intact tube.

Fig. 6.4 (a) Total energy change per atom, E_i , of zigzag tube (18, 0) versus axial tensile strain. (b) Energy change, u_i , of a crack front C-C bond in the same tube versus axial tensile strain. Circles are simulation results and dashed and solid lines are the regression curves by Eq. 6.3 in which the dashed line is the curve for intact nanotube.

For an intact CNT, the process of C-C bond dissociation from one mode to the next as more C-C bonds are being broken is accelerated due to increasing γ_i . Furthermore, when the stress is low, more bonds contribute to the total time-to-failure of the tube, resulting in a flattening of the solid curve, and thus the stress versus logarithm of time-to-failure curve is approximately linear. Also observed is that, the larger “defects” (more C-C bond dissociations), the closer the time-to-failure curves. It is evident that lifetime degradation of the zigzag tube is slower than that of armchair or chiral tube, which is identified by the smaller gap, for example, between the curves of $i=0$ and $i=1$ in Fig. 6.5, as compared to the relatively larger ones in Figs. 6.6 and 6.7.

Fig. 6.5 Time-to-failure of a zigzag tube (18,0) without defect versus applied stress.

Fig. 6.6 Time-to-failure of an armchair tube (10, 10) without defect versus applied stress.

Fig. 6.7 Time-to-failure of a chiral tube (10, 5) without defect versus applied stress.

Comparing the time-to-fracture curves of the intact zigzag, armchair and chiral tube, as shown in Fig. 6.8, it is found that armchair tube has the longest lifetime, followed by

chiral tube and zigzag tube has the shortest, for the same relatively high level of tensile load, when the time summation of the first five broken bonds is adopted as the lifetime prediction. It is also inferred that armchair tube can sustain the highest tensile stress, Le., the highest 'fatigue strength', followed by chiral tube, and then zigzag tube.

Fig. 6.8 Comparison of time-to-failure of a zigzag, armchair and chiral tube without defect versus applied stress. Only the lifetime predictions of intact tubes (correspond to $i=0$ mode) are incorporated.

6.4.2 Life prediction of CNTs with SW defects

The time dependent fractures of a zigzag tube (18,0), armchair tube (10, 10) and chiral tube (10,5) with two different modes (A- and B-mode) of SW defects are investigated. SW defects having a negative effect on the mechanical properties were found in CNTs produced by arc-discharge and hydrocarbon decomposition synthesized methods [155, 156]. In Chapter 5, the fracture patterns of CNTs with SW defects of both A- and B-

mode, were presented. In this Chapter, time-dependent fractures of armchair, zigzag and chiral tube with the two types of SW defects are discussed. It has been demonstrated that SW defect is energetically favorable when the strain is larger than 5%-6% [71, 75]. However, the SW defects discussed here are assumed to be induced by the synthesis methods, regardless of the formation mechanisms. From the aforementioned lifetime prediction of intact CNTs, it was found that the time-to-fracture of a CNT is dominated by the lifetimes of a few C-C bonds after initial bond dissociation. Therefore, the lifetime of the first five broken bonds is also adopted to represent the lifetime of CNTs with SW defects.

6.4.2.1 CNTs with SW defect of A-mode

Molecular simulation results of energies of the C-C bonds around a SW defect of A-mode are tabulated in Table 6.2, for the purpose of illustration. It is seen from Table 6.2 that the C-C bond connecting the two heptagon rings in a CNT with SW defect of A-mode is the weakest one and most likely to be broken first due to the highest strain energy experienced. Therefore, the defect topography in CNTs has a significant influence on the site of crack initiation.

In the case of SW defect of A-mode, the C-C bond connecting the two heptagons (denoted as bond No. 1 in Table 6.2) with the highest strain energy is considered to be the first bond to be broken, irrespective of the type of CNT. The schematic diagrams of cracking mode with the first five broken bonds for a zigzag tube, an armchair tube and a chiral tube with a SW defect of A-mode, are respectively shown in Figs. 6.9-6.11.

Table 6.2 Energies of the bonds around a SW defect of A-mode at the strain of about 5%.

Bond No	Bond Energy (eV)		
	Zigzag-AM	Armchair-AM	Chiral-AM
1	1.51	2.14	2.32
2	1.17	1.85	2.07
3	0.65	0.56	1.68
4	0.72	0.42	1.69
5	0.56	0.50	1.73
6	0.93	1.22	1.82
7	1.26	2.04	2.11
8	1.17	1.89	2.04
9	0.64	0.60	1.43
10	0.72	0.45	1.36
11	0.55	0.52	1.50
12	0.92	1.22	1.85
13	1.25	2.02	2.14

In the case of CNTs with SW defect of A-mode, crack propagation path is related to the chirality of CNT, after the first bond dissociation. As shown in Fig 6.9, for a zigzag tube with a SW defect of A-mode, once the first bond linking the two heptagons

dissociates, the path of crack propagation is the same as that of the corresponding intact counterpart, along the direction perpendicular to load and almost independent to the defect site (pentagons and heptagons).

For an armchair tube with a SW defect of A-mode, as shown in Fig 6.10, the crack develops along the path where the defect exists, and ruptures along the circumference oriented 60° with respect to the axis of the tube. For a chiral tube with a SW defect of A-mode, as shown in Fig. 6.11, the direction of crack propagation is quite similar to that of an armchair tube with the same defect and is related to its chirality. Worth noticing is that cracks propagate along both directions of a CNT.

Fig. 6.9 Schematics of cracking modes of a zigzag tube (18, 0) with a SW defect of A-mode. The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

Fig. 6.10 Schematics of fracture modes of an armchair tube (10, 10) with SW defect of A-mode. The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

Fig. 6.11 Schematics of fracture modes of a chiral tube (10, 5) with SW defect of A-mode. The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

The strain energies per atom E_i , and the bond energies u_i verse tensile strain, for determining the values of a_i and b_i , respectively, for the armchair tube with a SW defect of A-mode, are shown in Fig. 6.12. As stated previously, the values of b_i of intact CNTs increase from one mode to the next as more C-C bonds are being broken within the crack. In the case of CNTs with a SW defect of A-mode, however, the value of b_0 associated with the first bond to be broken is generally larger than those values associated with the subsequent fracture modes (Fig. 6.11, and also referring to Table 6.1), suggesting that the crack initiation be rendered more prone by this type of SW defect.

Results of time-to-failures of a zigzag tube, an armchair tube, and a chiral tube with A-mode SW defect are shown in Figs. 6.13-6.15, respectively. It can be seen from Figs. 6.13-6.15 that, compared with the intact CNTs (Figs. 6.5-6.7), the process of C-C bond dissociation from one mode to the next is no longer accelerated for CNTs with A-mode defect, possibly because the crack-front bond relaxations after the first bond dissociation render the values of b_i corresponding to the subsequent bonds to be broken be smaller than the value of b_0 . It is found in Figs. 6.13-6.15 that the sustainable stress of the C-C bond to be broken first (referring to the dashed curves of $i = 0$) is generally lower than those of the subsequent bonds, due to the largest local strain energy (b_0) induced by this type of defect. It is evident that $t_1 \approx t_0$ holds for all the three types of CNTs (Figs. 6.13-6.15) and $t_3 \approx t_2 \approx t_1 \approx t_0$ holds for armchair and chiral tube (Figs. 6.14 and 6.15), implying that the lifetime of CNTs with SW defect of A-mode is more dependent on the lifetimes of the subsequent bonds after the first bond dissociation.

Note that overlapping of the curves of t_i ($i=0-3$) in Figs. 6.14 and 6.15 is related to the wave-like decrease of b_i as more C-C bonds dissociate.

Fig. 6.12 (a) Total energy change per atom, E_i , of armchair tube (10, 10) with SW defect of A mode versus axial tensile strain. (b) Energy change, u_i , of the strained bond at the crack front of armchair tube (10, 10) with SW defect of A-mode versus axial tensile strain. Dashed line and solid lines are the regression curves in which the dashed line is the curve for intact nanotube.

Fig. 6.13 Time-to-failure of a zigzag tube (18,0) with SW defect of A-mode versus applied stress.

Fig. 6.14 Time-to-failure of an armchair tube (10,10) with SW defect of A-mode versus applied stress. Empty circles are results of fatigue experiment of SWNT embedded in epoxy composites specimens for comparison.

Fig. 6.15 Time-to-failure of a chiral tube (10,5) with SW defect of A-mode versus applied stress.

Also implied in Figs 6.13-6.15 is that the lifetime degradation of zigzag tube is the fastest among the three types of CNTs with SW defect of A-mode, evidenced by the larger gap between the curves of $i=0$ and $i=1$ in Fig 6.13, as compared to the relatively smaller ones in Figs. 6.14 and 6.15.

Comparison of lifetime predictions of the three types of CNTs with A-mode SW defect is depicted in Fig. 6.16. It is noted that, with the same SW defect of A-mode and at the same stress level, the chiral tube is predicted having the longest lifetime relative to the armchair and zigzag tube.

As a brief summary, for a CNT with A-mode SW defect, while the defect topography has a significant influence on the site of crack initiation, the path of crack propagation is closely related to its chirality. This type of defect renders crack initiation more prone, but crack propagation is no longer accelerated, as compared with the corresponding

intact counterpart. CNTs with this type of defect are predicted to have longer lifetimes but lower fatigue strengths, at low strain level.

Fig. 6.16 Time-to-failure comparison of a zigzag, armchair and chiral tube with a defect of A-mode versus applied stress. Only the lifetime predictions of intact tubes (correspond to $i=0$ mode) are incorporated.

6.4.2.2 CNTs with SW defect of B-mode

Crack initiation of CNTs with this type of defect should be contemplated carefully. As stated previously, the C-C bond connecting two heptagon rings in a CNT with SW defect of A-mode is the weakest one and most likely to be broken first due to the highest strain energy experienced. For CNTs with a SW defect of B-mode, however, that is not the case. Molecular mechanics simulation results of energies and lengths of the C-C bonds around a SW defect of B-mode are tabulated in Table 6.3, for the purpose of illustration.

Table 6.3 Energies and lengths of the bonds around a SW defect of B-mode at the strain of about 5%.

Bond No	Bond Energy (eV)/ Bond Length (Å)					
	Zigzag-BM		Armchair-BM		Chiral-BM	
	Energy (eV)	Length (Å)	Energy (eV)	Length (Å)	Energy (eV)	Length (Å)
1	2.5	1.38	1.60	1.395	1.82	1.40
2	1.43	1.43	0.95	1.41	1.41	1.42
3	0.82	1.465	0.46	1.406	1.34	1.417
4	0.56	1.432	0.64	1.45	1.35	1.46
5	0.56	1.432	0.63	1.44	1.36	1.462
6	0.85	1.467	0.45	1.406	1.35	1.416
7	1.43	1.437	0.95	1.41	1.32	1.417
8	1.44	1.438	0.95	1.41	1.43	1.417
9	1.41	1.43	0.96	1.41	1.42	1.42

The five C-C bonds (denoted as bond No. 1, 2, 7-9 in Table 6.3) connecting the two adjacent heptagons are stressed compressively at different levels, as demonstrated by the bond lengths (Note that the original bond length of CNT in free state is about 1.42 Å in the present simulations), even when the tube is strained up to 5%. The bonds may undergo a change from compressive to tensile state, resulting in a decrease of the

potential energies with increasing tensile strain. As a result, the five C-C bonds are quite stable even when the tube is tensile strained (up to 5 %). The C-C bond of the heptagon rings (denoted as No. 4 or 6) is the bond stretched to the largest extent, and is considered as the bond to be broken first. The bonds denoted as No. 6 for zigzag tube and the one denoted as No. 4 for armchair and chiral tube are considered to be the first bonds to be broken. Once the first bond dissociates, molecular mechanics simulations revealed that the subsequent bonds to be broken are dependent on the chirality of the tube rather than the site of defect, and propagate along the circumferences of CNTs. Schematics of fracture modes of a zigzag, an armchair and a chiral tube with SW defect of B-mode are shown in Figs. 6.17-6.19, respectively. It is therefore that this type of defect has little influence on the path of crack propagation.

Fig. 6.17 Schematics of fracture modes of a zigzag tube (18, 0) with SW defect of B-mode. The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

Fig. 6.18 Schematics of fracture modes of armchair tube (10, 10) with the SW defect of B-mode. The number of broken bond(s) is denoted by parameter i . The crack front bond is highlighted by bold.

Fig. 6.19 Chiral tube (10, 5) with the SW defect of B-mode. The number of broken bond(s) is denoted by parameter i . The crack front C-C bond is highlighted by bold.

The strain energies per atom E_i , and the bond energies u_i verse tensile strain, for determining the values of a_i and b_i , respectively, for the chiral tube with a SW defect of B-mode, are shown in Fig. 6.20. As shown in Fig. 6.20(a), similar to the cases of both intact CNTs and CNTs with SW defect of A-mode, the slopes of the curves (a_i) decrease gradually with an increase of the number of broken C-C bonds for CNTs with SW defect of B-mode. It is seen from Fig. 6.20(b) that the strain energy of the crack front C-C bond (solid lines) increases after crack initiation, with a lesser extent relative to the case of intact CNTs, and so is the armchair tube (referring to Table 6.1). An exception is that for zigzag tube with B-mode SW defect, the values of b_i change in a complicated manner with increasing number of broken C-C bonds (referring to Table 6.1), after the first bond dissociation.

Shown in Figs. 6.21-6.23 are the results of time-to-failures for a zigzag tube, an armchair tube, and a chiral tube with B-mode SW defect, respectively. It can be seen from these figures that, for the armchair and chiral tube with this type of defect, the process of C-C bond dissociation is accelerated due to increasing γ_i , similar to the case of intact CNTs; for the zigzag tube, however, that is not the case. The overlapping curves of t_0 , t_1 and t_2 , shown in Fig. 6.21, suggest that the lifetime degradation of zigzag tube is the slowest among the three types of CNTs with this type of defect, and the lifetime is more dependent on the lifetimes of the subsequent bonds after the first bond dissociation

Fig. 6.20 (a) Total energy change per atom, E_i , of a chiral tube (10, 5) with defect of B-mode versus axial tensile strain. (b) Energy change, u_i , of a crack front C-C bond in a chiral tube (10, 5) versus axial tensile strain. Circles are simulation results and dashed and solid lines are the regression curves by Eq. 6.3 in which the dashed line is the curve for intact nanotube.

Fig. 6.21 Time-to-failure of zigzag tube (18, 0) with SW defect of B-mode versus applied stress.

Fig. 6.22 Time-to-failure of an armchair tube (10,10) with SW defect of B-mode versus applied stress.

Fig. 6.23 Time-to-failure of a chiral tube (10,5) with SW defect of B-mode versus applied stress. Empty circles are results of fatigue experiment of SWNT embedded in epoxy composites specimens for comparison.

Comparison of lifetime predictions of the three types of CNTs with B-mode SW defect is depicted in Fig. 6.24. It is noted that the lifetime curve of zigzag tube lies lower but flatter than those of armchair and chiral tube. Hence, the zigzag tube is predicted having the longest lifetime, although there is a slight decrease in fatigue strength.

As a brief summary, for CNTs with B-mode SW defect, while the defect has an influence on the site of crack initiation, the path of crack propagation is closely related to the chirality, similar to the case of CNTs with A-mode SW defect. Crack propagation in armchair and chiral tube with this type of defect is accelerated from one mode to the next within a crack, similar to the corresponding intact counterparts. The effect of SW defect of B-mode on crack development in zigzag tube is more prominent than that in armchair and chiral tube, resulting in an obvious change of its lifetime relative to the intact counterpart.

Fig. 6.24 Time-to-failure comparison of a zigzag, armchair and chiral tube with a defect of B-mode versus applied stress. Only the lifetime predictions of intact tubes (correspond to $i=0$ mode) are incorporated.

Here, for the purpose of direct comparison, time-to-failure curves versus applied stresses of the zigzag, armchair and chiral tubes of all of the three cases, i.e., the case of intact CNTs, CNTs with SW defect of A- and B-mode, are superimposed and depicted in Fig. 6.25. In the case of intact CNTs, it is found that while the armchair and chiral tube exhibit higher fatigue strength relative to the zigzag tube, time-to-fracture curve of the zigzag tube is flatter, suggesting that lifetime degradation is slower, than those of armchair and chiral tube.

Fig. 6.25 Comparison of time-to-failure curves versus applied stress of the three types of CNTs with and without SW defects of A- and B- mode.

As compared with the intact CNTs, a decrease in the maximum sustainable stress of the tubes with SW defects of both two modes is found. The sustainable stress reduction induced by SW defect of A-mode is more significant than that by SW defect of B-mode for armchair and chiral tube, but the reverse is true for zigzag tube. Lifetime degradations of the three types of CNTs with SW defect of A-mode and zigzag tube with SW defect of B-mode are found to be slower than those of the intact counterparts. However, SW defect of B-mode is found to have a limited influence on the lifetime degradation of armchair and chiral tube. In general, SW defects of A- and B-mode result in a flattening of the lifetime curve, suggesting a retardation of crack propagation, and thus elongates the lifetime, at low strain level.

6.5 Comparison with experimental data

Up to now, experimental data on time-dependent fracture (static fatigue) of individual CNTs are not available for direct comparison with the proposed life prediction model. Here, the fatigue S-N data of aligned SWNT bundles embedded in epoxy matrix under cyclic tensile load, indicated by empty circles, are overlaid in Figs. 6.14 and 6.23, for comparison.

It is found from Figs. 6.14 and 6.23 that while the fatigue experimental data of SWNTs fall within the proposed model predictions very well during $10^5 - 10^7$ cycles, they are scattered in a zone lying under the lifetime prediction curves during 10^1 to 10^4 cycles, possibly because the SWNT bundles tested in our experiment contain numerous defects on their walls, leading to a substantial reduction in fatigue strength of the SWNTs. It has been found that CNTs with defects have much lower fatigue strengths than those of the intact counterparts. Possible defects may be introduced during the process of CNTs, especially in long CNTs. As the length of the SWNT ropes hit millimeter level or more, the embedded SWNT bundle very likely contains preexisted flaws. Furthermore, more C-C bond dissociations in crack propagation on CNTs render the time-to-fracture curves flatter and closer to each other. Since only the lifetime of the first five broken bonds is adopted to represent the lifetime of CNTs, and issues such as frequency effect, size effect, multiple fractures, and the matrix material effect are not addressed (all these factors do exercise influences, in one way or another and to various extents, on the lifetime of a material under long-term loading), it is reasonable that the fatigue experimental data are scattered in a zone lying under the lifetime curves. Despite the aforementioned complications, the proposed model seems to give

reasonable predictions for the available data of SWNT bundles embedded in epoxy composite.

6.6 Conclusions

A model is proposed for predicting time-dependent fracture of CNTs, based on the classical kinetic concept of solid fracture and a concept of strain energy concentration. The time-dependent fracture behaviors of a zigzag, armchair and chiral tube with and without SW defects (A- and B-mode) subject to axial tension were studied by molecular mechanics simulations and a numerical scheme using crack front strain energy concentration.

The crack initiation and propagation is found to be related to the local strain energy concentration on the crack-front bond being ruptured rather than the average strain energy in a whole CNT. For CNTs with SW defects of A- and B-mode, while the defect has an influence on the site of crack initiation, the path of crack propagation is related to the chirality.

For intact CNTs, the time-to-failure is dominated by the lifetimes of a few bonds after initial bond dissociation when applied load is large while more bonds contribute to the overall lifetime when applied load is small. It is found that armchair and chiral tube exhibit higher fatigue strength compared to the zigzag tube. However, lifetime degradation of an intact zigzag tube is slower than those of armchair and chiral tube.

The SW defects have significant influences on the bond strain energy transfer and thus the lifetime as well as the fatigue strength. Effects at different level on the fatigue

strength and lifetime of the CNTs induced by SW defects depend on both the modes of defect and the types of CNTs. In general, CNTs with SW defects are predicted to have a longer lifetime at low strain level, with a reduction in fatigue strength. Reduction of fatigue strength induced by SW defect of A-mode is more significant than that by SW defect of B-mode for armchair and chiral tube, but the reverse is true for zigzag tube. Lifetime degradations of the three types of CNTs with SW defect of A-mode are found to be slower than those of the intact counterparts. While SW defect of B-mode is found to have a limited influence on the lifetime degradation of armchair and chiral tube, lifetime degradation in zigzag tube with this type of defect is found to be slower relative to the intact counterpart.

Comparisons were made with available experimental measurements. The fatigue experimental data of SWNT bundles embedded in epoxy composite fall within the range of predication of the proposed model reasonably well. The proposed approach can be applied to other nanostructures, provided that the path of crack propagation is deterministic.

Chapter 7 Conclusions and Recommendations

7.1 Conclusions

With the emphasis placed on exploiting the remarkable mechanical properties of CNTs for advanced composite materials, we have carried out studies on the interfacial characteristics between the CNTs and the matrix materials, the tensile stiffness and strength, the long-term fatigue behaviors and mechanisms, as well as time-dependent fracture predictions of CNTs and their composites. In the following, results achieved to date are outlined.

1) Interfacial characteristics between CNTs and matrix materials.

The interfacial characteristics of CNT-reinforced composites were studied by simulating CNT pullout from several thermoplastic polymers, using molecular mechanics approach. Interfacial shear stresses of CNT/polymer composites were then derived from pullout energies using micromechanics formulation. Results suggested that the interfacial shear stresses between CNTs and polymers are significantly higher than most micro fiber-reinforced polymer composites. It is concluded that, the adhesion between the CNTs and the matrix materials with no chemical bonding assumed, is attributed, to a larger extent, to the electrostatic and van der Waals interactions. The nature and magnitude of electrostatic and van der Waals interactions rely on the choice of polymer matrix and also the conformations of the polymers, which has been exemplified by the phenyl-groups and the helical conformations of the polymers.

The influences of the conformational changes on the pullout energies and hence the interfacial shear stresses were evaluated through two optimization procedures while CNT was being pulled out from the embedding polymers. Results suggested that the conformational changes have no influences on the simulation results of the pullout energies, which is because the pullout energy is dependent on the difference of energies between the fully embedded CNT and the complete pullout configuration.

Temperature, as a contributor to interfacial adhesion, was also examined. The temperature dependence of the selected composite systems is believed related to the “annealing process”. With the temperature elevated, kinetic energy is introduced, which accelerates the thermal motion of CNT/polymer systems, and thus the polymer atoms can overcome the local energy barrier to reach a better-optimized conformation to interact with the circumferences of the CNTs, resulting in increased interfacial adhesion. As compared with the pullout energies at 0 K, the values of the pullout energies of CNT/polymers at elevated temperatures increase substantially. The temperature dependent contributions to the interfacial strength of CNT-reinforced polymer composite could be attributed to (i) the increase in electrostatic and van der Waals interactions between CNT and polymer with the increase in temperature, and (ii) the increase in mechanical interlocking induced by mismatch in CTEs and the deformations of CNT and polymer.

2) *Tensile test of SWNT bundles.*

Tensile strength and Young’s modulus of CNTs were characterized for SWNT bundles through experimental method. In addition to obtaining the values of tensile strength and Young’s modulus through tensile tests, analyzing the failure loads of the sub-bundles

statistically not only will provide information on the tensile strength distribution of the SWNT sub-bundles, but also will shed light on the tensile strength distribution of individual SWNT and on the structural characteristics of SWNTs. The strength and Young's modulus of SWNTs were estimated in the range of 6.6 to 35 GPa (mean value of 14.72 GPa) and 600 GPa, respectively. Analyzing the failure loads of the sub-bundles spanning from low to high load (1.92 - 35 GPa) through limited number of kinks on each stress-strain curve, the strengths of SWNT sub-bundles were well fitted to a two-parameter Weibull distribution with Weibull modulus of 1.71 and characteristic strength 17.8 GPa. The former indicates a large scattering of the distribution. Based on the local load shearing mechanism in the SWNT bundles and the weakest link concept, it is believed that the strength distribution of the SWNT sub-bundle is close to that of individual SWNTs.

3) Fatigue behaviors and mechanisms of CNTs under tension.

Tension-tension fatigue behavior and fatigue mechanisms of unidirectional, aligned SWNT rope reinforced epoxy composite was studied to unlock the long-term performance of SWNTs. The slope of S-N curve of the SWNT in SWNT/epoxy composite obtained is flat, similar to those of carbon fiber-reinforced epoxy composites, the fatigue strength of SWNT in epoxy is at least 1.5 times that of carbon fibers. Comparing the S-N curve of SWNT/epoxy composite with pure epoxy specimens, the reinforcing effect of SWNT/epoxy composite is more prominent at high cycles than that at low cycles, suggesting that SWNT could be fatigue resistant reinforcement with good long-term mechanical properties. Fatigue morphology were revealed through SEM examinations. Morphology of the fatigue fracture surface of SWNT reinforced epoxy involves matrix plastic deformation and SWNT-bridged

matrix cracks. Evidence of good wetting and adhesion between SWNTs and epoxy was demonstrated.

Fatigue failure mechanisms at nanometer level were revealed through TEM. Observed damage and failure modes include: 1) splitting of SWNT bundles; 2) kink formation and subsequent failure in SWNT; and 3) fracture of SWNT bundles. Patterns of crack propagation under tension in SWNTs were studied by molecular mechanics simulations, where defect-free SWNTs and SWNTs with two different modes of Stone-Wales defects were studied. It is demonstrated by the results of molecular mechanics simulations that the observed fracture surfaces of SWNT can be reproduced reasonably well, suggesting possible fatigue failure mechanisms of SWNT in the composite.

4) A Kinetic model for predicting time-dependent fracture behaviors of CNTs.

A model is proposed for predicting time-dependent fracture of CNTs, based on the classical kinetic concept of solid fracture and a strain energy concentration concept. The time-dependent fracture behaviors of a zigzag, armchair and chiral tube with and without SW defects subject to axial tensions were studied by molecular mechanics simulations and a numerical scheme using crack front strain energy concentration.

The crack initiation and propagation was found to relate to the local strain energy concentration on the crack-front bond being ruptured rather than the average strain energy in a whole CNT. While SW defect has a significant influence on the site of crack initiation, the path of crack propagation is related to the chirality.

It is found that the time-to-failure of the CNT is dominated by the lifetimes of a few bonds after initial bond dissociation when applied load is large while more bonds

contribute to the overall lifetime when applied load is small, resulting in the logarithm of time-to-failure of CNTs being approximately linearly related to applied stress. The SW defects have significant influences on the bond strain energy transfer and thus the lifetime as well as the fatigue strength. Effects at different level on the fatigue strength and lifetime of the CNTs induced by SW defects depend on both the modes of defect and the types of CNTs.

Comparisons were made with available experimental measurements. Despite complicated factors, such as frequency effect, size effect, multiple fractures, etc., exercise influences, in one way or another and to various extents, on the lifetime of a material under long-term loading, the fatigue experimental data of SWNT bundles embedded in epoxy composite do fall within the range of predication of the proposed model reasonably well.

7.2 Recommendations

Based on the work accomplished to date, subsequent further investigations may be carried out on the following aspects:

1) Fatigue model of CNT/polymer composite.

Some conventional fatigue models have been well established for composites reinforced with micro-sized fiber to predict the long-term performance of that material. It is expected that these models of microfiber-reinforced unidirectional composites can be adopted and modified to develop a fatigue model of CNT/polymer on the basis of in-

depth understanding of the interfacial behavior of CNT/polymer, the fatigue failure mechanisms of CNT-reinforced polymer composites.

2) Study of relationship between interfacial strength and fatigue behavior of CNT/polymer composite.

It is clear that the interfacial characteristics greatly influence the mechanical properties of composites, including the long-term behavior of composite materials. Good interfacial adhesion results in improved fatigue resistance. The theoretical model, combined with molecular simulation, will be carried out by using the well-established classical elastic shell theory in combination with the conventional fiber pullout model to further study the interfacial bonding characteristics of SWNT/polymer.

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